TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

THE IMPACT OF MIXTURE COMPOSITION AND PRE-TREATMENT PARAMETERS ON THE EFFICIENCY OF CELLULOSE ESTERIFICATION REACTION BY REACTIVE EXTRUSION

MASTER THESIS

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Tallinn 2023

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THESIS TASK

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Thesis topic:
(in English) The effect of mixture composition and pre-treatment parameters on the efficiency of the cellulose laurate esterification reaction
(in Estonian) Segu koostise ja eeltöötluse parameetrite mõju tselluloos-lauraadi esterdamise efektiivsusele

Thesis main objectives:

The objectives are to develop mixture pre-treatment methodology and optimize mixture composition.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature survey	10.2021
2.	Preparation and analysis of oven pre-treated samples	05.2022
3.	Preparation and analysis of US pre-treated samples	10.2022
4.	Preparation and analysis of samples with catalyst	12.2022
5.	Preparation and analysis of ratio modification	02.2023
6.	Summarizing the test results and writing the thesis	05.2023

Language: English **Deadline for submission of thesis:** "26" may 2023a

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CONTENTS

PREFACE

This thesis was completed at the Tallinn University of Technology, in the Institute of Materials and Environmental Technology, in the biopolymer technology laboratory. The research was conducted under the guidance of Viktoria Gudkova and Illia Krasnou. This study was supported by the Estonian Research Council via project RESTA10 "Chemical valorization of cellulose in environment of ionic liquids".

The author would like to express deep gratitude to supervisor, Viktoria Gudkova, and co-supervisor, Illia Krasnou, for their comprehensive support and guidance throughout the development of this work. The author would like to thank the Institute of Chemical and Biological Physics for conducting the NMR tests and early stage researcher, Nutan Bharat Savalet, for helping with the results analyzes. Additionally, special thanks are extended to Kirke Maria Lepik, a student who provided valuable assistance during the practical work.

The thesis describes the cellulose esterification reaction through a three-minute reactive extrusion process in an ionic liquid and co-solvent environment, resulting in the synthesis of cellulose laurate. The work aim is to achieve effective cellulose esterification reaction with a mixture pre-treatment via 3-minute reactive extrusion. The work main objectives are to develop mixture pre-treatment methodology and optimize mixture composition.

Keywords: cellulose, esterification, ionic liquids, reactive extrusion, master's thesis.

LIST OF ABBREVIATIONS

ATR	Attenuated Total Reflectance
[mTBNH][OAc]	Ionic liquid 5-methyl-1,5,7-triazabicyclo[4.3.0]non-6-enium acetate
AGU	anhydroglucose unit
cat	Catalyst
CL	Cellulose laurate
cm-1	Wavenumber
DMA	Dimethylacetamide
DMAc-LiCl	N,N dimethylacetamide-lithium chloride
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DMSO-TBAF	Dimethyl sulfoxide-tetrabutylammonium fluoride
DS	Degree of substitution
exDMSO	Dimethyl sulfoxide added to mixture after pre-treatment (before extrusion)
exVL	Vinyl laurate added to mixture after pre-treatment (before extrusion)
FTIR	Fourier transform infrared spectroscopy
IL	Ionic liquid
kHz	Kilohertz
m.ratio	Modified ratio
MAS	Magic-angle spectrum
MCC	Microcrystalline α-cellulose
NMMO	4-methylmorpholine-4-oxide
NMR	Nuclear magnetic resonance spectroscopy
preDMSO	Dimethyl sulfoxide added to mixture before pre-treatment
preVL	Vinyl laurate added to mixture before pre-treatment
rpm	Rotations per minute
RT	Room temperature
RTILs	Room-temperature ionic liquids
US	Ultrasonic bath
VL	Vinyl laurate

INTRODUCTION

Plastic waste has become a major global concern, with massive amounts produced and landfilled on a daily basis, causing severe environmental consequences. The negative effects of plastic pollution, such as ocean contamination, wildlife extinction, and ecosystem disruption, have heightened the need for more sustainable long-term solutions. [1] In this context, there has been a lot of interest in finding alternative solutions to replace currently widely used fossil-based plastics.

Cellulose, as one of the most common natural polymers derived from plants, provides a promising avenue for a variety of applications, including the development of sustainable alternatives to traditional fossil-based plastics. With its potential as a raw material for bioplastics production, cellulose holds promise in addressing the environmental challenges posed by conventional plastics. It is widely available, renewable, and biodegradable option for a wide range of applications. [2]–[4]

To make cellulose thermoplastic and therefore suitable as a raw material for the plastic industry, it requires appropriate modifications. Cellulose possesses a strong network of hydrogen bonds, which complicates its processing. However, through chemical and physical modification, the physicochemical properties of cellulose can be significantly changed to obtain the desired functionality, thereby improving its ease of use. [5]–[7]

Cellulose esterification has emerged as a promising approach in the quest for sustainable alternatives to conventional plastics. This process enables the synthesis of long-chain cellulose esters, which have shown remarkable mechanical and performance properties. These long-chain cellulose esters offer a viable solutions to produce various bioplastics, including films, coatings, and packaging materials. It is possible to contribute to a more sustainable future and reduce the reliance on fossil-based materials by utilizing the potential of cellulose esters. [1]

Cellulose laurate is a compound that falls under the category of ester derivatives of cellulose. Cellulose laurate is an esterified combination of cellulose and vinyl laurate. It has thermoplastic properties, which means it can be melted and reshaped when heated. Due to this property, cellulose laurate can be processed using a variety of thermoplastic techniques, such as extrusion or injection moulding. The thermoplastic properties make it suitable to be used for a variety of products such as films, fibers, coatings, packages and more. Cellulose laurate paves the way for environmentally friendly materials that reduce the negative effects of plastic waste. [8]–[10]

Reactive extrusion is a technique that uses mechanical shear forces and heat to speed up the chemical reaction between cellulose and vinyl laurate, resulting in the formation of cellulose laurate. The extruder is made up of a barrel with a rotating screw that aids in material mixing and transport. Typically, the barrel is heated to provide a suitable temperature for the reaction. [11]–[13]

Ultrasonic assisted treatment is a relatively new method, that has been used as an additional method in the creation of cellulose laurate. Ultrasonic waves can be used to treat cellulose, which improves the accessibility and reactivity without damaging the material. When comparing to traditional methods, it provides advantages such as faster reaction time, lower energy consumption, and higher product quality. [14]–[16]

The thesis describes the cellulose esterification reaction through a three-minute reactive extrusion process in an ionic liquid and co-solvent environment, resulting in the synthesis of cellulose laurate. The aim is to achieve effective cellulose esterification reaction via reactive extrusion in three minutes. The main objectives are to develop the mixture pre-treatment methodology and optimize the mixture composition. Attempting to find the optimal methods to achieve the best results. The key substances in this process are microcrystalline α-cellulose, ionic liquid [mTBNH][OAc], co-solvent dimethyl sulfoxide, and vinyl laurate.

The first section of the thesis gives an overview of the subject by discussing the basis, used materials, and employed methods. The second part describes the preparation of cellulose laurate samples. It includes a detailed description of the preparation process, employed techniques, and established parameters. The third part is dedicated to the methodology, providing an overview of the three testing methods used: fourier transform infrared (FTIR) spectrometry, nuclear magnetic resonance spectroscopy (NMR) and solubility test. The analysis and discussion of the test results are carried out in the fourth part of the study. Each tested aspect is examined separately, focusing on various pre-treatment parameters such as the time and temperature, application of ultrasonication, effect of the mTBN catalyst, and the modification of VL to MCC ratio.

1 THEORETICAL OVERVIEW

1.1 Cellulose

Continuing the current trend, 12 billion tons of plastic waste will be landfilled or released into the environment by the end of 2050 [1]. Therefore, there is a great environmental need to replace currently used fossil-based plastics. Cellulose is a suitable choice for a replacement because each year plans produce more than 100 billion tons of cellulose, hundreds of times more than the produced amount of plastics in the same period. [17], [18] Cellulose-based polymers could provide alternatives to oil-based polymers in numerous fields. That limitless raw material source could help the rising demand for eco-friendly and biocompatible resource-efficient goods. [19] Cellulose is already an essential raw material for several industries for making textiles, papers, food, cosmetics, and biomaterials [2].

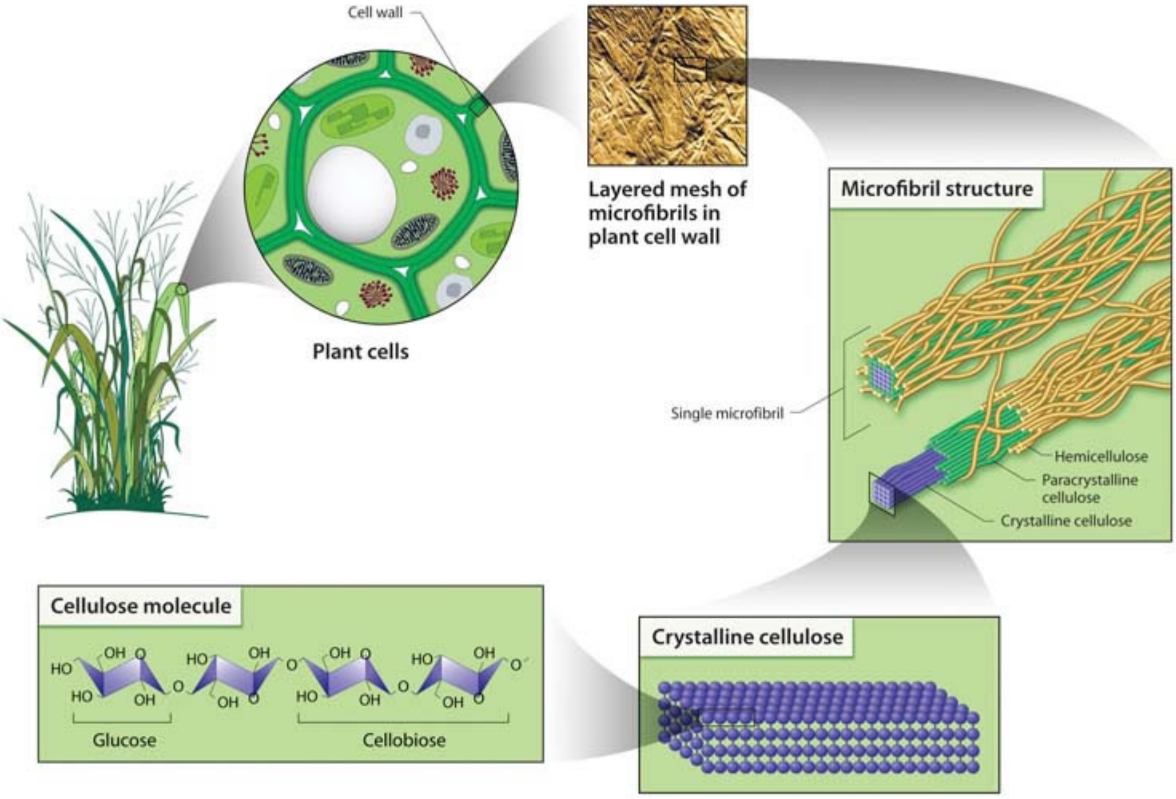


Figure 1.1. Cellulose in nature [20]

Cellulose is an essential component in the construction of a plant's primary cell walls, as it provides structural strength and rigidity by helping to maintain intracellular structures. (See Figure 1.1, which shows the cellulose in the plant cell.) For example, approximately up to 47% of the wood consists of cellulose. Cellulose is one of the most abundant organic macromolecule and common natural polymers, which is considered a renewable material. [3], [21]–[23]

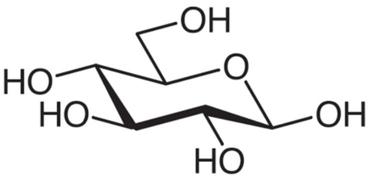


Figure 1.2. Glucose molecule [24]

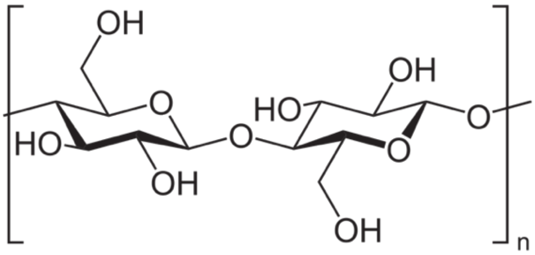


Figure 1.3. Cellulose molecule [25]

Cellulose is a polysaccharide (Latin for "many sugars") [26] with a linear chain consisting of two linked β-D-glucose units (figure 1.2) that are linked by glucoside linkages. Each anhydroglucose unit (AGU) is rotated 180° from the other, forming cellobiose (figure 1.3). Cellulose monomers, AGUs have three hydroxyl groups – the primary one at the sixth carbon and the secondary ones at the second and third carbons. The AGUs are bonded via 1,4-β-glycosidic linkages. These hydroxyl groups can react similarly to alcohol: forming esters, ethers, and oxidizes. [3], [23], [27], [28]

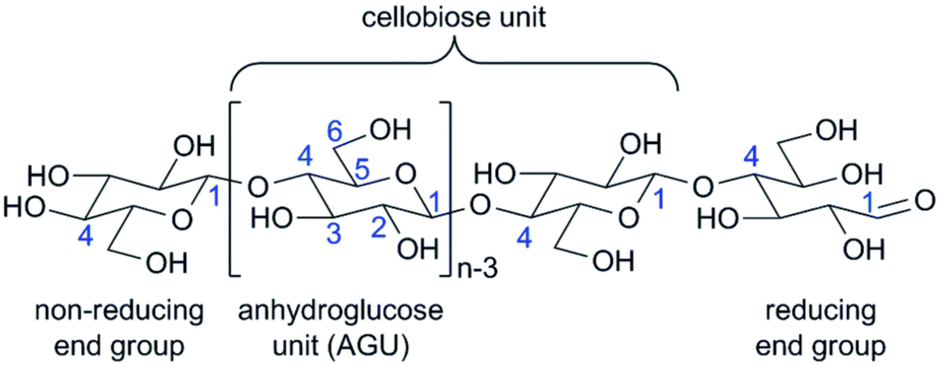


Figure 1.4. Cellulose molecular structure [28]

The cellulose hydroxyl group forms strong intramolecular and intermolecular hydrogen bonds, which significantly affect the properties of cellulose. This strong inter- and intra-hydrogen bonding network (figure 1.5) makes cellulose hydrophilic and thermally unprocessable (degradable by heat). Although cellulose is insoluble in traditional solvents (such as water), its physical and chemical properties can be significantly modified to achieve the required function, making it easier to use. [5]–[7] Therefore, the hydroxyl groups of cellulose need to be modified by breaking the strong hydrogen bonding network to improve the solubility and make it processable by giving it thermoplastic properties so it could be used in processing by existing methods [29].

