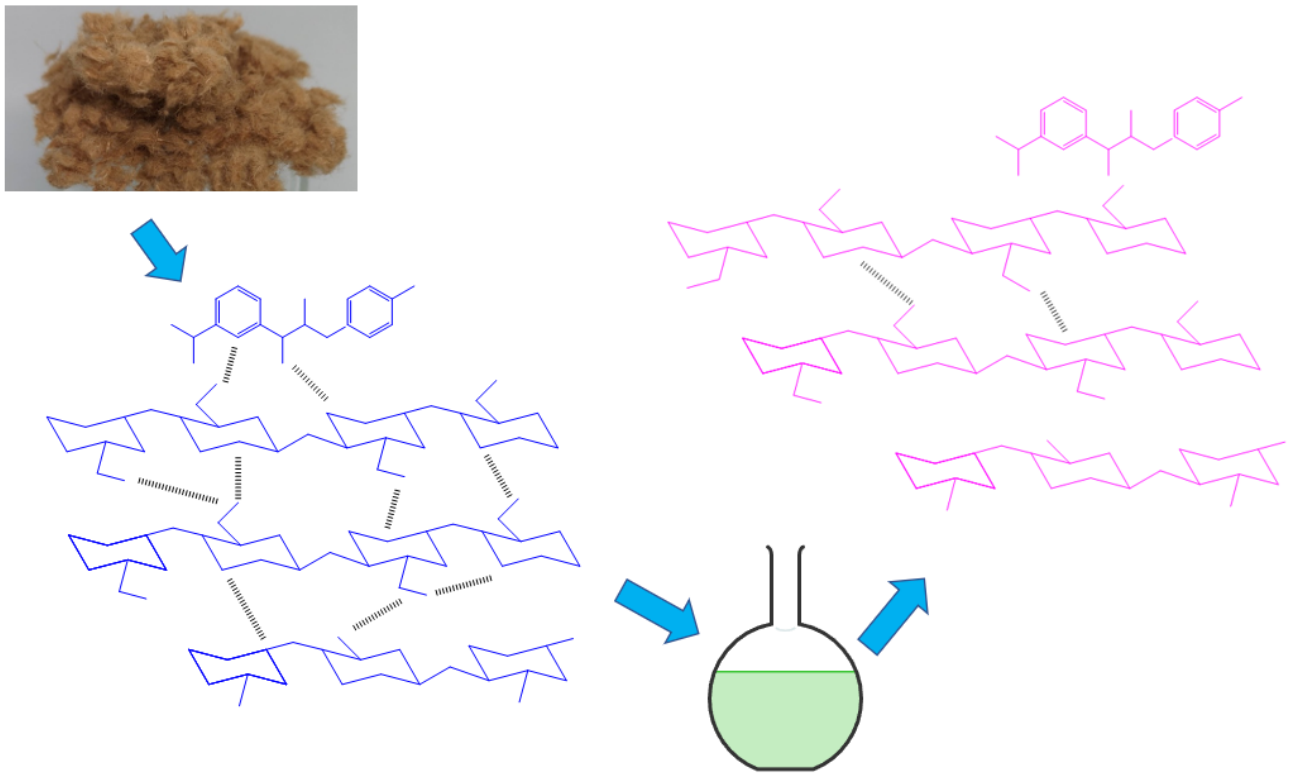


Cyclic carbonates as green reactants for improving thermoplastic properties of lignocellulosic materials

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Abstract

Lignocellulosic materials are attractive raw materials for producing thermoplastics with more sustainable manufacturing. They come from a renewable source that can reduce the dependency on conventional fossil-based feedstock and has good tensile properties. However, their polymeric chains have poor mobility because of the multiple hydrogen bonds of their hydroxyl groups, which is an essential obstacle for thermoplastic processing. To improve their thermoplasticity, their hydroxyl groups can be converted by chemical modifications that introduce the side groups that can increase the flowability of their chains. In this study, unbleached softwood kraft pulp was oxyalkylated with cyclic carbonates (propylene carbonate and ethylene carbonate), acting as a reactant and medium. These two reactants create low environmental impacts because of their biodegradability and low toxicity. In addition, they are also safer compounds from their high boiling point, flash point, and vapor pressure. The influence of temperature, catalysts, and reaction time were investigated. The molecular structures, purity, and thermal properties of the modified products were also evaluated. The chemical modification with ethylene carbonate provides the highest yields and appears to be the most effective pathway to substitute hydroxyl groups with the alkyl side chains. In addition, the products from the chemical modifications with ethylene carbonate have a higher purity and are easier to separate than the products from the chemical modifications with propylene carbonate. Increasing the temperature and amount of catalyst promotes the substitutions on the hydroxyl group. Finally, the modified pulp from chemical modification with ethylene carbonate at a higher temperature and amount of catalyst has better thermal properties than the unmodified pulp. The glass-transition temperature (T_g) of the modified pulp can be detected at approximately 180 °C while the T_g of its raw material is above 220 °C, so the polymeric chains of modified pulp become more flowable.

Keywords: Lignocellulosic materials, thermoplasticity, oxyalkylation, propylene carbonate, ethylene carbonate, yields

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

BSKP	Bleached Softwood Kraft Pulp
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
EC	Ethylene Carbonate
EO	Ethylene Oxide
E'	Storage modulus
MUSKP	Modified Unbleached Softwood Kraft Pulp
MW	Molecular Weight
PC	Propylene Carbonate
PO	Propylene Oxide
USKP	Unbleached Softwood Kraft Pulp

Contents

List of Acronyms **vii**

List of Figures **xi**

List of Tables **xiii**

1 Introduction **1**
1.1 Objectives . . . 2
1.2 FibRe . . . 2

2 Background **3**
2.1 Unbleached Softwood Kraft Pulp (USKP) . . . 3
2.1.1 Cellulose . . . 3
2.1.2 Hemicellulose . . . 4
2.1.3 Lignin . . . 4
2.2 Thermoplastics from lignocellulose . . . 4
2.3 Cyclic carbonates . . . 5
2.4 Chemical modification of lignocellulose with cyclic carbonates . . . 6

3 Methods **8**
3.1 Raw Materials . . . 8
3.2 Chemicals . . . 8
3.3 Chemical Modifications of Unbleached Softwood Kraft Pulp . . . 9
3.4 Modified Unbleached Softwood Kraft Pulp (MUSKP) Seperarations . . . 9
3.5 Characterization . . . 9
3.5.1 Yields . . . 9
3.5.2 Attenuated total reflectance-Fourier infrared Spectrometry (ATR-FTIR) . . . 10
3.5.3 Soxhlet Extractions . . . 10
3.5.4 Dynamic Mechanical Analysis (DMA) . . . 10

4 Results and Discussion **11**
4.1 Comparison of the Conditions of Chemical Modifications of USKP with Cyclic Carbonates 11
4.1.1 Chemical Modification with PC and K_2CO_3 . . . 12
4.1.2 Chemical Modification with PC and DBU . . . 13
4.1.3 Chemical Modification with EC and K_2CO_3 . . . 13
4.2 Influence of Parameters on Chemical Structure of MUSKP . . . 15
4.2.1 Chemical Structure of MUSKP from Chemical Modifications with PC and K_2CO_3 15
4.2.2 Chemical Structure of MUSKP from Chemical Modifications with PC and DBU 16

4.2.3 Chemical Structure of MUSKP from Chemical Modifications with EC and K_2CO_3 17
4.3 Corrective Weights of MUSKP 18
4.4 Dynamic Mechanical Analysis (DMA) 24

5 Conclusion **26**

6 Future work **27**

Bibliography **29**

A Appendix 1 **II**
A.1 Calculation of Reactive Groups in Cellulose and Hemicellulose II

List of Figures

2.1 Molecular structure of lignocellulose fibers component.(reproduced from Han Young Jung[1]) . . . 3
2.2 Molecular structure of EC (Left) and PC (Right) . . . 6
2.3 Reaction pathways between cyclic carbonate and functional groups in lignocellulose . . . 7

4.1 Brown effluent . . . 12
4.2 Relationship between the amount K_2CO_3 and the weight of MUSKP from the chemical modifications with EC at 180 °C . . . 14
4.3 MUSKP from the chemical modifications with PC and K_2CO_3, USKP (green), MUSKP 150°C, 0.125 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (red), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (purple), MUSKP 180°C, 0.625 g K_2CO_3, and 1 h (orange), MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (brown) . . . 15
4.4 MUSKP from the chemical modifications with PC and DBU, USKP (green), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.125 g DBU, and 2 h (orange), MUSKP 180°C, 0.625 g DBU, and 2 h (purple) . . . 16
4.5 MUSKP from the chemical modifications with EC and K_2CO_3, USKP (green), MUSKP 180°C, 0.125 g DBU, and 2 h (purple), MUSKP 180°C, 0.625 g DBU, and 2 h (orange), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red) . . . 17
4.6 Soxhlet Extraction of MUSKP from the chemical modifications with PC and K_2CO_3, USKP (green), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (purple), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (orange) . . . 19
4.7 Soxhlet Extraction of MUSKP from the chemical modifications with PC and DBU, USKP (green), MUSKP 180°C, 0.125 g DBU, and 2 h (orange), MUSKP 180°C, 0.625 g DBU, and 2 h (red), Extracted MUSKP 180°C, 0.125 g DBU, and 2 h (purple), Extracted MUSKP 180°C, 0.625 g DBU, and 2 h (blue) . . . 20
4.8 Soxhlet Extraction of MUSKP from the chemical modifications with EC and K_2CO_3, USKP (green), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (purple), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), Extracted MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (orange), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red) . . . 21
4.9 Residuals of the extracts after evaporation, USKP (I), MUSKP from PC and K_2CO_3 (II), MUSKP from PC and DBU (III), and MUSKP from EC and K_2CO_3 (IV) . . . 22
4.10 Ring-opening polymerization(Side reaction of cyclic carbonates) . . . 23
4.11 Normalized spatially offset storage modulus (E') versus temperature. The red and black lines are duplicate measurements of unmodified pulp, the blue line is MUSKP with lower water content, and the green line is MUSKP with higher water content . . . 24

List of Tables

2.1 Physical properties of EO, EC, PO, and EC 5

4.1 Condition Parameters and Results of Chemical Modifications 11
4.2 Condition Parameters and Corrective Weights of the Modified Pulps 18

A.1 II

1

Introduction

Softwood pulps are an attractive alternative to raw materials for making thermoplastics due to the declining availability of fossil fuels and increasing environmental awareness. It is a renewable and structurally strong biopolymer from biomass. It has better tensile strength and fracture toughness properties than hardwood pulps[2]. The main process for producing softwood pulps is kraft, called softwood kraft pulp. Unbleached softwood kraft pulp (USKP) compositions are cellulose, hemicellulose, and lignin. All lignin in USKP can be bleached and removed to produce bleached softwood kraft pulp (BSKP). The compositions in USKP and BSKP create strong intra- and inter-interactions via for example hydrogen bonds from their hydroxyl groups, so it lacks flowable properties attributed to thermoplastics. Melt-flow occurrence of polymer requires a higher temperature than its glass transition temperatures (T_g), but T_g of unmodified biomass can be over 200 °C[3]. Their temperatures of melt-flow behavior are usually higher than their decomposition temperatures, so the unmodified biomass is unusable in conventional and economical thermoplastics processing. Chemical modifications of the hydroxyl groups within the lignocellulose components can reduce hydrogen bonding and increase free volume from introduced side groups. As a result, chain mobility and thermoplasticity are improved[4][5].

