TALLINN UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

MECHANOCHEMICAL VALORISATION OF PAPER AND CARDBOARD WASTE INTO THERMOPLASTIC PACKAGING MATERIALS

PABERI- JA PAPIJÄÄTMETE MEHHANOKEEMILINE VÄÄRINDAMINE TERMOPLASTSETEKS PAKKEMATERJALIDEKS

MASTER'S THESIS

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Tallinn 2022

(*On the reverse side of title page*)

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Department of Materials and Environmental Technology

MECHANOCHEMICAL VALORISATION OF PAPER AND CARDBOARD WASTE INTO THERMOPLASTIC PACKAGING MATERIALS

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Thesis topic:

(in English) *MECHANOCHEMICAL VALORISATION OF PAPER AND CARDBOARD WASTE INTO THERMOPLASTIC PACKAGING MATERIALS*

(in Estonian) *PABERI- JA PAPIJÄÄTMETE MEHHANOKEEMILINE VÄÄRINDAMINE TERMOPLASTSETEKS PAKKEMATERJALIDEKS*

Thesis main objectives:

1. To synthesise cellulose esters by modifying surface properties of cellulose fibres
2. To perform compression moulding procedure for the synthesised products
3. To analyse the synthesised products and draw conclusions

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature overview, first tests with mechanochemical synthesis in order to obtain a cellulose derivative (cellulose acetate)	May 2021
2.	Synthesis of cellulose laurate and cellulose oleate	Nov 2021
3.	Compression moulding of produced samples and analysis of them (FTIR, DSC, SEM, solubility tests, microscopy)	March 2022
4.	Analysis of the experimental work, preparation of the final thesis form	May 2022

Language: english **Deadline for submission of thesis:** "24" May 2022

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PREFACE

The current topic chosen for the thesis was initiated as a topic for a project by the author’s supervisors. The author of the work conducted research about the basics of cellulose, paper and cardboard production, waste management, its modification opportunities by obtaining information from the literature. The experiments were carried out in the Laboratory of Polymers and Textile Technology at Department of Materials and Environmental Technology in Tallinn University of Technology.

I would like to express my special gratitude to one of my supervisors Dr. Illia Krasnou as the course of the practical work and discussions demanded a lot of time and attention from his side. I thank my second supervisor Prof. Andres Krumme for the support and initial discussions that were necessary for the main understanding of the work at hand. I pass on extra gratitude to the laboratory of the Polymer department for providing with the tools and equipment and the assisting personnel – Tea-Mall Krumme. Finally, I bring out the Early Stage Researcher Nutan Bharat Savale for her willingness to answer my urgent, but important questions while working in the lab. Thank you!

Keywords Cellulose, Esterification, Mechanochemical valorisation, Thermoplastic, Master’s thesis

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List of abbreviations and symbols

DP – Degree of polymerisation
DS – Degree of substitution
AGU – An anhydroglucose unit
DMF – Dimethylformamide
$SO4^{2-}/ZrO_2$ - Zirconium oxide sulphate
LiCl/DMAc - LiCl/N,N Dimethylacetamide - Lithium chloride/N,N dimethylacetamide
DMSO/TBAF - Dimethyl sulfoxide/tetramethylammonium fluoride
NMMO - N-methylmorpholine N-oxide
SO_4^{2-}/M_xO_y – A solid superacid catalyst, where M could be either Ti, Zr, Fe
mm – Millimetre
nm – Nanometre
m - Metre
DMSO – Dimethyl sulfoxide
PUR – Polyurethane
SEM – Scanning electron microscopy
DSC – Differential scanning calorimetry
FTIR – Fourier transform infrared spectroscopy
CA – Cellulose acetate
CL – Cellulose laurate
CO – Cellulose oleate
CAP – Cellulose acetate propionate
CAB – Cellulose acetate butyrate
CAT – Cellulose triacetate
HCl – Hydrochloric acid
NaOH – Sodium hydroxide
T_g – Glass transition temperature
T_m – Melting point/temperature
T_c – Crystallisation temperature
ACP – Alpha cellulose paper
IL – Ionic liquid
COO - An ester group
COOH - A carboxylic acid group
OH - An alcohol/hydroxyl group
CAT – Triacetate
LCCE – Long chain cellulose esters
CDI - N,N'-carbonyldiimidazole
$SOCl_2$ - Thionyl chloride

$C_2Cl_2O_2$ - Oxalyl chloride

h_0 - Charge thickness

h_f - The demanded thickness of the formed part

h - The speed of closure of the upper mould

$I_{C=O}/I_{C\text{-}O\text{-}C}$ – A parameter, which has been obtained by dividing the height of the carbonyl group peak by the height of the ether bond group from FTIR analysis

INTRODUCTION

Cellulose can be characterised as a hydrophilic and hygroscopic material which potential has not yet been thoroughly used by humankind. According to the numerous studies performed in the past the matter of hydrophilic nature can be processed to hydrophobic output if appropriate chemistry and technique are used and therefore, a lot more useful applications can be found for the modified version of cellulose material. Besides the wider range of applications, cellulose can be abundantly found on Earth (which is a renewable material of environmentally friendly origin) that in the case of smart processing technologies, could be a solution for completing the green turn goals. Esterification is recognised as one option as a successful modification technique implemented and researched in the past. The technique will be introduced and implemented in the main body of the current work.

The Master's thesis at hand handles various aspects of cellulose, the production of paper and cardboard, valorisation of cellulose material into thermoplastic cellulose esters, determining and analysing the properties of produced cellulose derivatives. The aim of the thesis is to produce surface modified cellulose fibres with thermoplastic properties and to apply the developed technology for paper and cardboard recycling.

The possibility of utilising the waste generated from paper and cardboard residues to produce cellulose derivatives is high in Estonia if it is being collected separately and directed to relevant factories which can transform the material into other outputs with corresponding and novel technologies. The relevant statistics on the waste material in Estonia are brought out in the main body of the thesis.

In the course of working on the project courses and the Master's thesis itself, the intention was to focus on solving environmentally related issues. For example, if it is possible to process the matter with minimum need of resources such as solvent and water. Another aspect was to discover new environmentally friendly chemical routes in the industry – that are briefly mentioned in the upcoming introductory part.

By conventional methods, the most widely manufactured cellulose acetate is achieved through the use of pyridine-acyl chloride or anhydride reactions [1]. So far in the polymer industry, synthesis is conducted by utilizing acetic anhydride and a solvent LiCl/N,N-Dimethylacetamide. In addition, sulfuric acid was added to the media in order to catalyse the reaction. However, the solvent and the catalyst mentioned before are not green by nature – implementation of mentioned substances causes pollution. [2]

Consequently, HCl was produced as a by-product, which was detrimental to the environment and caused the decomposition of cellulose. By now, on the market can be found several non-derivative solvent systems which are successful and efficient in dissolving the cellulosic material. N-methylmorpholine N-oxide (NMMO), N,N-dimethylacetamide-lithium chloride (DMAc-LiCl), and dimethyl sulfoxide-tetramethylammonium fluoride (DMSO-TBAF) are some examples that can be brought forth. Solvent systems, however, suffer from a number of drawbacks, including their high cost, the requirement of remarkable amounts of chemicals, the volatility, and the toxicity of the solvents. Besides, carrying out the recovery process of used solvents is toilsome. [1]

In terms of new solvent applications, ionic liquids have been shown to be a promising system that is both feasible and effective. It is possible to recycle ILs for repeated use and they do not produce toxic or explosive gases. It is also worth pointing out the following admirable properties of ionic solvent systems for cellulose specifically - great thermal stability and dissolution performance, negligible vapour pressure, relatively low viscosity and also selectivity and yields have been improved. [1]

In addition to ionic liquids, synthetic processes such as mechanochemical esterification are also used to mitigate the negative environmental impact. Mechanochemistry comprises chemical reactions in which mechanical force is used to stimulate and sustain the reaction in the grinding procedure. Due to the efficient chemical transformation generated by mechanical forces achieved in ball milling, it is worth studying to see the value of cellulose in industrial sectors. In the past, mechanochemical methods have been used to investigate cellulose esterification. The majority of the research has focused on the reaction using short chain fatty acids in the presence of solvents. Thus, esters made of long chain fatty acids have also become a necessary topic to be studied and worked on globally. [1]

A lot of organic reactions have been conducted based on the principles of a solvent-free technique. Cellulose composites are one of those materials that can be produced by using solvent-free principles in mechanochemical devices. A ball-mill reactor is an example of a simple and efficient instrument for the successful production of cellulose materials. It is possible to process the material in the device both in wet and dry conditions. [2] Based on the former research results, it must be kept in mind that the amount of time provided for the milling actions is mostly an essential factor for mechanochemical procedures. The factor depicts the mechanical energy that is fed into the operation. [3]

Furthermore, an example can be brought forth in the area of green catalysts. During the last decades a solid superacid catalyst with a type of SO_4^{2-}/M_xO_y has gained interest in the industry due to having better properties than ordinary catalysts used, such as liquid superacid and liquid acid. Many reactions have been carried out on the industrial scale with that kind of a green catalyst. [2]

However, in the current thesis, the main emphasis is set on the principle of producing the cellulose derivatives via mechanochemical reaction only.

CHAPTER 1. LITERATURE OVERVIEW

Literature overview provides the reader with the most relevant information in order to understand the main aspects of the work.

1. MATERIALS

1.1 Pristine cellulose

Cellulose is known as the most resourceful and ubiquitous natural polymer on Earth. Annually it is globally produced about $1.5*10^{12}$ tons and the amount can be compared to the number of planetary reserves of fossil and mineral fuels that can be found from different sources on the planet. Cellulose has been proposed as a solution to many environmental and recycling related issues due to the properties the material owns. It is a renewable and biodegradable natural polymer. Cellulose can be implemented in a wide range of applications if the polymer is modified by the usage of physical and chemical techniques. There are diverse options found for modification and therefore, there can be produced cellulose materials with versatile structures. Possible applications for cellulose can be fillers, composite materials, textiles, papers, advanced functional materials, coating materials and so on. [4]

1.1.1 Origin of pristine cellulose

Cellulose originates from such sources as plants, minerals, animals, fungi and algae. However, most of the cellulose is provided by plant fibres. In the next table (*table 1*) it has been provided with the information about the content of cellulose that different sources consist of. [4]

Table 1. Sources of cellulose and the amount of the polymer in each of the sources [4]

Source of cellulose	**Weight per cent (wt%)**
Wood	40-50
Bagasse	35-45
Bamboo	40-55
Straw	40-50
Flax	70-80
Hemp	75-80
Jute	60-65
Kapok	70-75
Ramie	70-75
Cotton	90

DP (degree of polymerisation) depends on the origin of the cellulose. The ones achieved from nature are in the range of 1000 – 30 000 and the chain length falls between 500 – 15 000 nm. DP of samples achieved by isolation methods falls in the range of 800 – 3000. Values of DP have been averaged because cellulose samples tend to be polydisperse. Viscosity measurements, chromatography and light scattering are one of the techniques found to measure molar masses of polymers and their distribution. [4]

1.1.2 Structure of cellulose

Figure 1 provides an understanding of the structural hierarchy of the cellulosic material from a tree scale to a molecular scale. [5]

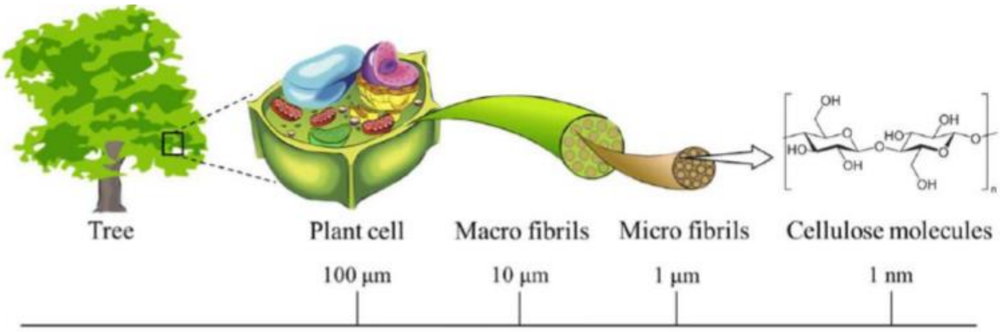


Figure 1. The illustration represents the structural hierarchy of cellulose (from *m* to *nm* scale) [5]

Regarding the molecular structure (*figure 2*), it is characteristic for cellulose to have D-glucopyranose ring units and these units are in $^4C_1$ – chair configuration. Due to such configuration, the units own the conformation of the lowest energy. The structure of cellulose is the same regardless of the source. Units are connected to each other by β-1,4-glycosidic bonds, allowing the polymer chain axis to rotate by 180°. The repeating unit of the natural polymer is called cellobiose and the length of it is 1.3 nm. In every anhydroglucose unit there can be found three hydroxyl groups that are reactive. One and only primary group is placed at the sixth carbon atom (C_6) in the plane of the ring and the other two secondary groups at the second and third carbon atom (C_2 and C_3). [4]

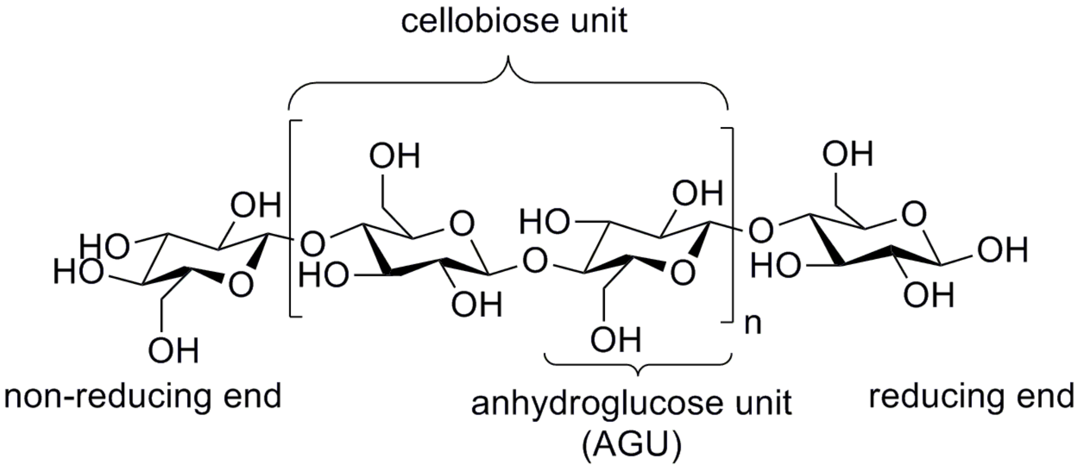


Figure 2. Structure of cellulose [6]

Cellulose is formed by polycondensation and as it is typical for the polymers polymerised in this way, the chain ends of the molecule are not chemically the same. At one end, the nonreducing end can be found and at the other one, the reducing end group. Nonreducing end prefigures an anomeric carbon (C) atom that is connected by the glycosidic bonds. The reducing end group consists of a D-glucopyranose unit and the unit is in equilibrium with the aldehyde function. [4]

In cellulose structure, there are several hydrogen bonding systems and they have a remarkable effect on the properties of the polymer. Due to the strong systems of hydrogen bonds, cellulose cannot dissolve in various kinds of solvents (or it is strictly limited), hydroxyl groups are reactive and samples of cellulose are crystalline. Also, around the C atoms in the molecule, there are hydrophobic regions that have an effect on overall properties and solubility as well. [4]

There are three OH groups that are found from AGU, the O atoms from the D-glucopyranose ring unit and the glycosidic bond. They interact with each other by producing intermolecular (a connection with another polymer chain) or intramolecular (a connection within the chain) hydrogen bonds. [4]

Intermolecular hydrogen bonding ensures the firm interaction between the polymer chains. These bonds are located between neighbouring macromolecules. To be more precise, intermolecular hydrogen bonding occurs along the plane in the crystal lattice of native cellulose (in cellulose I polymorph), mostly between the O atom at C_3 and the OH (hydroxyl group) at C_6. The whole hydrogen bonding system (fragile C-H-O bonds and hydrophobic interactions included) causes the polymer to be assembled into layers and several three-dimensional arrangements. [4]

1.1.3 Reactivity of cellulose

As of now, it is clear that each anhydroglucose unit contains three hydroxyl groups, cellulose can be characterised as an active chemical based on its molecular structure. Hence, cellulose reacts primarily through these hydroxyl groups. In terms of reactions, cellulose material possesses the principles of chemistry of alcohols due to the fact that cellulose is a carbohydrate compound, and therefore, the pristine matter can be converted to various common derivatives in the category of alcohols (e.g. esters and ethers). Therefore, cellulose can be treated with various reactions that fall into the category of alcohols, e.g. esterification, etherification, and oxidation. [7]

Laboratory studies have reported that the primary alcohol defined as the hydroxyl group located at the position of C_6 is able to act 10 times faster in terms of reactivity than the other secondary alcohol (hydroxyl) groups. [7]

1.2 Paper and cardboard

1.2.1 Production of paper and cardboard

Common materials, such as pulp and paper are produced from raw materials that contain cellulose fibres - typically wood, recycled paper, and agricultural waste. According to information about developing countries, almost 60% of cellulose fibres come from raw materials that do not originate from wood. These raw materials are such as sugar cane fibres (with an alternative name called bagasse), jute, flax, cereal straw, sisal, bamboo, reeds and esparto grass. [8]

In the pulp and paper industry, there are several activities carried out for the proper production of pulp and paper. At first, it is needed to prepare the raw material by performing operations such as wood debarking and chip producing. Then the next activities are pulp manufacturing (in which chemical and mechanical means are engaged), pulp bleaching, paper production and further fibre recycling. In industries, mills that are accustomed to processing pulp and paper may be found as integrated or separately existing entities. The pulp that is manufactured will be implemented as a source of cellulose for further fibre production and conversion into the desired products like paper and cardboard. [8]

Regarding the pulps manufactured in a chemical way, the process starts with the cooking of the raw materials. The alternative name for cooking is digesting and during the operation there will be included processes such as sulfite and sulfate (kraft). In the case of applying the kraft process, the pulp derived from it will be suitable for packaging, as well as high strength paper and board. The main objective of bleaching regarding the chemical pulps is to ensure that there will be no residues of lignin left after the cooking process. Chemicals such as oxygen, ozone, chlorine, hydrogen peroxide, etc., help convert lignin into another form (alkali soluble). An alkali (e.g. sodium hydroxide) is involved in the bleaching for the extraction of alkali soluble lignin. [8]

The pulp that is manufactured in a mechanical way can be completely suitable for the production of printing papers. In this operation, it is possible to make the pulp without the bleaching process and due to the low brightness of the pulp, one of its main applications for it is newsprint. However, there are not many options available for the usage of paper of low brightness. That is the reason it is still needed to bleach the mechanically made pulp to implement the products later in copying, printing and packaging. Thus, the original lignin included in the raw pulp is bleached by treating the mass with hydrosulfites and peroxides. [8]

Nowadays, in the mills it is preferred to use oxygen at the beginning of the bleaching operation. The main cause relies upon the fact that it will make it possible to go through the bleaching process without using any sort of chlorine chemicals. Total chlorine-free processing enables the effluents that are generated after the aforementioned process to direct them to recovery apparatus (here is meant boiler) for the generation of steam. After that, electricity is generated from the steam, reducing the overall amount of contaminants discharged compared to the processes where chlorine chemicals are applied. [8]

After the bleaching process has taken place, the organic substances that are also soluble are eliminated from the pulp. The prepared pulp can then be either dried for transport (used as the market pulp) or directed into further manufacturing on site, usually in a mill that is "integrated‟. Paper and cardboard are manufactured from the pulp in a way that fibres and fillers are precipitated from a suspension (that is in a fluid form) and the precipitates fall onto a moving forming machine that further removes water from the mass. Excess water in the net web is then eliminated by pressing and drying (for example, drying on a series of calender rolls) operations. Finally, to meet the specific properties of the manufactured paper, chemical additives are used. Pigments may be implemented in case of the desired colouring is needed to achieve. [8]

1.2.2 Volumes of paper and cardboard waste and recycling

In the current sub-chapter the information about the situation of cardboard and paper waste generated in Estonia in recent years has been brought out based on the statistics. The information helps to understand the potential of turning the waste into useful applications. According to the report about the waste statistics in Estonia evaluated in the years 2014 to 2018 by Estonian Environmental Agency, a remarkable amount of paper and cardboard has been created. In 2018, a total amount of approximately 95 tons of paper and carton remnants were collected in different forms such as packaging, scrap paper and small fractions resulting from mechanical treatment of other wastes. During these aforementioned years, the total amount of those residues created and the recovery of them did not variate notably. However, there are indications in numbers that let the specialists in the Environmental Agency conclude about the involvement of additional handling equipment implemented in the recycling of the waste. Therefore, the amount of waste recycled has increased in Estonia (meant in the area of Estonia). Over 70 per cent of paper and cardboard waste was exported to other countries for recycling. Since 2016, about 3000 tons of remnants have been imported from Finland. The degree of purity designates what proportion of the waste material can be recycled by existing technologies. From the scheme (*figure 3*) below, the same information has been provided in the illustrated way. [9]

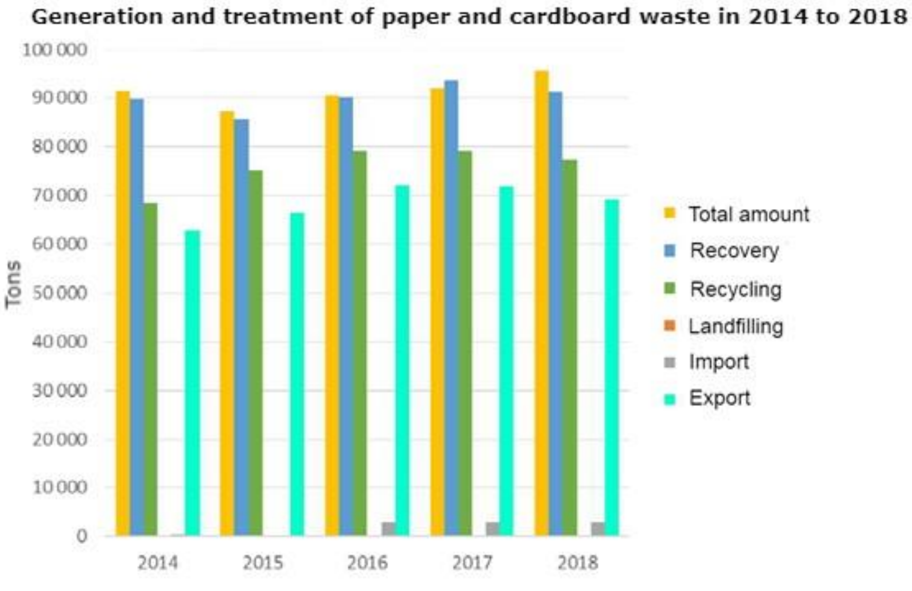


Figure 3. An overview of the generation and treatment of paper and cardboard waste in Estonia in years 2014 to 2018 [9]