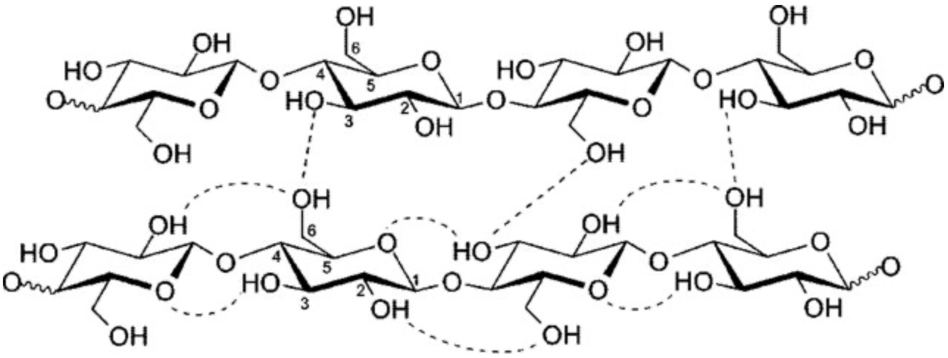


Figure 1.5. Inter- and intramolecular hydrogen bonds in cellulose [19]

1.2 Cellulose modifications (esterification)

Even though cellulose is essentially insoluble in traditional solvents, the physicochemical properties can be significantly changed with chemical modification to achieve the required function, making it easier to use. *Modified cellulose* mainly means that the hydroxyl groups in the cellulose backbone have been chemically modified. The primary hydroxyl group has higher reactivity than the secondary hydroxyl groups. [30] For example, common cellulose modifications of hydroxyl groups are oxidation, esterification, etherification, urethanization, and amination. [31]

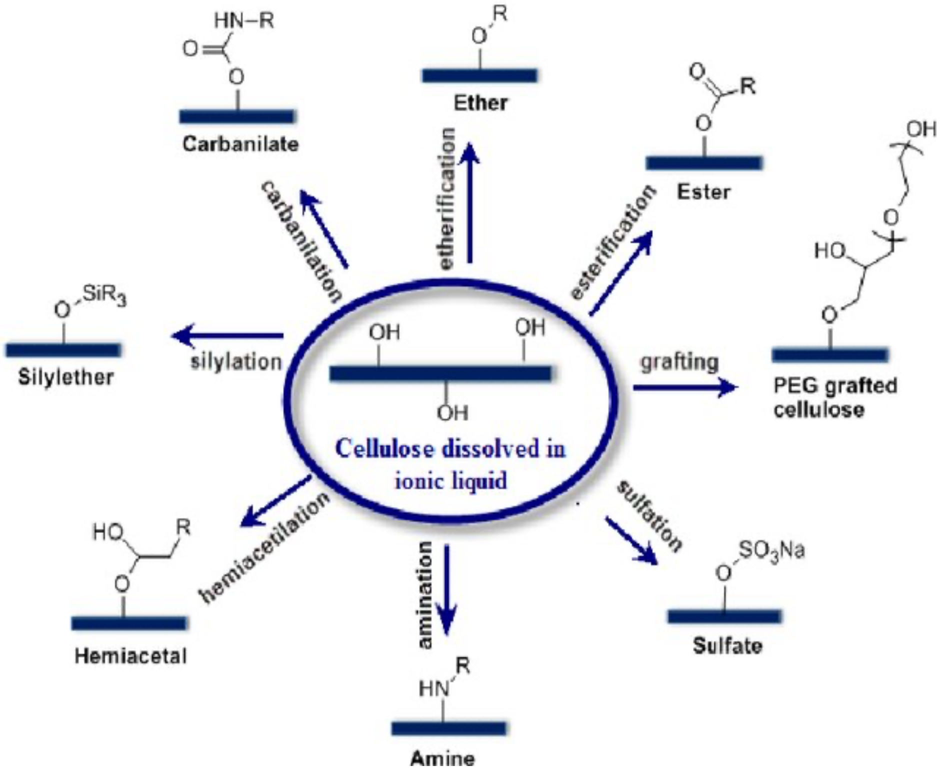


Figure 1.6. Example of possible chemical modifications of cellulose dissolved in ionic liquids [32]

One relatively new cellulose modifying method is esterification by reactive extrusion in an ionic liquid environment to obtain cellulose esters. The obtained cellulose esters differ from the original cellulose regarding their physical and chemical characteristics and dissolve in various solvents [4].

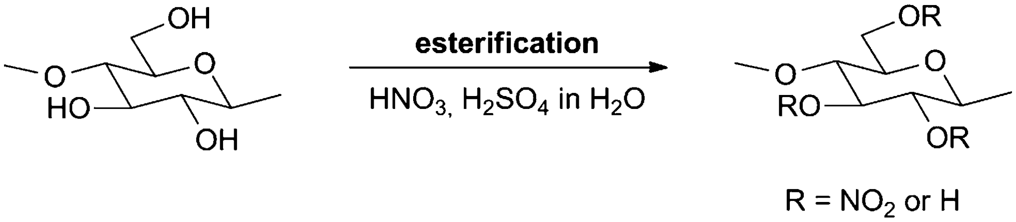


Figure 1.7. Example of cellulose modification (esterification) [28]

In this practical study, cellulose is modified in the esterification process, in which cellulose reacts with the vinyl ester to generate a new ester bond. In this process, the hydrogen in the cellulose hydroxyl group is replaced with a lauryl group. In practice the ionic liquid (described in more detail in section 1.2.1) and dimethyl sulfoxide (described in more detail in section 1.2.2) are used to dissolve cellulose and catalyse the reaction. Vinyl laurate (described in more detail in section 1.2.3) is used to form an ester bond with cellulose.

1.2.1 Ionic liquid as cellulose solvent

Ionic liquids (IL) are a group of salts that consist entirely of ions. Room-temperature ionic liquids (RTILs) occur as liquids at relatively low temperatures having a melting point at room temperature. They can contain both organic and inorganic ions, with one or more cations and anions. Ionic liquids' high polarity, due to their ionic character, gives them remarkable peculiarity to enhance biopolymer dissolving capacity. The acidic protons substantially increase solubility by forming hydrogen bonds with the hydroxyl group of cellulose molecules. [19]

Previous studies have found that the interaction between the ionic liquid and cellulose is stronger than the cellulose intermolecular bonds. This causes the cellulose to dissolve by forming hydrogen bonds between the cellulose and the ionic liquid's acetate [25]on. The advantages of ionic liquids over traditional solvents are their high thermal and chemical stability, immeasurably low vapor pressure, non-flammability, and the ability to mix with various solvents. [33]–[35]

Ionic liquids can replace the dangerous chemicals and unstable organic compounds that have been used so far. It is considered a safe and effective cellulose solvent. Also, it is possible to recover a certain amount of IL after usage, leading to lower overall process costs and raw material consumption. [36], [37]

Ionic liquid 5-methyl-1,5,7-triazabicyclo[4.3.0]non-6-enium acetate [mTBNH][OAc] [38] is used in this work (shown in the Figure 1.8). There were found any published studies that used the ionic liquid [mTBNH][OAc] for the synthesis of cellulose laurate. Common cellulose solvents such as N,N dimethylacetamide-lithium chloride (DMAc-LiCl), dimethyl sulfoxide-tetrabutylammonium fluoride (DMSO-TBAF), and 4-methylmorpholine-4-oxide (NMMO) are frequently used. Compared to [mTBNH][OAc], these substances are considerably more toxic, harmful to the environment and/or cannot be recycled. [39]–[41]

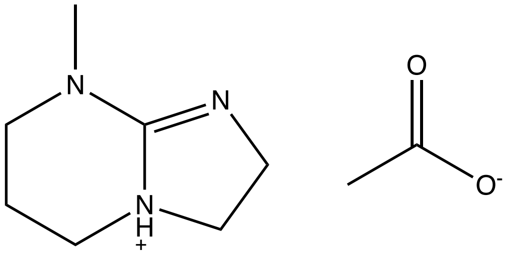


Figure 1.8. Chemical structure of ionic liquid 5-methyl-1,5,7-t triazabicyclo[4.3.0]non-6-enium acetate [mTBNH][OAc] [42]

The [mTBNH][OAc] ionic liquid consists of two components: a cation [mTBNH] (super-base moiety) and an [OAc] anion (acetic acid moiety). The mTBN super-base component acts as a catalyst in the esterification reaction. [43], [44] It could be added to the reaction mixture to promote the esterification of cellulose with vinyl laurate.

1.2.2 Dimethyl sulfoxide as co-solvent

Dimethyl sulfoxide (DMSO) with the chemical formula of (CH3)2SO (on Figure 1.9) can be used as an organic co-solvent with ILs for cellulose dissolution.[37] The use of DMSO has been mentioned in several literature sources as co-solvent in cellulose esterification prosses. While DMSO can swell cellulose and facilitate its dissolution, complete solubility is often not achieved without the addition of other solvents. [14], [45]–[47]

It is an aprotic solvent, meaning it does not donate a proton to the solvent environment and acts as a hydrogen bond acceptor. Because of this property, DMSO can break the hydrogen bond network of cellulose and dissolve the polymer. Therefore, DMSO can improve the solvent process by reducing the IL viscosity without blocking the ability to dissolve cellulose and increase the IL's esterification reaction. [47], [48] It has been found that adding DMSO increases the efficiency of cellulose esterification, resulting in a product with a higher degree of substitution because DMSO contributes to the catalysing effect of the ionic liquid reaction. The high boiling point of DMSO (189°C) is also advantageous in processing. [49], [50]

Furthermore, the quantity of IL required can be reduced by utilizing DMSO as a co-solvent in cellulose bond-breaking processes, making the overall process cheaper and more sustainable. In general, DMSO is considered a relatively safe solvent, and it can even be considered a biocompatible substance. [47], [51], [52]

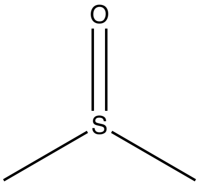


Figure 1.9. Chemical structure of DMSO $(CH_3)_2SO$ [42]

1.2.3 Vinyl laurate as the esterification reagent

In this research, the vinyl laurate ($C_{14}H_{26}O_2$) is used to esterify cellulose. Vinyl laurate is used as the esterification reagent to form an ester bond with cellulose in a given co-solvent system. Vinyl laurate can react with cellulose hydroxyl groups (-OH). In this reaction, the vinyl laurate double bond breaks, and the carbonyl group (C=O) molecule reacts with a cellulose hydroxyl group to form a new chemical bond known as an ester bond. This reaction results in the formation of a vinyl laurate ester group attached to the cellulose molecule.

Using vinyl esters to esterify cellulose can result in the production of acetaldehyde as a by-product, but fortunately, it is usually easy to remove from the reaction medium. Since acetaldehyde is a known carcinogen, it is important to evaluate and reduce any risks related to the production of cellulose esters. [53], [54]

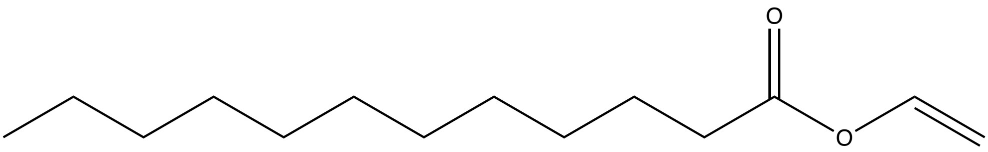


Figure 1.10. Chemical structure of vinyl laurate ($C_{14}H_{26}O_2$) [42]

1.3 Cellulose laurate

Cellulose laurate, an ester derivative of cellulose, has received a lot of interest due to its unique properties and its potential as an environmentally friendly alternative to conventional plastics. Previous studies have commonly produced cellulose laurate by using lauroyl chloride and lauric acid as reagents. However, these substances produce acidic environments and cause cellulose degradation. [55]–[57]

Researchers have recently investigated an alternative strategy in the esterification process by using vinyl laurate as a reaction reagent. Vinyl laurate has various advantages over lauroyl chloride and lauric acid, including shorter reaction time, improvements in reaction efficiency and less side reactions. Also, it is considered more environmentally friendly option. [10], [55]–[57]

It has been discovered that cellulose laurate behaves as a plasticized polymer without the need for additional plasticizers, distinguishing it from other biopolymers. Its thermoplastic properties enable material melting and reshaping when heated, making it compatible with various thermoplastic techniques such as extrusion and injection moulding. These cellulose laurate characteristics enable a wide range of applications, making it suitable material for larger scale production. It can be used to make films, fibers, coatings, packaging, and other products. [8]–[10]

By offering an environmentally friendly alternative, cellulose laurate contributes to reducing the negative effects of plastic waste. Its recyclability and biodegradability make it an attractive choice for sustainable materials, paving the way for a greener future.[10]

1.4 Reactive extrusion

In the plastics industry, an extruder is commonly used in the melting, mixing, and moulding of materials. It is a versatile tool used to shape molten plastic into a variety of products such as profiles, tubes, sheets, and other desired shapes. Extruders can vary depending on the application area and desired end result. An extruder is typically made up of a heated cylinder with an internal rotating screw that conveys and mixes the plastic mass. In general, raw material is fed into the extruder, where it is mixed and moved forward with the help of screws. Through the application of heat, the material undergoes melting or a chemical reaction, depending on the requirements. The process concludes with the material exiting the extruder from die. [11]–[13] The key components of an extruder are depicted in Figure 1.11.

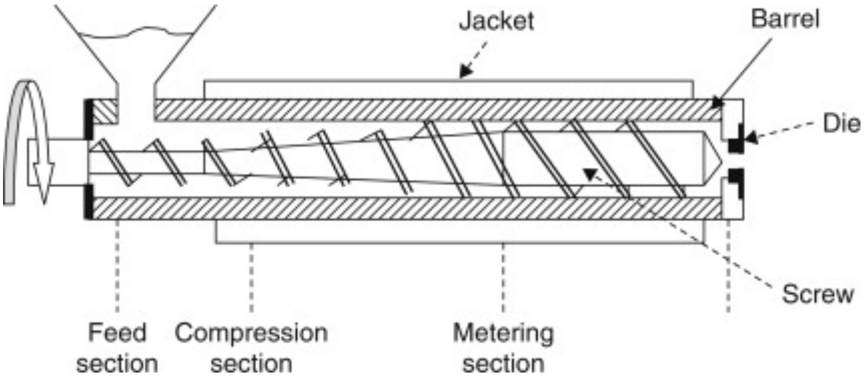


Figure 1.11. Basic structure of a extruder [13]

A reactive extrusion enables to conduct of chemical reactions during the material processing process. It is used to make chemical changes or synthesize new compounds. Reactive extruder combines mechanical mixing and heating processes with chemical reactions. The technique of using mechanical shear forces and heat can be used to accelerate the chemical reaction between cellulose and vinyl laurate.[12], [58]

Long-chain cellulose esters can be synthesized using reactive extrusion. The degree of substitution of the product can also be controlled by changing the extrusion process. During reactive extrusion, the mechanical forces generated by the rotation of the screws contribute to the breakdown of the fibrous structure of cellulose and the disruption of hydrogen bonding, facilitating the occurrence of the reaction. The rotation of the screws also helps the modifying agent reach the cellulose molecules. Studies have shown that reactive extrusion can successfully synthesize cellulose esters with different degrees of substitution in a short period of time.[9], [39], [58]

The mini extruders (with small capacities) are commonly used for producing smaller quantities, making them suitable for development and experimentation. These extruders could have a material feedback system, which is highly beneficial because it allows to control the prosses length (the reaction time). Also, material feedback systems help to reduce waste by using smaller quantities of material in compounding processes. Industrial-scale extruders typically do not have a material feedback system, and the reaction time depends on the extruder length and screws extruder.[9], [58], [59]

1.5 Ultrasonic treatment

The ultrasonic (US) bath can be used as a sonicator, to generate high-frequency energy in liquids. [60] Ultrasonic assisted treatment, has been used as an is a relatively new additional method in the creation of cellulose esters. Ultrasonic waves can be used to treat cellulose by improveing the accessibility and reactivity without damaging the material. When compared to the conventional methods it provides advantages such as faster reaction times, lower energy consumption, and higher product quality. [16]

The ultrasonics positive effects are frequently linked to cavitation, which refers to the development of cavities or bubbles inside a liquid medium. In the presence of cavitation, several effects have been observed. Cavitation can cause chemical activity that enables reactions which would not typically occur. It is known for increasing the chemical activity, suspended particles fragmentation or rupture, surface erosion, fragmentation rupture, liquid mixtures emulsification and small particles dispersion in liquids.[61], [62]

High-intensity energy produced by ultrasonic waves can aid to brake or weaken the surface structure of the material, allowing for better penetration of chemicals or solvents during the process. Based on written sources, ultrasonic waves have been found to breakdown and loosen the cellulose molecular bondage during the pre-treatment process and help the vinyl laurel particles to pass through the cellulose. The US has a strong effect, and it accelerates the reaction. In theory, this should also reduce pre-treatment time and energy consumption without losing the result. [14], [15], [61]

The efficiency of the reaction is affected by the frequency, temperature, and duration of the ultrasonic process. Previous studies have found that an ultrasound frequency between 10-100 kHz is optimal for promoting the degradation and breakage, depending on the cellulose type and other parameters. [63], [64]

When compared to traditional procedures for cellulose processing and modification, using US as a pre-treatment step can offer a more energy- and environmentally friendly approach. [62]

2 PREPARATION OF THE CELLULOSE LAURATES

In the current study, 27 different samples of cellulose laurate were prepared. In general, the preparation procedure can be divided into: mixture preparation, pre-treatment of the mixture before extrusion, reactive extrusion, and post-processing. The preparation procedure is described in the following parts 3.1 to 3.4.

The current research studied the effect of different variables on the esterification reaction's efficiency. Variables can be broadly divided into mixture composition and mixture pre-treatment variables. A detailed description of different variables is presented in part 3.5 of this chapter.

Figure 2.1. Cellulose laurate preparation main steps

2.1 Preparation of mixtures for extrusion

The following substances were used in the preparation of the reaction mixtures:

- Microcrystalline α-cellulose (MCC) - Carl Roth, CAS nr 9004-34-6, with the density of 1.5g/cm3
- Ionic liquid (IL) 5-methyl-1,5,7-triazabicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]) – Lioutin Group OY, ≥ 98,0%
- Dimethyl sulfoxide (DMSO) – Fisher Chemical, 99,9%, CAS nr 67-68-5
- Vinyl laurate (VL) – Wacker Chemie AG, ≥ 98,0%, CAS nr 2146-71-6
- Super-base mTBN (cat) - Lioutin Group OY, ≥ 98,0%

Every mixture consists of microcrystalline α-cellulose, vinyl laurate, and ionic liquid [mTBNH][OAc]. Samples with a lower ionic liquid content have an extra DMSO (with a formula of $(CH_3)_2SO$). The ratio of IL to DMSO in the reaction mixture was 1:1 or 1:0. Every sample has a total weight of 10,00 grams. In later experiments, the catalyst is added to the composition and calculated according to the amount of solvent (DMSO and IL) in the mixture. The catalyst was tested in two amounts - 10% and 5% of the solvent in the mixture.