Etherification on the hydroxyl groups of lignocellulose compositions by the reaction with alkylene oxides, especially with propylene oxide (PO), is one of the most well-known chemical modifications[6]. The etherification with propylene oxide has selectivity on the phenolic hydroxyl group of kraft lignin[7] and offers good thermal properties that are preferable for thermoplastics synthesis. Similarly, the lower T_g of hemicellulose is the product of the reaction with PO[8]. However, the etherification of PO reaction on lignin must be performed in a pressurized reactor (10 - 20 bar) and temperature at 150 - 180 °C[9], while PO has high flammability, vapor pressure, and health hazards. Therefore, other chemicals with less hazardous properties are conducted to modify lignocellulosic polymers.

The chemical modifications of lignocellulosic polymers in biomass with cyclic carbonates are a promising pathway to valorize this renewable resource. Cyclic carbonates are interesting reactants in green chemistry principle because they are low toxicity and vapor pressure, high boiling and flash points, biodegradability, and high solvency[10]. They etherify with phenolic and aliphatic hydroxyl groups of lignocellulosic compounds and offer new properties of these biopolymers. Recently, several investigations about this procedure have been done, including corncob with ethylene carbonate[11], wood sawdust and peat with ethylene carbonate[12], lignin with propylene carbonate[13], condensed tannins, organosolv and kraft softwood lignin with vinyl ethylene carbonate[14], and propylene carbonate with xylan[15][16]. The investigations have indicated that the chemical modification of lignocellulose with cyclic carbonates can be conducted at temperatures of about 140 - 180 °C under atmospheric pressure. DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) and potassium carbonate (K_2CO_3) are pervasive catalyst. In addition, cyclic carbonates act as medium and reactant for most systems.

The relationship between modified lignocellulosic polymers with cyclic carbonates and their thermal properties is reported[9]. Soda lignin and condensed tannins are reacted with ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), and glycerol carbonate (GC) under solvent-free conditions, and (K_2CO_3) is a catalyst for all reactions. Glass transition temperature (T_g) of modified lignin and tannins were considerably lower when compared to their origins. VEC offered the lowest T_g of modified lignin and tannins because VEC induced a higher free volume of modified biopolymers than the other three cyclic carbonates. However, VEC is an expensive compound. Meanwhile, the modified products from GC have the highest T_g due to introducing new hydrogen bonds. The modified lignins from EC and PC have a slightly different T_g. They also have the potential to increase their free volume from chain extension by increasing the reaction time that can decrease more T_g. EC and PC have different advantages for the chemical modification of softwood kraft pulp. PC is preferable for process design because it is liquid, while EC is solid (melting point 34 to 37 °C). However, EC is more reactive than PC, which is more beneficial in the chemical reaction aspect.

This study presents the pathways for modifying the unbleached softwood kraft pulp to have better thermal properties for thermoplastic processing by cyclic carbonates (EC and PC) and catalysts (K_2CO_3 and DBU). The temperatures, reaction times, and concentration of catalysts that can impact the properties of products are evaluated to identify the most appropriate pathway in green chemistry and economic approaches. Modified and dried samples are weighed to estimate the yields of reactions. The deeper insights regarding their structure and reaction mechanism are characterized by FTIR spectroscopy while their thermal properties are analyzed by dynamic mechanical analysis (DMA).

1.1 Objectives

This study aims to illustrate a green pathway for modifying the properties of lignocellulosic fibers in the unbleached softwood kraft pulp (USKP) into preferable thermoplastic materials. The mechanism of reaction and properties of the modified products are analyzed to reach the following objectives:

1) To investigate the effects of parameters of chemical modifications with cyclic carbonates on lignocellulose fibers

2) To optimize the chemical modifications of unbleached softwood kraft pulp with cyclic carbonates

3) To reduce glass transition temperatures (T_g) of lignocellulosic fibers with cyclic carbonates

1.2 FibRe

This work is associated with FibRe, a Vinnova competence center, which is a research consortium between academia (Chalmers University of Technology and KTH Royal Institute of Technology), industry, and public organization partners. The vision is a sustainable society where thermoplastic fossil-based plastics are replaced by lignocellulose-based materials. This thesis is a part of the collaboration between Chalmers University of Technology and Tetra Pak.

2

Background

2.1 Unbleached Softwood Kraft Pulp (USKP)

USKP is lignocellulosic fibers that are produced by kraft cooking of softwood, which is the intermediate procedure of the kraft pulping process. USKP has a higher tensile index than unbleached hardwood kraft pulp (UHKP) because of fiber strength and length characteristics[17]. The largest composition in USKP is cellulose at approximately 65.2-69 % while hemicellulose is about 20-22 % and lignin is about 8.8-13.8 %[18].

2.1.1 Cellulose

Cellulose is the most abundant natural polymer and the major component of softwood (37-43%)[19]. It is a homopolysaccharide of glucose units linked together by β-(1$\rightarrow$ 4) glycosidic bonds. The multiple hydroxyl groups on the glucose from one chain form strong hydrogen bonds with oxygen atoms on the same or on another chain. The chains are packed into crystalline fibers referred to as "microfibrils" that align to form oriented sheets[20]. The fibrils consist of crystalline and amorphous regions. It is found as the lowest reactive composition in lignocellulosic materials[21], but some chemical reactions can be done on the amorphous regions[22], glycosidic bonds, and hydroxyl groups.

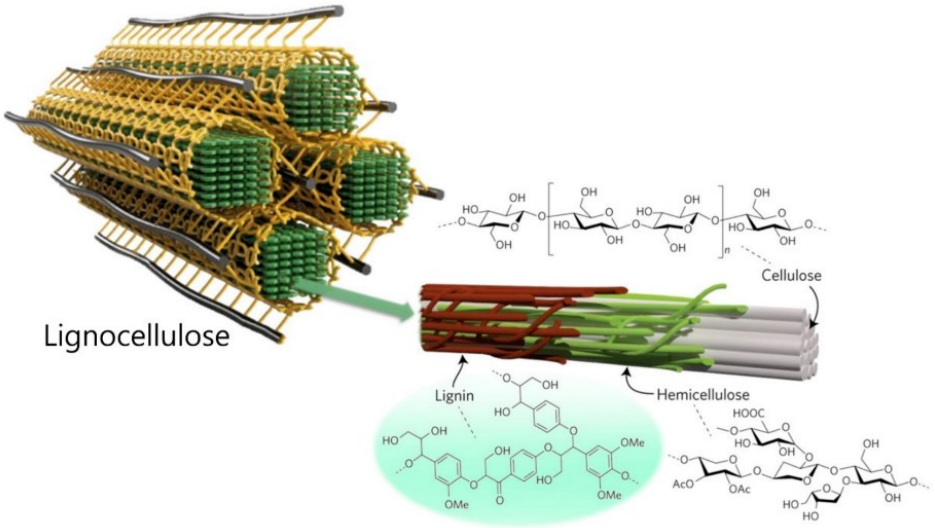


Figure 2.1: Molecular structure of lignocellulose fibers component.(reproduced from Han Young Jung[1])

2.1.2 Hemicellulose

Hemicellulose is a heterogeneous biopolymer composed of several sugars, such as xylose, arabinose, mannose, glucose, and galactose, that are C5 (pentoses) or C6 (hexoses) sugars[23]. The main hemicelluloses in softwood are arabinoglucuronoxylans (5–10%) and galactoglucomannans (20-25%)[24]. Xylans are the backbones of arabinoglucuroxylans and the homopolymer of xylose units linked with β-(1$\rightarrow$ 4)glycosidic bonds while glucuronic and arabinose are substituted side groups. The molar ratio of arabinose/glucuronic acid/xylose is 1:2:8[25]. The backbones of galactoglucomannans are formed by β-(1$\rightarrow$ 4) glycosidic bonds of glucose and mannose units, while galactose is the side group. Typically, overall molar ratios of galactose/glucose/mannose in softwoods are 0.5:1:3.5[25]. Hemicellulose is more reactive and soluble than cellulose. The presence of hemicellulose makes the cell wall of the plant strengthened by interaction with cellulose[26].

2.1.3 Lignin

Lignin is one of the most abundant natural polymers and consists of an aromantic structure[27]. Lignin is an important component of the middle lamella in the plant cell wall. The molecular structure of lignin is a randomly branched polyphenol that is composed of substituted phenyl rings and phenolic and aliphatic hydroxyl groups with numerous hydrogen bondings between hydroxyl groups and various ether oxygens and carboxylic acid groups[3][28]. Lignin monomeric composition varies widely among species. Hardwoods have a mixture of guaiacyl (G) and syringyl (S) units and a minor amount of p-hydroxyphenyl (H)-units, while softwoods are predominantly composed of (G)-units (around 90 %) with small quantities of p-hydroxyphenyl (H)-units[29]. Softwood lignin has higher cross-linked than hardwood lignin[30]. The different structures of lignins make (T_g) softwood kraft lignin higher than hardwood kraft lignin[31]. The appearance of lignin in the pulp contributes to the longitudinal Young's modulus of the fiber, so the unbleached pulp has a higher tensile index and superiority for use as stiffening reinforcement than bleached pulp [32][33].

2.2 Thermoplastics from lignocellulose

Thermoplastics are a class of polymeric materials that can be softened and melted by the application of heat and solidified after cooling. The general thermoplastic production processes are injection, molding, extrusion, blow molding, and thermoforming[34]. As a polymer, thermoplastics exhibit the glass transition temperature (T_g) defined as the temperature at or above which the molecular structure shows macromolecular mobility[35]. So, thermoplastics must be processed above this temperature.

The lignocellulosic materials are composite materials composed of cellulose, hemicelluloses, and lignin. The lignin coils hemicelluloses and cellulose and forms a rigid three-dimensional network that affects the thermoplasticity of the fibers because of the poor mobility of polymer chains[36]. Moreover, cellulose has massive intramolecular and intermolecular hydrogen bonds that make the wood fibers have melting points (T_m) and T_g higher than its decomposition temperature[3]. Therefore, unmodified wood fibers cannot be melt-processed directly through conventional extrusion or molding processing methods[37].

To increase the applications of lignocellulosic materials for thermoplastics, the chemical modifications of the hydroxyl groups within their components can intervene with hydrogen bonding and introduce side groups. These chemical reactions benefit their chain mobility and yield more thermoplasticity of lignocellulosic materials. Biomass from forestry and agricultural residues is etherified on its hydroxyl groups by propylene oxide (oxypropylation) and converted into viscous polyols that have the potential to be further processed to polyurethanes[38]. Meanwhile, the mixture of trifluoroacetic acid (TFA) and propionic anhydride reacts via esterification with hydroxyl groups of the wood and produce a product that exhibits thermoplasticity and good fluidity[39]. The disadvantages of these two modifications are the safety and environmental issues of the reactants. PO is an extremely flammable compound

with low vapor pressure and a carcinogenic effect[40]. TFA is a persistent chemical and hazardous to aquatic life. Meanwhile, propionic anhydride is a toxic, corrosive, flammable, reactive, and unstable compound that requires special handling conditions[41].