The recycling procedure regarding paper and cardboard waste will be explained in more detail. Recycling action starts with the collection of paper and cardboard waste from industries (which deal a lot with paper or cardboard), households and offices. The collected waste can be sorted and graded if the papermaker has such requirements. Recycling continues by mixing the waste with water, removing the belongings such as paper clips and staples and purifying the fibre. Based on the type of end use, it may be additionally essential to perform the de-inking (removal of ink) and bleaching procedure. If all such operations have been executed, then the waste will be converted into pulp and the pulp is ready for the manufacture of paper. The new paper product can be manufactured by either using only this recycled mass or mixing the recycled mass with the virgin one that originates directly from trees. [10]

From the perspective of individual cellulose fibres, it must be remembered that fibres hold on to recycling several times and then the pulp is not applicable to the same function anymore. Otherwise, the length of those fibres is too short and they begin degrading during the further recycling procedure. Therefore, the inappropriate material for recycling will be utilized as raw material for combustion processes (energy production), manufacturing of construction boards, or it is just placed onto the farmland. [10]

1.3 Modification of cellulose

Modifications in the molecular structure of cellulose are caused by reactions that result in the hydrolysis or oxidation of the polymer chain. These reactions take mostly place on the surface of fibrils or in amorphous areas. [4]

1.3.1 Dissolution of cellulose

According to literature, pristine cellulose has been proven to behave insoluble in liquids such as water and standard organic solvents. The essence of insolubility is caused by the fact that in the material, intensive supramolecular interactions take place as a result of hydrophobic interactions and hydrogen bond systems found among the macromolecules (inside and between them). [11]

Cellulose has been referred to as one of the most singular and plain structures found among polysaccharides. The construction of cellulose, therefore, determines the properties of the polymeric material and also notably the course of the process while chemical reactions take place. [12]

Among the major characteristics of cellulose containing materials is the presence of crystalline and amorphous phases. In other words, both the ordered and disordered regions determine the polymeric material to own a two-phase morphology, which plays a role in the accessibility of fibres and this property also determines the reactivity of the same fibres. The regions have been created due to the intramolecular and intermolecular hydrogen bonding found there in the material in a pattern form. Both conformational and mechanical characteristics are also influenced due to previous aspects. The intramolecular hydrogen bonds within molecules provide the cellulose molecule with its rigidity and shift characteristic, whereas the intermolecular hydrogen bonds between molecules assure the pristine cellulose its sheet-like character. Additionally, hydrogen bonds render cellulose insoluble in water and in many other organic liquids. [12]

Nevertheless, the dissolution behaviour of cellulose must be obtained as an unambiguous precondition for various actions. In the area of characterization, the aspect helps to determine the molar mass of the material and also the molar mass distribution. Secondly, it is essential to obtain solubility for shaping activities such as the manufacturing of fibres and membranes. Last but not least, homogeneous chemistry represents the third reason as one of the most vital pathways for designing polymeric materials of renewable resource origin. The designed polymeric materials are aimed to be relatively novel and functional as well. [11]

Due to the extended hydrogen bonds that can be found between cellulose chains, it is essential to choose suitable media and procedures for the successful dissolution of cellulose [4]. Formerly, there have been made efforts and proposals with an aim to systemise solvents that are applicable to cellulose [12]. However, by now, in general the solvents are still being divided into two main classes (*figure 4*) that are brought forth next [12];

1. Non-derivatising solvents – solvents that represent the idea that polymers in solution are dissolved only by means of intermolecular interactions [12],

2. Derivatising solvents – media where the dissolution of the material happens due to an occurring chemical reaction, and it results in the formation of covalent bonds as well as in the creation of "unstable" esters, ethers or acetal derivatives. [12]

Both types of solvents that were brought forth previously above can be even more classified into nonaqueous and aqueous systems [12].

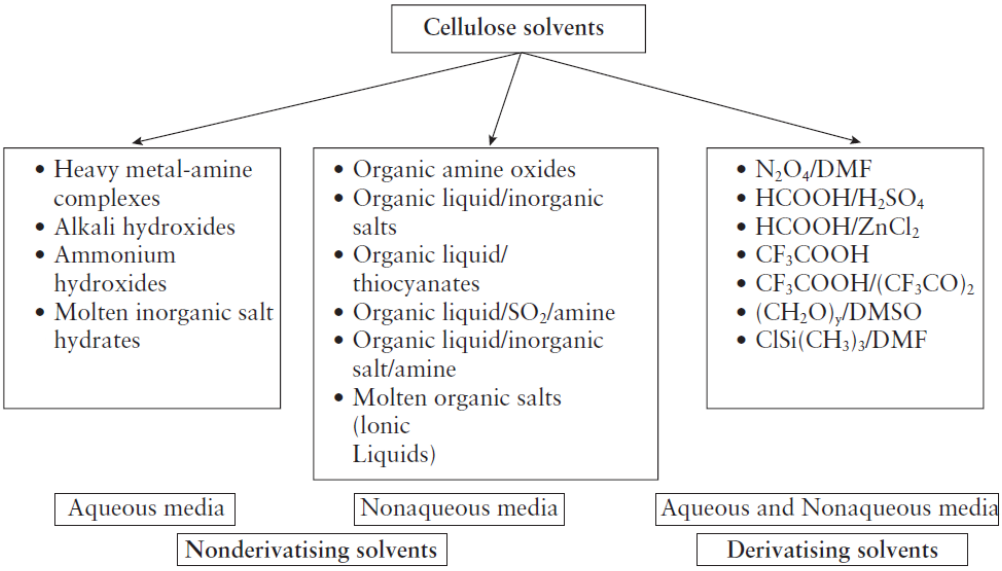


Figure 4. Categorised cellulose solvents [12]

1.3.2 Esterification of cellulose

Esterification reactions are known for their ability to alter the cellulose surface and as a result, the surface owns the hydrophobic characteristic. The main agents that are used in the process are acid anhydrides or acyl chlorides. [13] In this work, esterification with acyl chlorides is the reaction that will be implemented in the experimental work. Esterification itself has been defined as a process during which COO (an ester group) is attached to a molecule of the natural polymer. The process can happen due to the condensation mechanism taking place between COOH (a carboxylic acid group) and OH (an alcohol group). [13] In other words, hydroxyl groups of the cellulose are replaced by ester groups and the approach has been estimated as the most resultant property-modifying process of the natural polymer. [3]

The extent and how much the extent is limited during the esterification reaction depends on the properties of the polymer surface. Susceptibility and accessibility are the most important characteristics of the aspect. [13]

Cellulose can be esterified in three ways. The first option is that the esterification occurs in an environment between the material and an acid. In that case, a dehydration agent must be added. Secondly, cellulose would react with acid chlorides or acyl chlorides. The third option is reactions with acid anhydrides. All three reactions in the same order as they were described have been brought out below (*figures 5, 6 and 7*). [14]

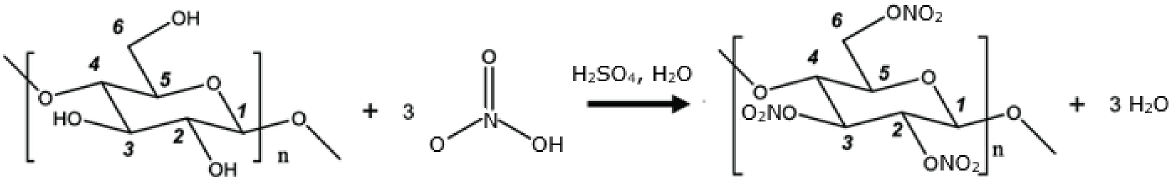


Figure 5. Synthesis of cellulose nitrate by reacting cellulose with an acid [14]

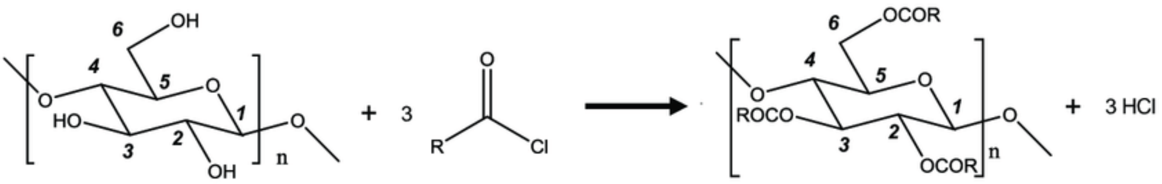


Figure 6. Synthesis of cellulose esters via acyl chloride reactions [15]

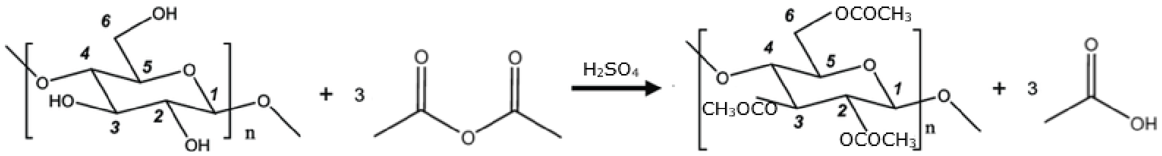


Figure 7. Acetylation of cellulose to CA as a result of using acetic anhydride [14]

The esters obtained are usually classified into the two separate groups, which have been brought out below.

1. Esters made of inorganic acids. For example, phosphate, sulfate and cellulose nitrate [14],
2. Esters made of organic acids. For example, acetophthalate, acetobutyrate and cellulose acetate. [14]

It has been scientifically determined that cellulose esters differ from the initial polymer due to their chemical and physical properties. In addition, the ester derivatives are soluble in numerous solvents. With an abbreviation of DS, the degree of substitution is an essential parameter to be regulated while producing derivatives. The parameter is a key factor in manufacturing various kinds of cellulose ester derivatives. *Figure 8* illustrates the essence of DS. [14]

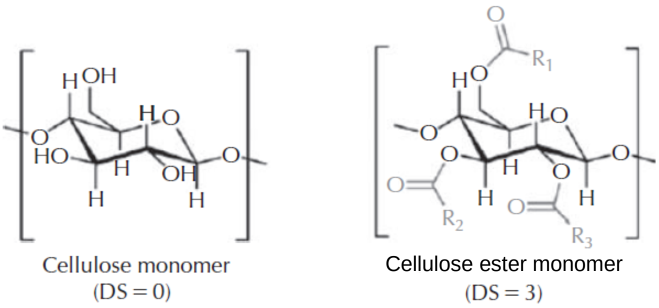


Figure 8. Depiction of the difference between cellulose and completely substituted cellulose ester monomers [16]

As of now, cellulose esters are implemented in such applications as coatings, plastics, membranes and films, etc. [14]

1.3.3 The most common short chain cellulose esters and their application areas

Cellulose acetate has been recognised as one of the most common esters produced worldwide in industries. The reaction for the production of cellulose acetate can also be called an acetylation reaction as the hydroxyl groups of cellulose are substituted with acetyl functional groups – $COCH_3$. Up until recent years, most of the cellulose acetate has been manufactured by the "acetic acid process". Perchloric or sulfuric acid are possible catalysts for that type of acetylation. It is a heterogeneous process during which swelling of cellulose in acetic acid takes place. After the step described above, the swelled polymer is acetylated by using acetic anhydride as an agent and a catalyst like perchloric or sulfuric acid. Finally, acetic acid is a by-product recovered by the end of the process. In the picture (*figure 7*) in the previous sub-chapter, the mechanism of the reaction has been provided. [13]

However, cellulose acetate can be successfully produced by following the principles of other synthesis routes as well, for example, by means of using acyl chlorides.

In *table 2* found below, all the commercial cellulose esters are presented there including the most common short chain cellulose esters with their potential application areas. [14]

Table 2. List of commercial cellulose esters found [14]

Cellulose ester	Typical reactant	Solvents	Main applications
Nitrate	Nitric acid	Acetone, methyl ethyl ketone, esters	Plastics, coatings, explosives, propellants
Secondary acetate (CA)	Acetic anhydride with subsequent hydrolysis	Acetone	Cigarette filters, textile fibers, films, plastics, coatings, membranes, drug matrices
Triacetate (CAT)	Acetic anhydride	Methylene chloride	Fibers, films
Propionate	Propionic anhydride	Acetone, ethyl acetate	Plastics, coatings, printing inks, films
Butyrate	Butyric anhydride	Acetone, ethyl acetate	Plastics, coatings, printing inks, films
Acetate propionate (CAP)	Acetic and propionic anhydrides	Wider range of solvents that CA	Plastics, coatings, printing inks, films
Acetate butyrate (CAB)	Acetic and butyric anhydrides	Wider range of solvents that CA	Plastics, coatings, printing inks, films

However, in the case of esters with short chains a matter of water sensitivity of the materials arises since short chain derivatives are known to be more sensitive to water. Also, processing the melt (for example, of cellulose acetate and cellulose propionate) has limitations due to the fact that the glass transition temperature tends to be high. Even the addition of plasticizers is not the most satisfactory solution to the problem. [3]

1.3.4 Long chain cellulose esters

Long chain cellulose esters with the abbreviation LCCE are recognised as bio-based cellulosic materials that have been produced from such input materials as long chain fatty acids. The chain length of the fatty substituent must be larger than C6. Relatively commercially widespread thermoplastic cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate are not among the category of LCCE as the chain length of fatty substituent reaches less than C6 in all three cases. Cellulose stearates, laurates and oleates are examples of LCCEs that can be brought forth. As well as their excellent mechanical properties, LCCEs also exhibit good barrier properties, which offer promising prospects in several areas such as bioplastics, coatings, and films. [17]

Cellulose esters with long fatty chains are prepared either by the homogeneous or heterogenous method. In 1985 McCormick et al. stated the homogenous cellulose esterification procedure in LiCl/DMAc solution offered several advantages over the heterogeneous method. In particular, side chains are more uniformly distributed along the backbone, more controllable DS is obtained, and slightly less reagent usage is required. [17]

However, long chain cellulose esters are most often produced under heterogeneous conditions even if the homogeneous method has its benefits. Since recycling the expensive lithium salt used in homogeneous methods is still challenging, heterogeneous routes are commonly chosen. As there is relatively poor ease of access for chosen esterification reagents to solid cellulose molecules, the DS is typically lower in heterogeneous reactions. [17]

According to work published by scientists Huang et al. long chain cellulose esters exhibit remarkably more advanced liquid repellent properties than short chain esters or the natural polymer itself. In the case of the long chains that were successfully grafted onto the polymer, the contact angles were about 30 degrees larger compared with natural (value 42.7°) and short chain ester derivatives (value 45.4°). Therefore, wettability had decreased when tested with water and the same trend applied to the surface energy of the derivative. The surface energy of the material was stated to be dependent on the amount of grafted carbon chains, not on the aspect of how many OH groups were replaced by ester groups. [3]

Willberg-Keyriläinen et al. in 2019 carried out a study in order to compare various esterification routes for LCCEs and to ascertain the most effective option. A variety of homogeneous and heterogeneous esterification methods were employed to produce the LCCEs with diverse side chain lengths - cellulose octanoates, cellulose laurates and cellulose palmitates. In total, four routes were tested during the research – CDI activation (N,N'-carbonyldiimidazole is an example of activating agents used there), vinyl transesterification, anhydride and fatty acid chloride routes. The scientists demonstrated that cellulose reactivity and degree of substitution are correlated with the esterification route and side chain length. A comparison of two pulps with different molar masses was conducted to investigate the impact of cellulose molar mass on reaction efficiency. [17]

In the case of the homogeneous esterification process, the acyl chloride option was proven to be the most effective and the output material the LCCEs exhibited the highest DS results. More specifically, based on the side chain length of the synthesised cellulose esters, the DS values varied from 0.3 to 1.3. The other routes exhibited lower DS values. Implementation of ozone to pre-treat cellulose pulp decreased its molar mass, which led to synthesized cellulose esters with a higher DS and greater reaction efficiency than initial untreated cellulose. The only effective way of achieving heterogeneous esterification was to use acyl chloride. It appears that the degree of substitution, rather than the length of the chain, determines the solubility of long chain cellulose esters;

higher substitution levels were associated with greater solubility of the synthesised esters of all fatty acid chain lengths. [17]

1.3.5 Reagents for the esterification reaction

As already presented in one of the previous sections, there are options found for suitable reaction agents. The reagents that have been successfully used in history and nowadays are acid or acyl chlorides, acid anhydrides and dehydration agents with acids. [14]

However, one of the most common reagents used so far is acyl chlorides. Acyl chlorides are produced (*figure 9*) as a result of the reaction taking place between carboxylic acid and reagents such as oxalyl chloride ($C_2Cl_2O_2$) or thionyl chloride ($SOCl_2$). As an acyl chloride compound contains in its molecule both the chlorine and oxygen atoms with electronegative traits, the reagent has been valued greatly as and acetylating agent due to its extremely reactive characteristic trait. [18]

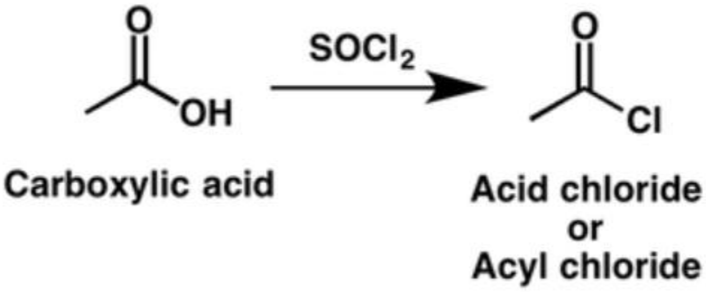


Figure 9. Creation of an acyl/acid chloride [18]

Acetyl chloride

Acetyl chloride with a synonym of ethanoyl chloride has been successfully used for the synthesis of cellulose derivatives. There are only two carbon atoms present in the structure, which determines the compound to be a short chain fatty acid. The molecular formula for the clear colourless liquid is C_2H_3ClO and the molecular weight of it reaches up to 78.5 g/mol. The structure of the liquid is presented in *figure 10*. [19]

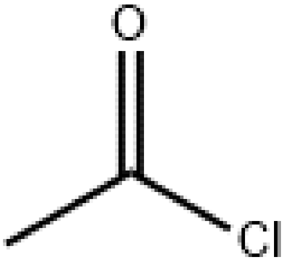


Figure 10. Structure of acetyl chloride [19]

The boiling point of the material has been estimated to be 52 °C. Density has been determined to be 1.104 g/mL. Acetyl chloride bottle should be stored at a temperature below +15 °C. In addition, the compound exhibits a strong pungent odour which must be kept in mind when dealing with the material in laboratories and industries. It has been determined that acetyl chloride is miscible with various chemicals such as ether, petroleum ether, chloroform, acetone, glacial acetic acid and benzene. [19]

Lauroyl chloride

Lauroyl chloride can also be used as a compound for the synthesis process of cellulose esters. Another name for the reagent is dodecanoyl chloride. Twelve carbon atoms are present in the structure of the reagent which also expresses the substance to be a long chain fatty acid. The molecular formula of the compound has been expressed as follows - $C_{12}H_{23}ClO$. The molecular weight of the compound has been measured to be 218.76 g/mol. The illustrative *figure 11* provides with structural formula of the lauroyl chloride compound has been brought out below. [20]

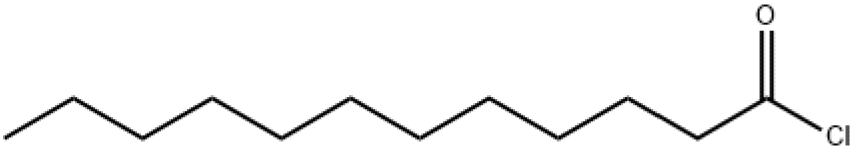


Figure 11. Structure of lauroyl chloride [20]

The density of the reagent is 0.946 g/mL. The compound must be stored below +30 °C and cannot be allowed to have any contact with either moisture or water. The liquid is colourless and the compound is able to dissolve in ethanol and methanol successfully. The boiling temperature falls into the range of 134 °C - 137 °C. [20]

Oleoyl chloride

Oleoyl chloride, in other terms octadecenoylchloride has 18 carbon atoms in its chain, which makes the reagent also a long chain fatty acid. The molecular formula of the compound has been described as $C_{18}H_{33}ClO$ and the molecular weight is estimated to be 300.91 g/mol. The density of the material is 0.91 g/mL and the boiling point was measured to be 193 °C. The storage temperature based on the literature data is -20 °C. [21] *Figure 12* expresses the structure of oleoyl chloride below.

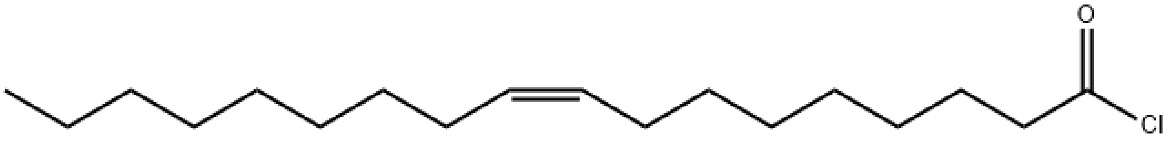


Figure 12. Structure of oleoyl chloride [21]

2. METHODS

2.1 Mechanochemical valorisation of cellulose

In recent years, customers and people involved in science and production have started to consider important how environmentally friendly the design and processing of chemical items are. Nowadays, sustainability is one of the most significant keywords in the chemical community. The goals are related to minimizing the usage of hazardous chemicals and taking over greener strategies. Cellulose is a great basis for improvement in the industry because it already has several applications where it is used as an everyday material. [22]

Mechanical methods are known to destroy or lessen the amount of interchain hydrogen bonds which are found in cellulose. The aim of using those methods is to alter the structure of the material but at the same time maintain the solid form. In addition, the modus can be characterized as a cost-effective way of improving the natural polymer fibres more accessible to various substances. [3]

Mechanochemistry has been evolving rapidly in materials science and chemistry. Implementing mechanochemistry technology and science helps scientists utilize the principles of technology and apprehend how mechanical processes affect chemical reactions. Although metals and minerals have been mechanically processed by various actions (such as comminution and mixing) found in the past, mechanochemistry became a considerable option valued since the late 1980s. This phenomenon may be the result of two aspects – increased utilization of mechanical alloying in metal industries and mechanical activation that was discovered in the field of organic reactions. [23]

Solid mechanochemistry in the field of polymeric materials cannot be generalised because a considerable amount of synthetically derived polymers are thermoplastic and such polymers cannot be processed by solid state milling techniques. Thermoplastics soften and melt during the heating action and mechanical energy dissipates and is absorbed, which is not the intention of the current technology. Therefore, un-melting polymers are applicable for the action and cellulose is one of the relevant and industrially essential materials that can be worked on. [23]

If cellulose is intended to be chemically utilized, heterogeneous processes are involved because cellulose is crystalline and the solubility of the material is low. In recent years it has been paid extra attention to technologies in which mechanical and chemical actions happen at the same time. The reason is the resulting higher efficiency and noticeable specific effects that may occur. [23]

There are several methods in the field of mechanochemical processing of cellulose polymers. Ball milling has been defined as a mechanical operation for grinding powders into blends and smaller particles. However, ball milling stands out for the principle of not having to involve organic solvents in operation. Therefore, the operation is environmentally friendly, swift, easy to work with and economical. [22]

2.1.1 Detailed description of the mechanochemical method

Ball milling is known for its simplicity, cost-effectiveness and fastness and therefore, as a green technology, it has much potential that could be developed via experience and research. Regarding the cellulose industry, technology has been involved in the production and chemical modification of derived cellulose particles. One of the successful examples is the manufacture of nanocrystals and nanofibers. [22]

There have been invented various kinds of ball mills that are adapted to diverse applications. In principle, a hollow cylindrical frame or shell starts revolving around its axis. The shell in use has previously been filled with spheres and those spheres can either be made of rubber, stainless steel, steel or ceramic. The technology relies on emitted energy that is caused by the collision and attrition between the spheres and the material (powder). Apart from numerous positive aspects of ball milling (reliability, the applicability of both the wet and dry conditions with a variety of materials, etc.), the running process may contaminate, produce nanomaterials with disordered shapes, cause noise and take a lot of time while cleaning and milling. [22]

Ball mills are divided into two groups by the way how they operate – direct and indirect milling. Regarding direct milling, kinetic energy is carried over right from the milling action by rollers or mechanical shafts onto the particles. In the indirect milling process, the mill body receives the kinetic energy from the external environment and then it is transferred to the milling environment. Indirect milling machines are most widely engaged in the cellulose chemistry area. Three types of machines for indirect milling found are tumbler ball, vibratory and planetary ball mills. [22] Those machines can be noticed in the picture (*figure 14*) below, whereas *figure 13* depicts the reaction mechanism of the mechanochemical procedure for the production of cellulose oleates at room temperature and for the duration of 3 hours.