Figure 2.2. Milled and vacuum-dried microcrystalline cellulose

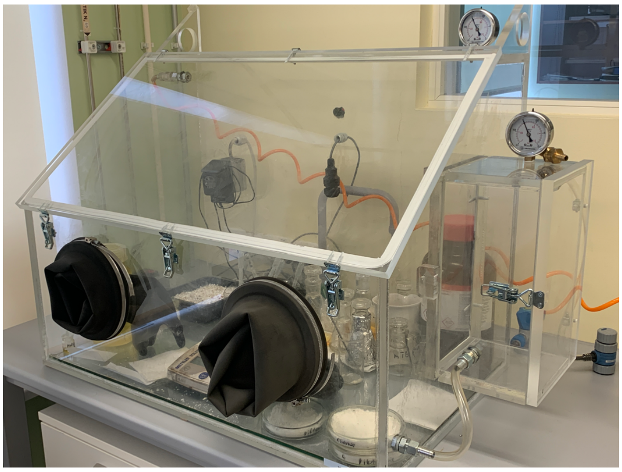


Figure 2.3. The glovebox

Before usage, the cellulose is dried in a vacuum oven at a temperature of 105°C for 24 hours to remove any excess moisture in the material. The dried material is stored in the glovebox (Figure 2.3) with an oxygen level below 1.00%. All the ingredients used for sample preparation were stored and mixed in a glovebox with low humidity levels.

Figure 2.4. Mixture before (left) and after (right) 20h at 40°C oven pre-treatment

The selected ingredients were weighed into a glass beaker (weighing bottle) of size 10ml and mixed thoroughly with a metal rod. The glassware was closed with a cap. (The ready-to-storage sample is shown in Figure 2.4, on the left side) Next, the sample was pre-treated either at room temperature in the same glovebox or at a higher temperature in the oven. For samples pre-treated in the ultrasonic oven, a beaker with a wider bottom of size 25ml was used to increase the treatable mixture surface area. After the pre-treatment period (example of sample after pre-treatment on Figure 2.4, on the right side), the sample proceeded directly to extrusion. If required, the variable ingredients (VL and/or DMSO) were added to the samples in a glovebox right before extrusion. Generally, the sample became visually darker and may have changed in structure to a rubberier mass.

2.2 Pre-treatment methods

In this study, three pre-treatment methods are used: RT-treatment (stored in glovebox during pre-treatment time), oven-treatment (pre-treated in conventional oven) and US-treatment (pre-treated in the ultrasonic bath). Different pre-treatment times and temperature combinations are used for all methods.

For RT-treatment the prepared mixture was stored in the same glovebox throughout the entire pre-treatment period. For the oven-treated samples the conventional oven was used. In 30 minutes, the oven containing the sample was pre-heated to the desired temperature. The sample was kept in the oven at an elevated temperature for a predetermined period. After the pre-treatment period, the sample was taken out of the oven and moved on to the extrusion step. Post the pre-treatment, the necessary variable ingredients were added for specific samples before extrusion.

After finding the optimal time and temperature for treatment in the oven, the ultrasonic bath was tried as another pre-treatment method. This study used the GT Sonic's ultrasonic bath (on Figure 2.5). The bath was filled with water so that all the sample in the container would be below the water line during the procedure. First, the bath water was preheated to the desired temperature. Next, the wax-sealed sample beaker was placed in preheated water, and the position was fixed between the wireframes. The sample was then processed at a frequency of 40kHz. After the pre-treatment time, the sample was removed from the bath and proceeded directly to extrusion.

Figure 2.5. US pre-treatment setup

2.3 Reactive Extrusion process

In this work, the cellulose esterification reaction is performed in a twin-screw extruder Haake MiniCTW of Thermo Fisher Scientific (Figure 2.6) with a rotating material feedback system.

Figure 2.6. Twin-screw extruder Haake MiniCTW of Thermo Fisher Scientific

Figure 2.7. The processed material exiting the extruder

Used parameters for reactive extrusion process:

Reaction temperature in compounder: 120ºC
Rotational speed of screws: 60rpm
Time of reactive extrusion: 3min

The pre-treated mixture was fed into a twin-screw mixing extruder once the machine had reached the set 120°C temperature. It took an average of 2 minutes to inject the mixture. During the mixture injection, the rotation speed of the screws was 30 rpm (lower than the processing speed) for the sample to be fed evenly into the extruder and to equalize the reaction time.

When the entire mixture was injected into the extruder, the speed was increased up to 60 rpm and the sample rotates in the extruder for 3 min. The reaction time in the extruder was chosen to be three minutes, as this period is common for industrial extruders. During this time, the cellulose is thoroughly mixed and further reacted with added components. The ionic liquid and dimethyl sulfoxide are used to dissolve cellulose and catalyse the reaction. By this, the VL can form an ester bond - the cellulose hydrogen atoms in the hydroxyl group are replaced by lauryl atoms (see Figure 2.8).

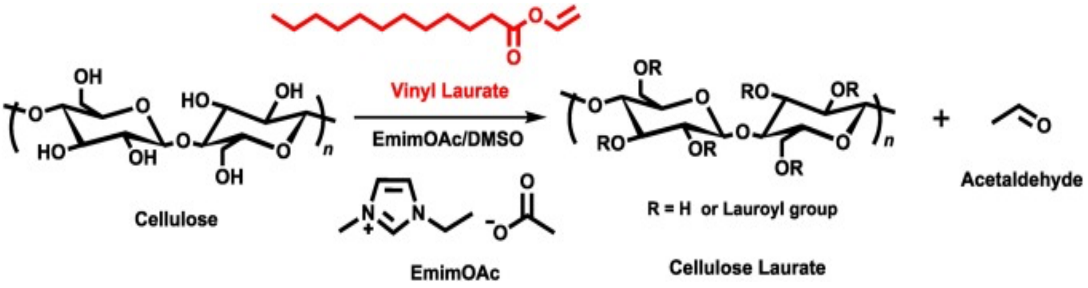


Figure 2.8. Reaction scheme of cellulose and VL [65]

After the time had passed, the extruder dye was opened, through which the processed material exits and was collected. If the mixture came out too slowly, the screw's rotation speed was increased to 100 rpm so that the material would exit faster and not stay in the extruder for more than the desired period. From there, the specimen was post-processed. Finally, the residues left inside the extruder were collected for the extraction of the ionic liquid for reuse.

2.4 Post-processing of samples after reactive extrusion

2.4.1 Specimen washing process

Specimen washing procedure consists of three main activities: washing, grinding, and drying. After reactive extrusion, the specimens must be washed to remove the solvent and the residual (unreacted) esterification agent from the extruded material. Both ethanol and distilled water were tested for washing, and the results were equivalent. The extruded specimens are washed in ethanol or distilled water at room temperature with a magnetic stirrer (2mag Magnetic stirrer MIX drive 6HT) for 1h. On the first washing, the extruded material stays a solid filament, but its color may slightly lighten during the washing process. This process was repeated 1-2 times. Then the samples were dried in a vacuum-oven for 24 hours at a temperature of 70°C.

After the first drying, the samples were milled and rewashed the same way until the washing liquid remained colorless (1-2 times) to obtain the purest possible result for further material analysis. Then, the grounded material was separated from the liquid with a nut filter and dried the in the vacuum-oven for 24h. The dried sample was stored in a zip bag. After every wash, the used liquid was collected for distillation to extract the ionic liquid from it for reuse. Separate tests were conducted to determine the effectiveness of the given washing technique. The results are shown in Appendix 2.

Different washing cycle lengths were also tested, and in the case of washing with water, it was found that the most profitable is washing twice for 2 hours. Specific changes were detected, which may indicate such a reaction or decomposition if the washing period exceeded 20 hours. No difference was found in the washing results between distilled water and ethanol, but washing with water is a more environmentally friendly method.

Figure 2.9. washing example of extruded material (before gringing)

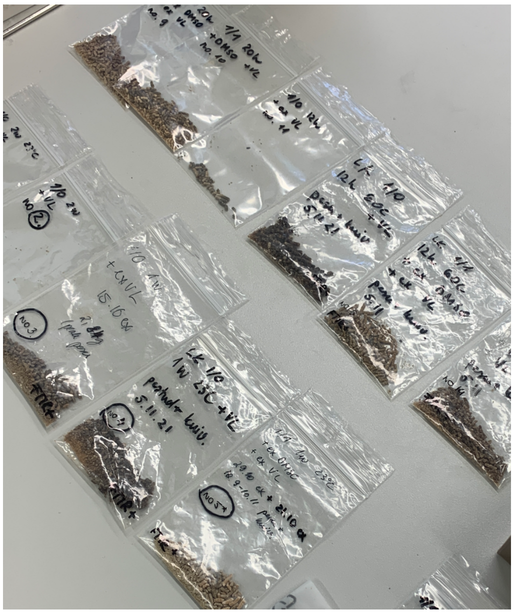


Figure 2.10. Finished samples (milled, washed and dried result)

2.4.2 Samples preparation for FTIR analysis

FTIR test was used as one method to analyze the samples. In this test, the close contact between the sample and the FTIR machine is extremely important. Therefore, a small amount of sample was pressed with a hydraulic hot press to avoid false information coming from the air between the material and ensure proper contact between the ATR crystal and the specimen. The powdered sample was pressed at an 80-100 bar pressure at 40 °C for 7-10 minutes.

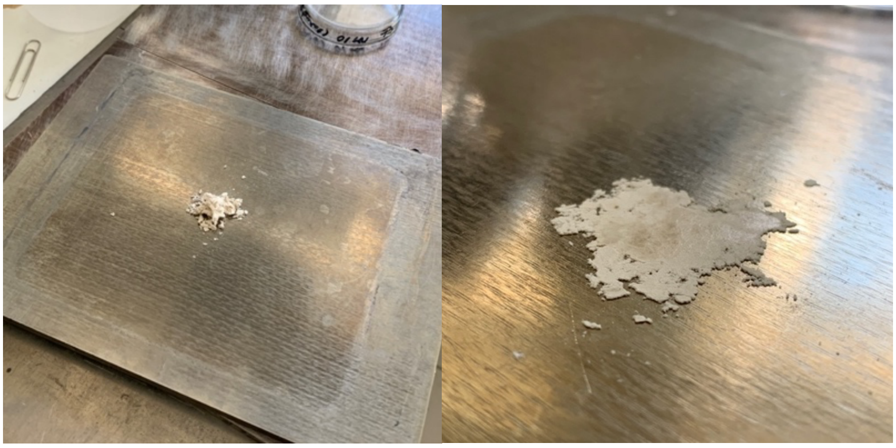


Figure 2.11. Sample before pressing (left) and after pressing (right)

2.5 Sample preparation parameters

In the current research study, the effect of different variables on the efficiency of the esterification reaction was studied. Variables can be broadly divided into mixture composition and mixture pre-treatment variables.

The pre-treatment conditions studied were the time of adding the components to the reaction mixture (from now on, referred to as the mixture composition), the pre-storage time and temperature, and the efficiency of the US method for the reaction. For the mixture composition, the co-solvents necessity and the catalyst's effect were tested. Changing the ratio of VL and MCC towards the success of the reaction was also examined in order to produce better reaction results. Therefore, 27 different reaction samples were prepared according to the data presented below to find the most optimal reaction mixture pre-treatment conditions, methods, and composition.

Comparable samples were made to determine whether the VL has an impact during pre-treatment or if it is beneficial only during the extrusion process. The VL was added either before pre-treatment time along with other fixed ingredients (IL and MCC), or after pre-treatment time, right before the extrusion process. These samples are displayed on the first two rows of the Table 2.1. For easier understanding, the amounts are given in grams and moles.

Table 2.1. – Samples compositions with variable ingrediencies adding times (before or after pre-treatment) combinations. Given in grams (and in moles).

Before pre-treatment (g(mol))				**After pre-treatment, before extrusion** (g(mol))	
IL	**MCC**	**VL**	**DMSO**	**VL**	**DMSO**
3,92 (0,074)	1,96 (0,012)	4,12 (0,018)			
3,92 (0,074)	1,96 (0,012)			4,12 (0,018)	
1,96 (0,037)	1,96 (0,012)	4,12 (0,018)	1,96 (0,025)		
1,96 (0,037)	1,96 (0,012)			4,12 (0,018)	1,96 (0,025)
1,96 (0,037)	1,96 (0,012)	4,12 (0,018)			1,96 (0,025)

Next, the impact of DMSO was examined. DMSO is often used in combination with IL to improve the solubility and processability of cellulose. It can also lower the cost of the reaction, as ionic liquids are generally expensive, and their synthesis is energy intensive.

The effect of DMSO addition time was also tested on three comparisons: all ingredients before pre-treatment, all ingredients after pre-treatment, VL before, and DMSO after pre-treatment (displayed on the three last rows of the Table 2.1).

The above-described compositions were tested at several pre-treatment time and temperature combinations. To assess the effect of pre-treatment time and temperature, the mixtures were treated in accordance with the Table 2.2. The mixtures at room temperature were held in the glovebox, and the samples at higher temperatures were treated in an oven with air. The room-temperature mixtures were kept in a glovebox, and the higher temperature samples were treated in the conventional oven (with air). Since no references were found in the literature, we conducted additional test to examine the impact of oven storage on VL and IL. The test was carried in oven for 20 hours at 40°C. The results are in presented in the Appendix 1.

Table 2.2. Mixture pre-storage conditions for reaction

Storage method	**Pre-treatment time**	**Pre-treatment temperature**
Glovebox	1 w	RT
	2 w	RT
Oven	20 h	40 °C
	12 h	60 °C
	4 h	70 °C

h - hour
w - week
RT - room temperature

The alternative pre-treatment method was tested after finding the most suitable composition with optimal time and temperature combination for pre-treatment in the oven. Since the work is intended as a possible further development on a pilot production line, it is necessary to reduce pre-treatment time because it is impractical to pre-treated mixtures in the oven for given long periods during production. As mentioned in section 2.2 Pre-treatment methods, the US method has a stronger effect and speeds up the reaction more than conventional oven pre-treatment, resulting in a shorter treatment time to achieve the same result. To assess the impact of US pre-treatment, all samples were prepared using the previously determined best combination of composition and ingredients addition times (preDMSO_preVL) and treated using the time and temperature combinations listed in Table 2.3.

Table 2.3. Mixture pre-storage conditions for US method

Storage method	Pre-treatment time	Pre-treatment temperature
US	4 h	50 ºC
	1 h	50 ºC
	1 h	80 ºC

In order to improve the vinyl laurate to cellulose monomer ratio, a comparison test was performed on two selected US samples. In the case of the oven pre-treatment, the VL amount could not be increased because the extruder used in this work is not hermetic enough and the liquids escape between the extruder gaps. However, with the US method, the mixture becomes more solid during pre-treatment than in the oven, so it is possible to increase the amount of VL.

Samples can have eighter 1,5:1 or 2:1 of molar ratio of vinyl laurate to the cellulose monomer, anhydro glucose (AGU). For 1,5:1 ratio, the maximum achievable degree of cellulose laurate substitution is 1,5. To increase the possible degree of substitution, the ratio was balanced to 2:1, meaning there is twice as much VL as there are AGU units. Samples whose ratio was balanced to 2:1 are marked with *"m.ratio"* at the end of the sample name (the naming of samples are explained in paragraph 2.6.).

Molar ratio of 1,5:1 composition
MCC – 1.96g
VL – 4.12 g
Solvent (DMSO and IL 1,5:1) – 3.92 g (DMSO – 1.96g; IL – 1.96 g)
Catalysis – amount not included in calculation
Total sample: 1.96+4.12+3.92 = 10 g

Molar ratio of 2:1 composition
MCC – 1.67g
VL – 4.66 g
Solvent (DMSO and IL 1:1) – 3.34 g (DMSO – 1.67g; IL – 1.67 g)
Catalysis – 0.33 g (10% of solvent)
Total sample: 1.67+4.66+3.34+0.33 = 10 g
The amount of catalyst was calculated in for the modified ratio recipe, because the tested samples that had catalyst in mixture gave better results in every tested condition. *

After analyzing the compositions and the pre-treatment methods with different time and temperature combinations, the effect of the catalyst was tested. To further enhance the experimental outcomes, the catalyst was introduced into the mixture. For that the IL mTBN superbase was used as catalyst. First, the effect of the catalyst was tested on the selected oven-pre-treated sample. From there, the studies were continued using the US-treatment. Two percentage amounts, 5% and 10%, were tested. The catalyst is added to the mixture based on the amount of solvent (DMSO and IL), and the quantity is calculated in grams. The total sample amount, including an additional 5% catalyst, is 10,20g for a ratio of 1,5:1 and 10,17g for a ratio of 2:1. For a 10% catalyst concentration with a 2:1 ratio, the total amount is 10.33g. The samples with catalyst have the abbreviation "cat" mention in their name.