2.3 Cyclic carbonates

Cyclic carbonates are organic compounds with a carbonate ester functional group. They have a great industrial interest due to their versatility in being used as reagents, solvents, diluents, and monomers for polymers[42]. The most attractive process for cyclic carbonates is the reaction between carbon dioxide (CO_2) and epoxides. In this process, a greenhouse gas (CO_2) is converted into useful chemical products with 100% atom efficiency as the following reaction(2.1).

$$R - CHCH_2O + CO_2 \rightarrow R - CHCH_2O_2CO \tag{2.1}$$

Another advantage of this reaction is thermodynamically favorable as a result of the high free energy of epoxides, which counterbalances the high thermodynamic stability of CO_2. Therefore, this process corresponds to the context of green chemistry as its atom economy and utilizes a renewable and widely available feedstock as CO_2[43] and becomes one of the most promising routes for carbon capture and utilization (CCU)[44].

The main drawback of this process is epoxides. The pervasive epoxides for the reaction with CO_2 are propylene oxide (PO) and ethylene oxide (EO), which are extremely flammable, volatile, and produced from non-renewable petroleum feedstock[43]. The reaction between EO and CO_2 produces EC, while PO reacts with CO_2 to form PC. Compared to their raw materials, EC and PC have higher boiling points and lower vapor pressures. They also have lower flammability from their higher flash points that are illustrated in table 2.1. Therefore, they are safer chemicals than their raw materials.

Table 2.1: Physical properties of EO, EC, PO, and EC

Chemicals	EO	EC	PO	PC
Appearence	Colorless gas	Colorless solid	Colorless liquid	Colorless liquid
Melting point (°C)	-112.5	34 to 38	-111.9	-48.8
Boiling point (°C)	10	248	34.23	241.6
Vapor pressure (mmHg)	1109.6 (20 °C)	0.0098 (25 °C)	445 (20 °C)	0.045 (25 °C)
Flash point(°C)	20	150	37	132

Additionally, PC is considered a green solvent due to its low viscosity, non-corrosive, colorless, and odorless solvent[45][46]. In the environmental aspects, PC is biodegradable in air and in water, where it slowly decomposes to low toxicity products such as propylene glycol and carbon dioxide[47]. EC has similar properties to PC, but it is a solid at room temperature, so it is less suitable to be used as a solvent[48].

2.4 Chemical modification of lignocellulose with cyclic carbonates

Cyclic carbonates are advantageous chemicals for the chemical modification of lignocellulosic-derived feedstock. Liu et al.[49] used EC to serve as both the reagent and the solvent in the chemical reaction with lignin. The main reaction is oxyalkylation on aliphatic and phenolic hydroxyl groups of its composition and creates longer side chains that are called grafting. Cellulose and hemicellulose consist of considerable aliphatic hydroxyl groups in their structure. In the case of lignin, it has both aliphatic and phenolic hydroxyl groups, but the appeared carboxylic acid in its structure from kraft cooking can also be alkylated by cyclic carbonates[27][50]. The carboxylic groups have the highest acidity compared to aliphatic and phenolic hydroxyl groups. Meanwhile, phenolic hydroxyl groups are more acidic than aliphatic hydroxyl groups because the phenyl ring is an electron-withdrawing group and increases deprotonation.



Figure 2.2: Molecular structure of EC (Left) and PC (Right)

Cyclic carbonates have two electrophilic sites: one carbonyl carbon atom (C=O) and two alkyl carbon atoms (C−C). The alkyl carbon atoms of cyclic carbonate alkylate phenols or carboxylic acids simultaneously release CO_2 (Scheme a) while carbonyl carbon atom reacts transesterification with aliphatic hydroxyl groups and forms the carbonate linkages (Scheme b)[27]. Two reactions pathways are illustrated in Figure 2.3. The electrophilicity of alkyl carbon atoms depends on the substituted group on the carbon atom. The methyl ($-CH_3$) group in PC is a stronger electron-donating substituent than hydrogen (−H) in EC. Consequently, EC has stronger electrophilic sites and becomes more reactive than PC.

Duval and Avérous[9] verified the reactivity of EC and PC by etherifying soda lignin at the same temperature(150 °C) under solvent-free conditions with K_2CO_3 catalyst. They found that EC provided a higher mass of the final product at a shorter reaction time than PC. Kühnel et al[27] also studied the degree of substitution (DS) of oxyalkylation of various lignin sources. Their cyclic carbonates were EC, PC, BC (Butylene Carbonate), and GC (Glycerol Carbonate). Although they raised the temperature to 170 °C and changed the catalyst to DBU, EC still delivered the highest DS.

Akil et al[15]. studied the reaction between PC in dimethyl sulfoxide (DMSO) and xylan (majority aliphatic hydroxyl compound) from oat spelt and beech wood. The reaction was operated at 140 °C and 160 °C with DBU catalyst, while the reaction times were 40, 80, 160, and 240 minutes. They found that higher temperatures and longer reaction times can increase the amount of substituted xylans. However, a higher temperature can induce DMSO degradation[51].

Kühnel et al.[13] varied the amount of PC and catalysts for oxyalkylation of lignin. The higher amount of PC can raise the substituted OH groups, but it can dilute catalyst concentration, slightly decreasing the DS value. Their investigations also included the comparison between DBU and K_2CO_3. DBU contributed higher conversion rates of the hydroxyl groups, longer grafted chains, and diminished crosslinking reactions, but it is a more harmful chemical for humans and long-term aquatic hazards[52].

Chamú-Muñoz et al.[11] studied chemical modification with EC on corncob that consists of cellulose, hemicellulose, and lignin. In the liquid phase reaction under ambient pressure, they discovered that temperature at 190 °C offered the highest gained weight, but extending the reaction time from 80 min to 120 min does not create significantly gained weight of modified lignocellulose materials.

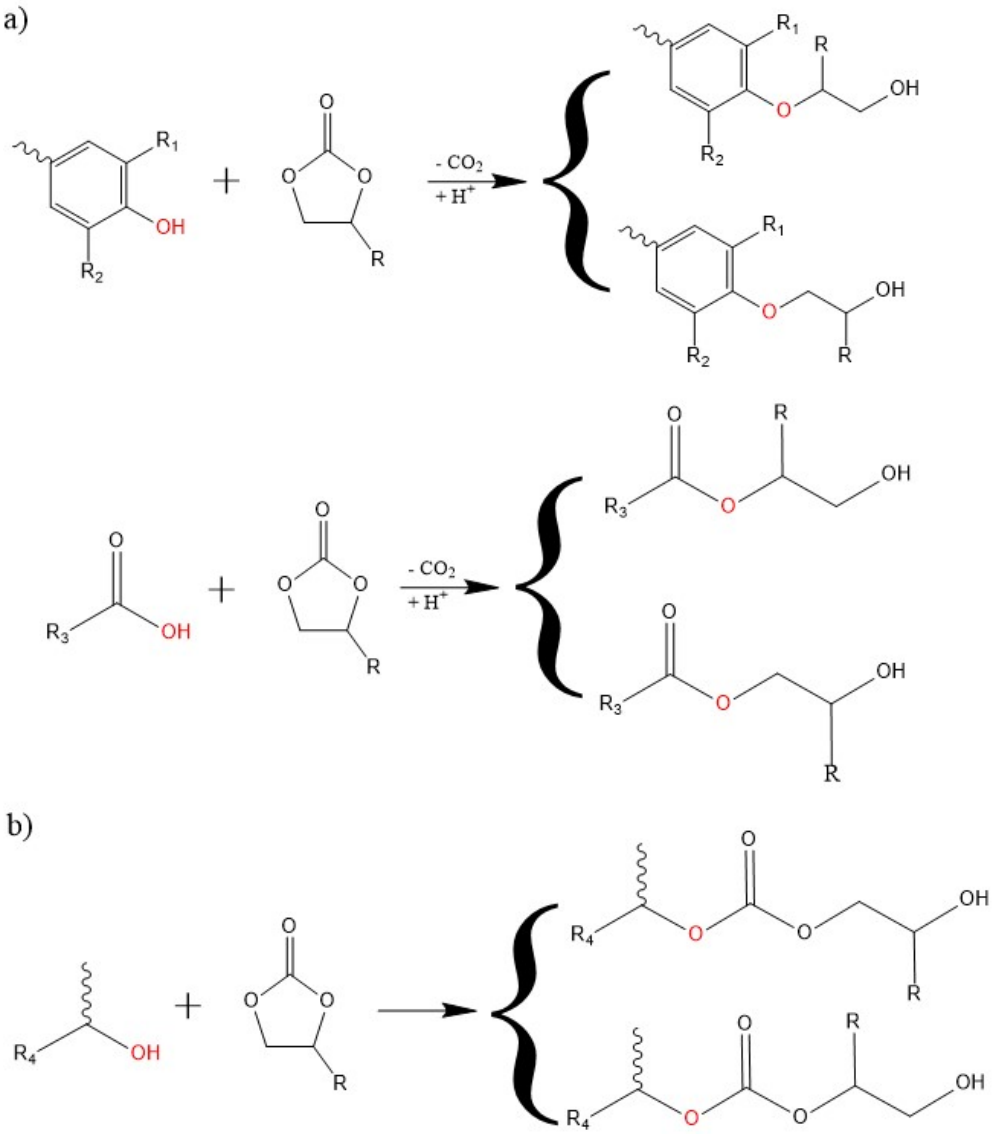


Figure 2.3: Reaction pathways between cyclic carbonate and functional groups in lignocellulose

3

Methods

3.1 Raw Materials

Never-dried unbleached softwood kraft pulp was freeze-dried. At laboratory condition, the moisture content in the pulp is 3.3%, determined by the difference between the weight of the pulp before and after drying in the oven at 70 °C for 24 h. The temperature and time for drying were verified by a stable weight of the dried pulp after 20 h, 22 h, and 24 h of drying. 1 g of pulp was identified components by composition analysis at the Competence Center FibRe. The total lignin was 13% or 130 mg from TAPPI T222 and TAPPI UM 250. The total monosaccharides were 83.7% (1.1%, 0.8%, 68.1%, 8.1%, and 5.6% for arabinose, galactose, glucose, xylose, and mannose, respectively) from SCAN CM-71:09. Xylans in softwood are arabinoxylans [24] so 1.1% of arabinose and 8.1% of xylose were assumed as the component that made the total content of xylans became 92 mg. The overall molar ratios of galactose/glucose/mannose in galactoglucomannans of softwoods are 0.5:1:3.5 [25]. They are isomers and have the same molecular weight (180 g/mol), so the contents of these three sugars in galactoglucomannans of the sample are 8 mg, 16 mg, and 56 mg, respectively. Consequently, 665 g of excess glucose was assumed as cellulose, and total hemicelluloses became 172 mg (80 mg of galactoglucomannans and 92 mg of xylans).

The contents of the reactive groups in cellulose and hemicellulose were estimated as their hydroxyl groups. The hydroxyl groups of hemicellulose were evaluated based on their composition structures (2 mol $-$OH per mol pentoses and 3 mol $-$OH per mol hexoses). The reactive groups of cellulose were considered accessible hydroxyl groups, which depend on the origin of the cellulose as well as on what types of treatments have been applied. The studies about the accessibility of the hydroxyl groups in USKP are limited, so this study used 11 $\times 10^{-3}$ mol/g accessible OH group content of cellulose similar as in BSKP [53]. The reactive groups in lignin were analyzed ^{31}P-NMR. As a result, the total content of the reactive groups was 10.92 $\times 10^{-3}$ mol/g (1.04 $\times 10^{-3}$ mol/g from lignin, 2.56 $\times 10^{-3}$ mol/g from hemicelluloses, and 7.32 $\times 10^{-3}$ mol/g from cellulose). The detail of calculations of total reactive groups in cellulose and hemicellulose can be seen in the Appendix 1.