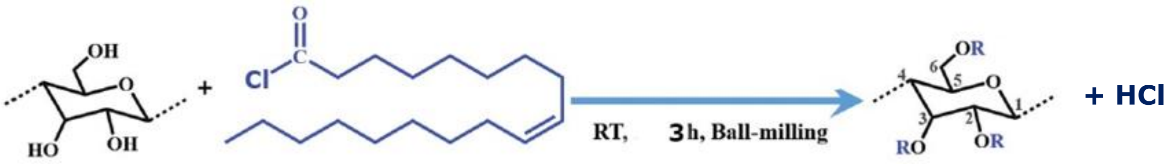


Figure 13. Reaction mechanism for the production of cellulose oleates with reaction parameters that were used in the current work at hand [24]

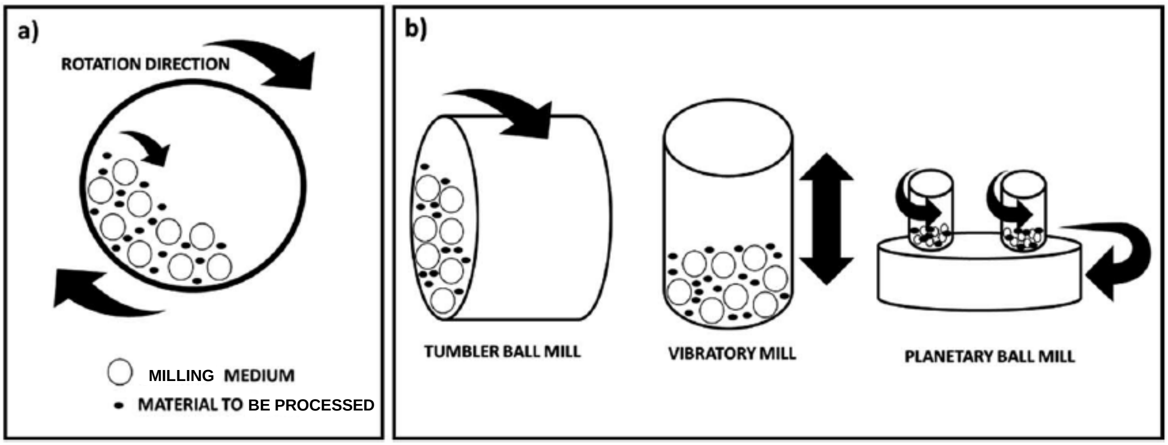


Figure 14. Scheme (a) prefigures the explanation about the ball mill working principle and scheme (b) prefigures variations of indirect mills that are popular in cellulose chemistry [22]

In the case of a tumbler ball mill, a cylinder that has been previously filled with steel balls is supposed to revolve around its longitudinal axis. The larger the diameter of the mill, the more efficient the procedure is regarding the tumbler ball machine. If the diameter is on the larger side, then the height of the fall for the objects found inside the mill is also remarkable and it results in higher energy transmission to the spheres. Vibratory mills have a working principle that differs from the one mentioned earlier. The container filled with the specimen and the grinding medium must operate at elevated vibrational frequencies in order to perform quick shaking movements. Factors that need to be considered while operating with vibratory mills are the amplitude and frequency of vibration and the amount of milling medium. The working principle for planetary ball mills begins by placing several vessels onto a disk and the disk performs the rotating supporting function. Vessels also rotate about their own axes while set on the disk. Regarding the planetary mill, the essential parameter is the size of containers because the larger the container, the more efficient the process is. Higher efficiency can be explained by the higher distance that a more spacious container provides and therefore, during the operation, kinetic energy is at high levels and stronger impacts happen in the vessel. [22]

After the ball milling operation has been carried out, the output material from the process differs from the initial one. Namely, the treatment alters the microscopic and macroscopic properties of the sample and the changes occur in thermal stability, morphology, structure and crystallinity. Moreover, cellulose destruction and its outcome depend on the media that has been used during the process. Therefore, different media have various effects on the destruction affecting the results of crystallinity, morphology and polymorphism. It has been concluded that solvents have an effect on the hydrogen bonding system among the cellulose particles. [22]

Research conducted on ball milling and the possible manufacturing of cellulose nanoparticles by Piras et al. found that ball milling operation is suitable for the chemical modification and production of cellulose nanofibers and nanocrystals. An important advantage of the method here is the ability to combine the mechanical treatment with chemical processes by applying minimal effort. However, it is necessary to keep in mind that the source of base material affects the efficiency of the process and the outcome properties. Therefore, careful selection of the raw starting material is a vital aspect. Ball milling has been customized for use in dry and wet (aqueous) conditions and it has been represented as a possible green and sustainable candidate to be used in industries. [22]

All types of suitable apparatuses for the mechanochemical processing of cellulose are listed in *table 3* below. The last two devices listed in the table demand that the material would be processed in the liquid phase, and therefore, shearing and impact forces during the operation are lower compared to the forces emerging in other devices. In addition, a grinder cannot work properly without any liquid because otherwise, there is the fear of overheating tendency. [23]

Table 3. Applicable machines in the field of mechanochemistry [23]

Category of device	**Another name**	**Action happening in the device**
Rotation mill	Drum mill, tumbling mill	Impact, shear
Planetary mill	-	Impact, shear
Vibration mill	Mixer mill, “high-energy mill”	Impact, shear
Attritor	Stirred media mill, bead mill, “high-energy mill”	Impact, shear
Grinder	Disk refiner	Shear/friction
Ultrasonic homogenizer	-	Cavitation
High-pressure homogenizer	French pressure cell	Shear

2.2 Main methods of materials characterisation

2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

In this work, the FTIR principle will be needed to ensure that the ball milling process has been successful. In other words, the FTIR machine is expected to show if the raw material has transformed into a cellulose derivative.

For understanding the structure of a material at the molecular level, infrared spectroscopy is an essential and crucial method to be used. Infrared (IR) spectroscopy can be used to determine the chemical composition and bonding arrangement of components in various sorts of polymers and polymeric materials. As an interferometer uses an active mirror in motion to create an optical transform of the infrared signal, FTIR spectrometers provide the IR spectrum by Fourier alteration of the signal as a result. Based on the Numerical Fourier analysis, the IR spectrum can be determined by examining the relationship between intensity and frequency. FTIR allows the study of gases, liquids, and solids and the sample to be measured can be prepared to a minimum extent. [25]

Based on the info from former esterification studies, it is expected that upon mechanochemical esterification, a new absorbance peak at 1731 cm^{-1} would be identified that results from the characteristic stretching vibration behaviour of the carbonyl group (C=O). Furthermore, a single absorptive band at 2901 cm^{-1} of non-modified cellulose material must transform into two absorptive bands (2901 cm^{-1} and 2857 cm^{-1}, respectively) in the modified cellulose sample due to the addition of more methylene groups (C–H bonds) from a chosen reagent. Further proof of the esterification process would be exhibited by the reduction in the intensity of the broad band at approximately 3344 cm^{-1}, designated to the cellulose O–H vibrations. [1]

2.2.2 Differential scanning calorimetry (DSC)

DSC is used to determine the melting temperature of the esterified cellulose surface layer. As the mechanochemical process happens on the surface of the cellulose ester particles, the properties of the surface layer are essential to determine.

The measuring process consists of determining the behaviour of a specimen upon heating and then comparing the outcome with a reference sample that goes through the same measuring conditions. In the apparatus, there is a built-in chamber consisting of two openings, one for the specimen and the other for the reference. The heat capacity property of the reference sample over the temperature extent that is observed during the experiment must be known. The specimen goes through a linear heating up activity while the temperature is gradually increased. However, the process is not linear anymore if the specimen undergoes a phase transition. As semi-crystalline materials have both the amorphous and crystalline regions, the matter can go through all three phase transitions – glass transition, crystallisation and melting. During these phase changes, exothermic or endothermic change occurs. Exothermic transition happens when the specimen absorbs heat and endothermic when it emits heat. [26]

The same temperature is obtained in both chambers, but it is needed to implement two separate heaters to ensure different values of heat rates for heating the two corresponding pans. In the case of two dissimilar heat flow values below the sample, slot has been obtained, the DSC notes down the heat flow dissimilarity as a function of temperature. The output of the operation is a graph where the heat flow is dependent on the temperature extent of the specimen analysis. [26]

Various thermal properties of polymers are possible to ascertain with the DSC analysis [26]. Melting point is one of them that is in the interest of the current work.

Based on the information regarding the melting point of the material as well as the glass transition temperature and the crystallization point, the best processing temperatures and thermal fingerprints of matters can be attained. [27]

2.2.3 Optical microscopy (OM)

An optical microscope has been built to operate with either one or more lenses in order to produce an enlarged figure of a sample that is being tested. A simple microscope has been designed for simpler evaluations of products as the magnification efficiency is not as sufficient as needed in the area of research, development and analysis. Therefore, if much larger magnifications are desired to be obtained, microscopy with more than one lens must be implemented into the process. The main idea of multiple lenses is that another lens compounds the effect of the first one. A compound microscope uses the aforementioned principle with two sets of lenses. *Figure 15* expresses the Ray diagram in the case of a compound microscope. [28]

The objective lens, which is located nearest to the object, forms a real image of the sample in an inverted and magnified version. The second lens is called the eyepiece, which functions as a simple magnifier with the aim of creating an enlarged and virtual figure of the initial specimen. [28]

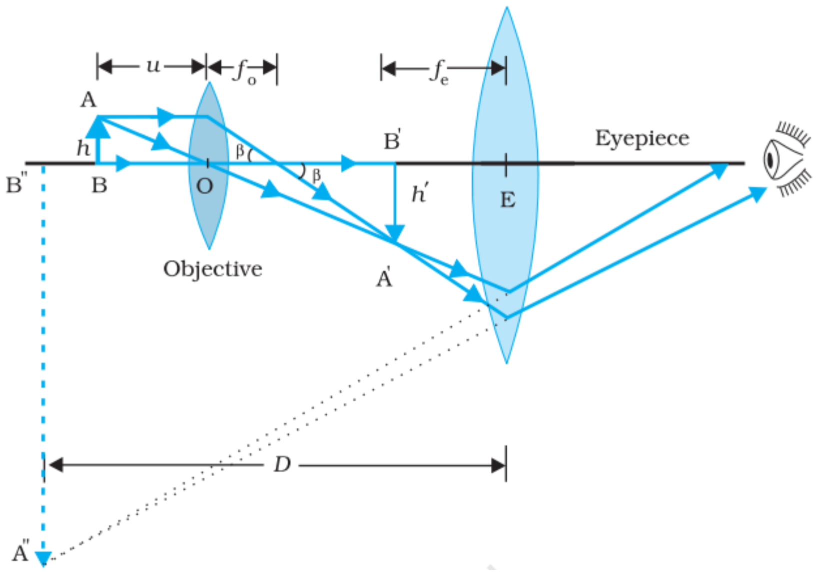


Figure 15. Ray diagram that applies to the principle of multiple lens microscope system [28]

2.2.4 Scanning Electron Microscopy analysis (SEM)

Scanning electron microscope belongs to the category of microscopes in order to provide the possibility of visualising structures of materials that are impossible to evaluate with the naked eye method. [29]

The SEM allows for direct observation and manipulation of the surface of a sample. The most important parts of the SEM machine are the sample chamber, an electron gun, an electron column and the essence of a vacuum created for the procedure. The electron column contains different types of lenses in order to carry out the procedure and a vacuum is necessary as electrons are not able to migrate long distances with the help of atmospheric air. [29]

The principle of the technology at hand is to capture and interpret obtainable signals that are emitted as a result of directing electron beams on the surface of the sample. The signals that are emitted have been determined to be of various types – heat, light, X-rays, electrons and these electrons that the sample absorbs or conducts during the procedure. All the aspects are depicted in a more detailed and illustrative manner in *figure 16*. Due to the occurrence of these signals surface morphology, chemical composition and structural organisation can be evaluated, estimated and characterised. [29]

SEM analysis will be an essential tool to study and analyse the synthesised materials in the current work. In its purest form, microcrystalline cellulose has been ascertained to contain even, rod-like bundles of cellulose material without small fragments from the outside. However, successfully modified thermoplastic cellulose derivatives should exhibit a more homogeneous appearance, sometimes mixed with loose and porous compositions. [1]

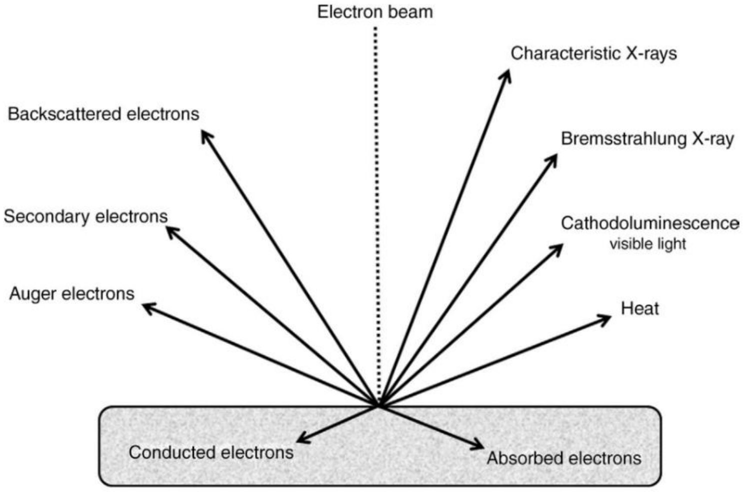


Figure 16. Signals that are emitted due to shooting electron beams onto the surface of the sample [29]

2.3 Processing methods for cellulose derivatives

2.3.1 Soxhlet extraction

The Soxhlet extraction practice has been recognized as one of the first and most practised tools for solid-liquid extraction of solid specimens. The well-known technique was first introduced in 1879 by Franz Ritter von Soxhlet, who was successful in the area of chemistry and nutritional psychology. In the area of analytical practices, the most challenging and toilsome aspect is the analysis of solid samples due to the essence of complex sample matrices. More specifically, a lot of procedures must be carried out before the final analysis can be conducted and analytes can be determined. The Soxhlet extraction method has been used for many years to extract and recover analytes from different solid matrices in an efficient manner. [30]

The experimental Soxhlet device is comprised of various components – a sample holder (in other words, the thimble), distillation flask, condenser part and siphon. The steps commonly involved in Soxhlet extraction are listed in the current paragraph. As a first step of the whole procedure, the solid material is placed onto the filter paper and the filter paper is folded in a way that the material would be wholly packed up by the filter paper. In the second part of the first step, the sample is correctly set into the thimble. Thereafter, in the distillation flask unit, there takes place generation of vapours of the chosen fresh solvent (e.g. acetone). The stream of vapours is directed through the thimble that contains the sample matter to be extracted. Finally, the vapours reach the upper part of the Soxhlet apparatus – condenser, where the same vapours are meant to be liquefied. By the time the level of the liquid in the thimble has reached the overflow stage or plane, a siphon belonging to the construction of the apparatus starts functioning by aspirating the solution and carrying the liquid back into the distillation flask. Additionally and more precisely said, the extracted solutes are directed into the bulk liquid. In a distillation flask, solutes are separated from solvents. Afterwards, the solute remains in the flask while fresh vapours of the solvent pass through the solid bed of the prepared specimen. Repetition is necessary until complete extraction has been achieved. [30]

Many types of solid samples are subject to Soxhlet extraction, including biological and environmental samples. *Figure 17* illustrates an example of a traditional Soxhlet apparatus. [30]

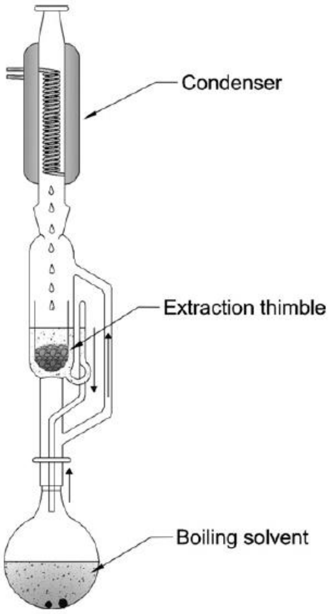


Figure 17. The conventional solution for Soxhlet extraction processes [30]

The author of the work was interested to find out whether there is a difference in the purity of the output material if a half amount of material (of the same synthesis product chosen randomly) was cleaned with usual manners and the second half of the same material was washed afterwards with Soxhlet extraction principles.

2.3.2 Compression moulding

The compression moulding process is known as a simple but not an automatic process for the production of plastic parts. Parts are formed by mounting the processable material into the mould cavity and then the upper part of the mould starts to move downwards with speed chosen for the closure action (*figure 18*). The polymeric matter is then squeezed or compressed and due to the hot plates of the mould, the molten substance starts to fill the cavities of the mould. Thereupon, the matter can cure and then the part is released. [31]

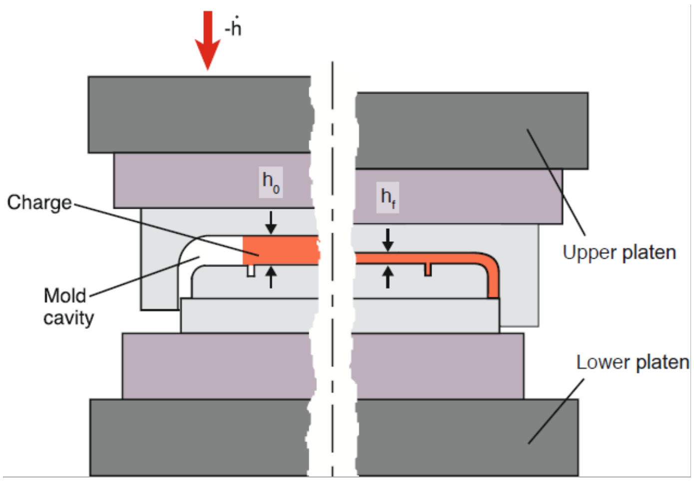


Figure 18. Compression moulding of plastics, where h_0 has been defined as charge thickness, h_f the demanded thickness of the formed part, and h the speed of closure of the upper mould [31]

CHAPTER 2. EXPERIMENTAL PROCEDURES

The current chapter expresses the origin of the raw material for the practical work, the necessary steps for synthesis and subsequent analysis.

3. SYNTHESIS OF CELLULOSE DERIVATIVES

The experimental work covered the production of 3 different cellulose derivatives – cellulose acetate (CA), cellulose laurate (CL) and cellulose oleate (CO). The equation depicting cellulose reacting with acyl chloride can be seen in *figure 6* of the current thesis.

As the process takes place in a rotating vessel following the rules of mechanochemistry, the reaction media is a solid phase. Therefore, no extra solutions or chemicals were included as chloride compounds are highly reactive. In the process of the thesis work, different molar ratios (AGU to acyl chloride) were tested for the production of cellulose derivatives via mechanochemical operation.

During the first stage of the experimental work, the essential task was to find out the most optimal molar ratio of the esterifying reagent for the production of cellulose esters and for the compression moulding procedure (the best material with satisfactory properties helps determine the aspect). Thus, a lot of synthesis operations were conducted following the same main principle of esterification. FTIR analysis was implemented as a detective tool in order to find out whether the esterification was successful.

3.1 Necessary preparational procedures before the mechanochemical reaction

In the current sub-chapter an overview of the original cellulose material will be provided and necessary steps before the synthesis are going to be brought forth.

3.1.1 Source of cellulose material and initial processing paper material

In this work the main implementable cellulose material originates from the white 100% α-cellulose paper produced by Hahnemühle. For one synthesis the initial material was randomly chosen cardboard material. The paper or cardboard had to be cut into smaller entities and milled with IKA A11 basic grinder in order to obtain smaller particles and a fluffy texture. The activity was necessary for ensuring the probability of a successful synthesis procedure as it is easier for the reagent molecules to obtain access to fibres of cellulose if the material has previously been processed into smaller entities. The milled matter was held in the vacuum oven for hours at temperatures between 50 °C and 80 °C to ensure there was no humidity found in cellulose at the beginning of the reaction process.

3.1.2 Production of regenerated cellulose cake

The current step was applied only for the production of regenerated cellulose oleates as this type of cellulose esters were the last to synthesise and it was noted that some improvement must be tried by engaging an additional step in work. In other words, the principles of the step were not utilised in the synthesis of cellulose acetates and laurates. Some cellulose oleates were made without the regeneration step as well.

The reason for engaging the step into the work was to test whether the properties of the output could be improved for the compression moulding procedure – to produce films of cellulose derivatives. More specifically, based on the results of produced CAs, CLs and some COs, it was evident that modification of initial cellulose material was not entirely performed – not to a full extent. With the regeneration process the results were hoped to be improved by activating (swelling) the cellulose before the reaction.

The information for the regeneration process was obtained from an article published by Hou et al. The study included the regeneration process for the production of cellulose oleates [24]. The same article used principles originating from one of the former articles that most of the same researchers had released a year before – preparation of thermoplastic cellulose grafted PUR [32].

According to the formerly mentioned articles, dissolution and regeneration activities on cellulose were carried out. As a first step in dissolving cellulose material in NaOH aqueous solution, 5 g of cellulose had to be weighed and set ready for the next step. Thereafter, 12.5 g of NaOH was poured into a beaker that contained 237.5 ml of distilled water. Mounting cellulose into the beaker containing NaOH and distilled water was the final step. The mixture goes then through the swelling procedure for 3 hours at room temperature. The following steps included placing the swollen mixture into the freezer at -18°C and letting the mass reach the frozen state. The next day the mass had to be melted at room temperature and stirred on a stove with a magnetic stirring bar. The aim of these little steps was to attain a homogenous cellulose solution.