Table 2.4. Treatment conditions for samples with mTHN catalyst

Catalyst amount of solvent	**VL to MCC ratio**	**Time and temperature**	**Treatment method**
5%	1,5:1	20h 40 °C	Oven
	1,5:1	4h 50 °C	US
	1,5:1	1h 50 °C	US
	2:1	1h 80 °C	US
10%	2:1	1h 80 °C	US
	2:1	1h 50 °C	US

All the prepared samples are compared with the reference sample. The reference sample consists of a mixture of preDMSO_preVL with the 1,5:2 ratio of VL to MCC. The reference sample was prepared in the same manner as the other tested samples in a glovebox. After mixing the ingredients, the sample was kept at room temperature for 1 hour and then extruded. The processing in extruder and post-processing were carried out under the same conditions as the rest of the samples.

2.6 Specimen naming

To make the analysis of obtained results easier, the naming system for the samples was developed. All the variables are coded in the names of samples for better understanding and evaluation of obtained results (naming is explained in Figure 2.13). Each sample was given a corresponding name based on the pre-storage time, composition, and method. The redundant and derived information is not written out in the name for shortening the names. The specimens that have been pre-treated in a glovebox or oven do not have a reference to this in writing (it is derivable from Table 2.2, based on temperature), therefore if the sample is pre-treated in an ultrasonic bath, it has a reference in parentheses in the appendices. The IL:DMSO ratio is not written out because it can be derived from the variable ingredients on the name (also derivable from Table 2.1). If a catalyst is added to the mixture, it is always added before the pre-storage time, which is why there is no "pre" or "ex" added in naming in front of it.

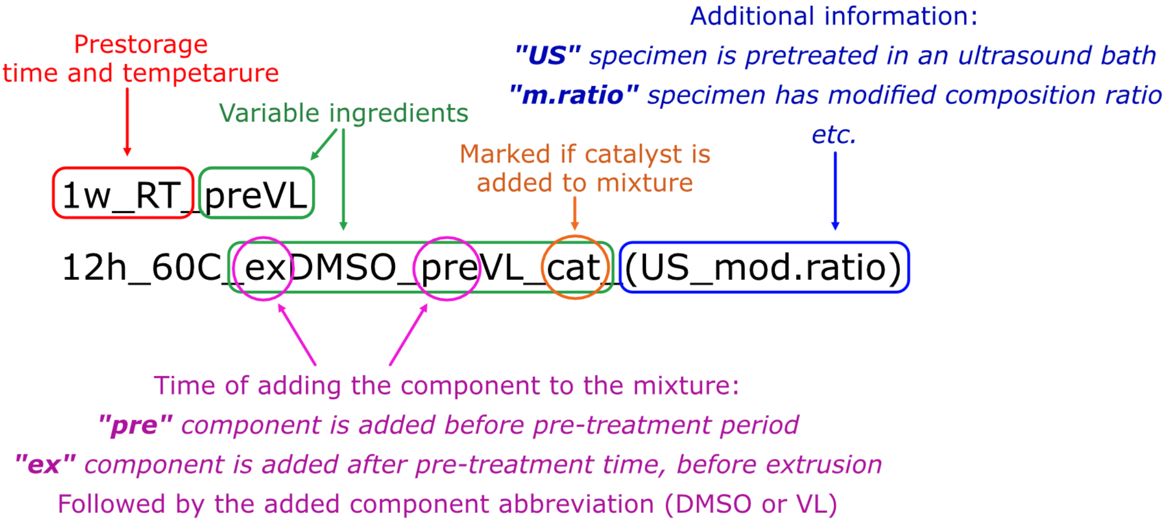


Figure 2.13. Specimen naming scheme

3 TEST METHODS

3.1 Fourier Transform Infrared Spectrometry

The Fourier Transform Infrared Spectrometry (FTIR) uses infrared radiation to measure the characteristic absorption of different chemical bonds to determine a substance's composition [66]. This work uses FTIR to detect a change in a sample and determine the reaction's success.

In this study used the FTIR spectrometer IRAffinity-1S with an ATR (Attenuated Total Reflectance) accessory (Figure 3.1). The ATR crystal provides good sensitivity and allows direct analysis of samples without extensive preparation. It enables to analyze wide range of materials from solid to liquid. [67], [68] For testing, the extruded material was washed according to the paragraph 2.4.1. and pressed according to paragraph 2.4.2. The post-processed material was placed on the crystal part and fixed. The spectra were measured in the range from 4000 cm^{-1} to 600 cm–1 with the resolution of 8 cm^{-1} and number of scans of 8.

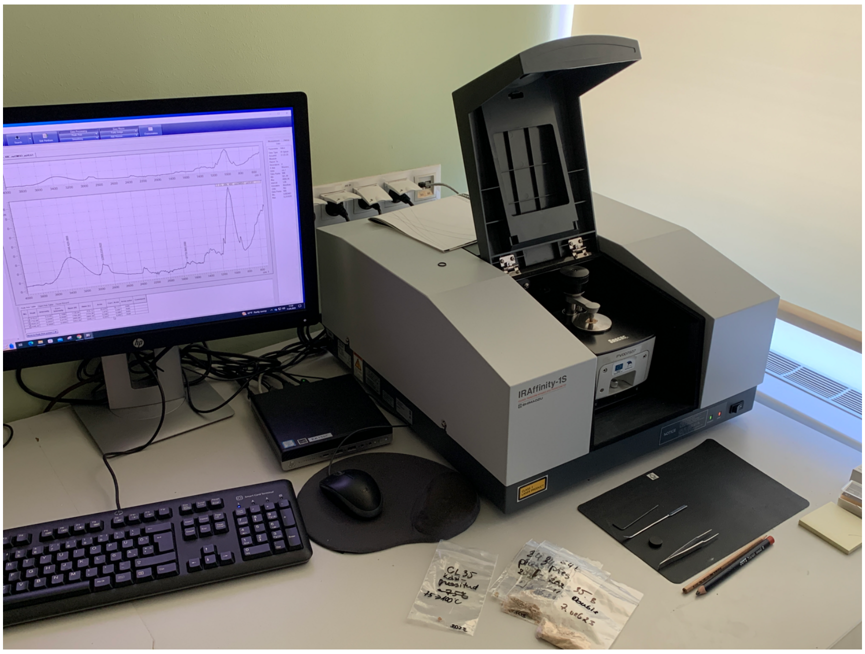


Figure 3.1. The FTIR spectrometer IRAffinity-1S with an ATR accessory

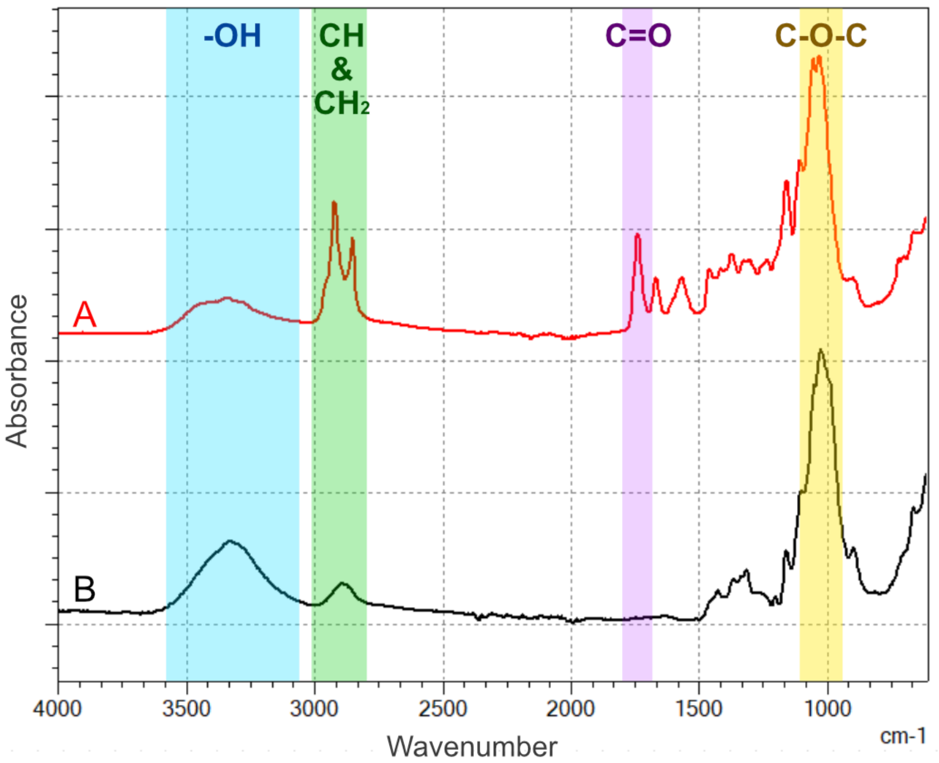


Figure 3.2. FTIR spectra for cellulose laurate (1h_50C_preDMSO_preVL_cat_(US_m.ratio)) (A) and MCC (B) with marked areas

The FTIR spectrum of cellulose is characterized by a peak in the region 3280–3410 cm^{-1}, which indicates the hydroxyl group (-OH). Vinyl laurate does not have a peak in the given region. However, the peak in the spectrum of the synthesized substance is still present to some extent. [69]–[71]

The vinyl laurate has characteristic peaks in the FTIR spectrum around 1740 cm^{-1} indicating a carbonyl group (C=O) and two close peaks in the region 2850–2924 cm^{-1}, indicating asymmetric and symmetric valence vibration of the methylene group (CH and CH_2). These appearances on the graph are a good first indication that named characteristic bands are in the synthesized sample. [69]–[71]

Cellulose esters have characteristic stretching vibration of the ether functional group (C-O-C bond) in the FTIR spectrum tends to occur around 1050 cm^{-1}. Even though cellulose also has a peak in that area, the C-O-C area in cellulose laurate has also been used in studies to calculate reaction success. [14], [72]

3.2 Nuclear Magnetic Resonance Spectroscopy

A solid Nuclear Magnetic Resonance (NMR) Spectroscopy analysis was performed on six selected washed and ground samples. 300-500 mg of the sample with the finest possible fraction was sent for analysis. Testing was performed by the Institute of Chemical and Biological Physics using a Bruker AVANCE-II spectrometer. Magic-angle spectrum (MAS) spectra of the 13C isotope were recorded at 14.1 T magnetic field using the home-built MAS probe for 25 x 4 mm Si_3N_4 rotors. During the test, the sample rotates at an angle of 54.74° with regard to the permanent magnetic field [73]. The magnetic induction was 14.1 T, and the spinning frequency was 12.5 kHz. With this method, it is possible to calculate a fairly accurate degree of substitution (DS).

The DS of the cellulose laurate refers to the average number of lauric acid ester groups per glucose unit in the cellulose backbone. A greater DS indicates a higher degree of substitution, meaning that more hydrogen units in cellulose have substituted with vinyl laurate ester groups. In theory, higher DS values increase the hydrophobicity and solubility of the cellulose laurate. In the analysis part of the work, the NMR DS results are compared with the FTIR C=O and -OH ratios.

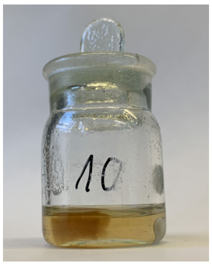
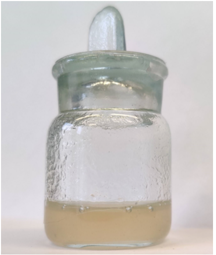
3.3 Solubility tests

The purpose of the solubility test was to evaluate the solubility of the obtained cellulose laurate samples in different organic solvents. Dissolution of cellulose laurate in different organic solvents is a method used to evaluate the solubility. It can provide useful information on the behaviour of cellulose laurate in solution, but it cannot provide a direct or quantitative method for determining the degree of substitution.[46]

Approximately 0.02 g of the sample and ~2g of the selected solvent were added to the beaker. The beaker was sealed with a wax strip to reduce possible evaporation of the solution from the container. Then it was magnetically stirred for 24 hours at RT. Later, the solution's physical appearance change was evaluated according to the scale in the table below (Table 3.1) solely based on visual observation.

The solubility of prepared cellulose laurate samples was tested in different organic solvents: dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and pyridine. Those polar aprotic solvents are more suitable for materials with lower levels of substitution and were selected for the solubility test based on the assumption that the reaction does not give high substitutions on the cellulose molecule.

Table 3.1 Solubility evaluation base scale

Scale	–	+	++	+++
Dissolution	No change in appearance	Surface swelling	Partially dissolved	Complete dissolution
Illustrative sample				

4 ANALYSIS AND DISCUSSIONS OF TEST RESULTS

4.1 FTIR value analysis and further method selection

The FTIR method is primarily used in this work to analyze the samples. Previous studies have used the FTIR spectra C=O peak quotient with C-O-C or -OH as a predictor of reaction success (those areas are explained in more detail in part 3.1). In this work, both methods were compared. The results are displayed in Figures 4.1 and 4.2.

Comparing the two graphs, it can be seen that the samples values and the relationship between them are quite the same, although the value scale is different for those quotients. Although the values are different, the ratio is relatively comparable and yields results that are roughly the same.

It was decided to use C=O/-OH in this work going forward because it seemed more appropriate for the context. In the analysis of the FTIR spectrum of cellulose laurate, the C=O/-OH ratio is probably more informative than the C=O/C-O-C ratio. Because cellulose laurate contains ester groups, the C=O peak is expected to be relatively strong, while the -OH peak is expected to be less distinct than in the cellulose FTIR spectrum. This change is very visual and easily estimated on the graph.

In the following work, the FTIR spectrum of carbonyl C=O (around 1740 cm-1) and -OH area (between 3300-3400 cm-1) ratio was calculated to determine the reaction success. The samples are compared with each other, and the effect of the variables on the reaction efficiency is evaluated.

Measuring the C=O to -OH absorption intensities ratio allows the estimation of substitution efficiency. The reaction results in the substitution of -OH groups with moieties containing the C=O group. Therefore, as the intensity of the C=O peak increases and the intensity of the OH peak decreases, it should indicate a better esterification of the cellulose macromolecule. However, it is important to note that the relationship between these peaks and DS value is not always accurate and can be influenced by a variety of factors.

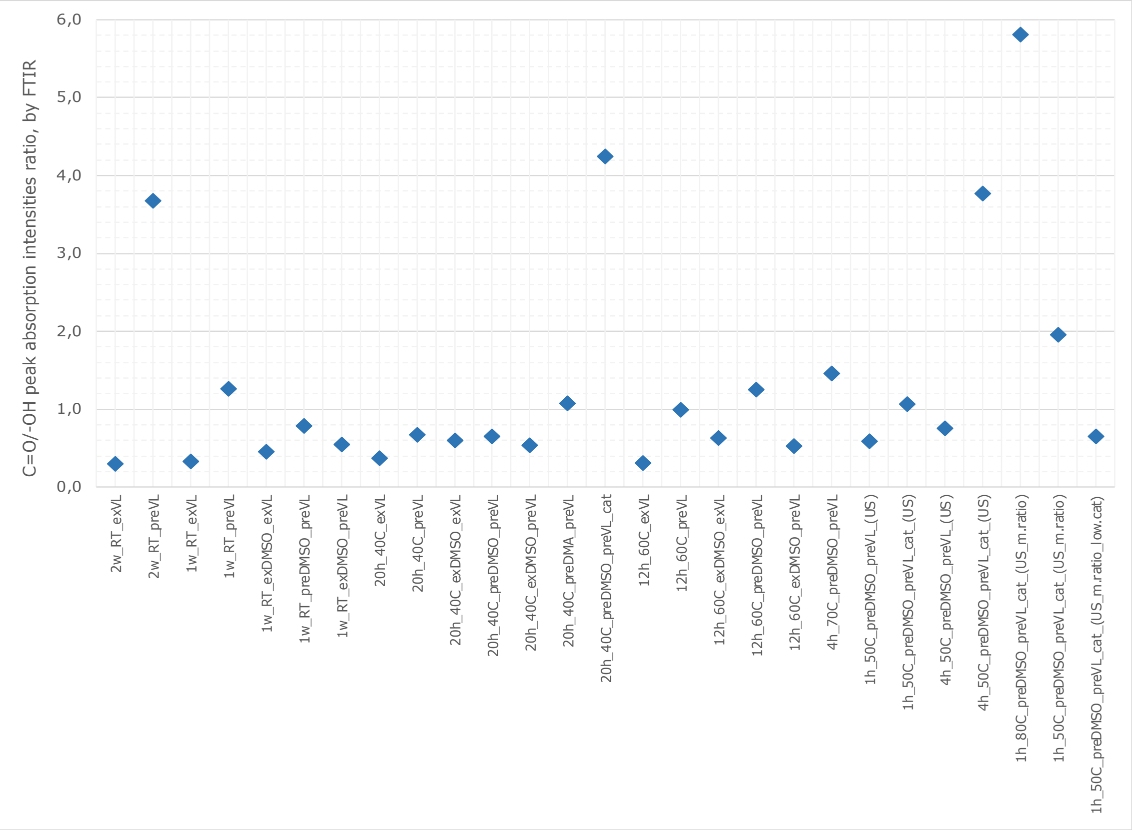


Figure 4.1. The absorption intensities of C=H to -OH peak hight ratios, measued by FTIR