3.2 Chemicals

PC (Propylene Carbonate, 4-methyl-1,3-dioxolan-2-one), EC (Ethylene Carbonate, 1,3-Dioxolan-2-one), DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene), and Potassium Carbonate (K_2CO_3) were 99% purity and purchased from Sigma-Aldrich, Germany. PC and EC represent cyclic carbonates in this study. Acetone (CH_3COCH_3) was an analytical reagent grade and 99.8% purity from Fisher Scientific, Finland. All chemicals were used without further purification.

3.3 Chemical Modifications of Unbleached Softwood Kraft Pulp

1 g of freeze dried USKP was pulled into smaller bits with tweezers that were more convenient for chemical reactions. The minimized size USKP was added to a round-bottom flask that connected to the condenser and flushed with nitrogen gas to disperse oxygen gas. 50 g of cyclic carbonates and catalysts were added to react with USKP in the flask. Then, the magnetic static mixer was put in the mixture. The flask was immersed in a silicone oil bath that was on Heidolph MR Hei-Tec magnetic stirrer. The target temperatures of the reaction were set and measured by a thermocouple.

The chemical modifications with PC and K_2CO_3 were used as the fundamental experiments to investigate the influence of temperature, amount of catalyst, and reaction time. The temperatures for the chemical reactions were selected at 150 and 180 °C while the amount of catalyst was 0.125 g and 0.625 g. The reaction time was 2 h. The condition that produced the highest weight of modified unbleached softwood kraft pulps (MUSKP) was done at 1 and 4 h.

The influences of reactant (EC) and catalyst (DBU) were investigated by the chemical reactions at the same temperatures, amount of catalysts, and reaction times. The consideration of yields and Green Chemistry were applied in this investigation.

3.4 Modified Unbleached Softwood Kraft Pulp (MUSKP) Seperarations

After reaching the reaction times, the reaction flask was cooled by distilled water to room temperature. The samples were collected from a round-bottom flask for vacuum filtration. The filter paper was put in the Buchner funnel that was installed on the vacuum flask. MUSKP was washed with distilled water, while the excess cyclic carbonates and soluble compositions were effluent and flowed through the filter paper. The washing was done until the effluence became colorless and had a pH of 7. The washed MUSKP was on the filter paper and kept on the watch glass for drying. The drying was operated by the oven at 70 °C for 24 h. After that, MUSKP was undergone characterization to evaluate the results of chemical modification with cyclic carbonates.

3.5 Characterization

3.5.1 Yields

The yields of the chemical modification of USKP with cyclic carbonate were calculated from the weights of MUSKP. The equation was applied from Duval and Avérous[9] and displayed below.

$$Yield(\%) = 100 \times \frac{m_f}{m_i(1 + \Delta M_{graft}[OH + COOH])} \tag{3.1}$$

m_f and m_i are the mass of dried MUSKP and USKP, respectively. ΔM_{graft} is the molar mass from the grafted chemical group which EC is 44 g/mol, and PC is 58 g/mol. [OH + COOH] is the total content of the reactive group in USKP, which is 10.92×10^{-3} mol/g.

3.5.2 Attenuated total reflectance-Fourier infrared Spectrometry (ATR-FTIR)

ATR-FTIR was performed to identify the changes in the chemical structure of USKP and MUSKP by measuring the aborbance. It is a Perkin Elmer Frontier FT-IR Spectrometer equipped with a diamond GaldiATR attenuated total reflectance (ATR) from Pike Technologies. The samples were placed directly on the ATR crystal without further preparation. The spectra were recorded between 4000 and 400 cm^{-1}, with 32 scans being collected with a resolution of 4 cm^{-1} at intervals of 1 cm^{-1}. 5 samples from each modification were replicated in analysis that generated 5 curves. After that, they were averaged and baseline subtraction was applied. Lastly, the peak of aromantic stretching (1509 cm^{-1}) that does not change during the chemical reaction was used to normalize the spectra.

3.5.3 Soxhlet Extractions

MUSKP, from the conditions which provided a proper yield of chemical modification with cyclic carbonates, was selected to purify with Soxhlet extractions. Acetone was used as a solvent for Soxhlet extraction of grafted sawdust by EC[12]. It was used to extract other organic compounds and has preferred properties because not too toxic and difficult to handle[54].

0.5 g of MUSKP was kept in the thimble and placed into an extractor. Acetone was loaded into a round-bottom flask that was under the extractor and in a water bath that was heated to evaporate the solvent. The evaporated solvent flowed into a condenser on top of the extractor, condensed into a liquid, and then flowed down to contact with MUSKP in the thimble. All extractions were run for 2 h, which resulted in 16 cycles or 8 cycles/h of acetone refluxing rate. This refluxing rate was applied to remove extractives from a fresh, softwood spruce thermomechanical pulp (TMP) by Soxhlet extractions[55]. After that, the thimble with MUSKP was taken out from the extractor to the oven to evaporate an excess solvent at 70 °C for 24 h. Then MUSKP from the extraction was weighed to identify % extracted yields from the equation 3.2.

$$\%Extracted\ Yields = 100 \times \frac{m_{a,ext}}{m_{b,ext}} \tag{3.2}$$

Where $m_{a,ext}$ and $m_{b,ext}$ represent the weight of MUSKP after and before the extraction, respectively. The % extracted yields were used to calculate the corrective weight of MUSKP by the equation 3.3

$$Corrective\ Weight(g) = \%Extracted\ Yields \times \frac{Weight_{MUSKP}}{100} \tag{3.3}$$

MUSKP from the extractions was characterized by ATR-FITR again to examine the chemical composition and compared to MUSKP before extraction.

3.5.4 Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of USKP and MUSKP were measured on DMA Q800 analyzer. 100 mg of samples were performed to analyzed with frequency at 1 Hz while heating and cooling rates were 3°C/min between 50 - 240 °C. The graph of relationship between min-max (0-1) normalized modulus and temperature was displayed. The glass transition temperatures (T_g) of the samples were taken at the point which the slope changed.

4

Results and Discussion

4.1 Comparison of the Conditions of Chemical Modifications of USKP with Cyclic Carbonates

The yields (calculated by equation 3.1) of conditions of chemical modifications varied from experiments 1 to 16 are discussed in this section. The parameters are reactants, catalysts, amounts of catalyst, temperatures, and reaction times. The complete experiments and results are displayed in the table 4.1.

Table 4.1: Condition Parameters and Results of Chemical Modifications

Experiments	Reactants		Catalysts		Temperatures (°C)	Reaction Times (h)	MUSKP Weights (g)	%Yields
	Names	Amount(g)	Names	Amount(g)				
1	PC	50	K_2CO_3	0.125	150	2	0.89	56
2	PC	50	K_2CO_3	0.125	180	2	1.04	66
3	PC	50	K_2CO_3	0.625	150	2	0.92	58
4	PC	50	K_2CO_3	0.625	180	2	1.14	72
5	PC	50	K_2CO_3	0.625	180	1	1.10	70
6	PC	50	K_2CO_3	0.625	180	4	2.02	128
7	PC	50	DBU	0.125	150	2	1.01	64
8	PC	50	DBU	0.125	180	2	2.88	182
9	PC	50	DBU	0.625	150	2	1.04	66
10	PC	50	DBU	0.625	180	2	2.50	159
11	EC	50	K_2CO_3	0.125	150	2	1.27	89
12	EC	50	K_2CO_3	0.125	180	2	2.34	163
13	EC	50	K_2CO_3	0.625	180	2	3.06	214
14	EC	50	K_2CO_3	0.375	180	2	2.78	194
15	EC	50	K_2CO_3	0.625	180	1	2.53	177
16	EC	50	K_2CO_3	0.625	180	4	3.15	220

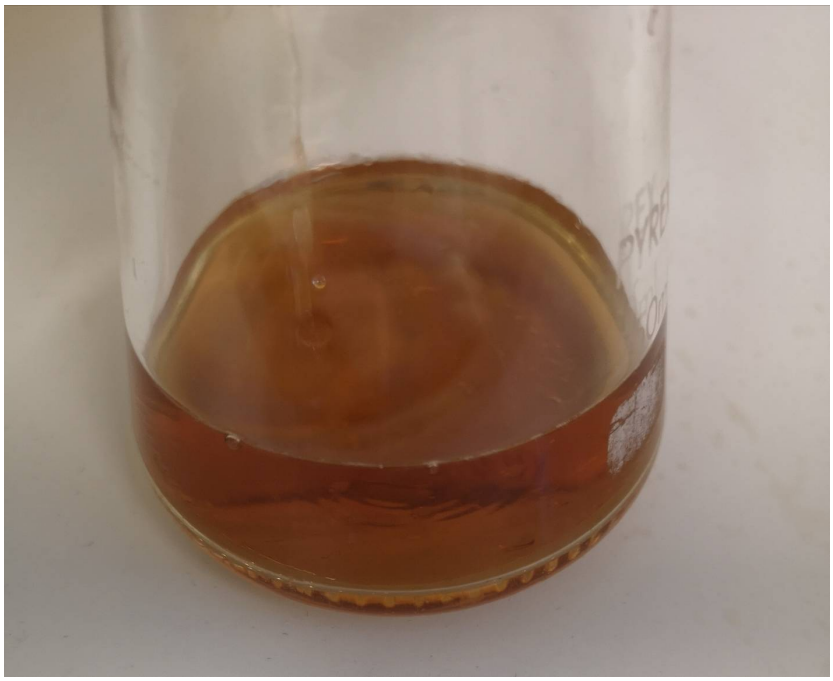


Figure 4.1: Brown effluent

All chemical reactions between MUSKP and cyclic carbonates produced the brown effluent that separated from the MUSKP by washing during the filtration, displayed in figure 4.1. Therefore, we can interpret that there are decompositions of some components in the pulps, which can be analyzed in future investigations.

4.1.1 Chemical Modification with PC and K_2CO_3

To evaluate the influence of temperature and amount of catalyst, experiment 1 (150 °C and 0.125 g of K_2CO_3) was defined as the reference condition. Experiment 2 (180 °C and 0.125 g of K_2CO_3) was used to consider the influence of temperature, while experiment 3 (150 °C and 0.625 g of K_2CO_3) was run to assess the impact of catalyst concentration. The combination of the influence of temperature and the amount of catalyst is seen in experiment 4 (180 °C and 0.625 g of K_2CO_3). All four experiments were done with the same reaction time at 2 h.

It is obvious that temperature increases the weight and yield of MUSKP. At the same amount of catalyst, the chemical modifications with PC at 180 °C offer higher weight and yield of MUSKP compared to the operations at 150 °C. The amount of catalyst rises the weight and yield of MUSKP, but at a lower temperature (150 °C), the higher amount of catalyst produced MUSKP at 0.92 g is a slightly higher weight than the product from a lower amount of catalyst condition (0.89 g). Thereby, at 150 °C, the concentration of K_2CO_3 has a minor effect on the yields of chemical modification of USKP with PC. Meanwhile, at a higher temperature (180 °C), the higher amount of K_2CO_3 increases the weight of MUSKP from 1.04 g to 1.14 g. The lower weight of MUSKP than USKP in experiments 1 and 3, along with the brown effluent from filtration, indicates that both conditions have more decomposition of lignocellulosic components than oxyalkylation.