As a first step in the preparation of regenerated cellulose ethanol gelation (the abbreviation is RCE), the homogenous solution had to go through a washing process several times with pure ethanol in order to ensure pure, neutral RCE. Thereafter the product was washed with distilled water in order to obtain RCW (regenerated cellulose water gelation) as a final result before synthesis. The material was then placed into the oven for drying at a temperature of 50°C. The material achieved was in a dry clump (also called a cake) form.

3.2 Synthesis procedure

3.2.1 Reagents utilised for the mechanochemical synthesis

The necessary reagents were obtained from the supplier Sigma-Aldrich and Fluka. Chemicals are brought out in *table 4*. The chemicals are in liquid form and were treated with the utmost care while using them for the reaction.

Table 4. Different reagents implemented in the mechanochemical reaction to produce various cellulose esters

Chemical	**Company**
Acetyl chloride	Sigma-Aldrich
Lauroyl chloride	Sigma-Aldrich
Oleoyl chloride	Fluka

3.2.2 Mechanochemical reaction

The processable cellulose material of 10 grams was placed into the planetary ball mill vessel (*figure 19*), which contained balls. In the case of regenerated cellulose oleate synthesis the mass of the initial cellulose cake was 5 grams as a lot of prework and chemicals were needed for the preparation of the cake weighing 5 grams only. The total weight of balls per 10 grams of cellulose was 800 grams and the average diameter of these spherical objects was 2.5 cm. The same balls were used for the production of a regenerated version of cellulose oleates as well and the weight of the balls remained the same (800 grams of balls per 5 grams of cellulose) as the reduction of the spherical objects caused inactivity of the mechanochemical process (no sound of the mechanochemical process was heard).

Figure 19. Result of one synthesis procedure where balls are found with the product in the vessel

A chosen reagent was added to the media and the amount of the reagent depended on the molar ratio of these two materials. In the beginning, different molar ratios were tested with every synthesis.

The duration of the procedure always remained the same throughout all the experimental procedures (syntheses) – 3 hours. The rolling unit onto which the vessel had been placed to spin was always used with the constant rotational speed of 250 rpm.

An explanation for calculating the amount of reagent to be used based on the example with acetyl chloride

The Cellulose AGU unit has a maximum of 3 -OH groups that could be substituted during the course of the reaction taking place. As in the current thesis, the author worked with acyl chlorides the equation in *figure 6* from the literature overview *section 1.3.2* describes the reaction mechanism properly. According to the equation, the -OH group shall be substituted with the main structure of the acyl chloride compound and only the Cl atom will be left out that reacts with the released H of the cellulose molecule and as a result, forms a gas HCl.

As was mentioned before, the one AGU unit has 3 -OH groups, but acyl chloride compounds (acetyl chloride, lauroyl chloride and oleoyl chloride) contain only 1 CO-R per 1 molecule. If the total substitution is desired, then the ratio of cellulose and the chosen acyl chloride must be 1:3. However, besides the 1:3 molar ratio, other molar ratios were also worked with (1:1, 1:2 and 1:4) in the current work at hand.

As the molar mass of one cellulose AGU unit is 162.14 g per 1 mol, the number of moles per 10 g of cellulose was necessary to be found. In the example below, the calculations have been made with the acetyl chloride compound.

Table 5. Summary table for the calculation of the number of moles for 10 g of cellulose

Cellulose material	Mass, g	Amount of moles, mol
1 cellulose AGU unit	162.14	1
10 g of cellulose	10	n_{10g}

$$n_{10g} = \frac{1\,mol * 10\,g}{162.14\,g} = 0.062\,mol$$

To find out how many moles of acetyl chloride were used per 10 grams of cellulose with total substitution, 0.062 mol was multiplied by 3.

$$n_{10g,1:3} = 0.062\,mol * 3 = 0.186\,mol$$

The number of moles was multiplied by the molar mass of the substance (acetyl chloride in the current example) and the mass of the acetyl chloride for 10 grams of cellulose was found. Finally, the mass had to be divided by the density to find the volume so that it would be easier to add the substance to the cellulose material by using the pipette.

$$m_{acetyl\ chloride} = n_{10g,1:3} * M = 0.186\,mol * 78.49\,\frac{g}{mol} = 14.6\,g$$

$$V_{acetyl\ chloride} = \frac{m}{\rho} = \frac{14.6\,g}{1.1\,\frac{g}{cm^3}} = 13.27\,cm^3 = 13.27\,ml$$

3.2.3 Washing procedure of the output material after the esterification reaction

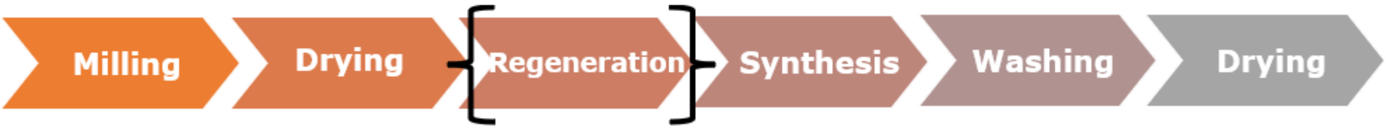
At first, the output was washed with acetone. In most cases, vacuum filtration was used instead of filtration with a simple filter at atmospheric pressure as the material contained tiny particles that would have passed the simple filtration system. Implementing acetone as the first chemical in washing ensured that all the material was removed from the vessel and surfaces from the balls. Thereafter, the material was washed with water by either using a vacuum filtration system or just passing the liquid through a simple filter.

In the case of one synthesis product (one regenerated cellulose oleate version), the Soxhlet extraction washing procedure was implemented as an extra after the simple washing procedure to see whether Soxhlet washing improves the purity of the final product.

3.2.4 Drying of the product

The product was left for drying in the vacuum oven for a day at temperatures between 50 °C and 80 °C before starting to analyse the output.

3.2.5 An overview of the general procedure until analysis steps



Milling

- Alpha cellulose paper
- Random cardboard waste

Drying

- Short-time drying
- Vacuum oven

Regeneration

- A mixture of cellulose, NaOH and water
- Freezing and melting of the mass
- Washing with ethanol 1st and 2nd with water

Synthesis

- 3 h, room T (°C)
- Cellulose material and a chosen reagent only

Washing

- 1st acetone
- 2nd water
- {Soxhlet washing as an extra tested for one synthesis only}

Drying

- Vacuum oven

3.2.6 Analysis of the output materials

The synthesised materials were analysed with different methods. All the products went through the FTIR, SEM, DSC, OM analysis and were also tested with solubility tests in 3 solvents (chloroform, acetone, DMSO) and compression moulding procedures to investigate if films of the derived materials could be created.

FTIR

- Determination if the material had been esterified

DSC

- Obtaining the melting point of the material

Compression moulding

- Preparaation of the film products

SEM 1 and 2

- 1 - Analysing the fibres of produced materials
- 2 - Analysing the structure of solution cast film sample materials

OM

- Analysing the structure of solution cast film sample materials

Solubility test

- Chloroform, DMSO and acetone

4. OVERVIEW OF ALL THE PRODUCED CELLULOSE DERIVATIVES

In order to provide the clearest information about the syntheses for the reader, *table 6* provides a compendious overview of all the produced cellulose esters with the molar ratios. In the list are included the regenerated cellulose derivatives – regenerated cellulose oleates from pure paper and one from randomly chosen cardboard waste. The total number of syntheses conducted during the Master's thesis reporting period is 15.

Table 6. All the produced cellulose esters with specified molar ratios

Polymer	**Molar ratio, AGU to acyl chloride**
Cellulose acetate	1:1
	1:2
	1:3
	1:4
Cellulose laurate	1:1
	1:2
	1:3
Cellulose oleate	1:1
	1:2
	1:3
Regenerated cellulose oleate	1:1
	1:1
	1:1
	1:1
Regenerated cellulose oleate from cardboard waste	1:1

5. CHARACTERISATION OF THE PRODUCTS BY FTIR

The current section provides the first understanding of the success or unsuccess of the conducted syntheses. FTIR analysis is able to ensure understanding regarding the modification of the material. Based on the preliminary data from the first reactions (production of CAs vs CLs vs COs), a decision was made on which reagent and molar ratio was chosen to carry out the rest of the experimental work. Description of the peaks (as an instruction to analyse FTIR correctly) is represented as one paragraph found in the introduction of the FTIR method, which is necessary for the characterisation of the synthesised samples. According to the same peaks, the occurrence of synthesis can be either confirmed or disproved. The FTIR machine utilised in the lab was INTERSPEC 200-X FTIR Spectrometer.

In the first FTIR graph (*figure 20*) of the current section, three different cellulose esters are compared with each other as they all have been synthesised with the same molar ratio (AGU to acyl chloride) 1:1. Based on the results of the analysis it was decided to conduct the remaining syntheses with oleoyl chloride compound (in blue) as peaks representing the esterified material exist in the graph and that was enough for the surface modification process of cellulose fibres. More specifically commenting on the graph, at wavelengths of 2901 cm^{-1} and 2857 cm^{-1}, two peaks indicating the methylene groups have arisen in the modified version of cellulose oleate (in blue) and cellulose laurate (in green) and the peak corresponding to carbonyl group exists at 1731 cm^{-1}. The wavelength at 1050 cm^{-1} represents the ether bond group which has been noted to exist for both the cellulose laurate and cellulose oleate samples. According to the analysis results for cellulose acetate in red, the same synthesis at hand was unsuccessfully conducted.

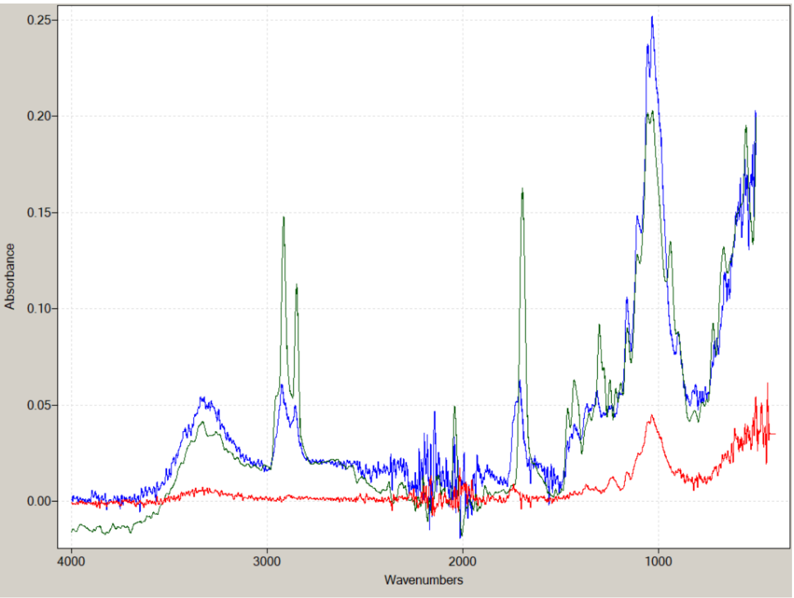


Figure 20. FTIR graphs illustrate graphically three synthesised cellulose esters in molar ratios of 1:1, where the *red* line represents CA, *green* CL and *blue* CO

In the next FTIR analysis result in *figure 21,* the same characteristic peaks that were used for the description of the previous analysis allow us to understand the influence of incorporating the regeneration step into the modification process. The line in pink represents the regenerated cellulose oleate version (also with the molar ratio of 1:1), whereas the blue represents the same cellulose oleate also captured in the previous FTIR analysis description. As a result, the regeneration process offers a high probability of improving the esterification process on the initial cellulose material, as the pink graph provided more advanced peaks at expected wavenumbers.

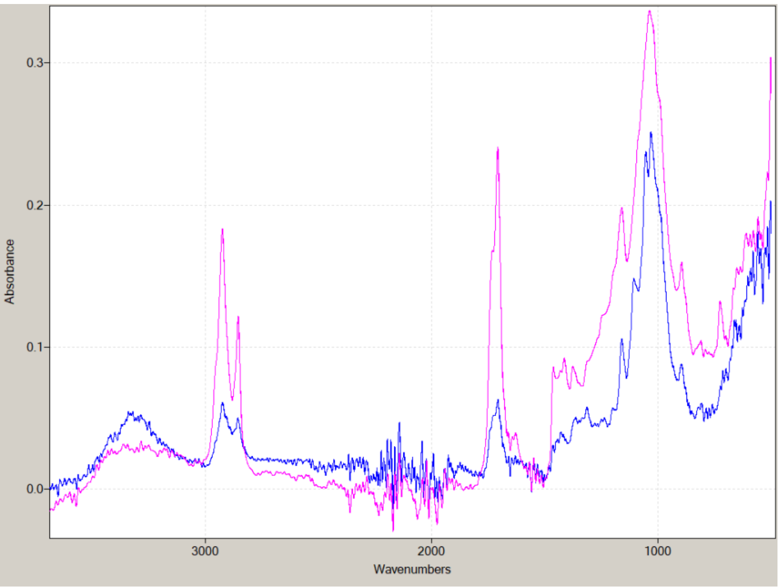


Figure 21. FTIR graphs illustrate the difference in the efficiency of the produced cellulose oleate *(in blue)* and regenerated cellulose oleate *(in pink)* products graphically with the molar ratio of 1:1

Table A1.1 in *Appendix 1* section expresses the extent of esterification brought out in numerical data for all the synthesised polymers. More specifically, the height of two peaks found at the corresponding wavelengths of approximately 1050 cm^{-1} and 1710 cm^{-1} were measured for all the samples.

The illustrative explaining figure based on the first regenerated cellulose oleate material can be noticed in *Appendix 1* section in *figure A1.1*. While taking a look at the table again, the value of $I_{C=O}/I_{C-O-C}$ parameter has been obtained by dividing the height of the carbonyl group peak by the height of the ether bond group. For both alpha cellulose paper and cardboard waste, there are expected to be found no remarkable peaks for carbonyl groups. Therefore, the $I_{C=O}/I_{C-O-C}$ value for alpha cellulose paper is low – 0.067. The higher the output for the parameter $I_{C=O}/I_{C-O-C}$ the more esterified the considered material is. A side note regarding the results for CA 1:4 and CL 1:1. The values were too optimistic (4.497 and 5.807, respectively) due to the very indistinguishable nature of the chosen curves, resulting in a high probability of inaccuracy.

The attempts of remeasuring did not improve the situation of the results for the two samples. However, by following the principle of the analysis and leaving the two previous polymers out, the least esterified materials were cellulose acetates and the most successful results came out as variations among the cellulose laurates and regenerated cellulose oleates.

All in all, the values of parameter $I_{C=O}/I_{C-O-C}$ varied significantly in all cellulose derivative categories, which makes the drawing of clear conclusions difficult based on the current analysis.

6. SUMMARY OF SYNTHESES

Syntheses exhibited different results. There are many nuances found during the reaction that play a huge impact on the result – on the synthesis product. For example, a number of important aspects are brought out that each help determine the properties of the end result - duration of the procedure, rotational speed, the temperature of the environment, molar ratio between the cellulose and reagent, size and weight of the balls. It can be stated as challenging to find suitable values for all parameters via testing in a relatively short period. As for the former studies, the previous publications have only listed a few specific parameters with which the tests were performed successfully.

Based on the results obtained from the FTIR analysis there are syntheses that were confirmed to be successful and a remarkable amount of them that had been left unmodified.

The preparation of the regenerated cellulose cakes takes time with a lot of effort and the reaction with post synthesis washing procedure is also time consuming where a remarkable amount of resources is being accumulated. Therefore, it demands practice and time to find the most optimal working solution for synthesis procedures.

However, in terms of the molar ratios it was clear that syntheses with molar ratios of 1:1 were ensuring satisfactory results in the modification of the material because the goal was to modify cellulose partially. Therefore, the same ratio was later used until the end of the experimental work. It is necessary to mention the aspect that synthesis with the molar ratio of 1:4 was harmful to the initial product (the amount of reagent was too aggressive towards the cellulose material) as there were noticed darker areas to be existing in the material.

In terms of esterifying reagents, it was decided to test the processing of the regenerated cellulose cake with oleoyl chloride only. Other chemicals were also performing well in the reaction procedures which results were confirmed by different analyses. However, oleoyl chloride was later preferred due to different aspects - successful FTIR results of cellulose oleates as a result of all three reactions, enough supply of the chemical in the lab for upcoming reactions and the reagent itself is a long chain fatty acid. The LCCE could exhibit more desirable properties in later applications of the produced cellulose ester than acetyl groups are able to ensure in cellulose acetate.

CHAPTER 3. RESULTS AND DISCUSSION

The current section focuses on the analysis of obtained cellulose derivatives and the probability of processing the materials further. The results are brought forth according to the categories – one type of cellulose ester at a time.

7. CELLULOSE ACETATE

Altogether four syntheses of cellulose acetates were made with various molar ratios of 1:1, 1:2, 1:3 and 1:4, in order to find the most efficient option for the mechanochemical esterification.

7.1 Solubility tests

At first, liquids (acetone, chloroform and DMSO) were poured into the three separate weighing bottles with lids placed on them. A small amount of material was mounted into the media to examine whether a type of cellulose acetate is able to dissolve in the medium. Thereupon, 10 minutes were given for the process and later the situation in the same bottles was evaluated. The same principle was applied to all the produced materials.

As a result, not any of the produced cellulose acetates were able to dissolve in the three different media. The first cellulose acetate product could have been contaminated with an unknown material which emitted from the surface of the balls. Before the very first mechanochemical procedure, the balls had remained unused for a long period of time. Therefore, the first product of the first synthesis was not the desired cellulose acetate. As for the other outcomes of syntheses, the reason for not dissolving may have been caused by the low extent of substitution of hydroxyl groups.

7.2 FTIR

According to the FTIR analysis results the chemical modification took place in synthesised cellulose acetates. By presence of absorbance peaks attributed to C=O group, CAs with molar ratios of 1:2 and 1:4 were evaluated as efficiently modified. Samples with molar ratios of 1:1 and 1:3 unexpectedly showed poor esterification.

7.3 DSC

The DSC for the materials were done by Perkin Elmer DSC 7. The analysis was made for two samples only – the melting point for the sample with the molar ratio of 1:2 was determined to be 135 °C (*figure 22*) and the melting point for the one with the molar ratio of 1:1 was 131 °C. Temperatures for the same polymer produced in different ratios fall into the same range – above 130 °C. The DSC graph for the CA material with the molar ratio of 1:1 and for all the other synthesised cellulose esters in the current work are brought out in *Appendix 3*.

Those two samples were chosen to be tested because the sample with the molar ratio of 1:2 was successfully synthesised according to FTIR analysis and the sample with the molar ratio of 1:1 did not contain any overreaction signs. Even though the sample with the molar ratio of 1:4 was chemically modified the output material exhibited a very dark colour which means that the ratio of reagent was too high for the mechanochemical reaction and therefore, the sample was excluded from the work.

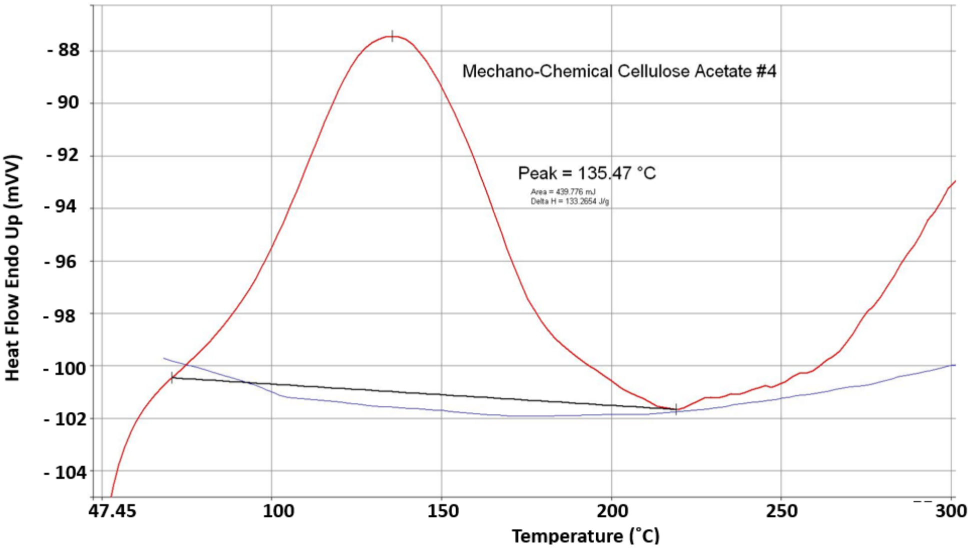


Figure 22. DSC graph presented as an example for the CA sample with the molar ratio of 1:2

7.4 Compression moulding

The previously determined DSC results were taken into account for the compression moulding procedure. The apparatus was heated up to 160 °C for approximately 25 °C over the average melting point of the polymer that was determined to be 133 °C. Compression moulding was unsuccessful – synthesised cellulose acetate materials remained in the same powdery form (*figure 23*). No film was produced from CA.

Figure 23. (a) The compression moulded CA sample with the molar ratio of 1:1, (b) CA sample with the molar ratio of 1:2

To summarise the results, the materials have been chemically modified, melting points were determined, but the thermal properties of cellulose acetates were not as great for film or sheet preparation by compression moulding. It is worth noting that molar ratio has no significant effect on processability of material by compression moulding.

7.5 SEM analysis

The SEM analysis was carried out with HITACHI TM-100 Tabletop Microscope. All the SEM figures in the current work can be found in *Appendix 2*. In *table A2.1,* the fibres of alpha cellulose are expressed, whereas the cellulose acetate with the molar ratio of 1:2 and the synthesis output tested with the molar ratio of 1:1 are depicted in *table A2.2*. However, *figure 24* below presents also the same figures in order to provide the reader with the primary understanding of SEM data.

The average width of alpha cellulose fibres was measured to be 22.08 μm. Based on the first impression obtained from the figures, there can be differences found among the images. Cellulose acetate 1:2 differs from the others structurally – the fibres have been processed into shorter fibres and are also densely packed. The figure of the cellulose acetate 1:1 resembles more to the figure of alpha cellulose, which may mean that modification has not taken place to a larger extent and most of the fibres remained in the long forms of fibres and contained a remarkable amount of unspecified residues between fibres. The residues can be either the undesired contaminants remaining from different processing procedures or the particles of the produced cellulose ester.