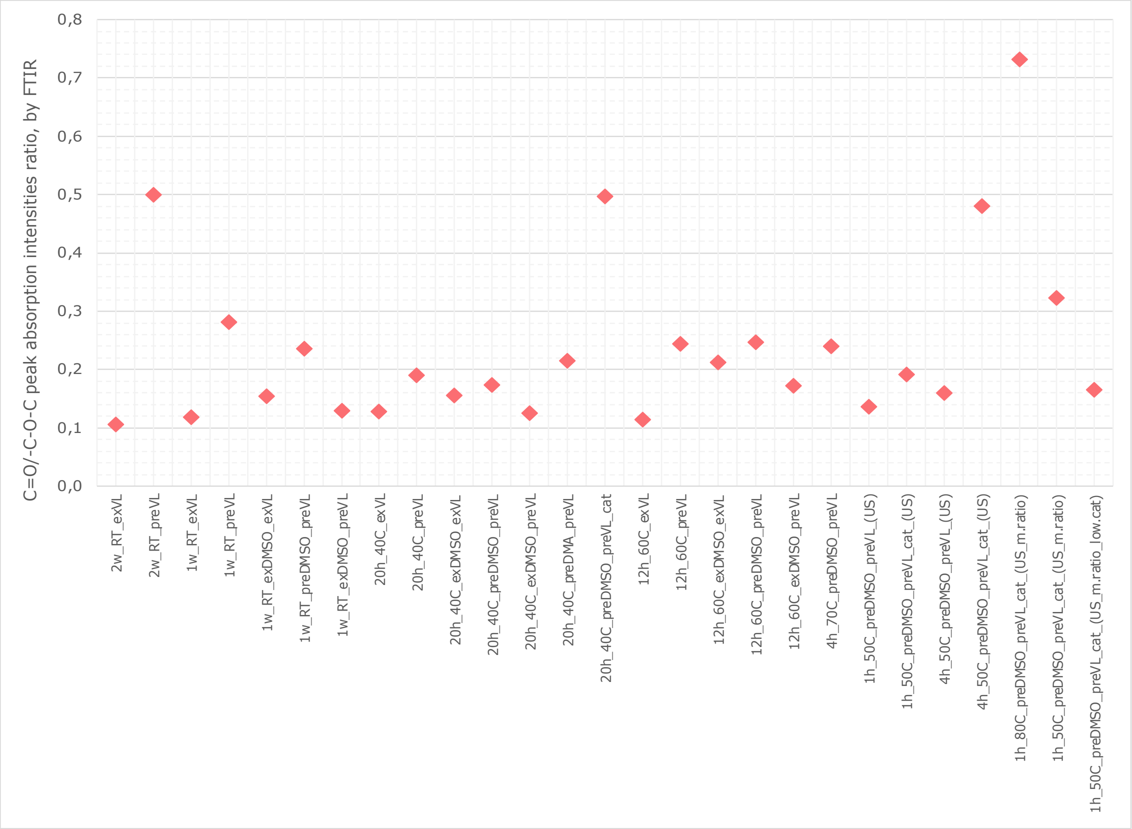


Figure 4.2. The absorption intensities of C=H to C-O-C peak hight ratios, measued by FTIR

To test this theoretical correlation, the available NMR values were compared with the FTIR C=O and -OH quotient. From this, it can be seen from Figure 4.3 that the corresponding relationship exists. The comparison chart shows the trend of between selected areas ratio increase with increasing DS. The used exponential trendline is calculated automatically by Excel ($y = 0{,}3888e^{2{,}4529x}$).

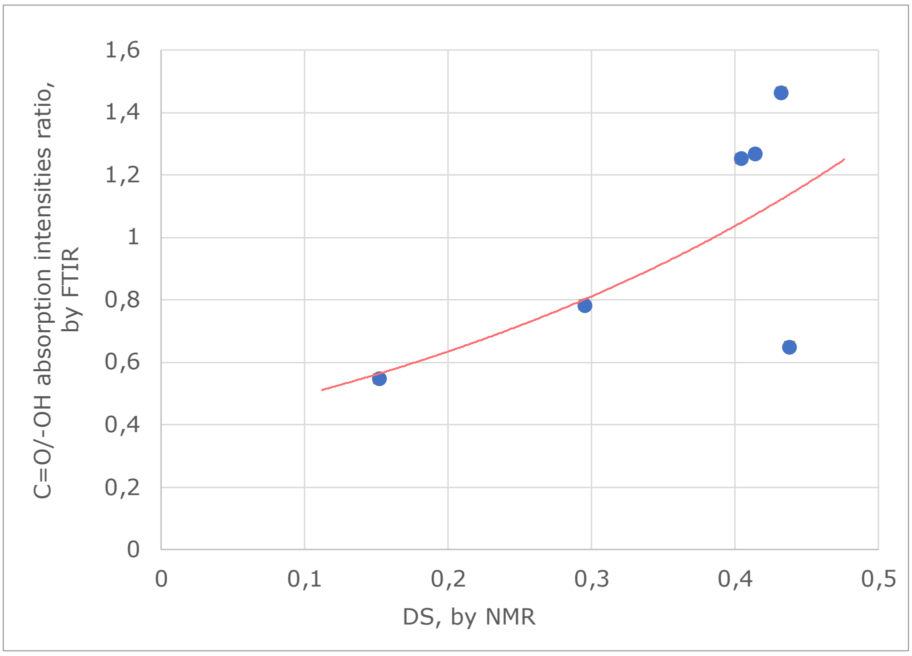


Figure 4.3. The C=O to -OH peak absorption intensities ratio, by FTIR, compared to DS, by NMR

In summary, the C=O and -OH ratio is used to determine the success of cellulose laurate synthesis, as C=O can specifically indicate the presence of the ester group in the cellulose laurate sample. This relationship can also provide correlative information on the material degree of substitution, which is a critical parameter for determining the material's properties.

4.2 The effect of component addition time and mixture composition

To assess the effect of VL and DMSO addition time, samples were prepared according to Table 2.1 in paragraph 2.5. It should be noted that samples containing DMSO contain half as much IL as those without DMSO. Because the amounts of IL differ, the time of adding the verging compositions has been compared in separate tables.

Table 4.4 compares the time of VL addition "preVL" (before pre-storage) and "exVL" (after pre-storage, right before extrusion) in three pre-treatment times: 12 hours, 20 hours, and one week. The results show that adding VL before pre-storage improves the results by an average of 2-3 times for all pre-storage times. This indicates that the reaction between VL and MCC starts already during the pre-treatment period, not only in the extrusion process. When VL is added to the mixture before the pre-treatment time, it has more time to react with the hydroxyl (-OH) groups on the cellulose chains.

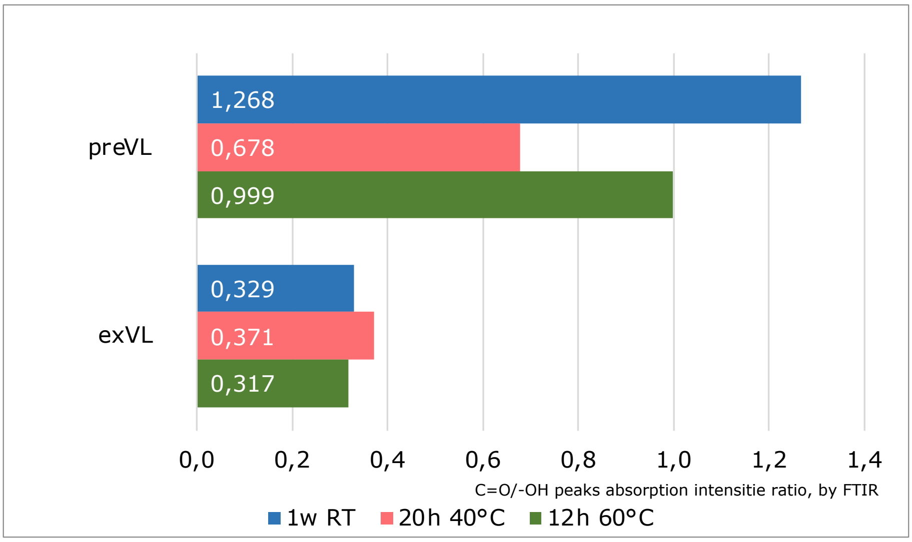


Figure 4.4. The effect of VL addition time on mixture composition on the efficiency of the cellulose esterification reaction determined by FTIR C=O and -OH peak quotients. A higher value indicates a more successful reaction.

The Table 4.5 compares the addition times of VL and DMSO combinations. There are three addition combinations: both added before pre-storage (preDMSO_preVL); VL added before and DMSO added after pre-storage (exDMSO_preVL); and both added after pre-storage (exDMSO_exVL). All the combinations are tested over the same three pre-treatment periods, as previously mentioned. The same pattern can be seen here as well; samples with all ingredients added before the pre-treatment time give better results.

Aside from the addition time of the components, the composition of the reaction mixture has a significant impact on the efficiency of the reaction. The effect of different compositions was tested along various pre-treatment times. This experiment had two constant components (MCC and IL) and two variable elements (DMSO and VL). The samples containing DMSO had a lower IL content (weight ratio 1:1).

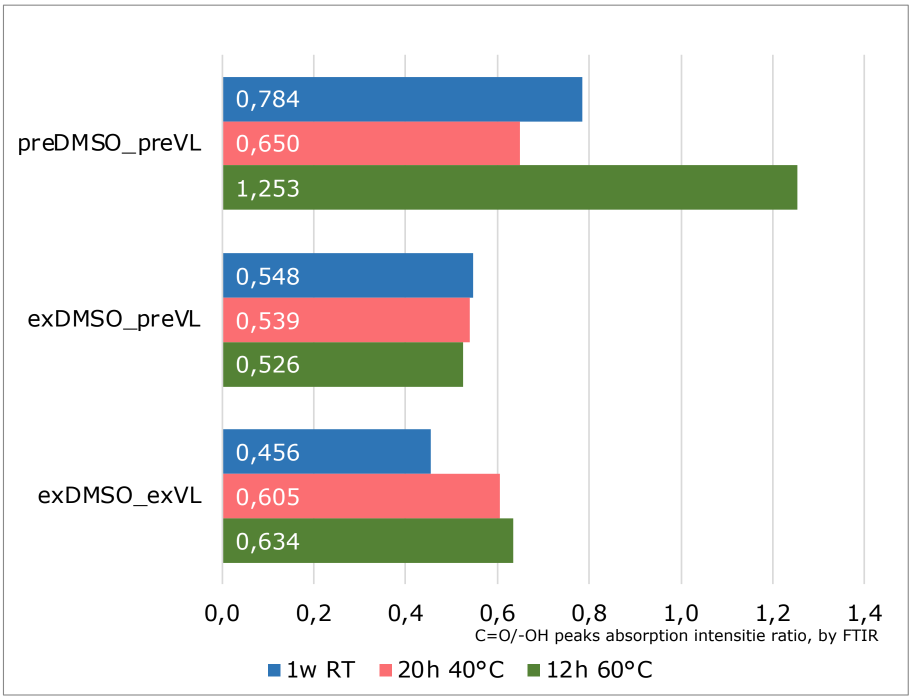


Figure 4.5 The effect of VL and DMSO combination addition time on mixture composition on cellulose esterification reaction efficiency as determined by FTIR C=O to -OH absorption intensities ratio. A higher value indicates a more successful reaction.

By comparing tables 4.4 and 4.5, it can be seen from the graphs that the time of adding VL affects the result the most. The best results were obtained when VL was added before pre-treatment time (preVL), both with and without DMSO (preDMSO_preVL). The best results were obtained with the shortest pre-storage time when both VL and DMSO were added before storage. The C=O peak is 1.253 higher than the OH group. Adding of DMSO right before extrusion did not affect effect on the results (exDMSO_preVL).

The mixtures with no DMSO and where VL was added after pre-treatment time right before extrusion (exVL) produced the worst results. The peaks observed in the FTIR spectrum of these mixtures are not detectable in the C=O region. Adding DMSO to the same sample after pre-treatment (exDMSO_exVL) improves the result to some extent. For all samples where some composition component is added after the pre-treatment time, the OH group continues to be significantly higher than the C=O peak.

In general, when variable ingredients are added after the pre-storage time, the results for all test periods are nearly identical. Larger differences can be observed for the same composition when the ingredients were added prior to the start of storage, and the ingredients had a longer time to affect the sample even during the pre-treatment period. The sample with the composition of preDMSO_preVL with 12 hours pre-treatment in oven gave the best results of composition and time combination was under the tested conditions.

4.3 Effect of pre-treatment period and temperature on reaction efficiency

After the composition analyse, the effect of pre-treatment time and temperature on the reaction efficiency was investigated. For this, samples with different compositions are compared under different pre-treatment time and temperature combinations. The pre-treatment period and temperature combinations are shown in more detail in Table 2.2 of paragraph 2.5.

All the results are presented on Figure 4.6. For a better comparison, the reference sample has been included in the table. When comparing the results with reference sample, it is evident that the values of all the samples are higher than the original reference. This is generally a positive indicator. The reference sample shows values closest to the composition of exVL for each tested period. This clearly demonstrates that although IL and DMSO play their role throughout the pre-treatment, their effect alone is limited. It is more advantageous to also include VL right before the pre-treatment.

In the test results, it was found that for the samples preVL and exDMSO_preVL, a longer reaction time favors the esterification reaction. The analysis show that a pre-treatment duration of two weeks yields highly favorable results. However, that long pre-treatment time, is not practical in the context of line production.

Based on the results, it can be observed that preDMSO_preVL exhibits promising outcomes at shorter durations, specifically at 12 hours and 4 hours. However, in terms of yield comparison, the result is still significantly lower, compared to the best result in the table (2w RT preVL).

Previous studies have also found that a longer reaction time favours the esterification reaction. The study "Preparation and characterization of cellulose laurate ester by catalysed transesterification," established that the vinyl laurate in a reactor at a temperature of 120 °C obtained the product with a higher degree of substitution if the reaction lasted for six hours instead of one hour. The degree of substitution was 2.74 and 1.97, respectively. [46]

The same study found that increasing the reaction time to nine hours lowered the degree of substitution to 2.55. From that, it can be concluded that too long reaction time can start to reduce/suppress the result and might have a thermally degrading effect on the cellulose macromolecules and the hydrolysis of the cellulose laurate ester. [46] The samples exVL and exDMSO_exVL decreasing values over time can be explained with possible degradation of the cellulose macromolecules and the hydrolysis of the cellulose laurate ester in the samples.

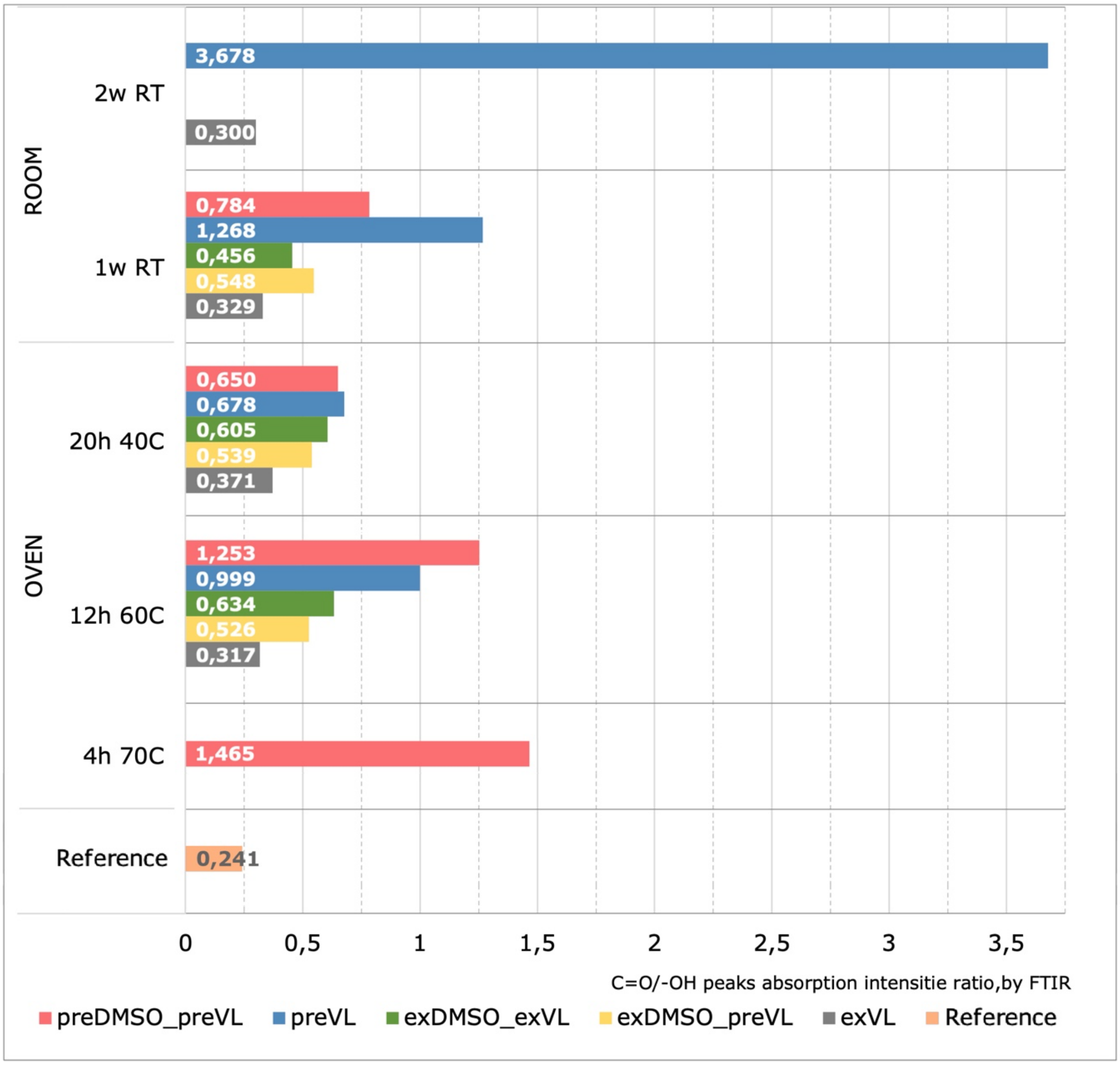


Figure 4.6. The impact of pre-treatment time and temperature on the reaction efficiency. The values given in the table are calculated by FTIR C=O to -OH absorption intensities ratio. A higher value indicates a better reaction. A value below 1 indicates that the -OH peak is still higher than the C=O peak.

