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

SYNTHESIS OF CELLULOSE ESTERS IN A NOVEL IONIC LIQUID AND TESTING THE EFFICIENCY OF ITS RECYCLING

TSELLULOOSI ESTRITE SÜNTEESIMINE UUDSES IOONILISES VEDELIKUS NING SELLE TAASKASUTUSE TÕHUSUSE TESTIMINE

BACHELOR THESIS

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Tallinn 2022

(*On the reverse side of title page*)

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Thesis topic:

(in English) *Synthesis of cellulose esters in a novel ionic liquid and testing the efficiency of its recycling*

(in Estonian) Tselluloosi estrite sünteesimine uudses ioonilises vedelikus ning selle taaskasutuse tõhususe testimine.

Thesis main objectives:

1. Synthesise cellulose esters in a novel ionic liquid
2. Test the effectiveness of recycling a novel ionic liquid
3. Optimise reaction conditions for cellulose stearate synthesis

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Synthesise cellulose esters in a novel ionic liquid	02.06.22
2.	Test the effectiveness of recycling a novel ionic liquid	02.06.22
3.	Optimise reaction conditions for cellulose stearate synthesis	02.06.22

Language: English **Deadline for submission of thesis:** "Synthesis of cellulose esters in a novel ionic liquid and testing the efficiency of its recycling" 02.06.2022 a

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PREFACE

This thesis was completed under the supervision of Dr. Elvira tarasova in the laboratory of polymers and textile technology of the department of materials and environmental technology of Tallinn University of Technology.

The author wants to thank Dr. Illia Krasnou for providing the recycled ionic liquid and rheology results, doctoral student Nuthan Bharat Savale for nuclear magnetic resonance spectroscopy results and analysis and of course Dr. Elvira Tarasova for all the guidance, motivation and expertise necessary to finish the thesis.

Within the work at hand, synthesis of cellulose esters by homogenous transesterification using a novel ionic liquid is described. Additionally the efficiency of recycling the ionic liquid is tested.

Keywords: cellulose, ionic liquid, esters, ionic liquid recycling, bachelor’s thesis

LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
CA	Cellulose acetate
CL	Cellulose laurate
CM	Cellulose myristate
CS	Cellulose stearate
DAC	Cellulose diacetate
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMSO	Dimethyl sulfoxide
DS	Degree of substitution
FTIR	Fourier transform infrared
IL	Ionic liquid
MCC	Microcrystalline cellulose
NMR	Nuclear magnetic resonance
THF	Tetrahydrofuran
VL	Vinyl ester
VOC	Volatile organic compound
[C4mim]Cl	1-butyl-3-methylimidazolium chloride
[mTBNH][OAc]	5-methyl-1,5,7-triazabicyclo[4.3.0]non-5-enium acetate

INTRODUCTION

Cellulose, being the most common polymer on earth, is a good candidate for producing biopolymers to replace the fossil-fuel based plastics currently causing irreparable ecological damage.[1] It has beneficial properties such as high mechanical strength and chemical resistance in addition to biodegradability already, but is neither thermoplastic nor soluble in most common organic solvents or in water and as such does not get used in industrial settings much.[2]

To make the polymer thermoplastic and give it solubility, derivatives of the molecule are synthesised. One such modification is esterification which results in cellulose esters which have the desired properties. With the reaction, the three hydroxyl groups in the molecule are turned into esters.[3]

A common cellulose ester that gets manufactured at industrial scales is cellulose acetate. It can be prepared without a large amount of dangerous solvents and longer esters do not get produced for that exact reason.[2] However, cellulose esters with longer aliphatic moieties ranging from 3 to 18 carbon long carbon chains have been synthesised in laboratory settings and their properties have been well studied and thermoplastic properties proven.[4]

The aforementioned resistance to solvents that cellulose has is caused by its strong inter- and intramolecular bonds that have to be overcome in order for it to dissolve — this has been a reason for the lack of commercialisation.[5] Traditionally strongly polar solvents are used to dissolve cellulose which are mostly are very environmentally unfriendly due to their volatility or their general toxicity and corrosive nature.[2] Somewhat recently, however,ionic liquids, which are touted as novel "green" solvents, have been used to successfully dissolve cellulose. They are essentially low melting point salts consisting of only ions that, due to their unique structure, stay in liquid form at room temperature.[6], [7] They are not volatile and some are non-toxic and can be recycled.[8]

Within the work at hand, the novel ionic liquid 5-methyl-1,5,7-triazabicyclo[4.3.0]non-5-enium acetate([mTBNH][OAc]) is tested for use in homogeneous transesterification of cellulose as to our knowledge it has not been involved in any research up until now.

The first part of the work gives a theoretical overview of cellulose, ionic liquids, synthesis of cellulose esters in ionic liquid and arguments for the sustainability and recycling of ionic liquids. The second part is the experimental part which is effectively divided into three sub-parts corresponding with the tasks of the work.

The aim of the thesis was catalyst-free synthesis of various cellulose esters in novel [mTBNH][OAc] ionic liquid with further recycling and reusing of IL in transesterification reaction of cellulose.