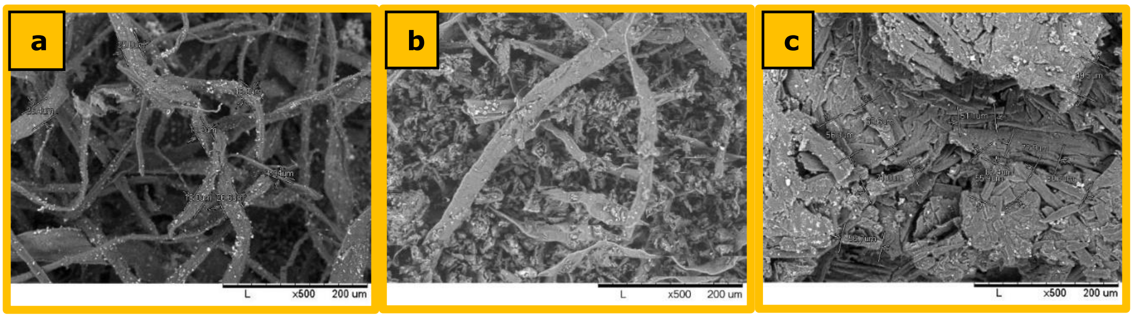


Figure 24. (a) The morphology of pure cellulose fibres, (b) The morphology of CA with molar ratio of 1:1, (c) The morphology of CA with molar ratio of 1:2

7.6 Solution cast films

Film solutions for all the produced and chosen cellulose derivative materials were prepared in a mass ratio that consisted of 10% of cellulose derivative material and 90% of DMSO. The total mass of the film solution sample was aimed to be 2 g. The purpose of the experiment was to obtain an overview of the structures of materials after they had gone through the stirring process for days in DMSO and drying activity for a day in a vacuum drying oven on the microscopy slides. Drying of the samples near 80˚C was conducted in order to investigate cellulose derivatives under the microscope without the presence of most of the DMSO substance. The film solutions that were spread onto the microscopy slides are illustrated in *figure 25*.

Figure 25. The prepared solution cast film samples, two CA samples are presented in the left upper corner of the figure

7.6.1 Optical microscopy analysis

As can be noticed from the figures regarding the cellulose acetates in *table A2.2*, there is a mixture of crystalline and amorphous areas found. More precisely said, in those microscopy figures, the darker area represents the crystalline area and the lighter one amorphous one. The main conclusion that can be drawn from the analysis of cellulose acetates is that the synthesised materials contain short fibres only. However, such a trait does not exhibit successful results in the production of films or composites.

7.6.2 SEM analysis

After the microscopy test, little amounts of two cellulose acetate films were scraped off from the same microscopy slides and were placed and stuck onto the SEM disc specimen. The figures are expressed in *table A2.2*. All these materials consist of layers of a cellulose derivative (no intermolecular crosslinking has occurred) which means no homogenous film forms have been created from the materials. Therefore, it can be claimed that the goal of obtaining a homogenous plastic film was not fulfilled.

8. CELLULOSE LAURATE

Altogether three mechanochemical reactions for the production of cellulose laurates were carried out with molar ratios of 1:1, 1:2 and 1:3. The output with the molar ratio of 1:3 was discarded as the material could not be processed after the post synthesis drying. The material remained liquid after repeated washing and further drying in a vacuum oven and thus, the material in liquid form could not be compression moulded or analysed.

8.1 Solubility tests

The produced two cellulose laurate materials with molar ratios of 1:1 and 1:2 were insoluble in all three solvents.

8.2 FTIR

Both syntheses for cellulose laurates were highly effective according to the FTIR data with expected characteristic peaks. However, synthesis with the molar ratio of 1:2 resulted in a dark coloured compound that could mean the amount of reagent was too high for the mechanochemical reaction. The spectra for CL material with the molar ratio of 1:1 is presented in *figure 20* in section 5 of chapter 2, where synthesised materials are analysed and characterised by FTIR.

8.3 DSC

Melting points for cellulose laurate were determined to be much lower than the ones for cellulose acetate. Temperatures of 63 °C (CL with a molar ratio of 1:1) and 61 °C (CL with a molar ratio of 1:2) fall into the same range as each other. The difference between the melting points of cellulose laurate and cellulose acetate amounts to up to 70 °C.

8.4 Compression moulding

In the case of cellulose laurates, the apparatus was heated up to 90 °C because the temperature had to exceed their melting point temperature (with an average of 62 °C obtained from the DSC analysis). The experimental work resulted in relatively successful outcomes as the materials were able to be heated up under pressure. However, a remark must be made regarding the cellulose laurate – after removal of the material found between the hot plates, a lot of oil was discharged. In conclusion, the most promising result was obtained with cellulose laurate with a molar ratio of 1:1 because the same matter with a molar ratio of 1:2 was burned to some extent (*figure 26*).

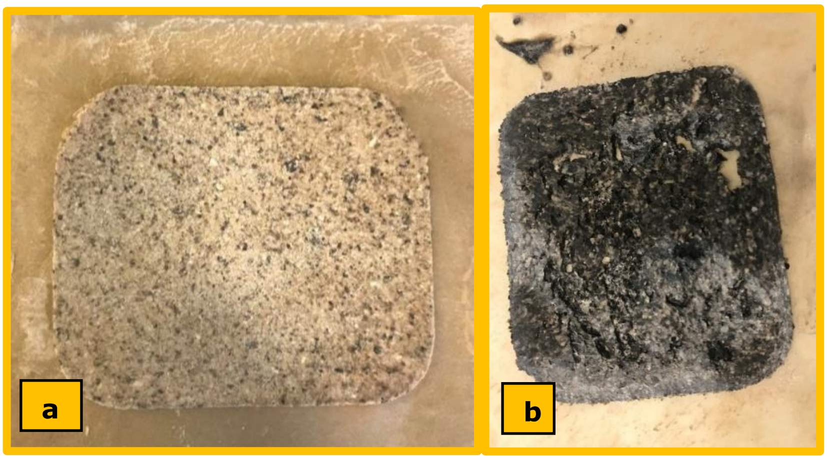


Figure 26. (a) The compression moulded CL sample with the molar ratio of 1:1, (b) CL sample with the molar ratio of 1:2

8.5 SEM analysis

According to the images obtained from *table A2.3,* the images exhibit the aspect that the processing of fibres has occurred. Fibres have been shortened and are more densely packed in both successfully mechanochemically synthesised materials.

8.6 Solution cast films

Film solutions were prepared in the same way as previously for cellulose acetates. No modifications in the film solution preparation procedures were made for the other materials as well.

8.6.1 Optical microscopy analysis

As can be noticed from the figures in *table A2.3*, there is a mixture of crystalline areas and amorphous areas. The analysis resulted in the fact that, as with cellulose acetates, cellulose laurates consist of only short fibres. However, as was already mentioned in the case of cellulose acetates, such a trait of the existence of short fibres does not exhibit successful results in the production of films or composites.

Another remark can be brought forth about cellulose laurate samples in *table A2.3*. Especially based on the second figure of them because there are specific circular objects found that show the existence of residues from other chemicals or just the fact that the microscopy slide was previously contaminated. Overall, very uniform images of a division of fibres have been obtained from the optical microscopy study.

8.6.2 SEM analysis

The SEM results for the film solution sample of cellulose laurates in *table A2.3* showcase the same tendency of consisting of layers of the derivative but not the existence of the homogeneous film form. The aim of achieving a homogenous plastic film was not completed.

To summarize the results for cellulose laurate synthesis, the reagent lauroyl chloride resulted in good esterification (according to FTIR). Still, the material is degraded and cannot form films or sheets by compression moulding or solvent casting.

9. CELLULOSE OLEATE

The syntheses of cellulose oleate were carried out with varying molar ratios of AGU to oleoyl chloride - 1:1, 1:2 and 1:3.

9.1 Solubility tests

The solubility test showed that all the produced samples were insoluble.

9.2 FTIR

All the produced cellulose oleates have been confirmed to be esterified according to the data from FTIR (*figure 27*). However, the peaks which are characteristic of esterified material could be improved to higher values. In the current thesis, the esterification of cellulose oleates was tried to improve by incorporating the regeneration process as one extra step in pre-synthesis activities.

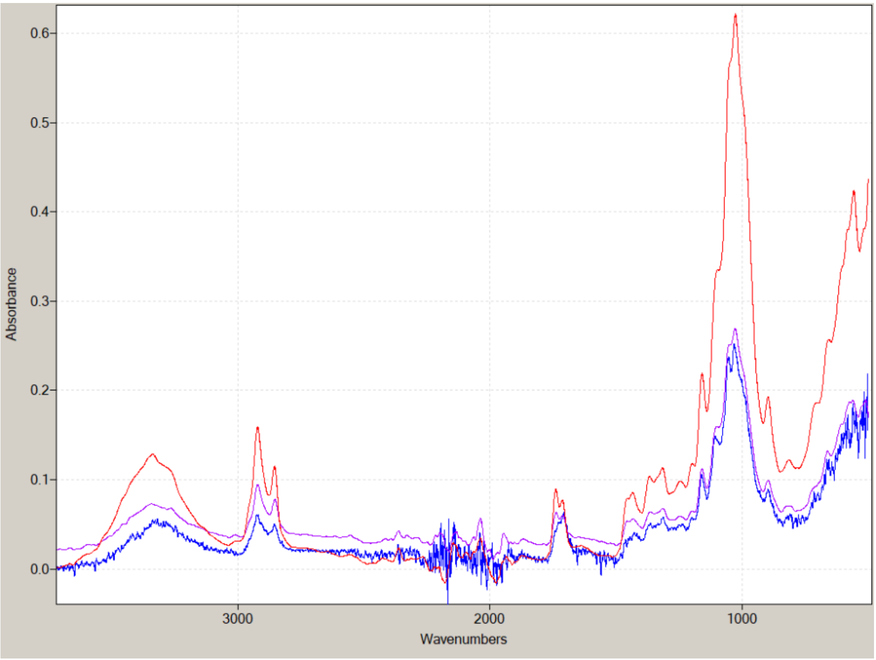


Figure 27. FTIR graphs illustrates graphically 3 synthesised cellulose oleates in molar ratios of 1:1 *(in blue)*, 1:2 *(in violet)* and 1:3 *(in red)*

9.3 DSC

DSC was implemented in order to obtain the melting points for prepared cellulose oleate specimens. The melting temperature for the sample with a molar ratio of 1:1 was determined to be 127 °C, the melting point for the second one with a ratio of 1:2 was 133 °C and the result for the third one with a ratio of 1:3 was measured to be of 131 °C. Melting points for cellulose oleate were determined to fall into a similar range as the temperatures measured for cellulose acetate – around 130 °C. Therefore, melting points of cellulose oleate are also measured to be higher than the results obtained for cellulose laurate.

9.4 Compression moulding

The outcome after the compression moulding operation was still powdery and therefore, it can be stated that the activity resulted in no change (*figure 28*). The temperature set for the machine was 150°C.

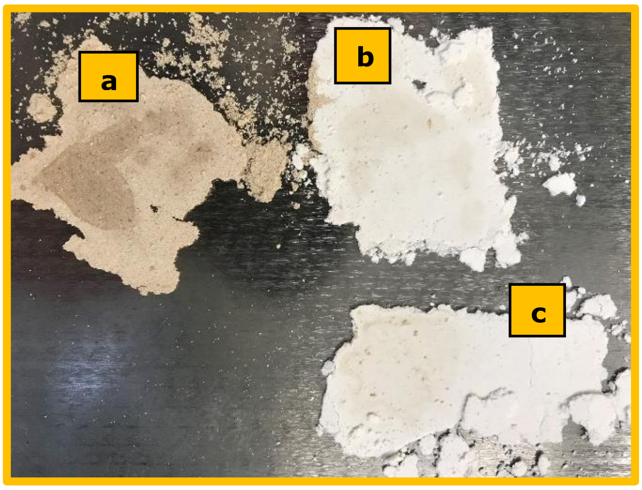


Figure 28. (a) CO sample with molar ratio of 1:1, (b) CO sample with molar ratio of 1:2, (c) CO sample with molar ratio of 1:3

9.5 SEM analysis

The results obtained from the SEM analysis in *table A2.4* shows that during the mechanochemical operation the processable materials had successfully been processed into shorter fibres which mostly have uniform lengths. However, the width of the samples varies, which means that the longer duration provided for the mechanochemical process may result in even more uniform dimensions of the fibres.

9.6 Solution cast films

9.6.1 Optical microscopy analysis

The main conclusion drawn from the microscopy analysis for cellulose oleates is that cellulose oleate fibres are uniformly packed and of uniform structure. The figures can be obtained in *table A2.4* in *Appendix 2* section.

9.6.2 SEM analysis

As with previous materials, no films or sheets were produced from the cellulose oleates. This was also confirmed by the SEM analysis (*table A2.4*), expressing the layers of fibres rather than the homogeneous film.

To summarise the results of cellulose oleate, the molar ratio could be set as low as 1:1, which is probably enough to modify the surface of fibres.

10. CELLULOSE OLEATE MADE OF REGENERATED CELLULOSE

To decrease the crystallinity of cellulose before esterification, pre-processing of cellulose into regenerated cellulose was performed as described in *sub-chapter 3.1.2*. In total, four reactions for the production of regenerated cellulose oleate were conducted. All of them were produced with molar ratios of 1:1.

10.1 Solubility tests

The results obtained for all the manufactured regenerated cellulose oleates exhibited behave insolubly in the chosen solvent systems. The fourth synthesis of regenerated cellulose oleate was determined to be well dispersed in the liquids but not dissolved.

10.2 FTIR

REG CO 1. The first regenerated CO showcased in pink (*in figure 29*) is being compared with the initial alpha cellulose paper and the unregenerated version of cellulose oleate. All three materials depicted in the exact figure have the same molar ratio - 1:1. REG CO has been successfully modified and esterified during the synthesis based on the conducted FTIR study. As a final note, the regenerated CO exhibited higher peaks in expected regions than the unregenerated CO, which allows estimating the regeneration procedure to be an efficient and necessary additional step for the whole procedure.

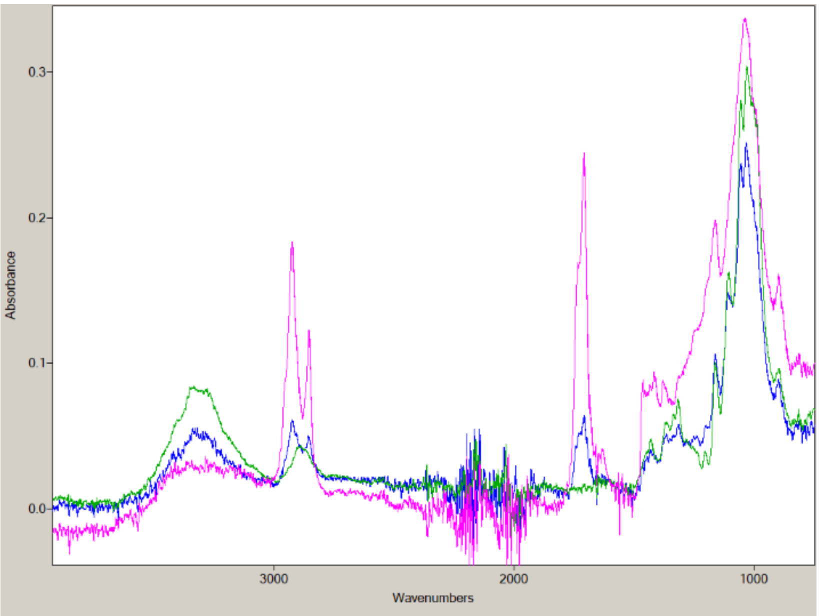


Figure 29. FTIR analysis for the REG CO 1 that has been expressed *in pink*, CO in blue and alpha cellulose paper *in green*

REG CO 2. Both the traditionally washed and extra Soxhlet washed materials have been esterified successfully. The modified materials exhibit peaks that were expected to be present in an esterified material. A considerable variation cannot be noticed between the quality of the extra Soxhlet extracted sample and the traditionally washed sample batch, which means that the Soxhlet procedure does not offer any additional value to the work in terms of the chemical composition of the material (*figure 30*). Therefore, there is no reasonable need to implement Soxhlet procedures for outcomes emerging from the upcoming synthesis processes.

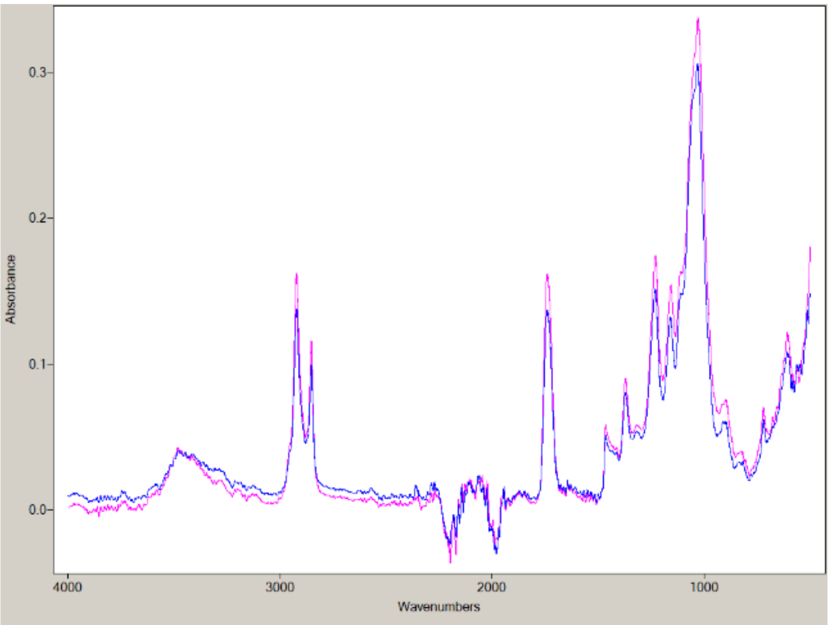


Figure 30. *The pink* line of the FTIR graph represents Soxhlet extracted sample and *the blue* the traditionally washed batch material

REG CO 3. The synthesis conducted with the double amount of balls exhibited no significant effect on the esterification efficiency, which was also confirmed according to the FTIR data *(*in *figure A1.2* in *Appendix 1)*. The idea was to investigate whether it affects the outcome and properties that emerged during the synthesis. There took no modification place as the curves around wavenumber at 3000 cm^{-1} and 1731 cm^{-1} are practically missing. Therefore, the theory of increasing the number of balls in the process did not result in the expected outcome as no successful esterification occurred in the mechanochemical operation.

REG CO 4. The fourth sample after FTIR analysis showed that the synthesis happened to a very low extent. The specific reason cannot be identified as the parameters set for the procedure were the same that have mostly been used throughout reporting period of the Master’s thesis.

10.3 DSC

REG CO 1. The melting point obtained in the first sample reached a level above 70 °C, namely 71 °C. Based on the information, the temperature needed for the compression moulding had to be set above 70 °C. While comparing the DSC temperature of REG CO with the previous cellulose oleate products (without the REG) and the DSC results obtained for the other regenerated samples, it is clear that the melting point of the first REG CO is almost twice lower than the melting points for cellulose oleates (without the REG) and regenerated cellulose oleate, which may suggest that the composition of the first REG CO is different from the others. SEM images of the first REG CO prove that the material contains either residues or contaminants from various stages of processing the polymer.

REG CO 2. The secondly produced regenerated cellulose oleate was divided into two portions. One portion of them went through the simple post synthesis washing procedure only. The second portion had been washed with the simple procedure and then additionally implemented the Soxhlet washing procedure with acetone for 3 hours. DSC for both samples was determined to be over 100 °C. For the Soxhlet extracted sample, the result reached up to 127 °C and the melting temperature for the other specimen of not Soxhlet washed one was measured to be 109 °C. The difference between these two melting temperatures is 18 °C which is a remarkable gap between the same material with the same ratios. The Soxhlet washing procedure could have extracted extra moisture from the sample that influenced the DSC results. However, the results show that the compression moulding procedure must occur at around 130 °C.

REG CO 3. The third process was conducted with a double amount of balls instead of the usual 800 grams. The operation was unsuccessful and therefore, no further analyses were made for the material.

REG CO 4. The melting point obtained for the fourth batch was measured to be 126 °C. No more extra remarks can be claimed on the fourth sample.

10.4 Compression moulding

The compression moulding machine was heated up to 130 °C. The test material was held under high pressure (50 to 70 bar) for 5 minutes. The result after the experiment was not the expected film form as the materials did not form into a molten sheet-like composition but remained in the powdery form that was able to decompose as the metal shaping frame element was either lifted or removed (*figure 31*). The author of the work proposes an aspect that may have influenced the properties of the produced samples and the compression moulding procedure to a remarkable extent. Namely, all the syntheses were able to be held only at room temperature as there was no regulation option provided by the machine. However, a number of research that was published by various scientists around the world conducted esterification reactions at elevated temperatures (e.g. at 50, 80 and 100 °C). Therefore, the thermal properties of the produced polymeric materials would have improved a lot, and the compression moulding procedure would have given the expected results.

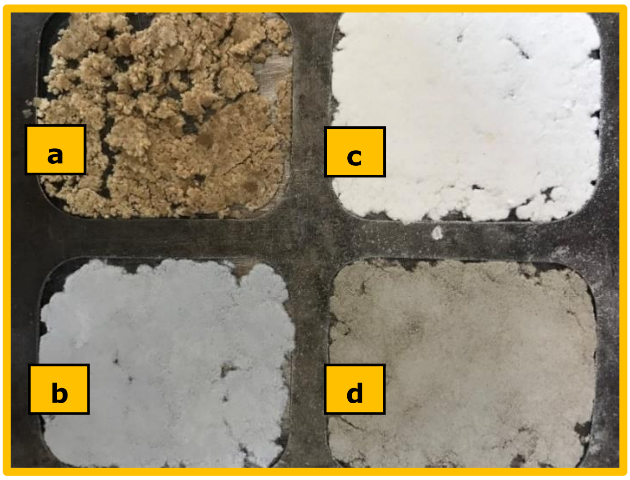


Figure 31. (a) The compression moulded REG CO 1 sample, (b) REG CO 2, (c) REG CO 4, (d) The cardboard-based REG CO sample which is described in the next chapter

10.5 SEM analysis

SEM analysis was carried out with the aim of investigating dry fibres of the esterified material, their structure and overall features. *REG CO 1.* For the first regenerated cellulose oleate process (*table A2.5*), longer forms of fibres remained during the esterification. Apart from the length of fibres, a remarkable amount of dust can be noticed from the figures that indicate the existence of residues resulting from improper washing either before or after synthesis or both combined. In addition, the small particles could also be the produced cellulose ester, which is difficult to prove.

REG CO 2. In figures obtained from *table A2.5* representing the regenerated cellulose oleate 2, the particles seem to be of the same width, long lengthwise and according to the second picture, the dust particles are also represented in the matter. The dust could have emerged due to the emitted particles of rubber cloth that had turned the reacted matter into grey form by the end of the esterification. In addition, the fibres are noted to be identical in these two figures (REG CO 2 without Soxhlet and Soxhlet version) originating from the same matter; only the difference lies in the post synthesis washing procedures.

REG CO 3. No SEM data cannot be brought forth for the third synthesis with the double amount of balls used as no value was seen in investigating the product that was not modified at all.

REG CO 4. The last synthesis product contains a lot of dust particles according to the corresponding figure from *table A2.5*. The fibres vary in their length. It is difficult to comment on any more remarks as the figures present disordered areas where some areas are covered more with contaminants than others. The contaminant may be the excess NaOH that was not successfully removed from the washing, the milling machine was not thoroughly cleaned previously, or the particles represent the modified cellulose ester.

10.6 Solution cast films

10.6.1 Optical microscopy analysis

REG CO 1. The first synthesised polymeric material REG CO 1 from *table A2.5,* contains long fibres (they form the crystalline area), but also the amorphous areas are represented. Longer fibres are known to be a better component for composites. Therefore, a given type of material could be tried to be mixed with fillers.