The C=O and -OH ratio is just one of several methods used to determine the success of cellulose acetate synthesis and other techniques, such as nuclear magnetic resonance (NMR) spectroscopy. It is important to establish consistent conditions and appropriate calibration standards when using the C=O and -OH ratio calculation method because it can affect the area's ratios. Since the tested material is not completely uniform and the FTIR measurement takes place at a selected location on the surface of the sample, the NMR test is considered more reliable and precise [67], [74].

Six samples were selected for the NMR analysis. The effect of pre-storage conditions (time and temperature) on the reaction can be evaluated based on four samples with the same composition (preVL_preDMSO) that are pre-treated at different length of time and temperature (1 week, 20 hours, 12 hours, and 4 hours).

Table 4.1. The DS values by NMR test on selected 6 samples

Pre-treatment conditions	**Sample composition**	**Degree of substitution**
1w RT	preVL	0,414
1w RT	exDMSO_ preVL	0,152
1w RT	preDMSO_ preVL	0,295
20h 40°C	preDMSO_ preVL	**0,438**
12h 60°C	preDMSO_ preVL	0,404
4h 70°C	preDMSO_ preVL	**0,432**

In conclusion, sample 2w_RT_preVL yielded the best test result. When comparing both NMR and FTIR measurements, sample 4h_70C_preDMSO_ preVL exhibited the most favourable outcomes. However, sample 20h_40C_preDMSO_ preVL, which showed the best NMR result, did not yield the expected outcome in FTIR analysis. Overall, it was observed that longer pre-treatment times yielded better results. However, considering the impracticality long pre-treatment in the line production perspective, it is necessary to explore more options, to find better method with lower time consumption and higher yield.

4.4 Pre-treatment in the ultrasonic bath

After analyzing the samples stored at room temperature and elevated temperature in the oven, the US method was introduced as another pre-treatment method. This method was implemented because, based on written sources, it was found that ultrasonic waves break down the cellulose structure better and help the vinyl laurel particles to penetrate through the cellulose molecule.

Based on previous knowledge, it was decided to continue the experimentation with a mixture composition of preDMSO_ preVL. To reduce the longitude of heat treatment during pre-treatment and make whole process more nature friendly regarding energy consumption the ultrasonic treatment was applied at next parameters: 50°C, the stable minimum that could be maintained using the given machine, and 80°C, the machine's maximum operating temperature. The US bath pre-treatment time and temperature combinations are shown on the Table 2.3 in paragraph 2.5.

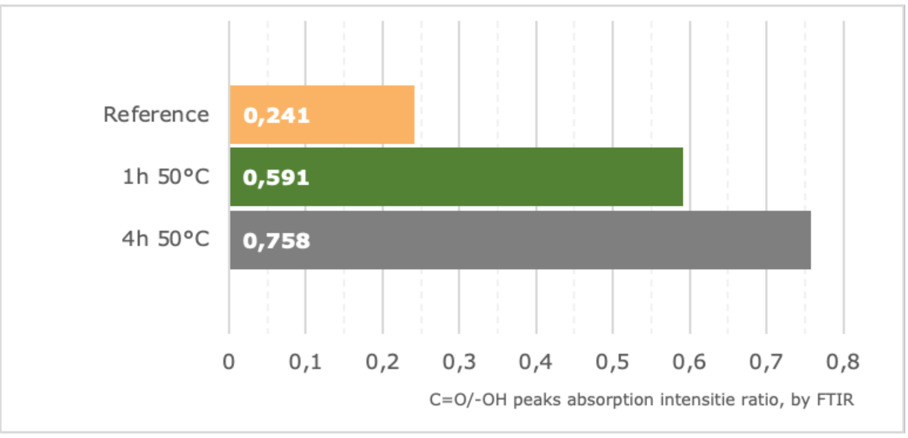


Figure 4.7. The 1h and 4h US pre-treated sample comparison.
At 50degrees on a sample compsition of preDMSO_preVL

Comparing the reference sample with 1 hour 50°C US-treated sample (both had the same duration from sample mixing to extrusion), we observe a more than double increase in the result. However, the precise impact of the ultrasound treatment remains unknown, as it differs from the reference sample in temperature elevation. By using the 4-hour 50°C US-treatment method, the result surpasses the reference sample by more than three times.

When comparing the two US-treated samples, which were pre-treated using US method at 50 degrees for 1 and 4 hours, it can be observed that there is an increase in the result with longer duration. Nonetheless, with only 1-hour US pre-treatment, an equivalent result was achieved compared to the longer pre-treatment times in previous tests (in an oven or at room temperature). Therefore, the US method allows for a significant reduction in pre-treatment time. Furthermore, the sample development was continued using US pre-treatment.

4.5 Addition of extra mTBN catalyst

To evaluate the effect of the catalyst, the best combination of pre-treatment parameters and composition was chosen. The superbase was added as a catalyst to oven-treated sample 20h_40C_preDMSO_preVL. The catalyst was added during mixture preparation in a glovebox with other chemicals. The amount of catalyst was calculated as 5% or 10% of the total amount of mixture solvents.

During practical work, it was observed that in the case of mixtures containing a catalyst, the material coming out of the extruder had a thicker consistency and was stickier. When cleaning the extruder, removing the excess material in the machine was more difficult. Also, based on the FTIR absorbance graph, the strong decrease in the -OH area was observed, which was not as visually evident in the previous samples. This finding is considered a positive indication of a successful reaction.

Figure 4.8. The sample after extrusion with no catalyst (left) and with catalyst (right)

As can be seen from Figure 4.9, the addition of 5% mTBN catalyst of mixture solvent amount, has a positive effect on all tested parameters. The -OH peak intensity decreased, and at the same time, the C=O peak increased significantly. Evaluating the value differences between oven pre-treated specimens, it can be seen that the result has improved more than 9 times.

Based on this positive result, the effect of the catalyst was also tested on US-treated samples. In the case of the 4-hour US-treated sample, a more than six times improvement in the result can be seen. In the case of the sample pre-treated for 1 hour in US, a two times improvement can be seen, but the overall result is significantly lower than the samples with a longer pre-treatment time. During the process of ester formation, the catalyst is often used in large quantities to enable the acylation reaction (catalyst action) while protecting the cellulose backbone from hydrolysis.

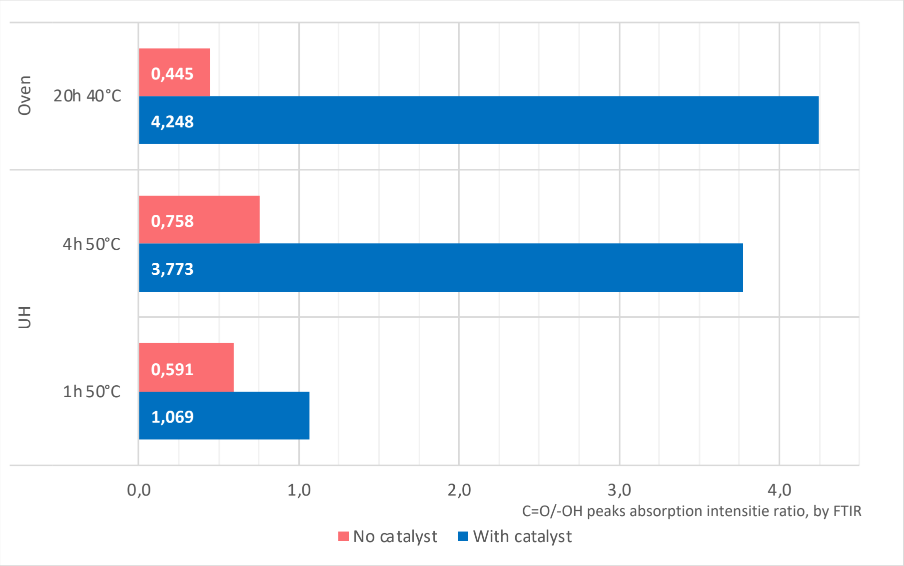


Figure 4.9. The 5% catalyst effect with composition of preDMSO_preVL on different pre-tretment conditions

After testing with 5% catalyst, it was decided to increase the amount of catalyst to 10%. The effect of the catalyst amount was tested with a 1-hour, 50°C US-treatment on a sample composition of preDMSO_preVL with a modified ratio (the ratio modification is described in paragraph 2.5 and analyzed further in the next paragraph 4.6). The results are presented on Figure 4.10. Increasing the amount from 5% to 10% gives almost three times better results. The use of a catalyst helps to increase the reaction rate and improve the efficiency of the esterification process. When comparing the reference sample (with a value of 0.241) to the sample with 10% catalyst, considering other modifications in the sample, we observe that the result has improved by more than 8 times.

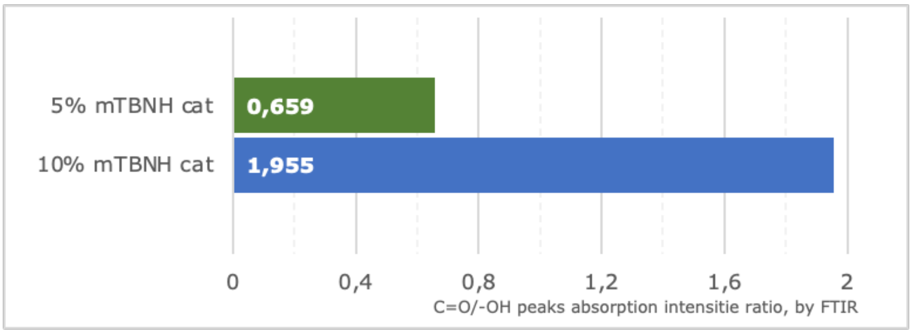


Figure 4.10. The 5% and 10% catalist effect on 1h at 50°C US-treated sample with composition of preDMSO_preVL with a modified ratio

In conclusion, a larger quantity of catalyst (under the tested conditions) leads to a more successful reaction. During this experiment, it was found that using 10% of the catalyst (relative to the total volume of the used solvents) yields approximately three times better results compared to using 5% quantity. It should be noted that the experiment was conducted with a modified composition ratio on the sample.

It can be assumed, although no experiments were conducted, that using a catalyst may allow for a reduction in the pre-treatment time, resulting in improved outcomes. This aspect was not included in the scope of this study and could be explored in future research.

4.6 Components ratio modification

When using the US method, it was discovered that the mixture became significantly more solid during the pre-treatment prosses compared to previous methods. Therefore, by employing the US-treatment, it was possible to increase the used VL amount in the mixture ratio of 1,5:1 to 2:1 of VL to MCC. The increase in quantity was not possible for other used methods, because the employ extruder was not hermetic enough to process samples with a large liquid volume. The VL to MCC ratio calculation is described in chapter 2.5.

The best sample, based on FTIR result analysis from the previous tests, was chosen to test the VL and MCC composition ratio modification. This sample was the one that underwent 1 hour of US pre-treatment at 50 degrees Celsius with the mixture composition of preDMSO_preVL_cat.

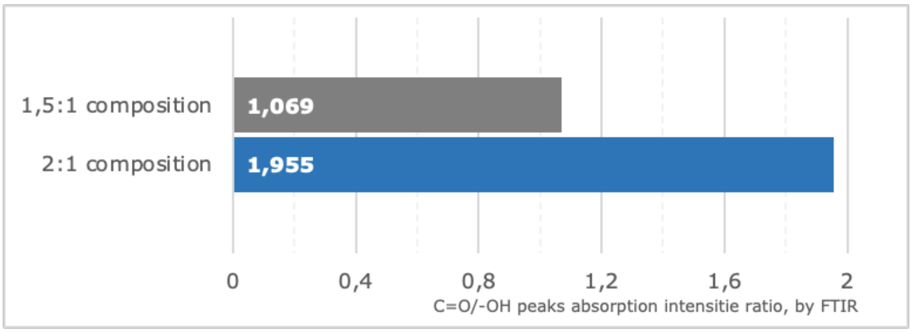


Figure 4.11. Improving the composition ratio on 1h_50C_preDMSO_preVL_cat_(US)

The experiment showed that improving the ratio almost doubled the value, as shown in Figure 4.11. This is because by increasing the ratio of VL to cellulose, more VL molecules are available for esterification with the hydroxyl groups of cellulose, leading to better reaction outcome.

Previous tests have also found that improving the ratio by increasing the amount of VL relative to AGU results in a better reaction. For example, this is confirmed in the study "Preparation and characterization of cellulose laurate ester by catalyzed transesterification." As a result of the mentioned research, it was discovered that improving the ratio from 3:1 (DS value 1,80) to 12:1 (DS value 2,63) gave a 1,4 times better DS result. [46]

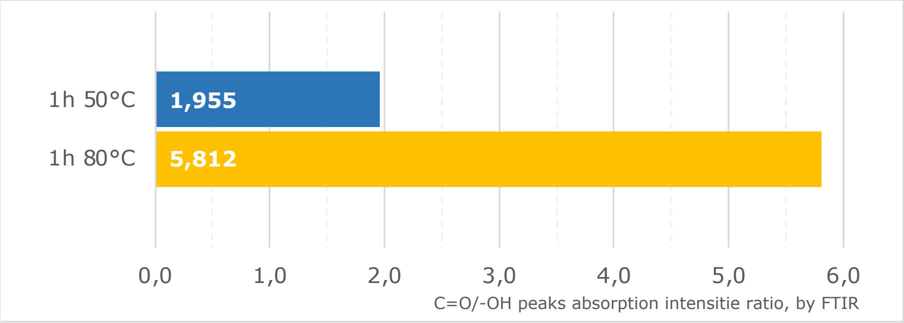


Figure 4.12. The 1h US pre-treated comparison of 50 and 80 degrees on sample preDMSO_preVL_cat_(US_mod.ratio)

The 2:1 ratio was also compared at two different temperatures, 50°C and 80°C in US, with a pre-treatment time of 1 hour. It was discovered that increasing the temperature by 30 degrees improved the result nearly three times. With this, the best result in the given research work was achieved. By increasing the ratio of VL to MCC in favour of VL and adding a catalyst, the US pre-treatment method was able to achieve a result over 24 times better (measured by FTIR, C=O/-OH peaks absorption intensities ratio, value of 5,812), than the reference sample (0,241).

In summary, by using the US-treatment method, it is possible to increase the amount of VL in the mixture. By increasing the amount of VL in composition leads to better results. The best result in the work was achieved with composition ratio of 2:1, along with 10% catalyst addition, using US-treatment for 1 hour at 80 degrees Celsius. Additionally, it is worth testing the given ratio of 2:1 of VL to MCC under different time and temperature combinations, which is a good step for further development of the work.

4.7 Solubility test

It is important to study the solubility of the synthesized samples in order to select suitable testing and processing methods. The solubility test results are presented in Table 4.2. The experiment was started with seven solutions: chloroform, 1,2-dichloroethane, tetrahydrofuran, dimethylacetamide (DMA), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine. However, three did not affect the CL samples (most had no visual change, and few swelled). Therefore, those three solvents chloroform, 1,2-dichloroethane, and tetrahydrofuran (tested on 14 specimens), are not shown in the table and were excluded from the experiment halfway. However, the solubility test can be repeated with named three solvents at higher DS-s of CL samples.