With the work at hand, the following tasks had to be done:

1. Synthesis of cellulose acetate, cellulose laurate, cellulose mysristate and cellulose stearate by homogenous transesterification of cellulose with vinyl esters in novel IL;
2. Optimization of reaction conditions in order to obtain cellulose esters with degree of substitution higher than 1;
3. Recycling and reusing of IL in order to evaluate an efficiency of IL recycling towards transesterification of cellulose.

1. THEORY OVERVIEW

1.1. Cellulose

1.1.1 Structure and properties

Cellulose is the most common polymer on earth, which most importantly has a structural role in plants, but can also be found in algae and even some bacteria.[9] The material has seen extensive use in its many forms throughout history and its general properties and limits are well known.

The structure of cellulose is similar to that of starch, as it has a structure of repeating glucose monomers(anhydroglucose units, aka AGUs) but, as opposed to the structure of starch, every second glucose unit is rotated 180° with respect to the previous one, as shown in figure 1.1.1.1.[10]

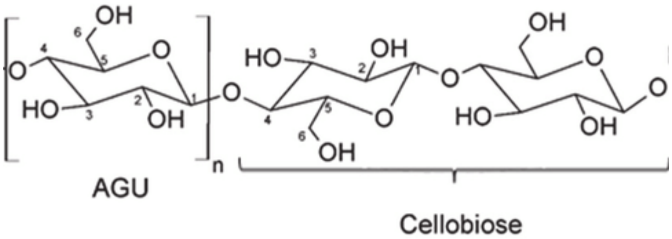


Figure 1.1.1.1 Structure of cellulose AGU and the repeating units forming cellobiose [11]

The mechanical strength and chemical resistance of the material comes from glycosidic bonds between the mentioned monomers and is further magnified by the presence of the many intermolecular and intramolecular hydrogen bonds shown in figure 1.1.1.2.[5]

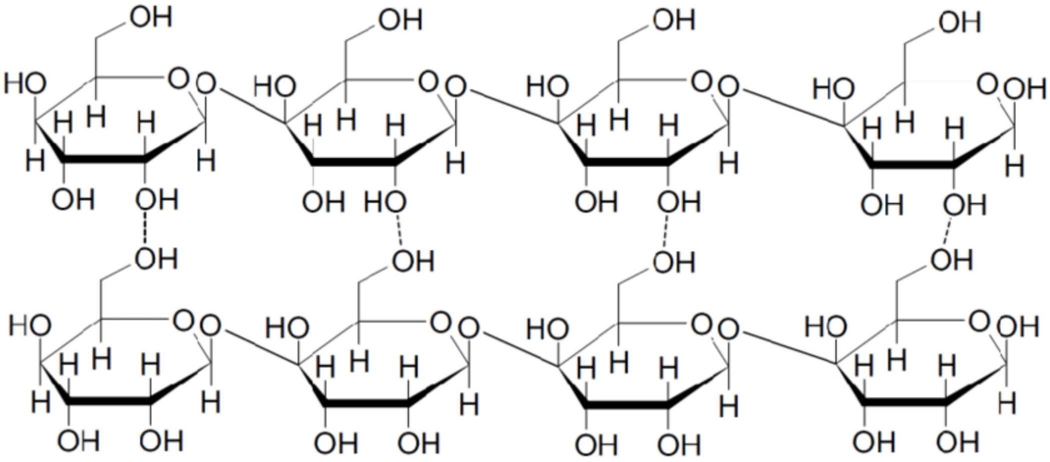


Figure 1.1.1.2 Cellulose molecule with hydrogen bonding represented by dashes [12]

The resulting high crystallinity means that only solvents that can compete for the intermolecular hydrogen bond interactions are viable, rendering water and most common organic solvents ineffective.[13]

The same bond structure is also responsible for cellulose not responding to thermal treatment as its theoretical glass transition temperature is higher than the point at which it starts to degrade.[14]

Although the plastic age we are currently living in has advantages, the environmental damage, due to overconsumption of short-term-use-plastics, is palpable.[1] As a consequence, science has turned to figuring out alternatives to the material, one of which are cellulose based plastics.[9]

As mentioned, though, cellulose isn’t thermoplastic in itself and its modification requires toxic and corrosive solvents which has made its application in industry minimal.[15]

1.1.2 Cellulose derivatives

A derivative is a compound which is derived from another similar one via a chemical reaction, mostly by the replacement of an atom or a group of atoms with another functional group.[16] In the context of cellulose derivatives the groups being replaced are -OH groups, of which 3 are connected to each AGU as seen in figure 1.1.1.1. Possible modifications are oxidisation-, esterification-, etherification- and other less common reactions.[17]

While cellulose has useful properties in its own right (high tensile strength, insolubility in water, biodegradability etc.) it is not viable in modern applications due to the undeniable versatility of plastics.[2] Hence the need for derivatives, which can give the polymer desirable properties like thermoplasticity and compatibility with other plastics like PLA.[2], [9]

Cellulose esterification

Cellulose esterification is done in principle the same way as any other cellulose modification - by reacting the -OH groups with substituent groups as a result, in this case, forming esters.[3] In doing so the resultant product is thermoplastic and possibly soluble in more common solvents than cellulose itself is.