REG CO 2. The next two figures from the same *table A2.5* originate from the same synthesis (not Soxhlet washed version and Soxhlet washed portion) and the inquiry expresses that the film solution samples contain a bunch of fibres (fibrous regions) whereas other areas are not mixed with fibres. The aspect expresses that the film solution samples are not homogeneous.

REG CO 4. The figure representing REG CO 4 in *table A2.5* from the fourth synthesis was captured to be more uniformly divided than the previous ones. The film solution sample of the same matter before the optical microscopy analysis was also noted to be most uniform while handling the solutions and applying them to the microscopy slides.

10.6.2 SEM analysis

SEM analysis on film solution samples showcased the same aspect as for all the other previously produced materials. All the figures of solution cast SEM for regenerated cellulose oleates in *table A2.5* state the same fact that incorporating the regeneration process into the production of cellulose esters alone does not improve the thermal properties of the material.

11. CARDBOARD-BASED CELLULOSE OLEATE

The synthesis with a randomly chosen cardboard waste type was rather curious testing in order to see if there is any remarkable difference present in the obtainable product compared to others that were previously prepared. The cellulosic input material chosen for the experiment is shown below in *figure 32 (a)*. The matter was easily cuttable and thin in its nature.

Preparation of the cardboard waste material for the regeneration process and cleaning of it was colourful when compared to the one with white cellulosic paper as the cardboard matter contains additives and colourants to some extent. Besides, the matter was easily processable during the regeneration operation as the fibres of the secondary material are known to serve in a shorter form than the ones that have not been recycled before.

Figure 32 (b) presents the structure of the regenerated cardboard waste clump after drying and before the sequent milling activity. The output from the esterification has been brought forth in *figure 32 (c)*.

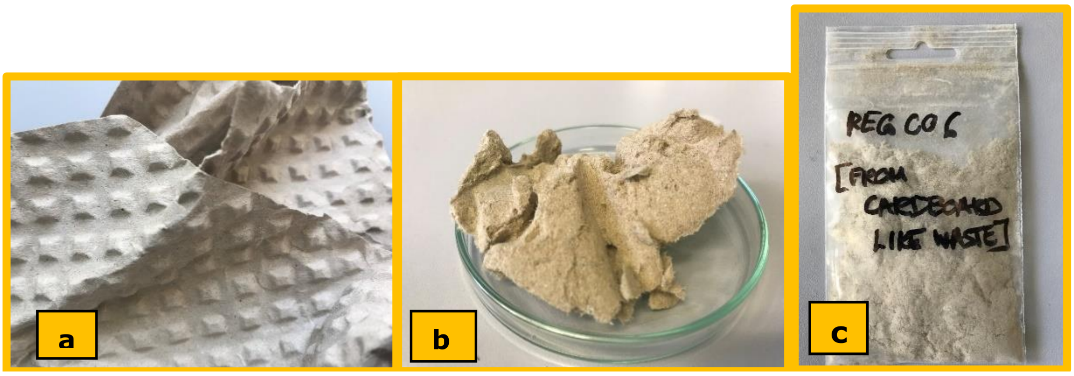


Figure 32. (a) The appearance of the input material, (b) Regenerated cardboard waste cake before the forthcoming synthesis procedure, (c) Regenerated CO from the cardboard waste

FTIR analysis showed that the whole process resulted in no modification of the material (*figure 33*). The specific reason is difficult to be identified as cardboard waste was easily processable and the parameters set for the process were not changed in comparison with the other processes. More tests must be made with the same material in order to draw specific conclusions from the results.

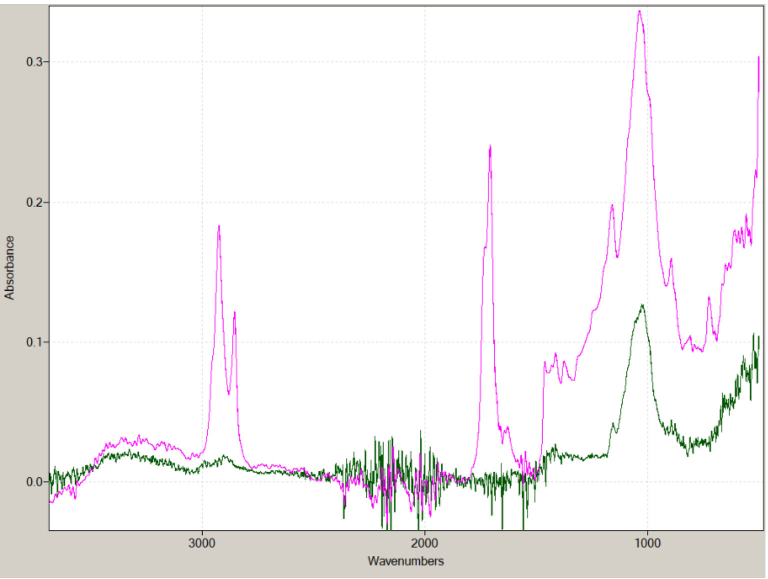


Figure 33. FTIR graphs for REG CO 1 from paper *(in pink)* vs REG CO from cardboard waste *(in green)*

The melting point obtained from the DSC analysis was measured to be of 121 °C. The compression moulding machine for the operation was set to 130 °C. Compression moulding of the material was unsuccessful as the material remained powdery after the procedure. The solubility test of the output also exhibited that the material was insoluble in all three chemicals (chloroform, acetone and DMSO).

SEM analysis for fibres of cardboard waste resulted in no remarkable comments. The average width for the initial cardboard waste material was measured to be 24.08 µm – the figure can be seen in *table A2.1*. The post synthesis SEM figure of the fibres in *table A2.5* showcases the fibres have remained in the long form, but an amount of contaminants amid the fibres can be noticed. The aspect may mean the purification step of washing off NaOH or oleoyl chloride has been successful enough.

The optical microscopy study of the processed material presented in *table A2.5* exhibits outstanding denser fibre areas with lighter areas. Thus, the film solution sample was not homogeneously dissolved in DMSO.

The SEM study of the solution cast film sample resulted in the fact (figure in *table A2.5*) that during the process, no homogeneous film structure was not formed as a result of the process. Instead, as for all the previous samples, there were present layers of fibres that are not the expected outcome for the Thesis.

SUMMARY IN ENGLISH

Based on the thorough and an abundance of literature sources and publications which have been published in recent years, cellulose chemistry exhibits a great potential to solve or mitigate various problems of huge importance and impactfulness on Earth. General ambitions set in the polymer and cellulose industry aim toward a transition from preferring polluting and unrecyclable chemicals over to environmentally friendly and recyclable alternatives, which allows reducing the environmental footprint of the planet and humankind in future and among future generations. In addition, the circular economy of materials is aimed to increase nowadays and in the near future, especially in European countries. However, the promising materials and technologies must be proven to be effective based on studies and experience. All the processes, from invention and pilot projects to carrying out the procedures to a large extent in society, demand a lot of practice, investment and time. In the current work, the main focus was set on the essence of mechanochemistry and the production of cellulose esters in a solid phase condition.

The current Master’s thesis covered aspects of pristine cellulose, esterification of cellulose, the estimated amount of residues of paper and cardboard waste generated in Estonia, production of paper and cardboard, mechanochemistry, the trends and progress taking place in the cellulose industry. The experimental part brought forth the practical activity – production of cellulose derivatives (CAs, CLs, COs and COs from regenerated cellulose cake materials), compression moulding of the synthesised materials and analysis of the obtained results.

In the experimental work, most of the esterification attempts succeeded in modifying the cellulose to the corresponding cellulose esters, the effectiveness of which was either confirmed or refuted by FTIR analysis. In addition, the DSC analysis was able to determine the melting point of all the chosen materials that were decided to be tested at the compression moulding procedure - 11 materials out of 15 synthesis outputs were attempted at the compression moulding test. However, the compression moulding, SEM and OM analyses exhibited that the given treatment (mechanochemical valorisation) did not guarantee the materials with the desired thermoplastic properties. Although, as a result of the synthesis, the cellulose derivatives were not mouldable, the FTIR analysis expressed success in the chemical modification of cellulose in a considerable number of samples. Thus, based on the info obtained from the experimental results, the mechanochemical approach is efficient in cellulose esterification by various types of esterification agents.

Emphasising once again, however thermal properties of the materials are not great for thermoplastic material. Also, unfortunately, it was found that materials could not be processed by compression moulding into films or sheets. Therefore, the development of soluble and thermoplastic cellulose esters by mechanochemical esterification is a big challenge.

After the mechanochemical treatment, the fibres were processed into shorter forms in most cases. However, cellulose oleates made of regenerated cellulose material were noted to remain in the longer forms of fibres but to contain a remarkable amount of dust amid the fibres when compared to the materials without the regeneration steps included in the synthesis. As stated in the analysis section, the residues can be either the undesired contaminants remaining from different processing procedures (NaOH or oleoyl chloride) or the particles of the produced cellulose ester. The properties of the potential material are affected by the length of the fibres found in cellulose products. The longer fibres could exhibit larger strength properties but at the same time maintain flexibility. The shorter fibres are great to be combined with fillers which could be used as composites in different application areas.

Based on research papers, elevated temperatures from 50 to 100 °C are efficient for esterification. This work shows that mechanochemical esterification at room temperatures and without catalysts could be used for surface esterification of cellulose materials, but not enough to obtain thermoplastic properties.

Nevertheless, the surface modification of cellulose with long chain fatty acids could be an efficient approach for the compatibilization of cellulose to polyolefins; the scheme is represented in *figure 34*. Surface modified cellulose from paper and cardboard waste could be a promising raw material for manufacturing fibre-reinforced plastics.

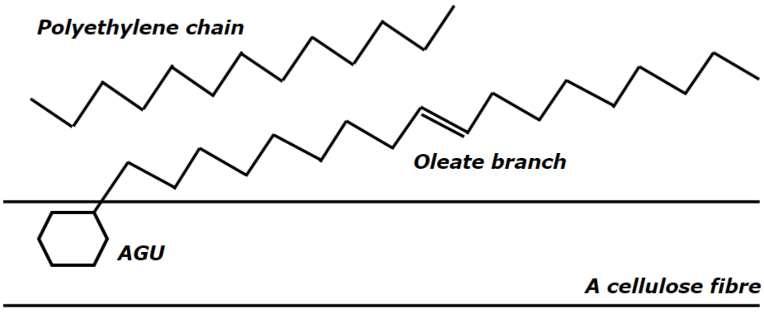


Figure 34. Compatibilization of cellulose to polyethylene

KOKKUVÕTE EESTI KEELES

Viimastel aastatel avaldatud põhjalike ja rohkete kirjandusallikate ja väljaannete põhjal on tselluloosi keemial suur potentsiaal lahendada või leevendada mitmesuguseid tohutu tähtsusega ja mõjukaid probleeme planeedil Maa. Polümeer- ja tselluloositööstuses on seatud üldised ambitsioonid seotud üleminekuga saastavate ja taaskasutamatute kemikaalide eelistamiselt keskkonnasõbralikele ja taaskasutatavatele alternatiividele. Taoline üleminek vähendab planeedi ja inimkonna keskkonnajalajälge nii tulevikus kui ka tulevaste põlvkondade seas. Lisaks on tänapäeval ja lähitulevikus eksisteerivas maailmas, eriti Euroopa riikide seas, suundumus suurendada materjalide ringmajanduse osatähtsust kogu majandussüsteemis. Paljulubavate materjalide ja tehnoloogiate tõhusus tuleb aga tõestada uuringute ja kogemuste põhjal. Kõik protsessid alates leiutamisest ja pilootprojektidest kuni protseduuride laiapõhjalise kasutusele võtuni ühiskonnas nõuavad palju praktikat, investeeringuid ja aega. Käesolevas töös keskenduti põhitähelepanu mehhaanokeemia olemusele ja tselluloosiestrite tootmisele tahkes faasis.

Käesolevas magistritöös käsitleti tselluloosi materjali olemust, tselluloosi esterdamist, Eestis tekkivate paberi- ja papijäätmete hinnangulist kogust, paberi ja papi tootmist, mehhanokeemiat, tselluloositööstuses toimuvaid trende ja edusamme. Eksperimentaalne osa tõi välja praktilise tegevuse, mis viidi läbi Taltechi Ülikooli laboris - tselluloosi derivaatide (CA-d, CL-d, CO-d ja CO-d valmistatud regernereeritud materjalist) valmistamine, sünteesitud materjalide vormimine survevormimise teel ja tulemuste analüüsimine.

Eksperimentaalse töö käigus õnnestus enamike sünteesikatsete tulemusena modifitseerida tselluloosi vastavateks tselluloosiestriteks, mille tulemuslikkust kas kinnitas või lükkas ümber FTIR analüüs. Lisaks oli võimalik DSC analüüsiga määrata kindlaks nende kõikide toodetud materjalide sulamispunkti, mida otsustati kaasata testimiseks survevormimise katses – testides survevormimise katses ühtekokku 11 produkti 15st kogutoodetud materjalist. Küll aga selgus survevormimise, SEM ja OM analüüside tulemusena see, et antud töötlus (mehhanokeemiline väärindamine) ei taganud materjalile siiski termoplastseid omadusi. Isegi hoolimata tõsisasjast, et FTIR analüüs väljendas tselluloosi keemilise modifitseerimise edukust märkimisväärsel hulgal proovidel. Küll aga saab katsetulemuste põhjal väita, et mehhanokeemiline lähenemine on tõhus tselluloosi esterdamiseks kasutades selleks erinevat tüüpi esterdamisvahendeid.

Materjalide termilised omadused ei ole termoplastseid materjale iseloomustavate omadustega võrreldes eriti märkimisväärsed. Samuti leiti kahjuks, et materjale ei saa töödelda survevormimise abil kiledeks või lehtedeks. Seetõttu on lahustuvate ja termoplastiliste tselluloosi estrite väljatöötamine mehhaanokeemilise väärindamise teel suur väljakutse.

Pärast mehhanokeemilist töötlemist purustati kiud enamasti lühemateks osadeks. Siiski täheldati, et regenereeritud tselluloosmaterjalist valmistatud tselluloosi oleaadid säilitasid pikemad kiudusid, kuid sisaldasid märkimisväärsel hulgal osakesi, võrreldes materjalidega, kus sünteesis regenereerimisetappi ei kasutatud. Nagu analüüsijaotises öeldud, võivad jäägid olla kas erinevatest töötlemisprotseduuridest jäänud soovimatud saasteained (NaOH või oleoüülkloriid) või toodetud tselluloosestri osakesed. Potentsiaalse materjali omadusi mõjutab tselluloositoodetes leiduvate kiudude pikkus. Pikematel kiududel võivad olla suuremad tugevusomadused, kuid samal ajal säilib paindlikkus. Lühemaid kiude sobib suurepäraselt kombineerida täiteainetega, mida saab kasutada komposiitmaterjalina erinevates kasutusvaldkondades.

Uurimistööde põhjal on esterdamiseks tõhusad kõrgendatud temperatuurid 50 kuni 100 °C. See töö näitab, et tselluloosmaterjalide pinnaesterdamiseks võib kasutada mehhanokeemilist väärindamist toatemperatuuril ja ilma katalüsaatoriteta, kuid antud tingimused pole piisavad materjali termoplastsete omaduste arendamiseks.

Sellegipoolest võib tselluloosi pinna esterdamine pikkadest ahelatest koosnevate reagentidega olla tõhus lähenemisviis tselluloosi ühildumiseks polüolefiinidega. Paberi- ja kartongijäätmetest toodetud tselluloosi derivaat on paljulubav tooraine kiudtugevdatud plastide (komposiitplastide) tootmiseks.

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APPENDICES

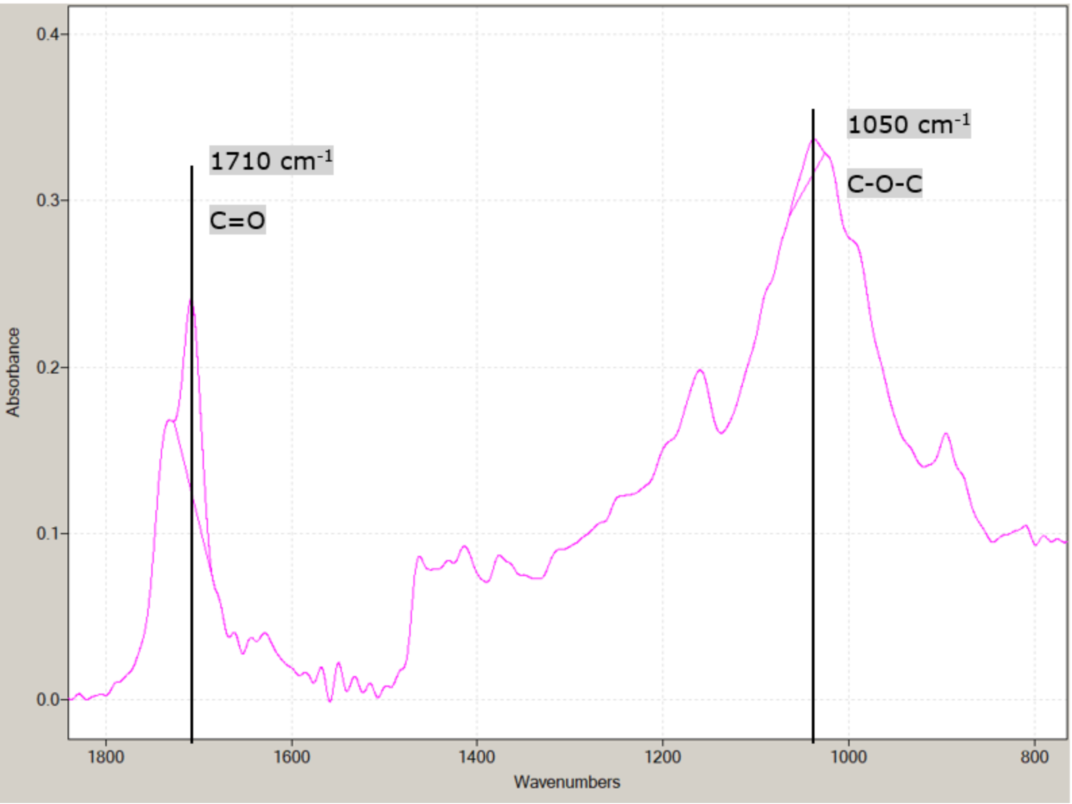


Figure A1.1 REG CO baseline

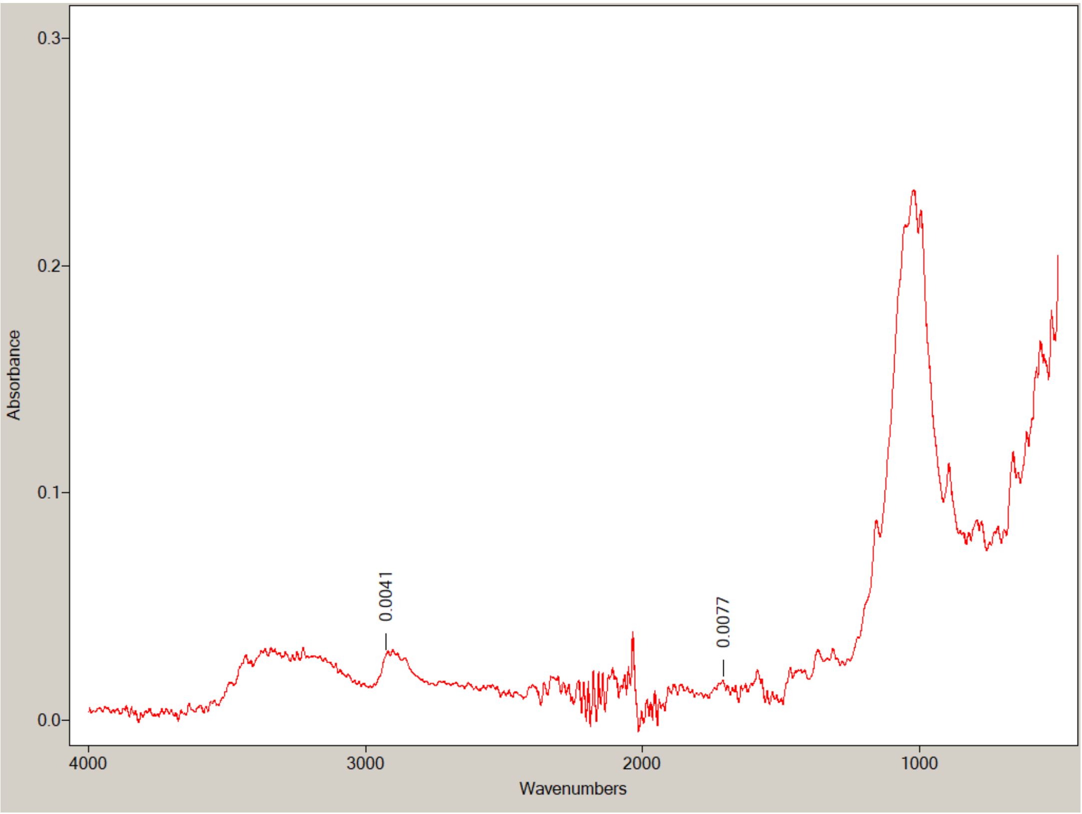


Figure A1.2 FTIR graph for the REG CO 3 synthesis with more balls

Table A1.1 Essential parameters obtained from the FTIR analysis for all the polymers

Polymer	**Molar ratio, AGU to acyl chloride**	**Chemical bond**	**Peak position**	**Height of peak**	$I_{C=O}/I_{C-O-C}$
Alpha Cellulose Paper	-	C=O	1706	0.0035	0.06
		C-O-C	1053	0.0519	
CO	1:1	C=O	1706	0.0498	1.34
		C-O-C	1053	0.037	
CO	1:2	C=O	1709	0.0108	0.53
		C-O-C	1052	0.0202	
CO	1:3	C=O	1713	0.0198	0.34
		C-O-C	1053	0.0579	
CA	1:4	C=O	1737	0.0715	4.49
		C-O-C	1052	0.0159	
CA	1:3	C=O	1711	0.0046	0.86
		C-O-C	1057	0.0053	
CA	1:2	C=O	1740	0.0861	0.34
		C-O-C	1029	0.2526	
CA	1:1	C=O	1739	0.0049	0.22
		C-O-C	1034	0.0222	
REG CO 1	1:1	C=O	1706	0.2141	2.83
		C-O-C	1041	0.0755	
REG CO 2 Without Soxhlet	1:1	C=O	1724	0.0051	0.92
		C-O-C	1056	0.0055	
REG CO 2 Soxhlet	1:1	C=O	1724	0.0045	1.18
		C-O-C	1056	0.0038	
REG CO 3	1:1	C=O	1710	0.005	0.56
		C-O-C	1053	0.0089	
REG CO 4	1:1	C=O	1729	0.0114	2.47
		C-O-C	1048	0.0046	
REG CO cardboard	1:1	C=O	1729	0.0165	1.91
		C-O-C	1056	0.0086	
CL	1:1	C=O	1693	0.1411	5.80
		C-O-C	1053	0.0243	
CL	1:2	C=O	1737	0.032	1.39
		C-O-C	1056	0.023	