Testing was continued with only the remaining four solutions: dimethylacetamide (DMA), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine. The selected solutions are used due to their high polarity and ability to dissolve a wide range of organic compounds, including cellulose derivatives [75].

Table 4.2. The solubility test results of all specimens used in written work. The solubility was evaluated according to the previously set parameters (described in Table 3.1).

Sample name	**DMA**	**DMF**	**DMSO**	**Pyridin**
2w_RT_exVL	-	+	+	+
2w_RT_preVL	+++	-	-	+
1w_RT_exVL	-	-	+	+
1w_RT_preVL	+++	++	+	+
1w_RT_exDMSO_exVL	-	+	+++	-
1w_RT_preDMSO_preVL	+++	+	+	+++
1w_RT_exDMSO_preVL	++	+	++	+
20h_40C_exVL	-	++	+	-
20h_40C_preVL	+	+	+	+
20h_40C_exDMSO_exVL	-	+	+++	++
20h_40C_preDMSO_preVL	+++	++	++	++
20h_40C_preDMA_preVL	+++	+++	+	+++
20h_40C_exDMSO_preVL	+	+	++	+
20h_40C_preDMSO_preVL_cat	+++	+	+	++
12h_60C_exVL	-	++	+	-
12h_60C_preVL	+	+	+	+
12h_60C_exDMSO_exVL	-	-	+	+
12h_60C_preDMSO_preVL	+++	+++	+	++
12h_60C_exDMSO_preVL	++	+	++	+
4h_70C_preDMSO_preVL	+++	+	+	+
4h_50C_preDMSO_preVL_(UH)	+	+	+	+++
4h_50C_preDMSO_preVL_cat_(UH)	+	+	-	+++
1h_50C_preDMSO_preVL_(UH)	+	+	+++	+
1h_50C_preDMSO_preVL_cat_(UH)	+++	++	++	++
1h_50C_preDMSO_preVL_cat_(UH_m.ratio)	-	-	-	+++
1h_50C_preDMSO_preVL_cat_(UH_m.ratio_low-cat)	+++	+	+	++
1h_80C_preDMSO_preVL_cat_(UH_m.ratio)	-	+	-	-

For the specimens pre-treated in the oven and glovebox, it can be seen that the samples where the substances were added after the pre-treatment time (exVL) have a poorer dissolution result compared to the samples where all the ingredients were added before the pre-storage time (preDMSO_preVL). No visual change was detected (at least in one solvent) in those samples to which VL (with or without DMSO) was added after the pre-storage time (exVL and exDMSO_exVL). The mixtures to which all components were added at the beginning of the oven or RT pre-treatment time gave overall better solubility results. All these samples were completely dissolved or had at least a surface swelling in all tested solvents (except for 2w_RT_preVL).

It was observed that when both VL and DMSO are added to the mixture before oven pre-treatment, these samples show visual changes in the solubility test with all tested solvents. Furthermore, as previously observed in the FTIR test analysis (paragraph 4.2), samples where both VL and DMSO are added before pre-treatment also achieve higher results. Therefore, a correlation can be observed here, suggesting that better solubility is achieved when the reaction has been more successful. It is important to remember that cellulose itself does not dissolve, but its derivatives, such as cellulose laurate does. Hence, it can be inferred that the addition of VL and DMSO before pre-storage can influence the progress and efficiency of the reaction, promote solubility, and facilitate the formation of cellulose derivatives.

Comparing the NMR results and solubility, it can be seen that the samples with the highest DS values (20h_40_preVL_preDMSO and 4h_80C_preVL_preDMSO) are also relatively successful in the solubility test. And the sample with the lowest DS value (1w_RT_exVL) does not dissolve. Based on this, it can be concluded that the time of addition of the ingredients affects both the solubility success and the DS.

In the case of the samples pre-treated in the US, no correlation was found between the solubility and the FTIR value. Also, no correlation was found between catalyst and solubility. A consistent dependency was not found between successful solubility (complete dissolution) and FTIR results. Neither have some earlier studies found a definite relationship between the solubility of the samples and the degree of substitution. Since the samples were tested in polar aprotic solvents, which are more suitable for low-substitution materials, it would be worthwhile to test higher FTIR values samples in less polar solvents where samples with high substitution efficiency should dissolve well.

Presumably, it is not possible to produce uniformly substituted materials within the context of the current process. Since different parts of the same samples can have varying degrees of substitution, this can lead to uncertainties in the solubility test. One approach to achieving more uniform substitution levels would be to incorporate mixing of the sample during the pre-treatment process. It is also worth considering the idea that the solubility may be more related to the location of substitution in the cellulose molecule rather than the degree of substitution. Different substitutions on the surface of the fibrous structure can affect solubility differently.

Table 4.3. The summary of the solubility test results of 27 tested samples in DMA, DMF, DMSO, and pyridine. Evaluated according to the parameters described in Table 3.1.

	DMA	**DMF**	**DMSO**	**Pyridin**
Complete dissolution	**10**	**2**	**3**	**5**
Partially dissolved	2	5	5	6
Surface swelling	6	16	15	12
No dissolution	9	4	4	4

In conlusion, out of the 27 samples listed, the complete dissolution was observe in DMA (10 samples). However, the DMA also had the highest number of samples with no visual change observed (9 samples). Summarizing the table, DMF, DMSO, and pyridine caused most visual changes (surface swelling, partially dissolved or complete dissolution) in 23 samples out of 27.

Figure 4.13. Material obtained by dissolution. Made from oven-treated sample 12h_60C_preDMSO_preVL

4.8 Process productivity analysis

Already during the production of the first sample, it was clear that material loss was high during operation. In order to gain a clearer understanding, 14 samples were examined. All samples had an initial weight of 10g (when preparing the mixtures). This weight was compared to the sample weight after extrusion. Loss of material during pre-treatment was excluded because the sample was pre-treated in a closed container.

The loss after the extruder is about 48%, which means the outcome is 52% (average of about 5,16g) of the inserted amount. The loss of material during extrusion depends on many factors. The extruder is not entirely hermetic; therefore, some of the material (added liquid components) may escape between the extruder screws during the process. Because the mixture is quite sticky (especially when heated), the material can get stuck on the screws and extruder channel. Also, the feed channel will stay full of material, as there is nothing to physically pushing it out of the extruder.

Table 4.4. Material loss and yield analysis from initial mixture to post-processing

Initial mixture weight (g)	**Weight after extrusion (g)**	**Material loss in extrusion (%)**	**Weight after post-processing (g)**	**Material loss in post-processing (%)**	**Overall material loss (%)**	**Material yield (%)**
10,00	2,54	74,60	0,94	62,99	90,60	9,40
10,00	2,67	73,30	1,01	62,17	89,90	10,10
10,00	8,50	15,00	2,84	66,59	71,60	28,40
10,00	7,95	20,50	2,97	62,64	70,30	29,70
10,00	3,05	69,50	1,12	63,28	88,80	11,20
10,00	2,57	74,30	1,03	59,92	89,70	10,30
10,00	2,84	71,60	1,09	61,62	89,10	10,90
10,00	7,86	21,40	3,08	60,81	69,20	30,80
10,00	6,80	32,00	2,92	57,06	70,80	29,20
10,00	6,26	37,40	2,47	60,54	75,30	24,70
10,00	1,82	81,80	0,69	62,09	93,10	6,90
10,00	7,14	28,60	3,02	57,70	69,80	30,20
10,00	6,33	36,70	2,47	60,98	75,30	24,70
10,00	5,87	41,30	2,36	59,80	76,40	23,60
Mean	**5,16**	**48,43**	**2,00**	**61,30**	**79,99**	**20,01**
Standard deviation	**2,43**	**24,29**	**0,95**	**2,39**	**9,46**	**9,46**

The received extruded material is not yet in the final product, as it contains unreacted substances that need to be washed out. During the washing process, the IL and DMSO, as well as the unreacted VL, are washed out. The washing liquid is collected and then distilled in the laboratory so that it can be reused. Therefore, half of the extruded material weight is lost during washing. Measurements are visible in work appendices in Table 4.4. One part of the washing process is grinding the extruded material. This process also involves some material loss, as obtaining the exact same amount of material from the grounder is impossible. For similar reasons, there is some material loss in the crushed material washing filtration process. For these samples, the total loss in the process was about 80%.

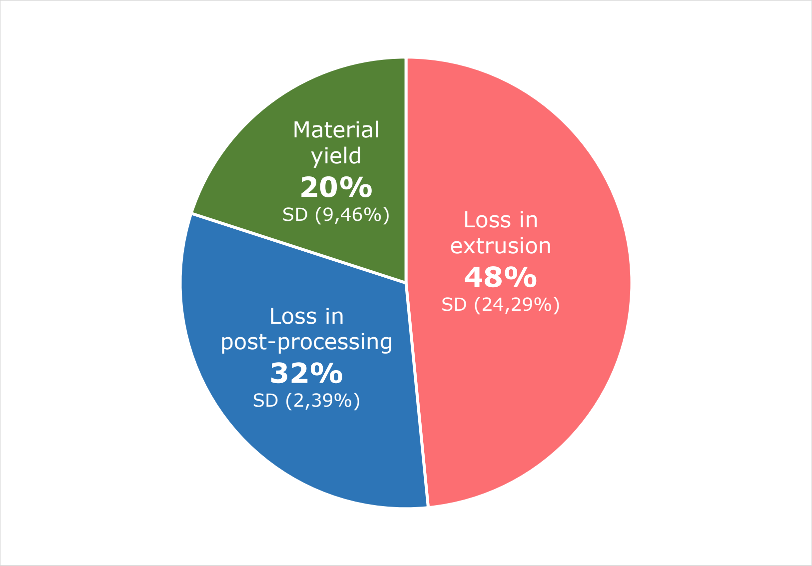


Figure 4.14. Process productivity conclusion - material loss and yield during extrusion and post-processing

The material residues are a major shortage in the given process. However, losses in the given sample making scale can be reduced in a variety of ways, including the use of a more hermetic extruder. Here it is important to keep in mind that the current project serves as a foundation for future development on a larger scale of continuous process line production. As production increases, the amount of material lost during extrusion decreases due to reduced residue left inside the extruder.

4.9 Possibility of completing reaction during US-treatment

During the course of the study, the specific impact of only US-treatment on the sample was investigated, driven by personal interest. To explore this, samples were prepared without extrusion. The results discovered that a significant amount of the reaction takes place already during the US pre-treatment stage. Figure 4.15 presents a comparative analysis showing the results, of the preDMSO_preVL_cat composition samples pre-treated 1-hour in US at 80°C, both before and after extrusion.

Based on these findings, an idea for further development arises – investigate the possibility of using only US treatment. Therefore, there should find the US conditions that give comparable or even better results without extrusion. This is not within the scope of the current thesis objectives but could be promising direction as a part of further research in doctoral studies.

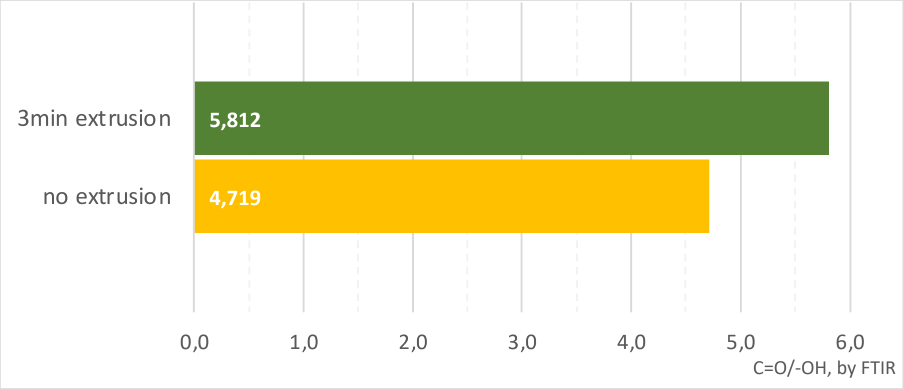


Figure 4.15. Extrusion effect on sample, tested on preDMSO_preVL_cat composition with 1h 80°C US pre-treatment

4.1 Economic Aspects

In today's economy, various factors play a crucial role in shaping industries and driving sustainable development. Bioplastics have often been considered a more environmentally friendly alternative to traditional plastic materials. Although bio-based materials are already available, their production is typically small-scale and expensive. There are currently several constraints in the industrial production of cellulose esters. For example, only certain cellulose esters can be produced on a large scale. In addition, compared to the conventional plastics, the reaction takes a long time to complete (with a high energy consumption) and requires an extensive amount of reagents. [19]

In the context of the green economy, there is a growing emphasis on sustainable practices and the adoption of environmentally friendly alternatives. One such alternative is the use of cellulose as a base material to make thermoplastic polymers, as it is derived from widely available renewable resources and does not compete with food-based raw materials. The substances used in the work are also safer than the most common components currently used in the industry cellulose derivatives. Current work uses vinyl laurate what is considered more environmentally friendly option over commonly used substances. In particular, sulfuric acid, a highly oxidizing chemical that is commonly used in the production of cellulose esters but is not used in this thesis project. [10]

It was discovered that it was possible to lower the used solvent IL by partially replacing it with co-solvent DMSO. Replacing half of the IL with the more cost-effective and widely produced substance DMSO offers significant economic benefits by reducing production costs by achieving comparable reaction results. [47], [51], [52]

The promotion of recycling is a vital economic aspect that aims to minimize waste and conserve resources. In this study, the methods employed allows to restore the solvents used in the reaction. After extrusion, in post-processing (sample washing), the used liquid was collected for distillation to extract the ionic liquid from it for reuse. Ionic liquids are currently expensive and recycling them would also reduce the cost of the process.

Moreover, it was established that distilled water can be used for samples washing, which is much more environmentally friendly compared to alcohol (ethanol) wash. Alcohol washing can have harmful effects on the environment, such as contributing to air pollution and water contamination through evaporation. In contrast, distilled water does not contain harmful chemicals and poses no risk to the environment. Therefore, using distilled water for sample washing is a sustainable and environmentally friendly alternative to alcohol.

Energy efficiency is a crucial consideration in today's economy, aiming to maximize output while minimizing energy consumption. In this study, it was found that the use of US-treatment significantly reduced the reaction time, achieving equivalent results in just 1 hour compared to conventional methods that took 20 hours. The research identified techniques to shorten the duration of mixture pre-treatment, although additional work is required for large-scale application and implementation.

The created cellulose laurate provides an environmentally friendly alternative, effectively reducing the adverse impact of plastic waste and promoting sustainability [10]. With its recyclability and biodegradability, cellulose laurate emerges as a desirable option for sustainable materials, contributing to a greener future. Additionally, the use of ionic liquids as substitutes for hazardous chemicals and unstable organic compounds in the process makes it a safe and efficient cellulose solvent. Furthermore, the ability to recover a certain amount of IL after use leads to cost savings and reduced consumption of raw materials [36], [37].

When analyzing from an economic perspective, it is important to take into account the yield, which refers to the amount of the reaction mixture that ultimately becomes the intended product. The extruder used in this project is suitable for the production of small quantities. As previously stated, the disadvantage of this extruder is its high material consumption, resulting in a yield of approximately 52% of the initial mixture amount. However, it is important to remember that this method is intended for making small mass specimens rather than mass production. When moving on to larger production, a different type of extruder would be used, resulting in a much lower material residue. In line production, there is not a significant loss of material in extruder. At the same time, the cost of post-processing somewhat remains, as complete substitution is not possible to achieve and a certain amount of unreacted VL residue is left. Additionally, it is difficult to predict the exact yield in this process, since the DS has been tested on only few specimens in the given work.

CONCLUSION

The thesis describes the cellulose esterification reaction in the reactive extrusion process in an ionic liquid and co-solvent environment, which results in the synthesis of cellulose laurate. The aim was to achieve effective cellulose esterification reaction with a mixture pre-treatment via 3-minute reactive extrusion. The main objectives were to develop mixture pre-treatment methodology and optimize mixture composition. The following materials were used: microcrystalline a-cellulose, esterification reagent vinyl laurate, ionic liquid [mTBNH][OAc], co-solvent dimethyl sulfoxide (DMSO), and mTBN catalyst.

The influence of the reaction mixture composition and the pre-treatment conditions on the efficiency of cellulose esterification reaction was analysed. During the study, 27 samples of cellulose laurate were synthesized under different pre-treatment conditions and mixture compositions. Current research has tested and examined the effects of pre-treatment time and temperature, reaction mixture composition, catalyst addition, application of US-treatment, and raising the VL to MCC ratio. The FTIR method was predominantly used for sample analysis, to estimate the substitution efficiency, by calculating the C=O to -OH peak absorption intensities ratios.

In this study, three pre-treatment methods are used: RT-treatment (stored in the glovebox during the pre-treatment), oven-treatment (pre-treated in the conventional oven) and US-treatment (pre-treated in the ultrasonic bath). Different pre-treatment times and temperature combinations are used for all the methods.