Many different reaction systems for esterification have been developed over the lifetime of cellulose chemistry. Some of the most common ones are dimethylacetamide/lithium chloride, dimethyl sulfoxide/tetrabutylammonium fluoride)and N-Methylmorpholine N-oxide.[18], [18] The routes of these reactions can be very different, in many different solution media and with varying degrees of complexity. Further explanation falls out of the scope of this report, but has been studied extensively by Willberg-Keyriläinen and Ropponen, 2019[19].

The cellulose ester that has found the most industrial use is cellulose acetate. It can be spun into fibres and can be prepared in large quantities without the use of highly hazardous solvents.[2] Practical considerations like the need for large amounts of hazardou solvents have made it infeasible to introduce cellulose esters longer than four carbons to large scale industry.[2] Both the length of the carbon chain of the ester attached and the degree of substitution (the amount of -OH groups replaced) have a dramatic impact on the properties of the product.

Degree of substitution

An important outcome of cellulose modification is the degree of substitution (DS). It is defined as the average number of -OH groups substituted throughout the cellulose chain. Each cellulose unit has 3 hydroxyl groups with the maximum DS being 3. However, in practice, an average is found because in most cases there will not be complete replacement due to a myriad of factors relating to irregularities in cellulose structure and intermolecular forces.[20]

While different acyl groups connected to cellulose will have different properties, it is still worth mentioning some property changes that take place with a change in only the DS. Taking lauroyl cellulose as an example, it was found that, broadly speaking, the elastic modulus and tensile strength increased with an increase in DS, as did glass transition temperature. Interestingly, after peaking at DS of 2.4 the values dropped, so there is something to be said about finding the optimal DS rather than the maximum.[21] While just an example of one ester, similar correlations of mechanical properties and also solubility have been found with other cellulose esters as well.[21], [22]

Ester chain length

As important as DS seems to be, the length of the connected acyl group also plays a major role in determining the properties of the formed substance. The major impacts of lengthening the acyl chain length are increased thermoplastic behaviour, heightened maximum stress level, lower strain at breaking point and increasing resistance to both acids and bases.[22]

It has been found that the chain length also has an effect on the maximum degree of substitution. In a range of studies done by Willberg-Keyrilainen, 2020 they found that as the length increased from 6 carbons to 18 carbons, under similar conditions, the DS values dramatically decreased from 1.3 to 0.8.[4] Along with a decrease in degree of substitution it was found that water vapour permeability, when the substance was formed into a film, decreased inversely with the increasing of the ester length.[4]

1.2 Ionic liquids

1.2.1 General info

Ionic liquids(IL) are a relatively new group of substances with a lot of research surrounding them being done in recent years and at large volumes.[23] The most simple explanation pegs them as compounds composed only of ions that have a melting point below 100 °C - so liquid salts.[6] Some ionic liquids are even liquid at room temperature, aptly garnering them the moniker room temperature ionic liquids.[8]

The reason they have such a frenzy of research around them is their many unique properties compared to organic solvents which they are quickly replacing. Importantly, they have a very low vapour pressure (so do not emit volatile organic compounds) and have a high potential for being able to be modified for specific purposes and optimising reactions.[18] They are also able to be removed from solution and recycled, making them, theoretically at least, viable for industrial use.[18]

Other properties that make them advantageous include thermal stability over a wide temperature range, being non-flammable and most importantly, being very good solvents.[8] Due to ILs allowing customization, though, there are many properties, such as solubility in water and hydrophobicity which can be modified using different ions or by slightly changing the structure of either of the ions .[8]

ILs have been applied in many different use cases in different areas of chemistry and are pertinent for cellulose chemistry as well. They are being touted as more “green” than conventional solvent systems, although these claims are dubious to say the least.[24].

1.2.2 Structure and properties

ILs consist of only cations and anions, thus having a similar molecular makeup as salts. What differentiates them from regular salts, though, is the shapes of the cations and anions which has a dramatic impact on how the compound behaves. The ions for ILs can both be very large and misshapen (figure 1.2.2.1), making the formation of a lattice structure difficult as the molecules can not pack as closely together. This in turn means the substances remain liquids at high temperatures.[7]

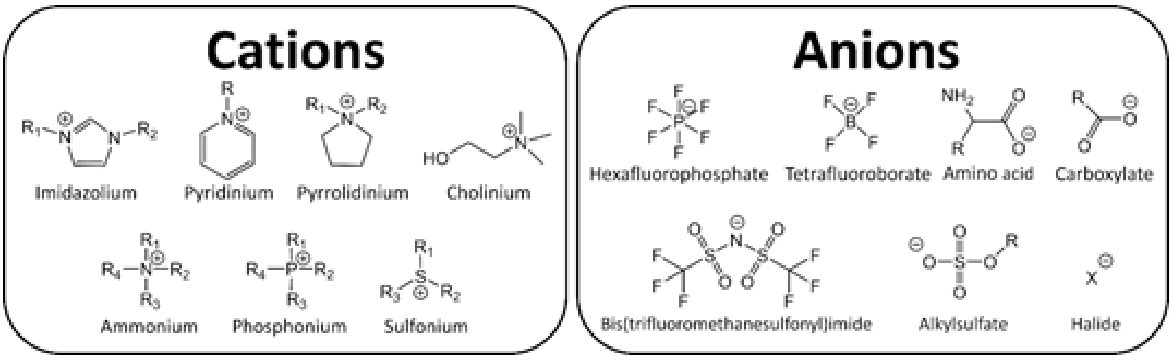


Figure 1.2.2.1 Some typical ions present in ionic liquids and their unorthodox molecule shapes[25]