Since the chemical modification at 180 °C and 0.625 g of K_2CO_3 produced the highest yield, this condition was changed the reaction time from 2 h to 1 h (experiment 5) and 4 h (experiment 6). The weight of MUSKP from 1 h of a chemical reaction is 1.10 g, slightly lower than 2 h (1.14 g). However, the reaction time at 4 h provides a considerably higher weight of MUSKP at 2.02 g.

4.1.2 Chemical Modification with PC and DBU

The influence of the catalyst was tested by replacing K_2CO_3 with DBU for the chemical modification with PC, and the weight of MUSKP was measured. The approach for the experiment is the same as the chemical modification with PC and K_2CO_3, and the reaction time is 2 h for all experiments. Experiment 7 was the basis of chemical modification with PC and DBU. The temperature and amount of catalyst are low (150 °C and 0.125 g). This condition produced MUSKP at the weight of 1.01 g, which is a higher weight than MUSKP from the chemical modification with PC and K_2CO_3 at the same temperature and amount of catalyst.

The impact of temperature was studied in experiment 8. Increasing the temperature from 150 to 180 °C provides a highly higher weight of MUSKP at 2.88 g. Meanwhile, increasing the amount of DBU (experiment 9) from 0.125 g to 0.625 g at the temperature of 150 °C offered a product at 1.04 g. Consequently, the amount of DBU has a minor effect on the chemical modification of USKP with PC at the temperature of 150 °C which is similar to the chemical modification with PC and K_2CO_3.

In contrast, the combination of higher temperature and amount of DBU (180 °C and 0.625 g) in experiment 10 produced MUSKP at 2.5 g, which is lower than MUSKP from experiment 8. It can be predicted that there are more decompositions from alkaline hydrolysis. At high temperatures, only dilute basic compounds can stimulate the partial separation of the cellulose fibers from the cell wall[56]. Alkaline hydrolysis can reduce the degree of polymerization and crystallinity while structural linkages between lignin and carbohydrates are separated[57]. As a result, the weight of the product becomes lower because of the decomposition of its components.

The separation of MUSKP from the chemical modification with PC and DBU is more difficult than the chemical modification with PC and K_2CO_3 because DBU has a lower solubility in water, so it consumes a higher amount of water for washing.

4.1.3 Chemical Modification with EC and K_2CO_3

In the aspect of reactants, EC was applied in the investigation to compare with the result from the chemical modification with PC. K_2CO_3 was selected to be the catalyst in this chemical modification because of lower environmental impacts and more convenient separation of the product. The approach for the experiment is the same as the chemical modification with PC and K_2CO_3, but the experiment for investigating the influence of the amount of catalyst at 150 °C was excluded from the study because it has a minor effect on the weight of MUSKP, which found in the chemical modification with PC and both two catalysts (K_2CO_3 and DBU). Experiment 11 was the basis of chemical modification with EC and K_2CO_3. The temperature, amount of catalyst, and reaction time are 150 °C, 0.125 g, and 2h, respectively. This condition produced MUSKP at the weight of 1.27 g, which is a higher weight than MUSKP from the chemical modification with PC and K_2CO_3, and PC and DBU at the same temperature, amount of catalyst, and reaction time.

The effect of temperature on the chemical modification with EC is considered in experiment 12 which the temperature is risen to 180 °C while the amount of K_2CO_3 and reaction time are constant. The weight of MUSKP is 2.34 g which is higher than the weight of MUSKP from the chemical modification with PC and K_2CO_3 but is lower than the chemical modification with PC and DBU at the same condition and reaction time.

The combination of the influence of the temperature and amount of catalyst was examined in experiment 13. The temperature is 180 °C and the amount of K_2CO_3 is 0.625 g, while the reaction time is still constant. The weight of MUSKP is 3.06 which is the highest among the chemical modifications of USKP with cyclic carbonates at the reaction time of 2 h. Therefore, it is interesting to run the chemical modification with the intermediate amount of K_2CO_3 at the temperature of 180 °C (experiment 14) that produced MUSKP at 2.78 g. The reletionship between the amount K_2CO_3 weight of MUSKP from the chemical modifications with PC at 180 °C is displayed in figure 4.2.

As the highest weight of MUSKP is produced from experiment 13, the condition was varied its reaction time from 2 h to 1 h (experiment 15) and 4 h (experiment 16). The weight of MUSKP from 1 h of a chemical reaction is 2.53 g which is lower than 2 h. However, the reaction time at 4 h provides a slightly higher weight of MUSKP at 3.15 g.

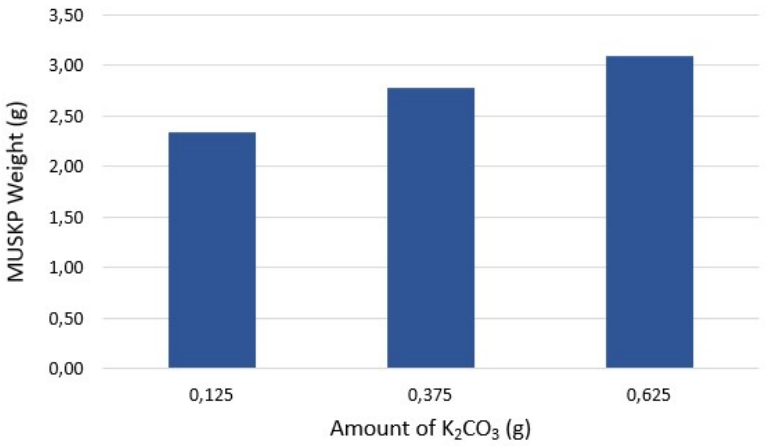


Figure 4.2: Relationship between the amount K_2CO_3 and the weight of MUSKP from the chemical modifications with EC at 180 °C

4.2 Influence of Parameters on Chemical Structure of MUSKP

The parameters of the conditions of chemical modification varied from experiments 1 to 16. The products of the chemical modifications are MUSKP, and analyzed their chemical structure by ATR-FTIR. The absorbance at the wavenumber 3550 - 3200, 3000 - 2840, and 1760 - 1740 cm^{-1} that represents hydroxyl (O−H), alkyl (C−H), and carbonyl (C=O) groups, respectively. The peaks of hydroxyl groups indicate the aliphatic and phenolic hydroxyl groups that can create the hydrogen bonds between the polymeric chains in the samples. In the meantime, the signals of alkyl and carbonyl groups present the level of substitutions on the original hydroxyl groups in USKP. Therefore, the samples which are expected to have lower T_g than USKP having better signals of alkyl and carbonyl groups and lower peaks of hydroxyl groups.

4.2.1 Chemical Structure of MUSKP from Chemical Modifications with PC and K_2CO_3

The samples from the chemical modifications with PC and K_2CO_3 in experiment 1,2,4,5 and 6 were selected to be analyzed. The curves of absorbance of all MUSKP samples are illustrated in figure 4.3.

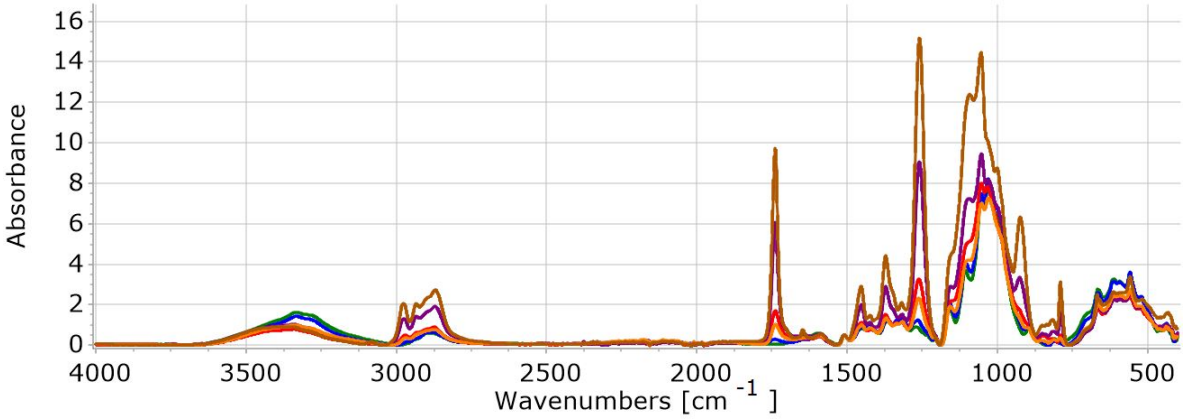


Figure 4.3: MUSKP from the chemical modifications with PC and K_2CO_3, USKP (green), MUSKP 150°C, 0.125 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (red), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (purple), MUSKP 180°C, 0.625 g K_2CO_3, and 1 h (orange), MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (brown)

From the figure 4.3, the green line represents the curve of USKP that has the strongest signal of the hydroxyl group (3550 - 3200 cm^{-1}) and, the lowest signal of alkyl (3000 - 2840 cm^{-1}) and carbonyl (1760 - 1740 cm^{-1}) groups. The chemical modification at 150 °C and 0.125 g of K_2CO_3 (blue line) has minor effects on the chemical structure because the signal of the hydroxyl groups is slightly lower than USKP, while the signal of alkyl and carbonyl groups are very little difference when compared to the raw material. The signal of alkyl and carbonyl groups is stronger when the chemical modifications operate at 180 °C and the amount of K_2CO_3 at 0.625 g (purple line). In this curve, the signal of hydroxyl groups is considerably lower than USKP. The peaks of alkyl and carbonyl groups increase when the reaction time is extended to 4 h (brown line). Decreasing reaction time (orange line) to 1 h and amount of K_2CO_3 to 0.125 g (red line) is negative to chemical modification. The peaks of alkyl and carbonyl groups are almost similar to the chemical modification at 150 °C and 0.125 g of K_2CO_3.

4.2.2 Chemical Structure of MUSKP from Chemical Modifications with PC and DBU

The samples from the chemical modifications with PC and DBU in experiment 8 and 10 were selected to be analyzed. The curve of the sample from the chemical modifications with PC and K_2CO_3 at 180 °C and 0.625 g of K_2CO_3 (experiment 4) is included for comparison. The reaction time of these three experiment was 2 h. The curves of absorbance of all MUSKP samples are illustrated in figure 4.4 .