Appendix 2. Morphology of fibres

Table A2.1 Figures of fibres of the raw material obtained by SEM analysis

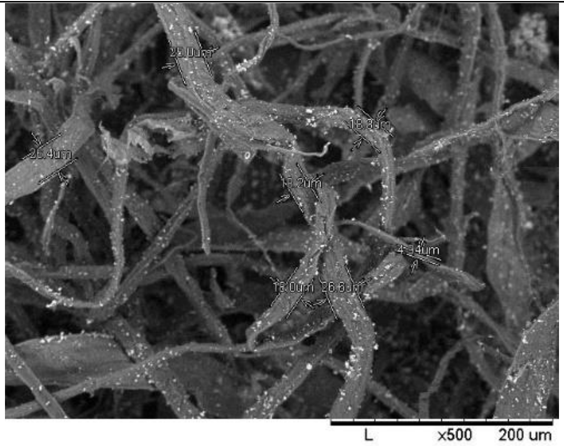
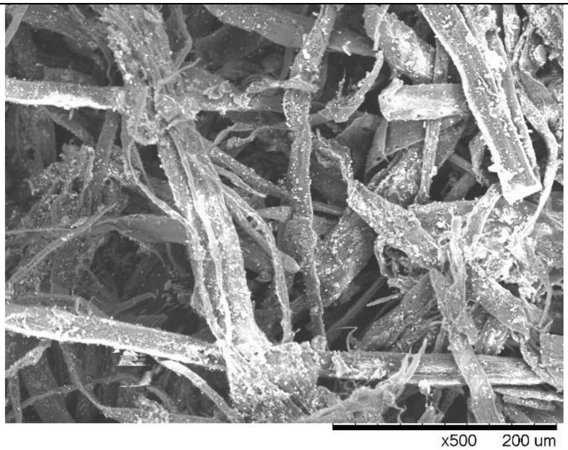
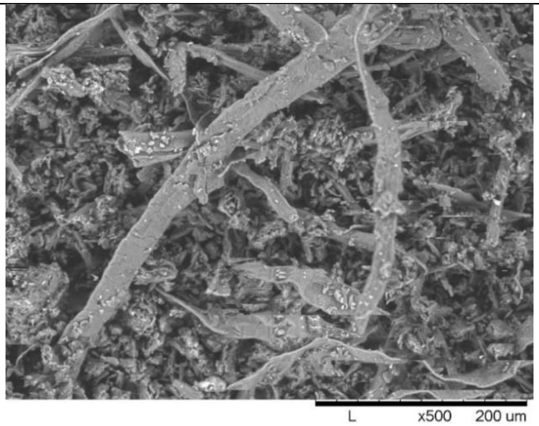
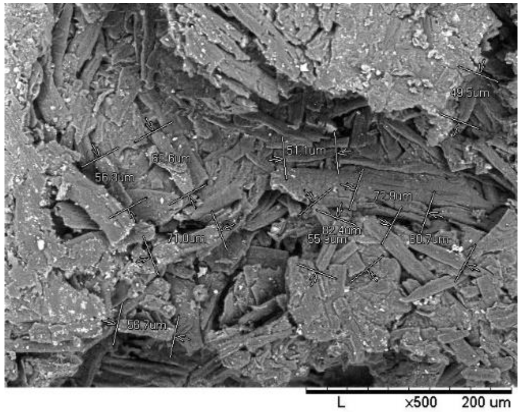
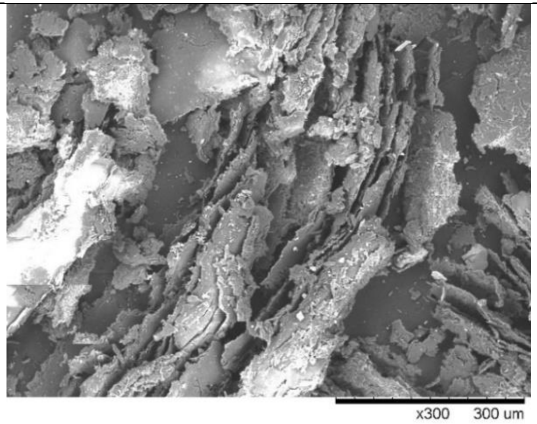
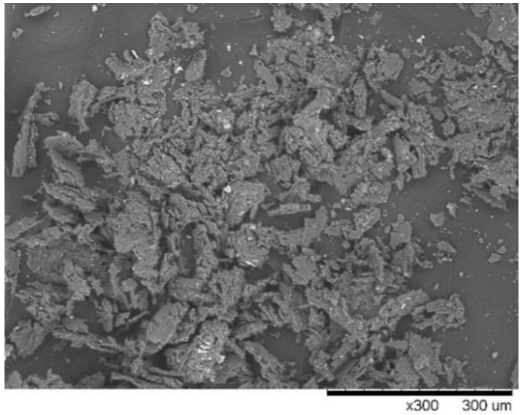
Initial alpha cellulose paper material	Initial randomly chosen carboard waste material
	

Table A2.2 SEM data for fibres of analysed cellulose acetates

	Cellulose acetate	
Molar ratio	**1:1**	**1:2**
SEM analysis for the post synthesis fibres		
SEM analysis for the solution cast film samlpes		

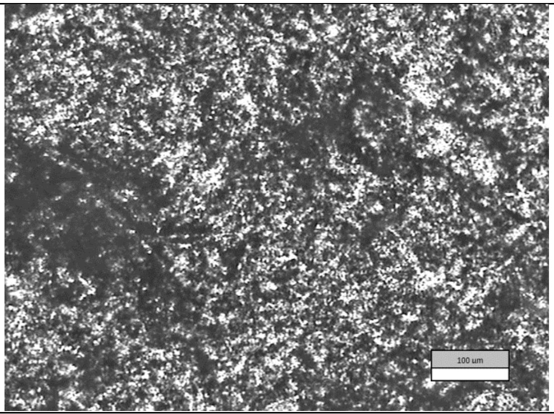
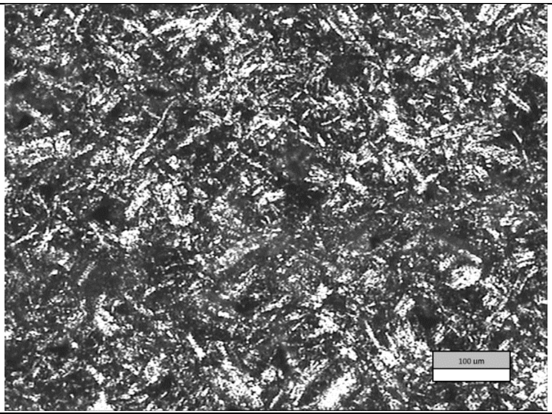
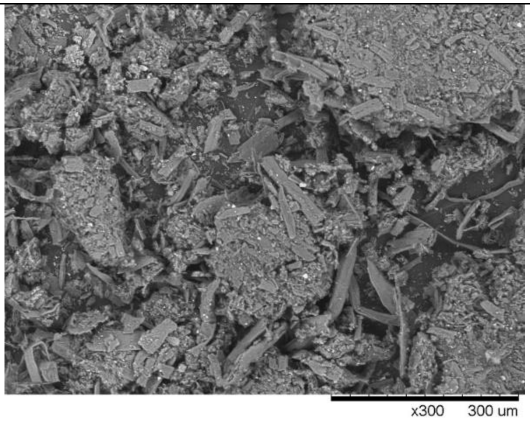
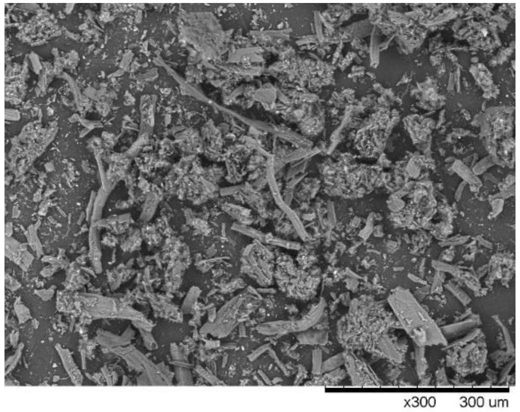
Optical microscopy analysis for the solution cast film samlpes		

Table A2.3 SEM data for fibres of analysed cellulose laurates

Cellulose laurate		
Molar ratio	**1:1**	**1:2**
SEM analysis for the post synthesis fibres		

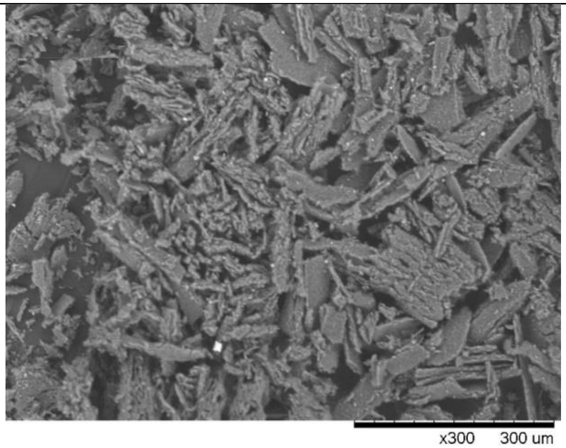
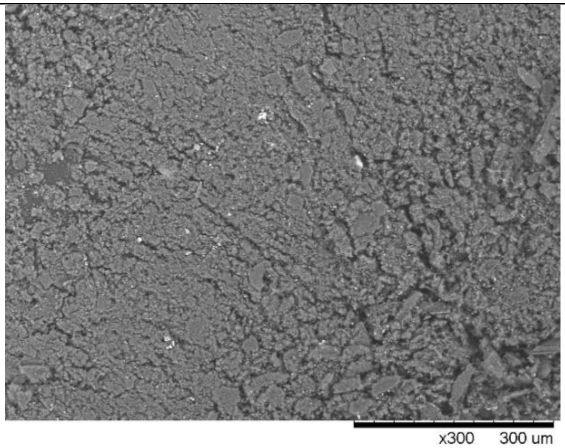
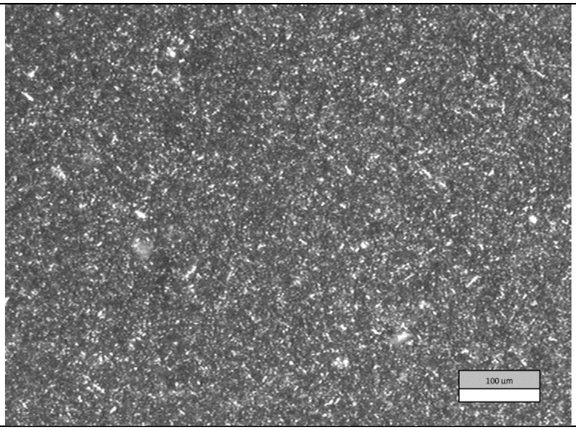
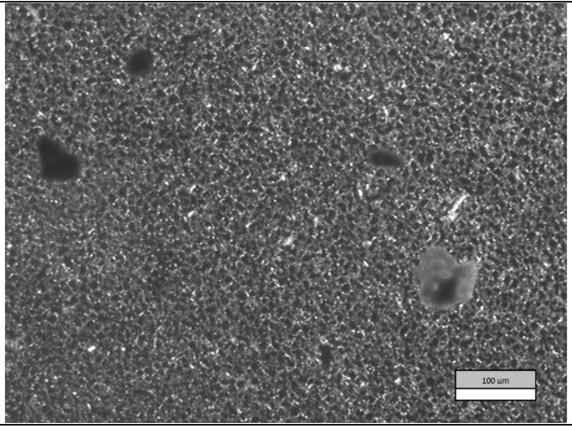
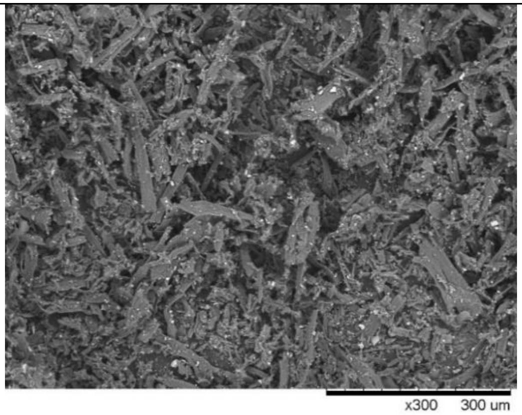
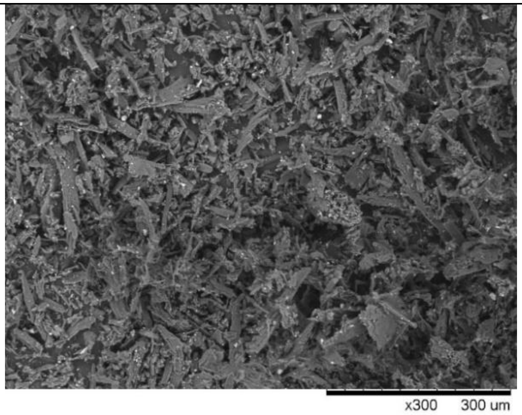
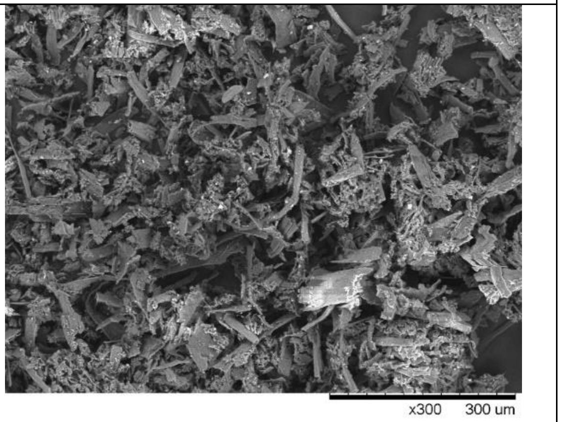
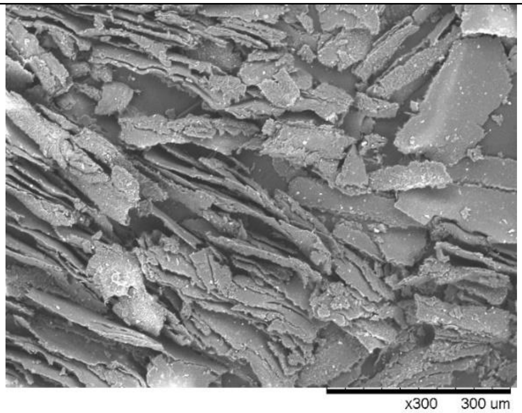
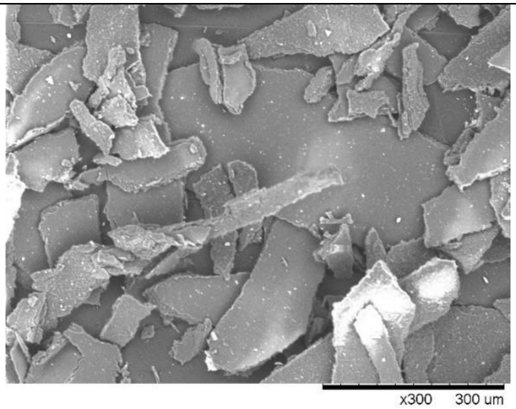
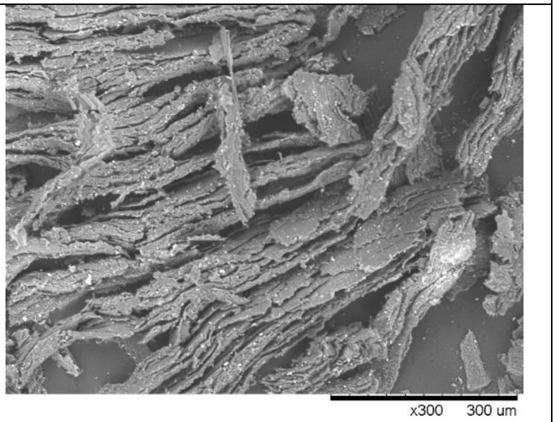
SEM analysis for the solution cast film samlpes		
Optical microscopy analysis for the solution cast film samlpes		

Table A2.4 SEM data for fibres of analysed cellulose oleates

Cellulose oleate			
Molar ratio	**1:1**	**1:2**	**1:3**
SEM analysis for the post synthesis fibres			
SEM analysis for the solution cast film samlpes			

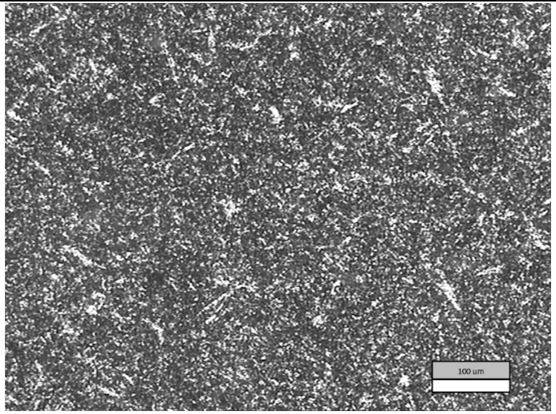
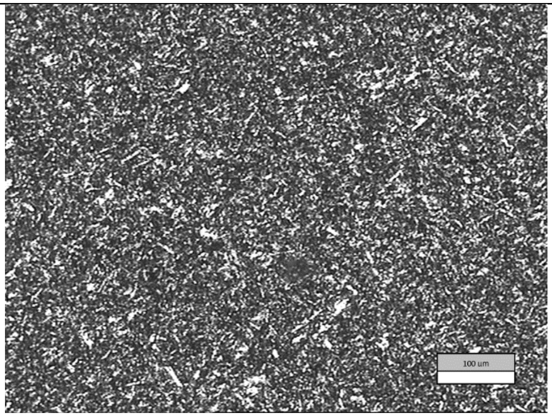
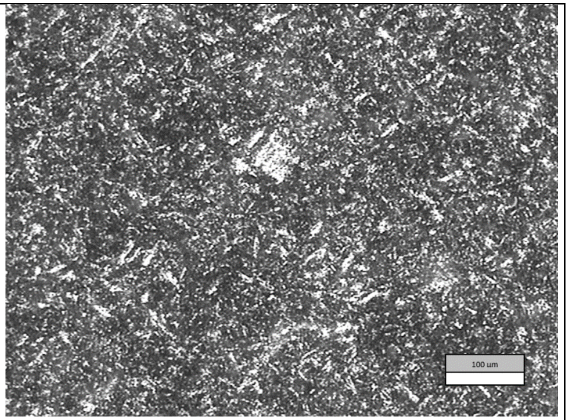
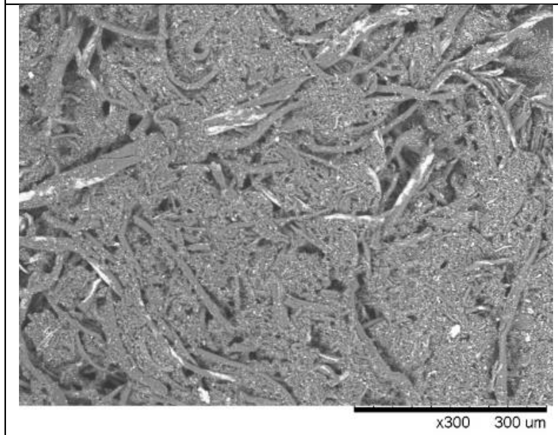
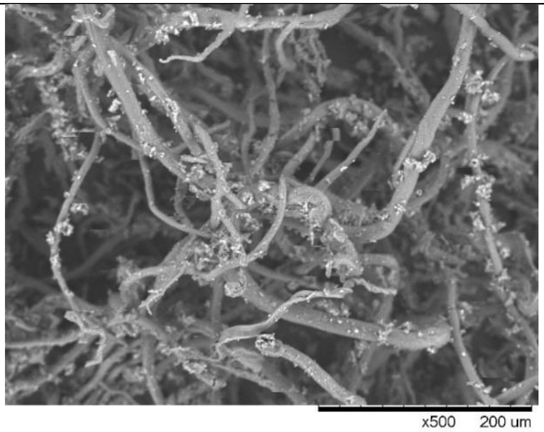
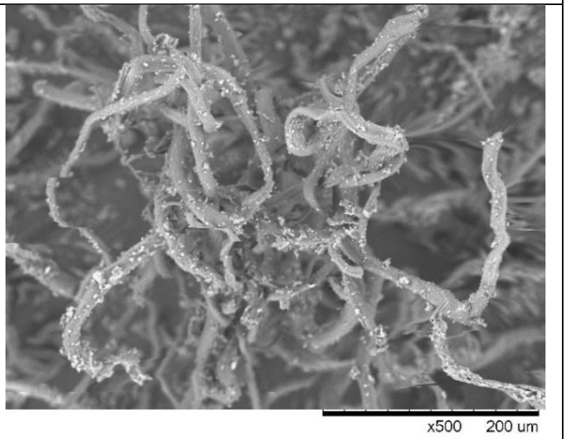
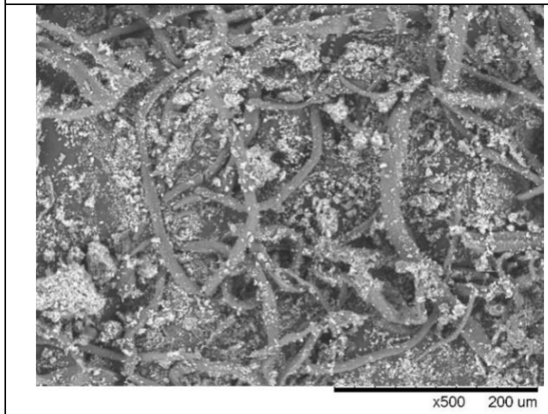
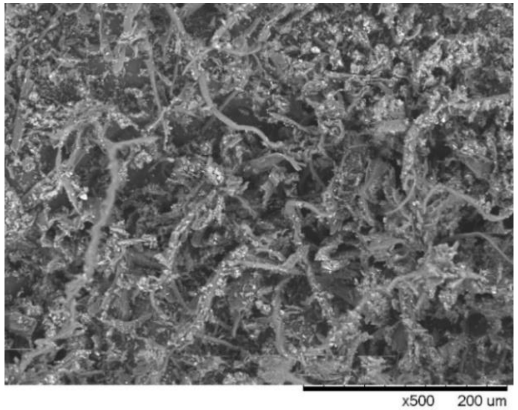
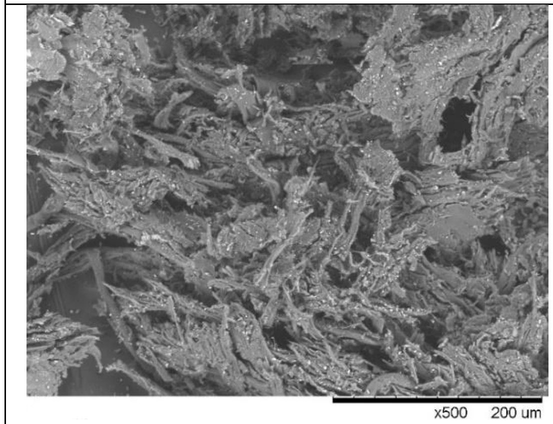
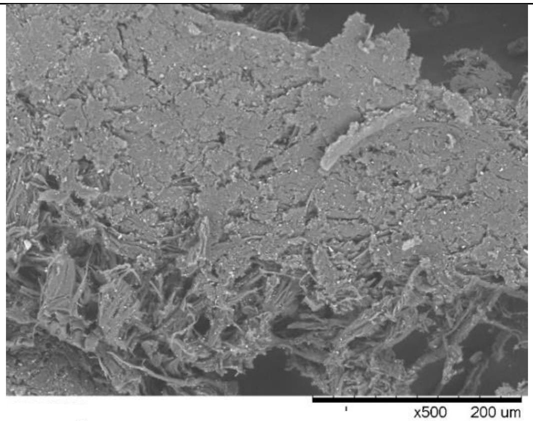
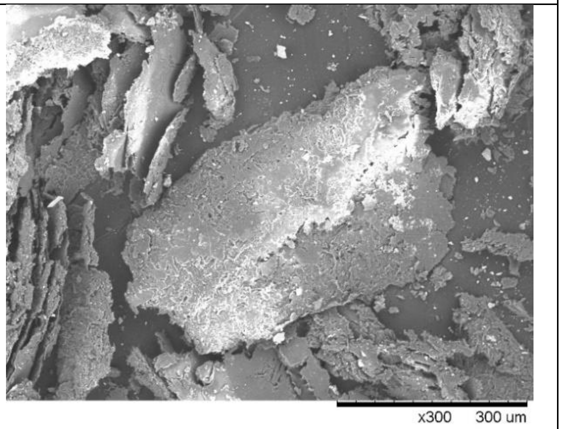
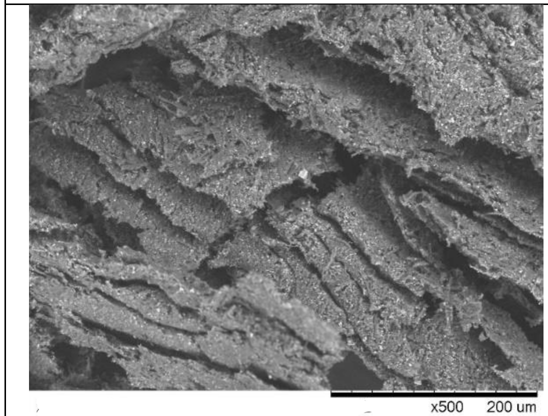
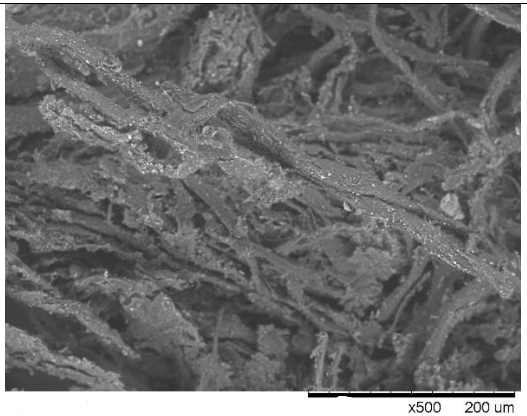
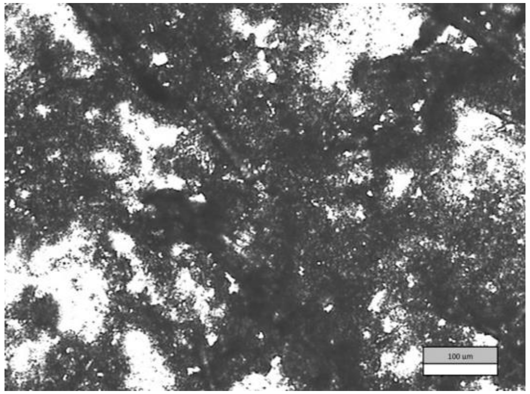
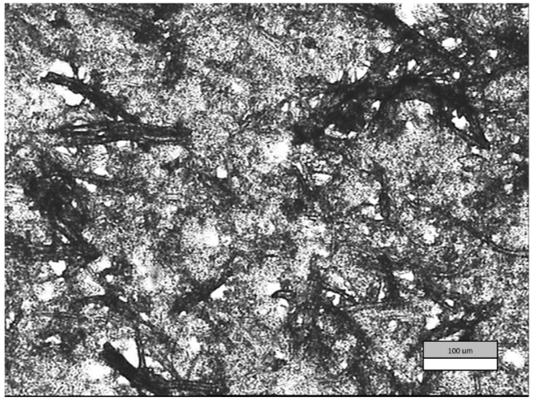
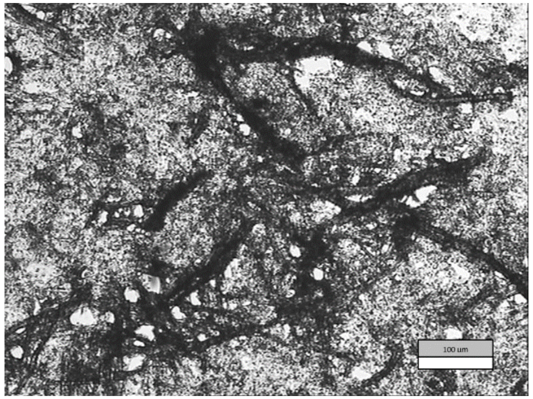
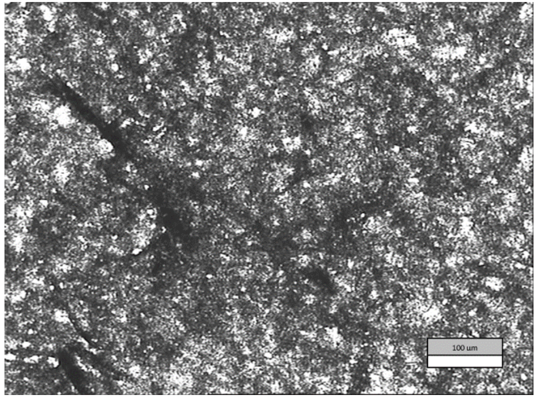
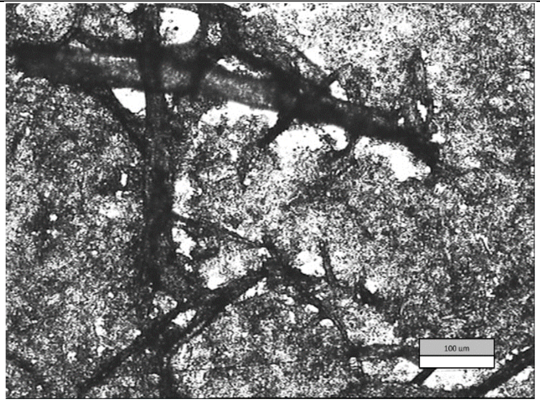
Optical microscopy analysis for the solution cast film samlpes	 	 	