Most commonly the ions in ILs consist of a positively charged organic cation and a negatively charged anion, both of which can be either organic or inorganic. The cation generally contains either a nitrogen or phosphorus atom. Halides, hexafluorophosphates, tetrafluoroborates, alkyl sulphates, talylates, methanesulfonates and bis(trifluoromethylsulfonyl)imides have been recognized as possible anion part.[8]

As emphasised, resulting from there being a huge number of different cation-anion combinations, there is also an almost unlimited amount of variation and potential for customization for properties like thermal stability, vapour pressure and other physicochemical attributes.[25]

1.2.3 Project ionic liquid [mTBNH][OAc]

The ionic liquid used throughout the experimental portion of the thesis is 5-methyl-1,5,7-triazabicyclo[4.3.0]non-5-enium acetate which is abbreviated to [mTBNH][OAc]. Its structure is illustrated in figure 1.2.3.1. It is synthesised by Lioutin Group OY in Finland. It is very novel and has not been involved in any other research up until now, as far as we know. It is said, however, that the dissolution and regeneration properties are similar to that of [mTBDH][OAc] by the manufacturer.[26] Based on that, we know that it does indeed dissolve cellulose as it has been applied to the Lyocell process and is distillable as was demonstrated by Elsayed et al.[27]

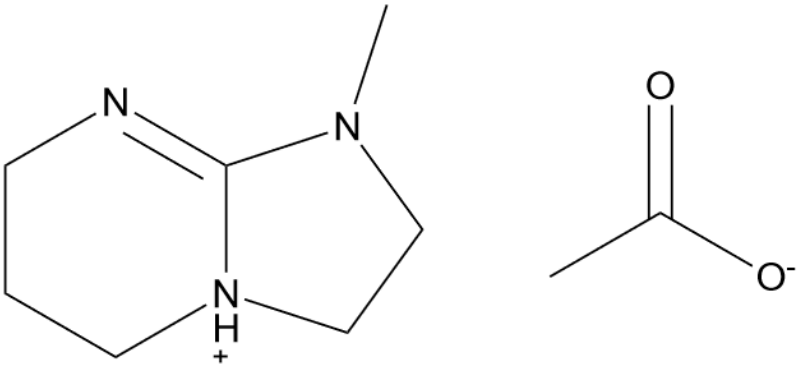


Figure 1.2.3.1 The ionic liquid 5-methyl-1,5,7-triazabicyclo[4.3.0]non-5-enium acetate

1.3 Synthesis of cellulose esters in ionic liquid

Ionic liquids(ILs) have become a viable option as a cellulose solvent.[9] For esterification in IL, a homogenous transesterification reaction takes place by which the esterification is done in solution.

Esterification involving ILs is able to be performed at room temperature and in solution, which means less steps and energy use.[28] Additionally, it is noteworthy that, for some ILs, (Emim]OAc for example), it has been reported that they not only dissolve the cellulose, but also act as a partial catalyst or serve as a part of the reaction in further derivation.[29] The project IL [mTBNH][OAc] presumably has analogous organocatalytic properties as there would invariably be traces of the superbase mTBNH in the mixture. This presumption is based on the superbase TBD having such properties and being similar in structure.[18]

Most traditional cellulose esters, and many new ones, have been synthesised using ILs as solvents and either acid chlorides or acid anhydrides.[28]

As mentioned, the effectiveness of a solute dissolving cellulose is contingent on its ability to interfere with the hydrogen bonding present throughout the polymer as a consequence of the -OH groups in the structure.[18] Due to this, not all ILs can be used, obviously, and effectiveness varies from one IL to the next.

Regarding the anions in ILs OAc- , HCOO- , (MeO)2 PO2- and Cl- have been shown to dissolve cellulose very well. Although, it has been found that the cations play some role in the process also.[30]

The general reaction scheme for synthesis of cellulose esters can be seen in figure 1.3.1.

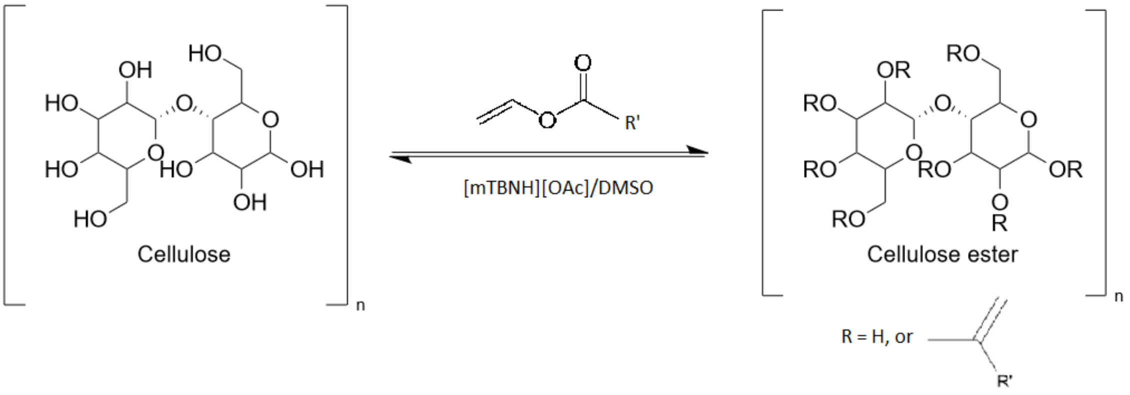


Figure 1.3.1 Cellulose transesterification reaction scheme

1.3.1 Cellulose acetate

Cellulose acetate (figure 1.3.1.1) is one of the most common cellulose derivatives that is produced at industrial scales and has been used historically as photography film and as aircraft dope.[31]