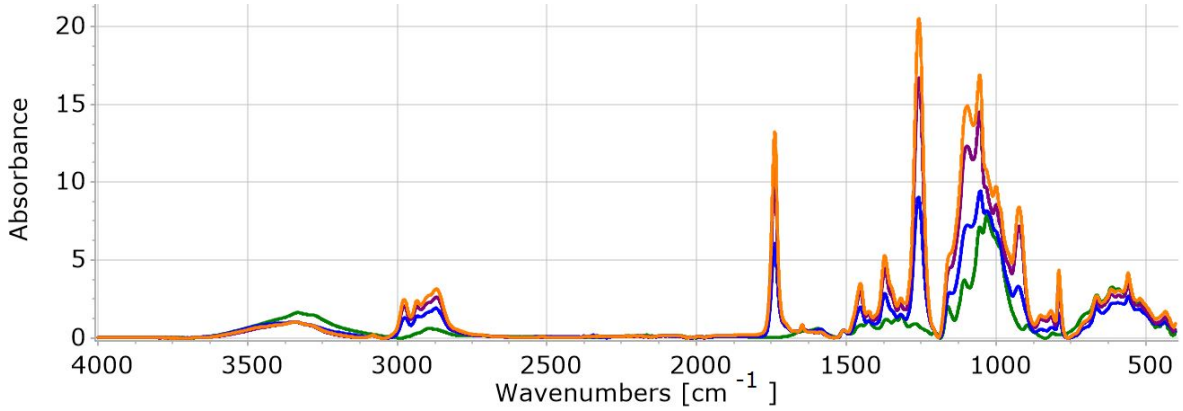


Figure 4.4: MUSKP from the chemical modifications with PC and DBU, USKP (green), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.125 g DBU, and 2 h (orange), MUSKP 180°C, 0.625 g DBU, and 2 h (purple)

From figure 4.4, the green line represents the curve of USKP like the previous figure. The peaks of the hydroxyl groups (3550 - 3200 cm^{-1}) of all three samples are almost similar and lower than the green line. The signal of alkyl groups of MUSKP from the chemical modification with PC at 180 °C and 0.125 g of DBU (orange line) is slightly higher than MUSKP from the chemical modification with PC at 180 °C and 0.625 g of DBU (purple line) but clearly higher than MUSKP from the chemical modification with PC at 180 °C and 0.625 g of K_2CO_3 (blue line). The obvious difference of peaks can be seen in the range of carbonyl groups (1760 - 1740 cm^{-1}), in which the sample from the chemical modification with PC at 180 °C and 0.125 g (orange line) is clearly higher than purple and blue lines.

4.2.3 Chemical Structure of MUSKP from Chemical Modifications with EC and K_2CO_3

The samples from the chemical modifications with EC and K_2CO_3 in experiment 12 and 13 were selected to be analyzed. The curves of two samples from the chemical modifications with PC and DBU at 180 °C (experiment 8 and 10) are included for comparison. The reaction time of these four experiment was 2 h. The curves of absorbance of all MUSKP samples are illustrated in figure 4.5.

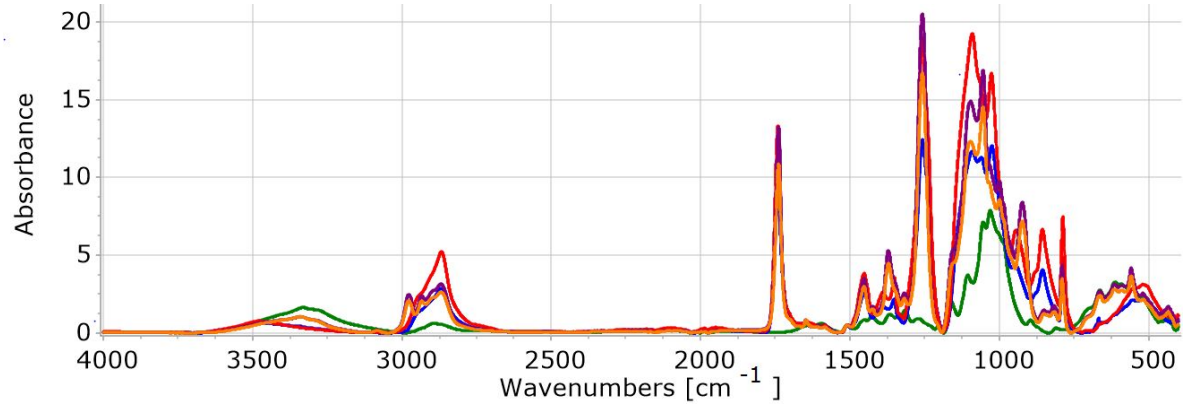


Figure 4.5: MUSKP from the chemical modifications with EC and K_2CO_3, USKP (green), MUSKP 180°C, 0.125 g DBU, and 2 h (purple), MUSKP 180°C, 0.625 g DBU, and 2 h (orange), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red)

From the figure 4.5, the green line represents the curve of USKP like the previous figure. The chemical modification with EC at 180 °C and 0.125 g of K_2CO_3 (blue line) has the peak of hydroxyl groups (3550 - 3200 cm^{-1}) at different positions from two samples from the chemical modification with PC and DBU(orange and purple lines). The peaks of the alkyl groups (1760 - 1740 cm^{-1}) are at almost the same absorbance. The curve of MUSKP from the chemical modification with EC at 180 °C and 0.625 g of K_2CO_3 (red line) has the same signal of the hydroxyl group as the blue line. However, the peak of the alkyl groups is obviously higher than the other three lines. It has a different shape from the orange and purple lines, which are the products of the chemical modification with PC because EC does not introduce the methyl group ($-CH_3$) to USKP. Therefore, the application of EC with a higher temperature and amount of K_2CO_3 is the most efficient condition to introduce the alkyl side groups to USKP. The process is also more eco-friendly because it does not require DBU, which negatively impacts the environment.

4.3 Corrective Weights of MUSKP

Since the conditions in all experiments were at a high temperature and in presence of Lewis bases. They are possible for the ring-opening polymerization of a five-membered cyclic monomer, which is the side reaction of PC and EC[58][59]. The contaminants from the side reaction can cover the surface of MUSKP and make the weight of MUSKP become wrong. Therefore, the main purpose of the two previous sections is to identify the conditions that produce MUSKP with the proper weights and chemical structure. After that, those samples were taken to Soxhlet extractions to evaluate the corrective weights. From table 4.1, the samples of MUSKP from experiments 4, 6, 8, 10, 12, and 13 were tested for their corrective weights by the Soxhlet extraction because they have appropriate weights and signals of substituted groups (alkyl and carbonyl groups). USKP was used as the reference in this investigation, and the results are reported in the table 4.2. The extracted yields are the ratios between the mass of MUSKP after and before extractions which are calculated from 3.2. After that, the extracted yields are used to estimate the corrective weight of MUSKP, according to 3.3.

Table 4.2: Condition Parameters and Corrective Weights of the Modified Pulps

Samples	Reactants		Catalysts		Temperatures (°C)	Reaction Times (h)	% Extracted Yields	Corrective Weight (g)
	Name	Amount(g)	Name	Amount(g)				
USKP	-	-	-	-	-	-	99	0.99
MUSKP	PC	50	K_2CO_3	0.625	180	2	66	0.76
MUSKP	PC	50	K_2CO_3	0.625	180	4	70	1.42
MUSKP	PC	50	DBU	0.125	180	2	54	1.54
MUSKP	PC	50	DBU	0.625	180	2	66	1.66
MUSKP	EC	50	K_2CO_3	0.125	180	2	105	2.46
MUSKP	EC	50	K_2CO_3	0.625	180	2	104	3.22

The reference sample, USKP, has extracted yields at 99%, so before and after, the extracted sample has almost the same weight.

MUSKP from the chemical modification with PC and K_2CO_3 at 180 °C with 2 h of reaction time (experiment 4) has extracted yield at 66% so its corrective weight reduces from 1.14 to 0.76 g. Meanwhile, when the reaction time is extended to 4 h, the extracted yield is 70% that, making the corrective weight of MUSKP from the chemical modification with PC and K_2CO_3 at 180 °C with 4 h of reaction time (experiment 6) to become 1.42 g from its initial weight at 2.02 g. Although increasing reaction time provides higher extracted yield, the chemical structures of the two samples that are characterized by ATR-FITR (figure 4.6) are almost similar. The curve of the extracted sample from the chemical modification at 2 h (red line) and 4 h (orange line) are difficult to distinguish. Both samples also have similar peaks of hydroxyl groups (3550 - 3200 cm^{-1}), but lower signals of alkyl (3000 - 2840 cm^{-1}) and carbonyl (1760 - 1740 cm^{-1}) groups compared to their MUSKP before extractions (blue and purple lines). According to the lower weight of MUSKP and signals of substituted groups (alkyl and carbonyl groups), it indicates that there are contaminants from the side reaction that consists of alkyl and carbonyl groups covering the surface of MUSKP. They cause the incorrect weight of MUSKP before Soxhlet extractions because they cannot be separated by water which is applied in the separation but can be removed by organic solvents.

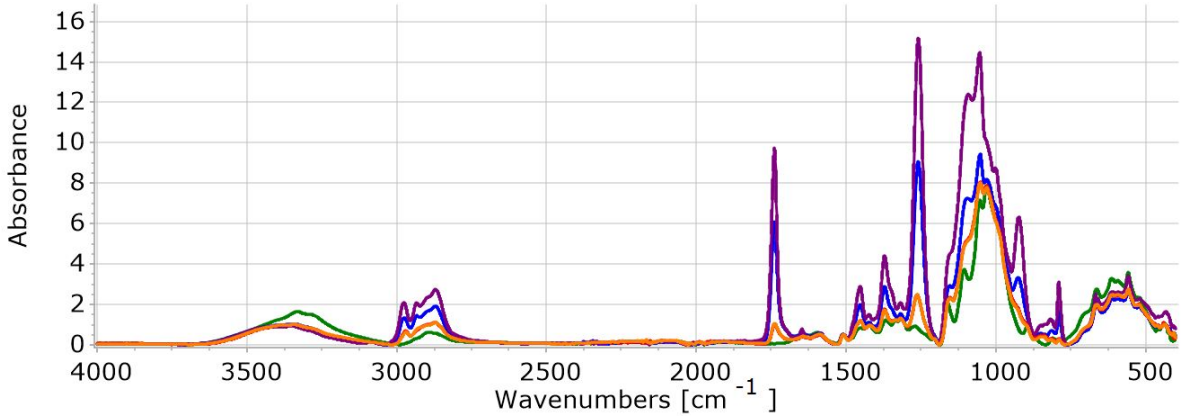


Figure 4.6: Soxhlet Extraction of MUSKP from the chemical modifications with PC and K_2CO_3, USKP (green), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (purple), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 4 h (orange)

The samples of MUSKP from the chemical modification with PC and DBU that are selected to study by Soxhlet extraction come from the synthesis at 180 °C with 0.125 (experiment 8) and 0.625 g (experiment 10) of DBU. The reaction time of these two experiment was 2 h. The sample from the chemical modification with 0.125 g of DBU has an extracted yield at 54% that decreases the weight of MUSKP from 2.88 to 1.54 g. The sample from the chemical modification with 0.625 g of DBU has an extracted yield of 66%, higher than the synthesis with 0.125 g of DBU. So, the corrective weight of MUSKP from this condition is 1.66 g. When we investigated the chemical structure of extracted MUSKP from chemical modification with PC and DBU with ATR-FTIR, we found almost the same occurrence as the samples from the chemical modification with PC and K_2CO_3. From the figure 4.7, the signals of the hydroxyl groups (3550 - 3200 cm^{-1}) of the extracted samples (purple and blue lines) are not too much different from MUSKP before extractions (orange and red lines). However, the difference in the peaks of alkyl (3000 - 2840 cm^{-1}) and carbonyl (1760 - 1740 cm^{-1}) groups are quite clear. The signals of hydroxyl groups of the extracted samples are lower than the initial MUSKP for both chemical modifications. In the region of the carbonyl group, two extracted samples have the same level of absorbance, but signals of the initial MUSKP from the chemical modification with 0.125 g of DBU (orange and red line) are higher, so this condition generates more side reactions that form more carbonate compounds and decreases the purity of MUSKP.