Table A2.5 SEM data for fibres of analysed regenerated cellulose oleates either from paper or cardboard waste

Regenerated cellulose oleate (of paper or cardboard origin)			
Molar ratio	**1:1**		
SEM analysis for the post synthesis fibres	REG CO 1	REG CO 2 Without Soxhlet	REG CO 2 Soxhlet
	 	 	

	REG CO 4	REG CO from cardboard	
	 	 	
SEM analysis for the solution cast film samlpes	REG CO 1	REG CO 2 Without Soxhlet	REG CO 2 Soxhlet
	 	 	

	REG CO 4	REG CO from cardboard	
			
Optical microscopy analysis for the solution cast film samlpes	REG CO 1	REG CO 2 Without Soxhlet	REG CO 2 Soxhlet
			

	REG CO 4	REG CO from cardboard	
			

Appendix 3. DSC results

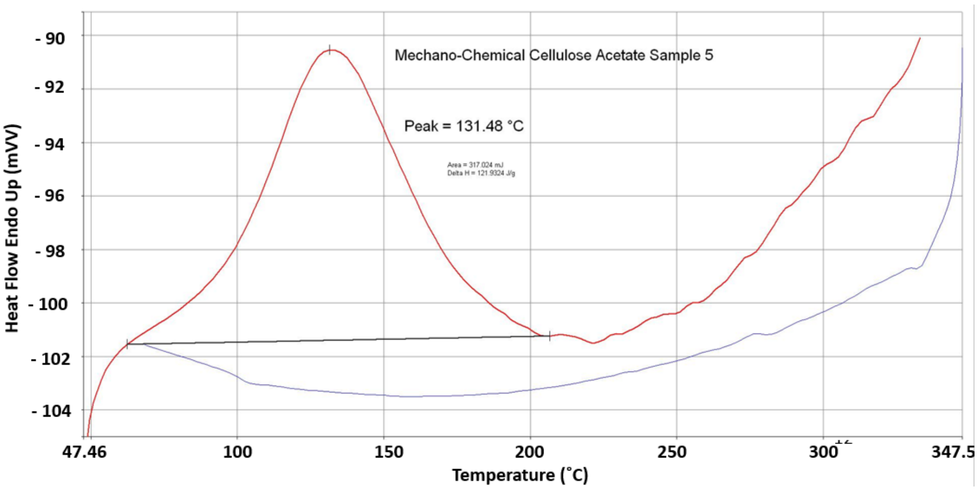


Figure A3.1 CA 1:1

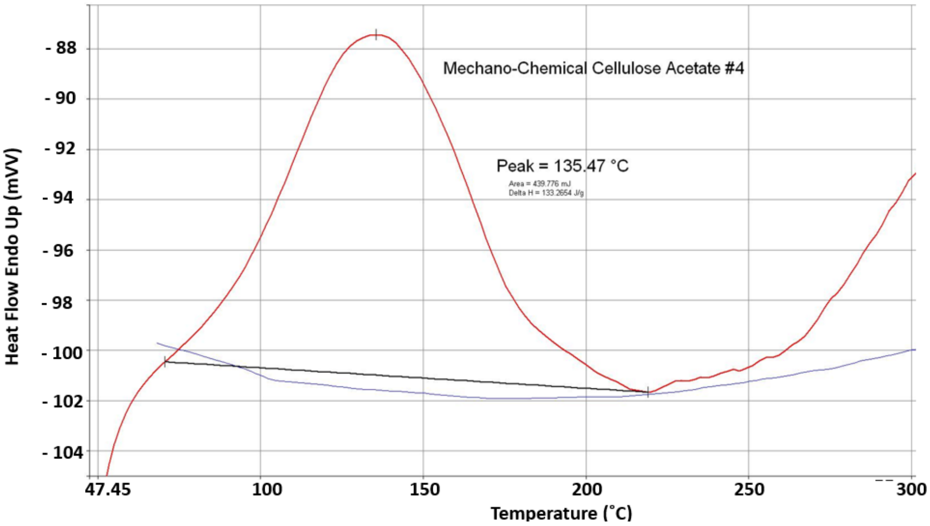


Figure A3.2 CA 1:2

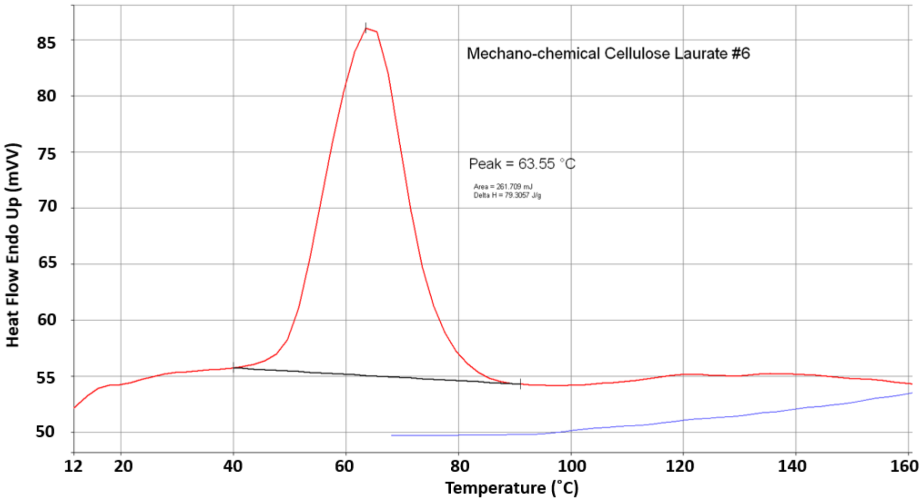


Figure A3.3 CL 1:1

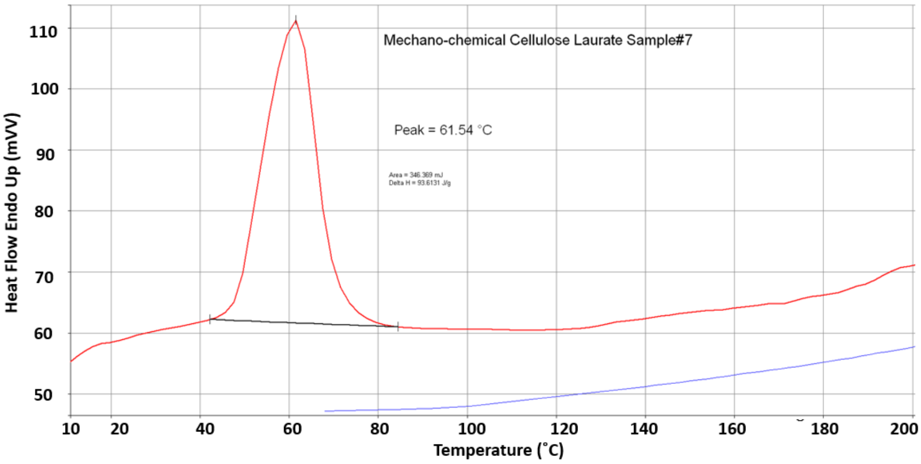


Figure A3.4 CL 1:2

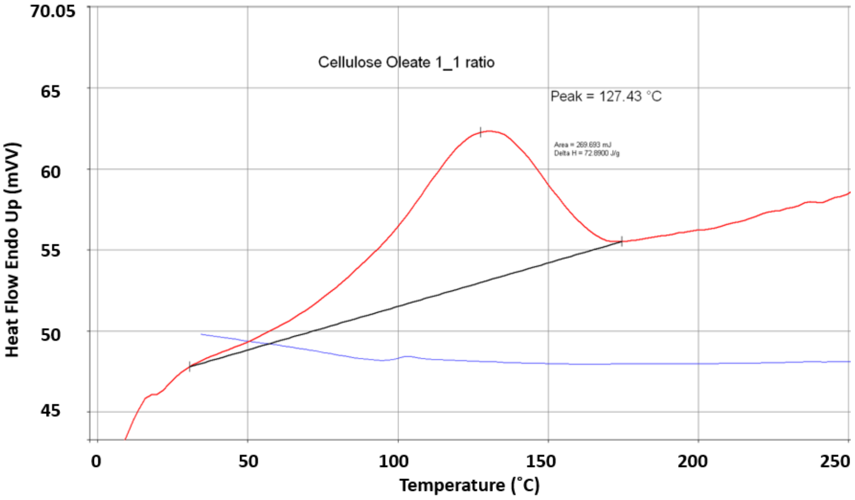


Figure A3.5 CO 1:1

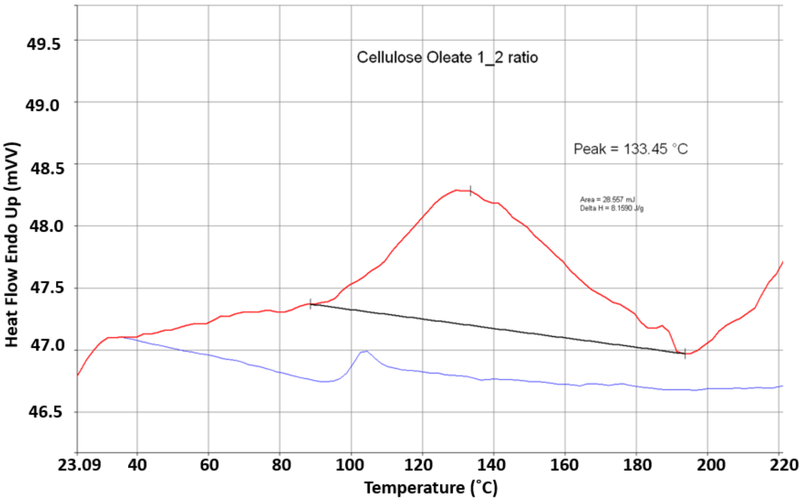


Figure A3.6 CO 1:2

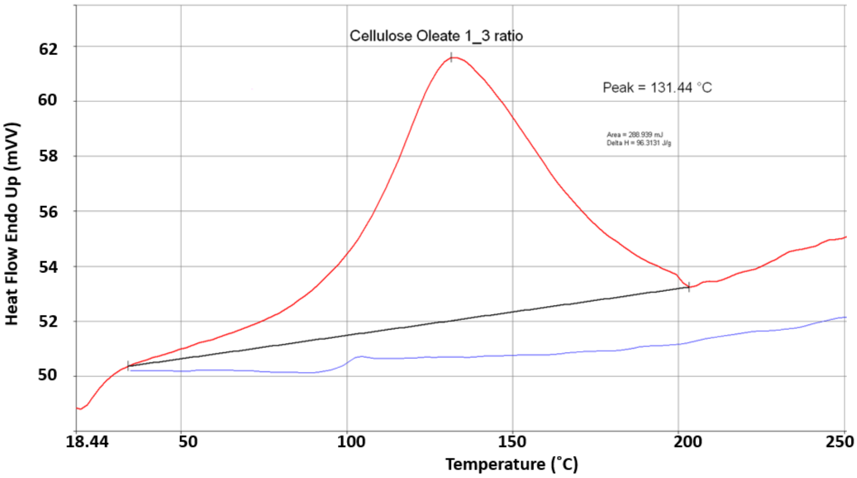


Figure A3.7 CO 1:3

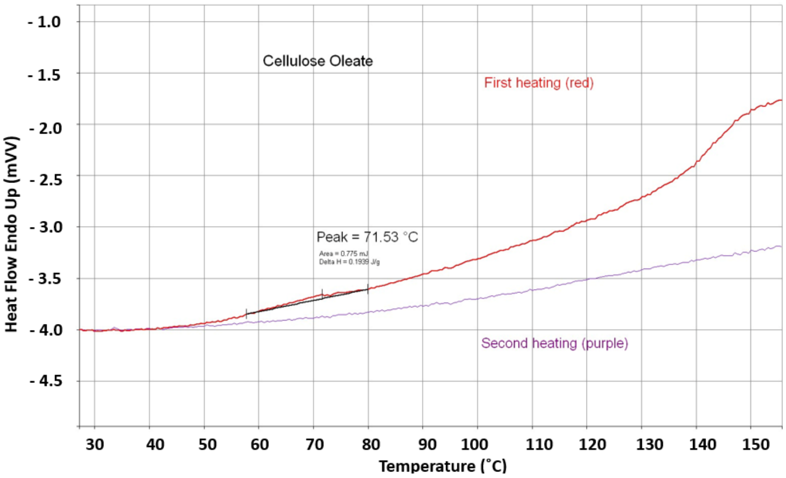


Figure A3.8 REG CO 1

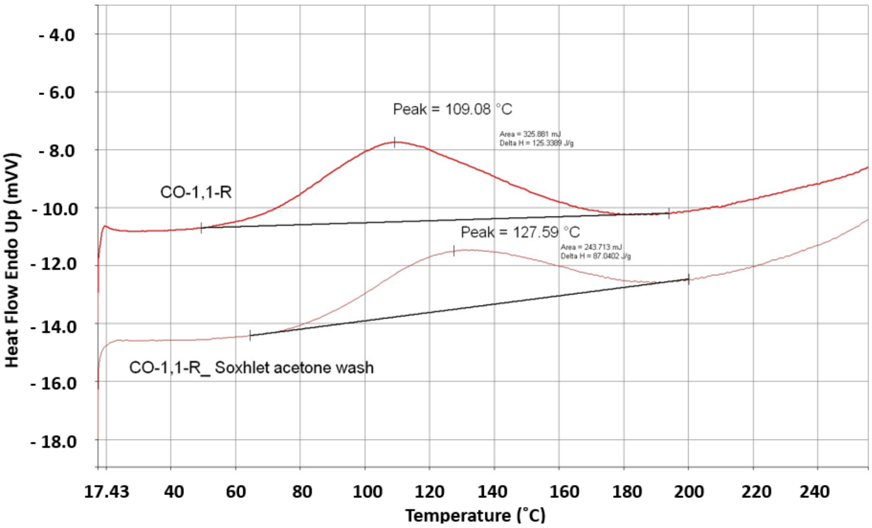


Figure A3.9 REG CO 2 Without Soxhlet and With Soxhlet

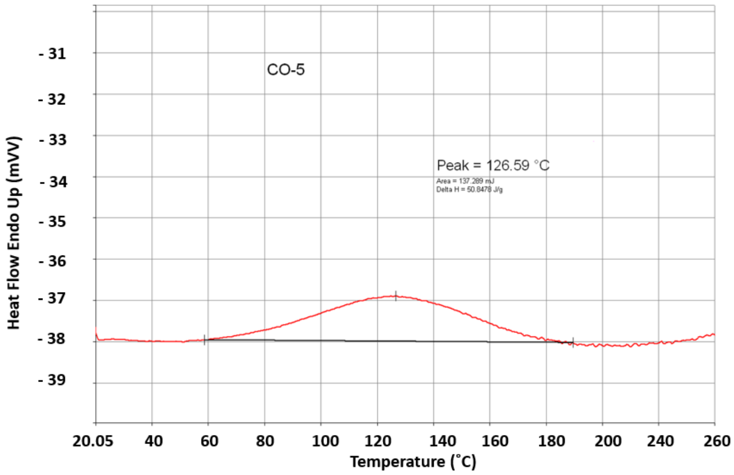


Figure A3.10 REG CO 4

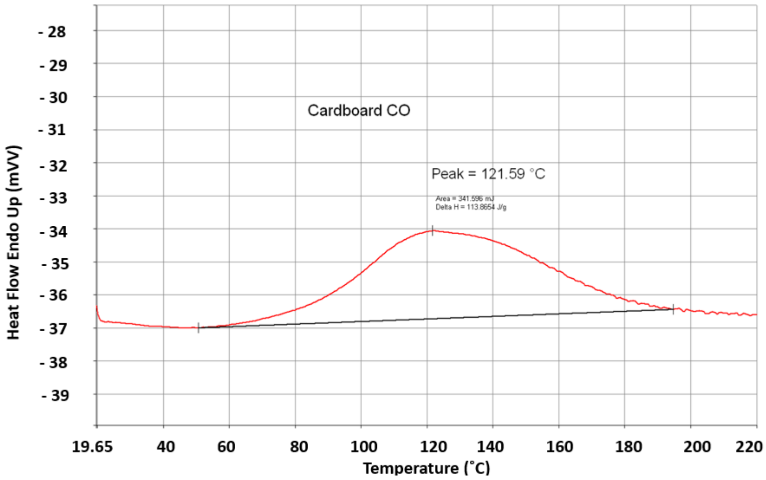


Figure A3.11 REG CO from cardboard waste