It has traditionally been prepared by dissolving cellulose in acetic acid and adding an acetic anhydride together with a catalyst. The resulting product is a very crystalline and high-melting point thermoplastic that, when fully substituted, does not dissolve in most common solvents.[32]

More recently, however, ionic liquids and homogeneous transesterification with an acetate vinyl has become a viable synthesis path for the polymer as well. One study had very good results (achieving a DS of 2.97) by using a DBU/CO_2 solvent system. Regurgitating what has already been said before, ILs are much more mild as far as solvents go and less impactful to the environment.[33]

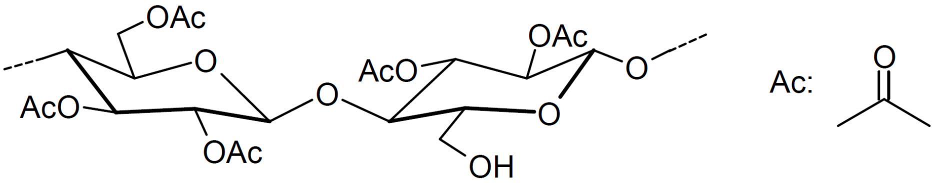


Figure 1.3.1.1 Structure of cellulose acetate[34]

1.3.2 Cellulose laurate

Laurate is a saturated straight-chain higher fatty acid and is an anion that is derived from lauric acid and has a carbon chain length of 12.[35]

For preparing a cellulose laurate the acid itself is sometimes used, but more often it comes from vinyl laurate(VL) or a lauroyl chlorine.[36], [37]

A comprehensive overview of cellulose laurate was done by Wen et al., 2017, who described a myriad of its properties, but most importantly synthesised it using a reaction system involving an ionic liquid as a solvent. The system used was 1-Allyl-3-methylimidazolium chloride/DMSO with DBU as a catalyst and vinyl laurate as the acylation reagent. The results were exceptionally good and the reaction product has potential to be used as a “green” packaging film.[37]

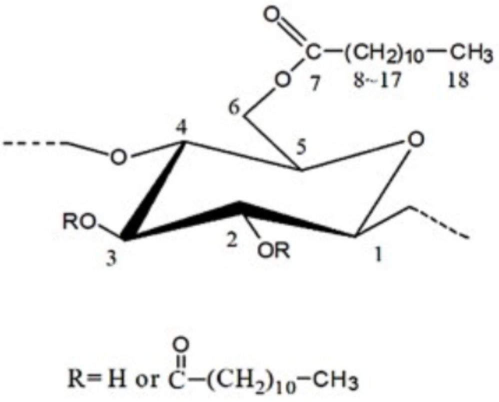


Figure 1.3.2.1 Structure of cellulose laurate [37]

1.3.3 Cellulose myristate

Myristate is an anion deriving from myristic acid. It has a 14 carbon backbone and is found in natural oils.[38]

Cellulose myristate (figure 1.3.3.1) has also been successfully synthesised in ionic liquids. One study that was evaluating fatty cellulose esters for antifriction properties found that cellulose myristate displayed the best antifriction properties when utilised as a potential biolube. Its having been synthesised with [C4mim]Cl (1-butyl-3-methylimidazolium chloride) as a solvent and achieving a DS of around 2 is very promising.[39]

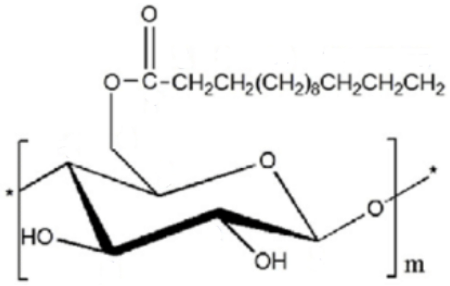
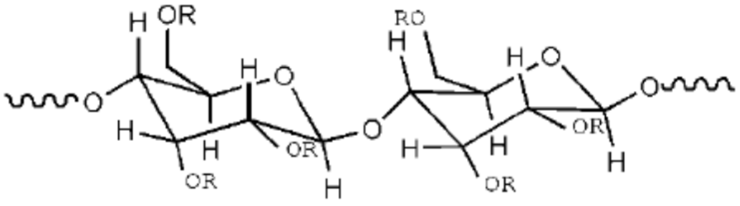


Figure 1.3.3.1 Structure of cellulose myristate [40]

1.3.4 Cellulose stearate

Stearate is also a fatty acid anion and comes from stearic acid.[41] It is naturally abundant in animal and vegetable fats and oils and essential in the structure of milk fats, lard and cocoa and shea butters.[42]