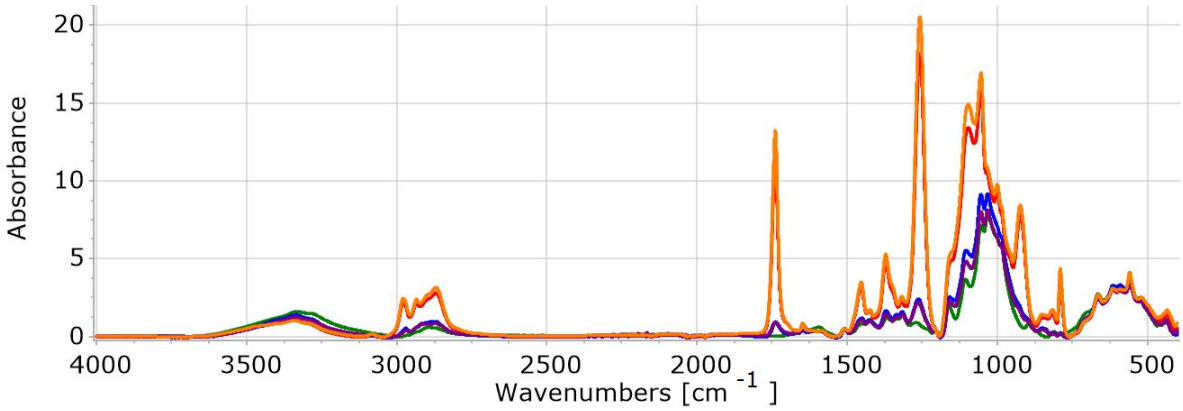


Figure 4.7: Soxhlet Extraction of MUSKP from the chemical modifications with PC and DBU, USKP (green), MUSKP 180°C, 0.125 g DBU, and 2 h (orange), MUSKP 180°C, 0.625 g DBU, and 2 h (red), Extracted MUSKP 180°C, 0.125 g DBU, and 2 h (purple), Extracted MUSKP 180°C, 0.625 g DBU, and 2 h (blue)

The samples of MUSKP from the chemical modification with EC and K_2CO_3 that are chosen to analyze by Soxhlet extraction are the products from the synthesis at 180 °C with 0.125 (experiment 12) and 0.625 g (experiment 13) of K_2CO_3. The reaction time of these two experiment was 2 h. The extracted yields of the sample from both conditions are a little higher than 100%. Therefore, the corrective weight of the samples from the chemical modification with 0.125 g of K_2CO_3 and 0.625 g of K_2CO_3 become 2.46 and 3.22 g, respectively. The extracted samples have a higher mass than their initial weight, 2.34 and 3.06 g. When we consider the chemical structure of extracted MUSKP from chemical modification with EC and K_2CO_3 with ATR-FTIR, we found different appearances from the chemical modifications with PC. From figure 4.8, we found that the initial and extracted MUSKP samples from the chemical modification with 0.125 g of K_2CO_3 (purple and orange lines) have an almost similar curve in the region of the hydroxyl (3550 - 3200 cm^{-1}), alkyl (3000 - 2840 cm^{-1}) and carbonyl (1760 - 1740 cm^{-1}) groups. The extracted sample from the chemical modification with 0.625 g of K_2CO_3 (red line) have slightly lower signals of alkyl (3000 - 2840 cm^{-1}) and carbonyl (1760 - 1740 cm^{-1}) groups than its initial sample (blue line). However, the peak of the alkyl group in the extracted MUSKP from 180°C and 0.625 g of K_2CO_3 is still higher than the extracted MUSKP from 180°C and 0.125 g of K_2CO_3. A higher weight but lower signals of substituted functional groups of the sample are opposite results and indicate that there are some errors in our method. A repeated experiment should be done to verify the results. However, when compared to the extracted MUSKP from the chemical modifications with PC and both catalysts, the peaks of alkyl and carbonyl groups in the extracted MUSKP from the chemical modifications with EC are significantly closer to the signals of initial MUSKP, so the corrective weights of MUSKP from the chemical modifications with EC maybe seem more reliable.

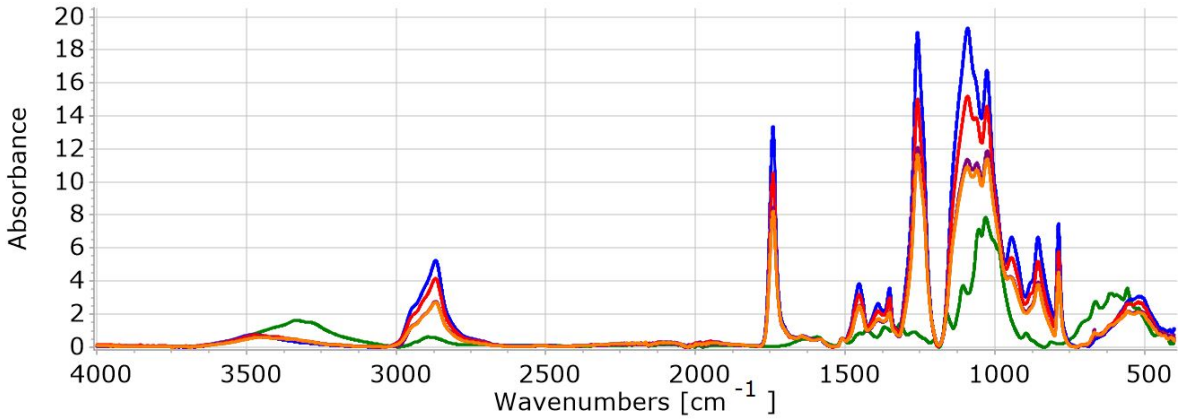


Figure 4.8: Soxhlet Extraction of MUSKP from the chemical modifications with EC and K_2CO_3, USKP (green), MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (purple), MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (blue), Extracted MUSKP 180°C, 0.125 g K_2CO_3, and 2 h (orange), Extracted MUSKP 180°C, 0.625 g K_2CO_3, and 2 h (red)

The extracts from Soxhlet extractions of the samples from the chemical modifications with PC and K_2CO_3, PC and DBU, and EC and K_2CO_3 at 180 °C and 0.625 g of catalyst have undergone additional analysis. The extracts consist of acetone, and the extracted compounds from MUSKP are evaporated to remove acetone. The residuals from evaporation are illustrated in figure 4.9.

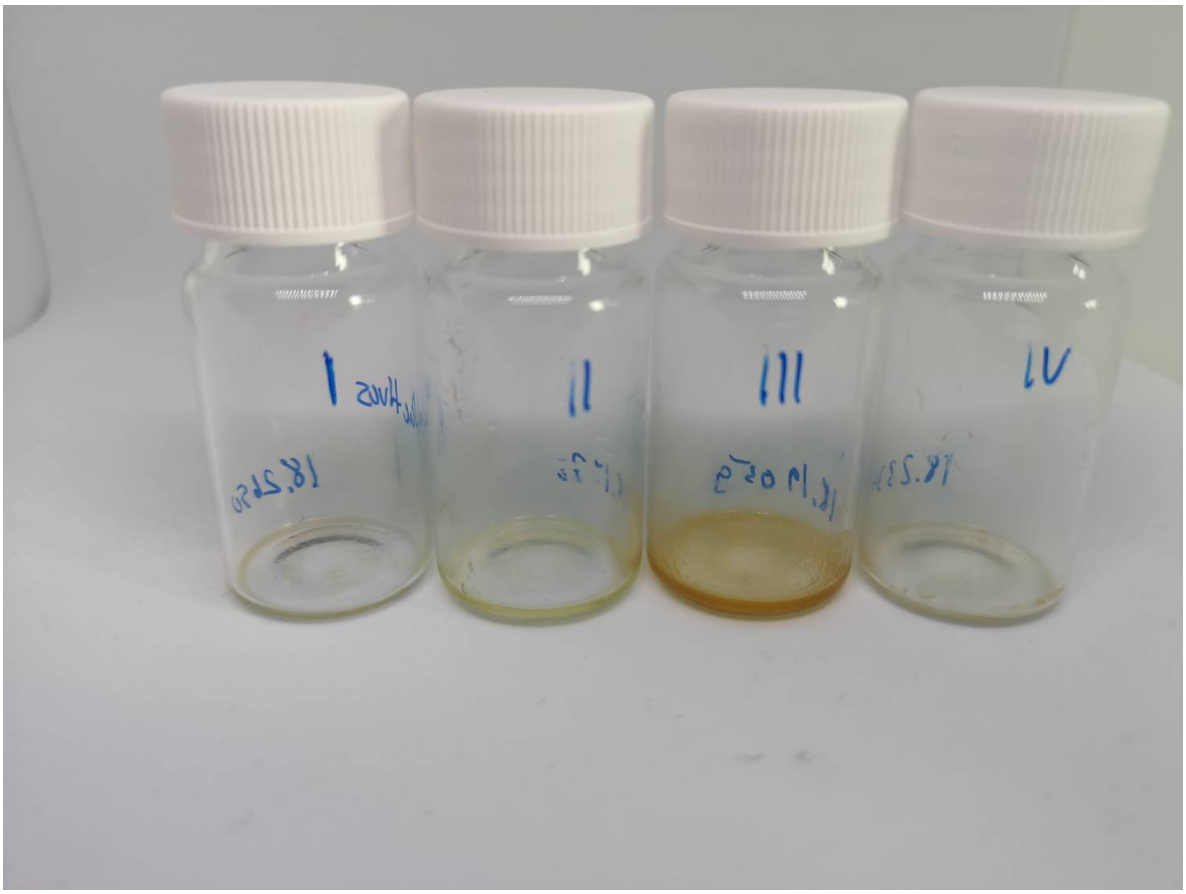


Figure 4.9: Residuals of the extracts after evaporation, USKP (I), MUSKP from PC and K_2CO_3 (II), MUSKP from PC and DBU (III), and MUSKP from EC and K_2CO_3 (IV)

From figure 4.9, bottle III, MUSKP from PC and DBU has the highest residual, so the contaminants from the side reaction at this condition are the most difficult to remove by water. The residual in bottle II, MUSKP from PC and K_2CO_3 is the second highest, so we can explain that the chemical modifications of USKP with PC have side reactions that generate insoluble compounds. In contrast, bottle IV, MUSKP from EC, and K_2CO_3 are almost similar to the bottle I, USKP, which have a little residual. This occurrence can be elucidated in two aspects. Firstly, EC can minimize side reactions that produce the insoluble contaminants and cover on the surface of MUSKP. Secondly, the compounds are soluble and washed out by the water during the separation. These two aspects ensure the advantages of EC over PC in terms of yield and convenience in separation. The side reaction of PC and EC maybe ring-opening polymerization[58][59], and the products which become the contaminants are dimers, trimers, and tetramers of cyclic carbonates[12]. The reaction scheme is illustrated in figure 4.10

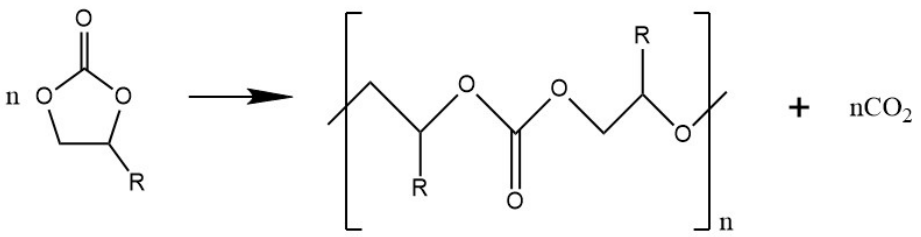


Figure 4.10: Ring-opening polymerization(Side reaction of cyclic carbonates)

R for EC is hydrogen ($-H$) while R for PC is methyl ($-CH_3$), which makes polymer from the side reaction have a different solubility. Therefore, it is very interesting to do an additional analysis of the effluence from the separation of MUSKP that is modified with EC. It can extend understanding of the chemical reaction between USKP and EC, which will be beneficial for process design.