The results revealed that the pre-treatment positively influences the esterification reaction, enabling the production of cellulose laurate with a higher degree of substitution compared to not pre-treated reference sample. Among the various methods investigated, it was found that US-treatment is the most advantageous, because successful results were achieved with lowest time and energy consumption.

It was found that the VL addition time to the reaction mixture plays a high role in the pre-treatment. The best results were obtained with mixtures where vinyl laurate was added before pre-treatment. In that case, the reaction between cellulose and vinyl laurate begins during the storage rather than later in the extruder. In addition, by using DMSO as a co-solvent, the amount of IL used can be reduced, without losing in reaction efficiency. Therefore, preDMSO_preVL was chosen as the most suitable mixture composition.

It was also found that including a mTBN catalyst in the mixture improves efficiency. By adding 5% catalyst (relative to the total solvent amount), the oven-treated sample gave

9 times, and the US-treated sample up to 6 times better FTIR values. Increasing the amount of catalyst also contributes to a more successful reaction. During the catalyst experiments, it was discovered that using 10% of the catalyst produced approximately three times better results than using 5%. It can be assumed, although no experiments were conducted, that using a catalyst may allow for a reduction in the pre-treatment time. This aspect was not included in the scope of this study and could be explored in future researches.

By using US method, it was possible to increase the used VL amount, because the mixture became significantly more solid during the pre-treatment process compared to previous methods. Increasing the volume was not possible for other methods because of extruder's inability to handle large liquid volumes. Therefore, the mixture ratio of 1,5:1 was increased to 2:1 of VL to MCC. The experiment showed that improving the ratio almost doubled in value. This is because of increased ratio of VL to cellulose makes more VL molecules available for esterification with the hydroxyl groups of cellulose, leading to better reaction outcome.

In conclusion of this practical study, it was determined that the optimal mixture composition was preDMSO_preVL with a 10% catalyst. The best result was achieved with a 2:1 ratio of VL to MCC. The most effective pre-treatment method was US-treatment for 1 hour at 80°C. In the outcome of this study, a remarkable achievement was obtained, surpassing the value of the reference sample (FTIR measured, C=O/-OH peaks absorption intensities ratio of 0,241) by a significant factor of 24 times (5,812).

From the NMR test, out of the 6 analysed samples, the highest tested degree of substitution (DS) was 0.438. The samples used for analysis were oven-treated, which had significantly lower FTIR values compared to the US-treated samples. Therefore, the final maximum achieved DS result is unknown.

It was determined that the most promising avenue for future exploration would be to continue analysing and experimenting with the ultrasonication (US) method. Further investigation of the US method offers the opportunity to optimize the cellulose esterification process, improving its overall efficiency and effectiveness by potentially achieving a complete reaction during the US pre-treatment process.

Based on these findings, an idea for further development raised, to investigate the possibility of completing the reaction during US-treatment. For that the US conditions that give comparable or even better results without extrusion must be found. This is not within the scope of the current thesis objectives, however, could be promising direction as a part of further research in doctoral studies.

This study has identified key parameters for the successful production of cellulose laurate in 3-minute extrusion. These findings lay a solid foundation for future advancements and potential implementation on a production line. The author claims that this work has good opportunities for further development because created cellulose laurate is a promising alternative material to traditional petroleum-based plastics in many areas.

KOKKUVÕTE

Lõputöös kirjeldatakse tselluloosi ümberesterdamise reaktsiooni reaktiivse ekstrusiooni protsessis ioonvedeliku ja kaaslahusti keskkonnas, mille tulemusena sünteesitakse tselluloosilauraadi. Eesmärk oli saavutada efektiivne tselluloosi esterdamisreaktsioon segu eeltöötlusega 3-minutilise reaktiivse ekstrusiooni teel. Peamisteks eesmärkideks oli segude eeltöötluse metoodika väljatöötamine ja segu koostise optimeerimine. Kasutati järgmisi materjale: mikrokristalliline a-tselluloos, esterdamise reagent vinüüllauraat, ioonvedelik [mTBNH][OAc], kaaslahusti dimetüülsulfoksiid (DMSO) ja mTBN katalüsaator.

Analüüsiti reaktsioonisegu koostise ja eeltöötlustingimuste mõju tselluloosi esterdamise reaktsiooni efektiivsusele. Uuringu käigus sünteesiti erineva segu koostise ja eeltöötlustingimustega 27 tselluloos-lauraadi proovi. Antud uurimustöös testiti ja analüüsiti eeltöötlusaja ja temperatuuri kombinatsioone, reaktsioonisegu koostist, katalüsaatori lisamist, ultrahelitöötluse kasutamise ning VL koguse tõstmise mõjusid. Proovide analüüsimiseks kasutati peamiselt FTIR-meetodit, et hinnata asenduse efektiivsust, arvutades C=O ja -OH piikide neeldumise intensiivsuse suhe.

Antud uurimustöö testis ja uuris eeltöötluseaja ja -temperatuuri kombinatsioone, reaktsioonisegu koostist, katalüsaatori lisamist, ultrahelitöötluse rakendamist ning VL koguse suurendamist. Proovide analüüsiks, et hinnata asenduse efektiivsust, kasutati peamiselt FTIR-meetodit, arvutades C=O ja -OH piikide neeldumise intensiivsuse jagatis.

Selles uuringus kasutatakse kolme eeltöötlusmeetodit: toatemperatuuril-töötlus (näidis hoiustati kindakapis eeltöötluse ajal), ahju-töötlus (eeltöötlus viidi läbi tavapärases ahjus) ja UH-töötlus (näidist eeltöödeldi ultrahelivannis). Kõikide meetodite puhul kasutati erinevaid eeltöötluse aja ja temperatuuri kombinatsioone.

Tulemused näitasid, et eeltöötlus mõjutab positiivselt esterdamise reaktsiooni, võimaldades luua kõrgema asendusastmega tselluloos-lauraat, võrreldes eeltöötlemata võrdlusprooviga. Erinevate uuritud meetodite hulgast leiti, et UH-töötlus on kõige kasumlikum, kuna edukaid tulemusi saavutati väiksema aja- ja energiakuluga.

Leiti, et vinüüllauraadi reaktsioonisegule lisamise aeg mängib eeltöötluses suurt rolli. Parimad tulemused saadi segudega, kus enne eeltöötlust lisati vinüüllauraati. Sel juhul algab reaktsioon tselluloosi ja vinüüllauraadi vahel juba eeltöötlemise algul, mitte alles hiljem ekstruuderis. Lisaks saab DMSO-d kaaslahustina kasutades vähendada kasutatava ioones vedeliku kogust, ilma, et reaktsiooni efektiivsus väheneks. Seetõttu valiti sobivaimaks segukompositsiooniks preDMSO_preVL.

Samuti leiti, et mTBN katalüsaatori lisamine segusse parandab tulemusi. Lisades 5% katalüsaatorit (võrreldes lahusti koguhulgaga), andsid ahjus eeltöödeldud näidised 9 korda ja UH-ga eeltöödeldud proov kuni 6 korda paremad FTIR väärtused. Samuti aitab katalüsaatori koguse suurendamine kaasa edukamale reaktsioonile. Katalüsaatori-katsete käigus avastati, et 10% katalüsaatori kasutamine andis ligikaudu kolm korda parema tulemuse kui 5%. Võib eeldada, kuigi katseid ei tehtud, et katalüsaatori kasutamine võimaldab ka eeltöötluse aega lühendada. See aspekt ei olnud antud uurimuses proovitud, kuid seda võiks uurida tulevastes uuringutes.

UH-töötlus kasutades oli võimalik suurendada kasutatavat VL kogust, kuna segu muutus eeltöötlusprotsessi käigus varasemate meetoditega võrreldes oluliselt tahkemaks. Mahu suurendamine ei olnud teiste meetodite puhul võimalik, kuna kasutatud ekstruuder ei suutnud käsitleda suuri vedelikukoguseid. VL ja MCC suhet 1,5:1 suurendati 2:1-ni. Katse näitas, et suhte suurendamine peaaegu kahekordistas tulemusi. Suurendatud suhe muudab esterdamisel VL molekulid tselluloosi hüdroksüül-rühmale kättesaadavaks, mis omakorda viib parema reaktsioonitulemuseni.

Antud praktilise töö lõpus selgus, et optimaalsem segu koostis oli preDMSO_preVL, koos 10% katalüsaatoriga. Parim tulemus saavutati VL ja MCC suhtega 2:1. Kõige tõhusam eeltöötlusmeetod oli UH-töötlus 1-tund temperatuuril 80°C. Töö lõpuks saavutati märkimisväärne tulemus, mis ületas võrdlusproovi väärtus (FTIR mõõdetud, C=O/-OH piikide neeldumis intensiivsuse suhe, 0,241) lausa 24-kordselt (5,812).

NMR-testi põhjal oli 6 analüüsitud proovist kõrgeim testitud asendusaste 0,438. Analüüsiks kasutatud proovid töödeldi ahjus, mille FTIR väärtused olid oluliselt madalamad kui UH eeltöödeldud proovidel. Seetõttu pole saavutatud maksimaalne asendusaste teada.

Tehti kindlaks, et kõige lootustandvam viis edaspidiseks uurimiseks oleks jätkata UH meetodi analüüsimist ja katsetamist. Edasine uurimistöö UH meetodi kasutamise kohta pakub võimalust optimeerida tselluloosi esterifitseerimis protsessi, parandades selle üldist efektiivsust ja tõhusust. Potentsiaalselt võiks saavutada täieliku võimaliku reaktsiooni juba UH-töötluse etapis.

Mainitud avastuste põhjal pakuti välja idee edasiseks arendamiseks, et uurida võimalust viia reaktsioon lõpule UH töötluse ajal. Selleks tuleb leida vastavad UH tingimused, mis annavad võrreldavaid või isegi paremaid tulemusi ilma ekstrusioonita. See aga ei kuulu käesoleva lõputöö eesmärkide raamidesse, kuid võib olla palju lubav suund näiteks doktoriõppe edasise uurimistöö osana.

Antud uurimustöö käigus määrati olulisemad parameetrid tselluloos-lauraadi edukaks tootmiseks 3-minutilise ekstrusiooniga. Need leiud loovad tugeva aluse edasisele võimalikule rakendamisele tootmisliinil. Autor väidab, et sellel tööl on head võimalused edasiseks arenguks, sest loodud tselluloos-lauraat on erinevates valdkondades paljulubav alternatiivmaterjal traditsioonilistele naftapõhistele plastidele.

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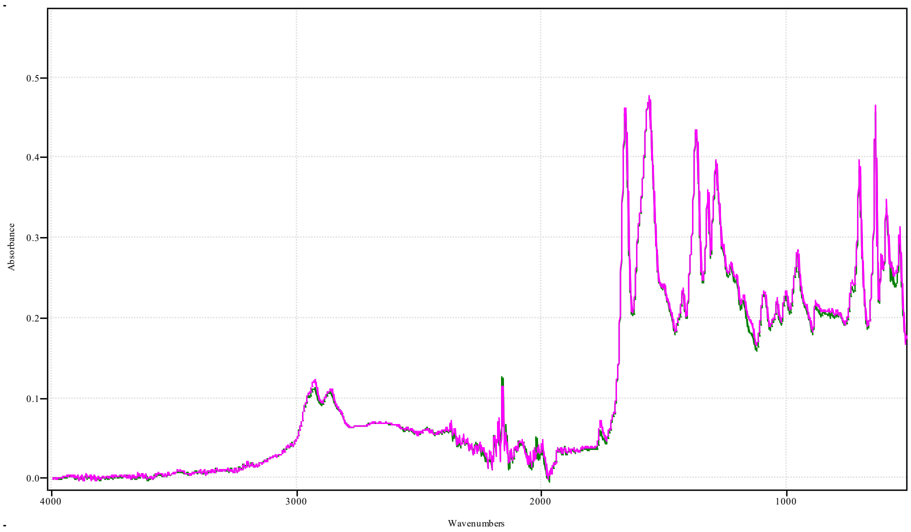
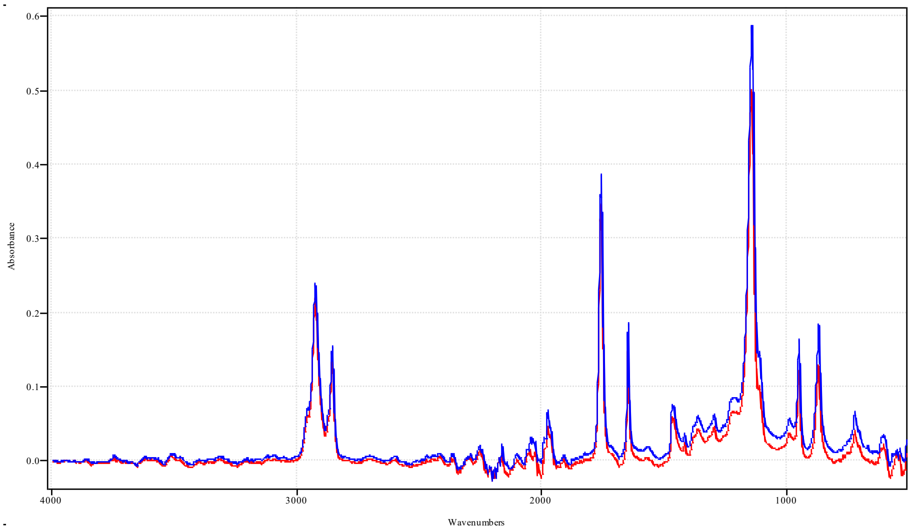
APPENDICES

APPENDIX 1 Oven storage effect on VL and IL

The test's purpose was to determine whether temperature changes VL and IL properties. For this, the untreated VL and IL were compared to the test samples, which were stored in oven for 20 hours at 40 degrees. Appendix figures 1.1 and 1.2 demonstrate, that there is no effect on tested condition for VL or IL chemical composition (the FTIR spectrum has not changed).



Appendix figure 1.1 – Untreated IL and oven-treated IL comparison.
Description of the samples shown in the figure:
Untreated IL (pink) and IL after 20h 40C oven-treatment (green).



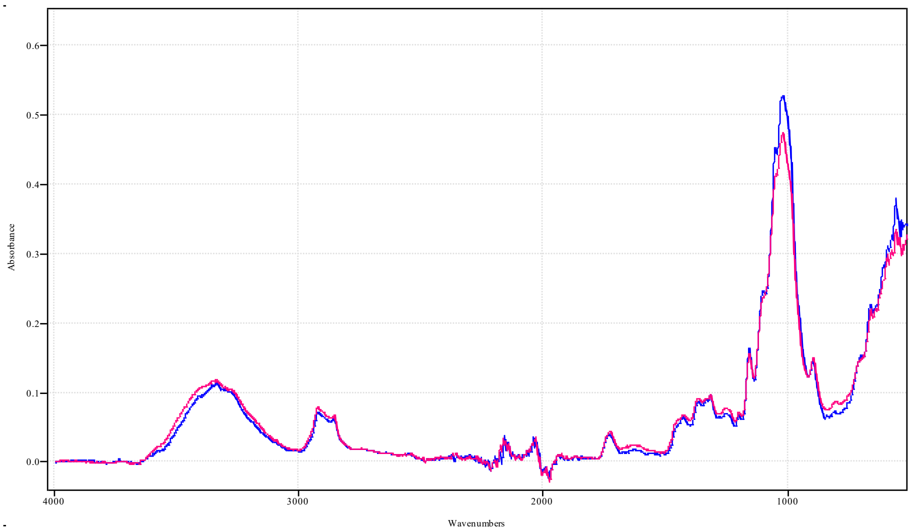
Appendix figure 1.2 – Untreated VL and oven-treated VL comparison.
Description of the samples shown in the figure:
Untreated VL (red) and VL after 20h 40C oven-treatment (blue).

APPENDIX 2 Purity of the sample after post-processing

The primary objective of this test was to confirm that the determined post-processing method (sample washing method) is sufficient to achieve a clean outcome. The purity of the sample after washing is vital, as an insufficient washing method may leave residual in the sample, thereby affecting the accuracy of the analysis.

To test it, one sample was dissolved in DMA. Then precipitated in ethanol and filtered. At the end of the process, there should be a pure product from which all unreacted substances have been fully removed. This dissolved sample was then compared to a sample washed by using the method described at the beginning of the work (2.4.1 Specimen washing process). This comparison can show whether the initial post-processing method is effective to obtain a clean sample, and whether the results are reliable.

As shown in Appendix figure 2.1, no observable changes were detected between these samples (particularly in the areas used for practical result calculations). Based on this, it can be concluded that the used washing method adequately removes excess substances, resulting in trustworthy outcomes.



Appendix figure 2.1 – Samples purity comparison. Description of the samples shown in the figure: washed specimen (red) and additionally purrifyed (dissolved) specimen (blue). Tested on sample - 20h_40C_preDMSO_preVL