As with the previous three esters, cellulose stearate (figure 1.3.4.1) has also been synthesised in ionic liquids. In one case [C4mim]Cl was used and a useable product was formed which could be further used for electrospinning.[43] Traditionally the cellulose ester has been synthesised using cellulose in acyl chloride, toluene and pyridine, acid chlorides under vacuum or aliphatic acids with trifluoroacetic acid so a much more mild reaction media is a welcome development.[44]



R=$C_{17}H_{35}CO$- or H according to the DS

Figure 1.3.4.1 Structure of cellulose stearate [45]

1.4 Sustainability and recycling

Ionic liquids are relatively expensive compared to conventional solvents. The project IL [mTBNH][OAc] costs around 1000€ per litre, for example. As such, efforts have gone into devising regeneration protocols. Not only are the substances themselves expensive, often a large quantity is needed. There is something to be said about economies of scale, though, as prices are expected to decrease going forward as they are being used in large scale operations more and more.[24]

Regarding recycling, there is no one method that works for all ILs. As there are so many possible molecules, there are also at least as many different ways to recycle them and the results are varied.

Taking the example of 1-allyl-3-methylimidazolium chloride, it was found after even 5 times of reuse that the purity of the IL was still at 99.56% using wiped film molecular distillation.[46] In a review by Dołżonek et al. it was found that for 1-Butyl-3-methylimidazolium chloride, which is one of the most used ILs, both filtration and rotary evaporation showed very good results as the compound could be reused up to ten times without losing any ability to dissolve.[47] In another study with 1-Butyl-3-methylimidazolium chloride/DMSO, it was found that after reuse 97% of the mixture could be recovered although the recovery procedure was not elaborated on.[18]

That being said, these results are from a laboratory setting, concerning only a few ionic liquids, so their scalability and ecological impact are equivocal.

1.4.1 Ecological claims and industrial scalability

Due to ILs not emitting volatile organic compounds (VOCs) they are, somewhat hastily, being published as a more sustainable solvent that is not environmentally harmful. While not emitting VOCs is a good sign, of course, in an extensive review article about IL recycling Abu-Eishah, 2011, highlights other important aspects to consider.[24]

As the solvents are, in the context of academic research, very new, there are a lot of unknowns. Not only is it important to look at the solvents on their own and how they are made, but also how they react with other compounds and what issues arise. Another thing to consider should be which resources are used up during the recycling process and what potential hazards stem from it.[24]

In a more recent review by de Jesus and Michael Filho published in 2022 and focusing solely on answering the question "Are ionic liquids eco-friendly?", even more concerning and importantly, more up to date, points were raised. It was concluded that not only is there a need for highly toxic reagents for the synthesis of ILs but that they themselves are often indirectly toxic and do not biodegrade. Also, while the lack of volatility is commendable, it is also an issue as it makes the recycling process more difficult.[48]

In a laboratory setting up to a 99% reuse rate has been achieved, but only 83% was recovered with distillation. It being the most prevalent and cheapest solution and giving a result like that does not bode well for industrial scaling. ILs being so susceptible to contamination is a major issue which makes it hard to justify their present cost and the "green" designation they have been given.[48]

2. EXPERIMENTAL PART

2.1 Methodologies and materials

2.1.1 Synthesis of cellulose derivatives in ionic liquid

Materials

The cellulose in the work was microcrystalline cellulose (MCC) which was purchased from Sigma-Aldrich and dried at 105°C for 24 h before use. Vinyls used for the acylation were >98% pure vinyl acetate, -laurate, -myristate and -stearate which were all purchased from Tokio Chemical Industry Co. The ionic liquid 5-Methyl-1,5,7-triaza-bicyclo-[4.3.0]non-6-enium acetate([mTBN][OAc]) was purchased from Liuotin Group Oy in finland. DMSO, which was used to lower the viscosity of the solution, was purchased from Fisher Chemical.

Precipitation of the esters was done into water and washed with either ethanol, acetone or in extreme cases toluene or hexane.

Cellulose esterification

Synthesis of cellulose esters took place in a heated reactor with a stirrer under nitrogen atmosphere.

2.1.2 Recycling of ionic liquid

Distillation of the ionic liquid was done by Dr. Illia Krasnou in a wiped film evaporation apparatus.

2.1.3 Sample Analysis

Fourier transform infrared spectroscopy

Fourier transform-infrared spectroscopy (FTIR) is a material analysis and identification method. It involves measuring the amount of infrared radiation the material absorbs. With certain molecules being excited to a higher energy level only by certain wavelengths it makes the molecules or functional groups present in the material identifiable. Usually the results are represented as a graph of the intensity of light at the detector in comparison to the wavenumber in cm^{-1}.[49]

The FTIR spectroscopy for all samples was done with an Interspec 200-X together with a Quest ATR accessory from Specac. Samples were analysed in the 500-4000 cm^{-1} wavenumber range with a resolution of 4 cm^{-1}.