4.4 Dynamic Mechanical Analysis (DMA)

The viscoelasticity of the modified pulp was characterized by DMA, while two samples of unmodified pulp (USKP) were included to be referenced. The extracted modified pulp for this characterization was produced from the chemical modification with EC at 180 °C and 0.625 g of K_2CO_3. This modified pulp was selected because it has a proper purity and the most different chemical structure from USKP. The strongest signals of the alkyl and carbonyl groups in this sample indicate that it has the highest oxyalkylation. The higher degree of oxyalkylation interferes with the hydrogen bonding patterns and increases the free volume of the polymer with a simultaneous reduction in the T_g[60]. One sample of MUSKP was characterized at 30 minutes after freeze-drying, while another sample was kept for 24 h before being analyzed by DMA. The collection of MUSKP is because we would like to estimate the influence of water as a plasticizer. Water is a ubiquitous plasticizer and is applied to biopolymers such as proteins and polysaccharides[61]. Generally, water can increase the molecular mobility of organic materials so T_g becomes lower, but in some cases, it creates the opposite impact[62]. The results are visualized in figure 4.11

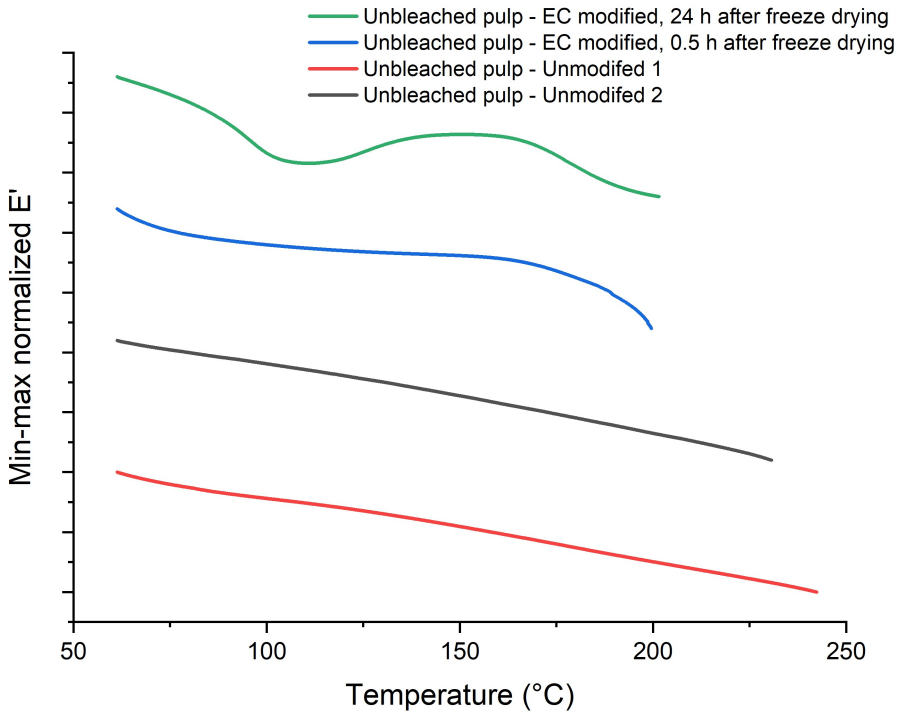


Figure 4.11: Normalized spatially offset storage modulus (E') versus temperature. The red and black lines are duplicate measurements of unmodified pulp, the blue line is MUSKP with lower water content, and the green line is MUSKP with higher water content

From the figure 4.11, the inflection point in the graph of the relationship between storage modulus (E') and temperature is expected to be T_g of the polymer[63]. The graphs of USKP (black and red lines) are similar to unmodified biomass in that T_g is above 220 °C because we cannot see the clear inflection point. For MUSKP with EC and low water content (blue line), the inflection point is approximately 180 °C and anticipated to be T_g, so oxyalkylation of EC increases the mobility of polymeric chains in lignocellulosic materials.

The presence of water in extracted MUSKP (green line) is obviously beneficial for polymeric chain mobility. The first inflection point can be detected at about 110 °C, but it is an artifact from water and disappears when water evaporates. After that, the second inflection point can be identified again at about 170 °C, which is expected to be T_g of this sample. According to the impact of water on polymeric chain mobility, the relationship between the water content and viscoelasticity of MUSKP should be investigated in more detail because it can improve the drying procedure and thermoplastic processing of MUSKP.

5

Conclusion

It has been shown that cyclic carbonates are green reagents and solvents for improving the thermoplastic properties of lignocellulosic materials. Cyclic carbonates are carbon capture and utilization products that can reduce CO_2 from the atmosphere. They are also safer compounds from their high flash point and low volatility. The reactions between lignocellulose and cyclic carbonates can be run under solvent-free conditions and ambient pressure. The desired reaction is oxyalkylation which modifies the hydroxyl groups of lignocellulose components in USKP. Meanwhile, the decomposition of lignocellulosic compositions and ring-opening polymerization are side reactions.

The chemical modification of USKP with EC provides the highest yield and appears to be the most effective pathway to oxyalkylate the hydroxyl groups in USKP. Most of the hydroxyl groups in USKP are substituted by alkyl side chains by the chemical modification with EC. The chemical reactions are operated with K_2CO_3 catalyst, which is inexpensive and has a low environmental impact. In addition, MUSKP from the chemical modifications with EC have higher purity and are easier to separate than the products from the chemical modifications with PC because the compounds synthesized by EC's side reactions can be removed by water, while the compounds from PC's side reactions require organic solvents to isolate from MUSKP. Temperatures and amounts of catalyst can increase the rate of oxyalkylation on the hydroxyl groups, but the influence of catalyst is more obvious at the higher temperature.

A proper introduction of alkyl side chains by EC makes MUSKP have better viscoelasticity. The analysis from DMA reveals that MUSKP from the chemical modification with EC has T_g at approximately 180 °C while the T_g of its raw material is above 220 °C. It is clear that the polymeric chains of MUSKP have more mobility, which is the result of lower hydrogen bonds between lignocellulosic components. Furthermore, the presence of water in MUSKP can be a plasticizer that can assist in the thermoplastic processing of MUSKP.

6

Future work

The chemical modification of USKP with EC expresses the possibility of producing thermoplastics from renewable sources. There are two main areas of further investigation to increase this possibility. Firstly, the effluence from the separation of MUSKP consists of excess EC and compounds from the side reactions. This study can offer detail about the chemical reactions in this system and how to recycle the excess EC. Another issue is the relationship between water content and viscoelasticity of MUSKP because it is essential data for designing the drying procedure and thermoplastic processing of MUSKP.

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Rattanapon Tansatien, Gothenburg, June 2023

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A

Appendix 1

A.1 Calculation of Reactive Groups in Cellulose and Hemicellulose

From the composition analysis of 1 g of USKP, the number of polysaccharides is displayed in the table

Components	MW(g/mol)	%	Amount(mg)
Arabinose	150	1.1	11
Galactose	180	0.8	8
Glucose	180	68.1	681
Mannose	180	5.6	56
Xylose	150	8.1	81

Table A.1:
Monosaccharides in USKP

From the molar ratio of galactose/glucose/mannose in galactoglucomannans of softwoods are 0.5:1:3.5 [25], galactoglucomannans of softwoods, 16 mg of glucose is in galactoglucomannans and 665 mg is in cellulose. It is separated to calculate the reactive groups.

Reactive groups in cellulose:

$$\begin{aligned} \textit{Reactive groups} &= 665\ mg_{cellulose} \times \frac{11 \times 10^{-3}\ mol_{OH}}{1\ g_{cellulose}} \times \frac{1\ g_{cellulose}}{1000\ mg_{cellulose}} \\ &= 7.32 \times 10^{-3}\ mol \end{aligned} \tag{A.1}$$

Reactive groups in Arabinose:

$$\begin{aligned} \textit{Reactive groups} &= 11\ mg_{arabinose} \times \frac{1\ g_{arabinose}}{1000\ mg_{arabinose}} \times \frac{1\ mol_{arabinose}}{150\ g_{arabinose}} \times \frac{2\ mol_{OH}}{1\ mol_{arabinose}} \\ &= 0.147 \times 10^{-3}\ mol \end{aligned} \tag{A.2}$$

Reactive groups in Galactose:

$$\begin{aligned} Reactive\ groups &= 8\ mg_{galactose} \times \frac{1\ g_{galactose}}{1000\ mg_{galactose}} \times \frac{1\ mol_{galactose}}{180\ g_{galactose}} \times \frac{3\ mol_{OH}}{1\ mol_{galactose}} \\ &= 0.133 \times 10^{-3}\ mol \end{aligned} \tag{A.3}$$

Reactive groups in Glucose (in galactoglucomannans):

$$\begin{aligned} Reactive\ groups &= 16\ mg_{glucose} \times \frac{1\ g_{glucose}}{1000\ mg_{glucose}} \times \frac{1\ mol_{glucose}}{180\ g_{glucose}} \times \frac{3\ mol_{OH}}{1\ mol_{glucose}} \\ &= 0.267 \times 10^{-3}\ mol \end{aligned} \tag{A.4}$$

Reactive groups in Mannose:

$$\begin{aligned} Reactive\ groups &= 56\ mg_{mannose} \times \frac{1\ g_{mannose}}{1000\ mg_{mannose}} \times \frac{1\ mol_{mannose}}{180\ g_{mannose}} \times \frac{3\ mol_{OH}}{1\ mol_{mannose}} \\ &= 0.93 \times 10^{-3}\ mol \end{aligned} \tag{A.5}$$

Reactive groups in Xylose:

$$\begin{aligned} Reactive\ groups &= 81\ mg_{xylose} \times \frac{1\ g_{xylose}}{1000\ mg_{xylose}} \times \frac{1\ mol_{xylose}}{150\ g_{xylose}} \times \frac{2\ mol_{OH}}{1\ mol_{xylose}} \\ &= 1.08 \times 10^{-3}\ mol \end{aligned} \tag{A.6}$$

The total reactive groups in arabinoxylans are the summation of the reactive groups in arabinose and xylose, so they are 1.23 $\times 10^{-3}$ *mol*.

The total reactive groups in galactoglucomannans are the summation of the reactive groups in galactose, glucose, and mannose, so they are 1.33 $\times 10^{-3}$ *mol*.

Finally, the total reactive groups of hemicelluse are the summation of the reactive groups in arabinoxylans and galactoglucomannans, so they are 2.56 $\times 10^{-3}$ *mol*.

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