Titration for determining the degree of substitution

Titration is a sample analysis method for determining the concentration of some substance or part of a substance. It is found by adding to the sample a certain amount of a substance that reacts with it in excess and then gradually adding a standard solution, known as a titrant, to the point at which the solution is neutral i.e. the excess substance is all used up.[50] This shows how much of the excess solution was actually reacted, from which the prior mentioned concentration can be deduced. In the context of cellulose esters it is used to determine the degree of substitution.

The titration method to determine the degree of substitution was based on the one described in "Standard Test Methods of Testing Cellulose Acetate" by ASTM international, more specifically the method for heterogeneous saponification.[51]

For titrants, a 75% by volume solution of ethanol, a 0.5 N solution of NaOH and a 0.5 N solution of HCl were prepared.

The titration itself was performed with the EasyPlus Automated Titrator by Mettler Toledo. First, a titration to neutralise the initially added NaOH with HCl was done after which an excess of 0.5 ml of the HCl solution was added to the solution for a back titration.

The ester content was calculated with the following equation: [4]

$$E(\%) = \frac{[(A-B)\cdot N_B - (D-C)\cdot N_A]\cdot M}{10\times w}$$

Where;

A = NaOH added to sample, mL

B = NaOH added to blank, mL

N_a = NaOH normality

N_b = HCl normality

C = HCl added to sample, mL

D = HCl added to blank, mL

M = molecular weight of the grafted ester residue

w = weight of the sample

Then the degree of substitution was calculated with the following equation:

$$DS = \frac{162E}{100M - E \times (M-1)}$$

Where;

162 = molecular weight of anhydroglucose unit.[44]

Rheology

Rheology is a study of flow and how polymeric fluids react to outside forces. It is used to assess the optimal environment for example polymer extrusion with the goal of certain properties.[52] When compared with a reference material a quantification of the thermoplastic properties can be gauged.

Rheology parameters of samples were measured with an Anton Paar PhysicaMCR50 rheometer with a cone-plate measuring geometry under nitrogen atmosphere.

To study rheological properties of recycled IL, a rheometer with cone-plate measuring geometry was used. Flow curves were obtained at a shear rate ranging from 0.001 to 100 s^{-1}.

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) is the most accurate method for assessing the atomic makeup of a material. The method is based on creating an energy transfer at the nuclear level from a lower level to a higher one using strong magnets and radio frequencies. From that energy level change there is an energy emission which corresponds to some specific radio frequency which is unique for each element.[53] NMR is used in cellulose chemistry for accurately determining the degree of substitution by ^{1}H NMR spectra analysis.

NMR analysis was done by doctoral student Nutan Bharat Savale for both ^{1}H and ^{13}C spectra with a Bruker AV-300 spectrometer. The samples were all measured in either pyridine-d6 or DMSO-d6 and at 25°C. Sample spectra were referenced with trimethylsilane(TMS).

^{1}H NMR spectroscopy was used to determine the DS of the synthesised cellulose esters as mentioned. It was done by taking an integral of the area of terminal methyl groups and AGU signals in the ^{1}H NMR spectra based on the method outlined in Lowman, 1998 with the following equation [54]:

$$DS = 10 \cdot \frac{I_{CH_3}}{(3 \cdot I_{AGU} + I_{CH_3})}$$

Where;

I_{CH_3} = integral of the area of terminal methyl groups

I_{AGU} = integral of the area of terminal AGU signals

2.3 Results and discussion

2.3.1 Synthesis of cellulose derivatives in ionic liquid

Within the work at hand an attempt to find a more sustainable solvent for creating long chain cellulose fatty acid esters is discussed. [mTBNH][OAc] was chosen as a cellulose solvent and homogenous transesterification was undertaken. The IL was chosen as it had potential for dissolving cellulose well and was also distillible. In synthesis with the IL no external catalyst was used which is a feature that many other synthesis routes lack.

Some optimal parameters had already been obtained from previous experiences in the lab. The mass percent of cellulose was kept at a constant 3.5%, the ratio of IL to DMSO used as a cosolvent was kept at 1:1, the ratio of AGU to vinyl ester was 1:3 and finally the reaction temperature and time were kept at 70°C and 2.5 h, respectively. The esters synthesised were cellulose acetate (CA), cellulose laurate (CL), cellulose myristate (CM), and cellulose stearate (CS).

Synthesis of Cellulose Acetate

Synthesis of cellulose acetate was done under the chosen parameters, however only a small amount of 2 grams of cellulose was used.

Analysis by way of ^{1}H NMR spectroscopy revealed that a very large majority of the AGUs had been substituted. This was evidenced by the peaks that correspond to AGU protons and a peak at 1.06 ppm that is indicative of CH_2 groups in figure 2.3.1.1.

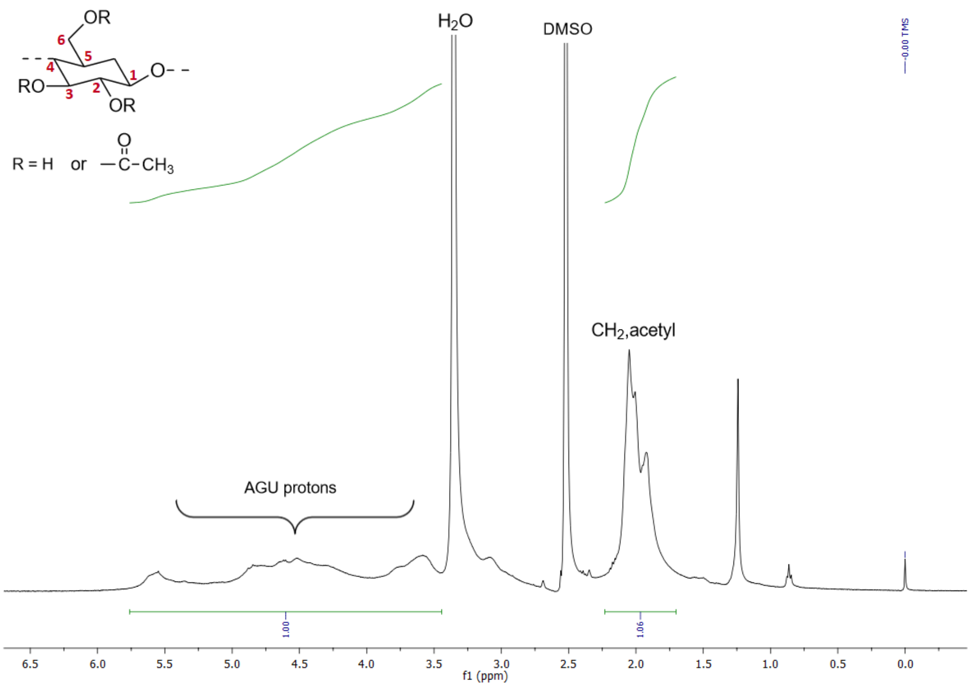


Figure 2.3.1.1 ^{1}H NMR spectra of CA

FTIR analysis of the sample also illustrated the result well. Looking at figure 2.3.1.6, we see a strong peak at around 1746 cm^{-1} and compared to other samples practically nothing at 3300-3500 which is an indicator for -OH groups in the AGU. No peaks around 2800-2900 cm^{-1},which usually characterise CH_2 groups, is an expected outcome.

A comparison FTIR analysis was also done with commercially available cellulose diacetate (DAC). The spectra were remarkably similar. Only slight differences around the 2800-2900 cm^{-1} and 3300-3500 cm^{-1} wavenumbers can be observed which could correspond to some unreacted cellulose or be a result of remnants from the IL playing a role. In any case, this is still a remarkably good result.

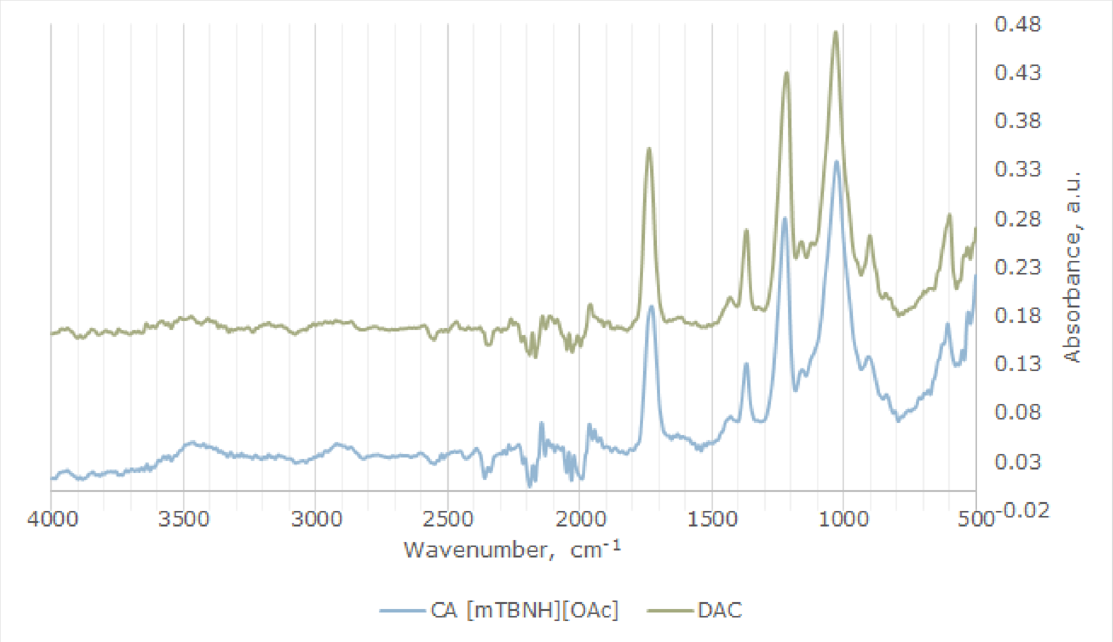


Figure 2.3.1.2 CA synthesised in [mTBNH][OAc] FTIR spectra compared to commercially available DAC

Synthesis of Cellulose Laurate

Synthesis of CL followed the same process and parameters. The product was soluble in DMSO, THF(tetrahydrofuran) and pyridine, which enabled NMR measurements to be done. ^{1}H NMR and ^{13}C NMR spectra were measured shown in figure 2.3.1.3 and figure 2.3.1.4, the first of which enabled DS to be calculated.

Looking at the ^{1}H NMR spectra, several characteristic peaks are revealed. The peaks from 6.00 to 3.50 ppm are proton signals assigned to H-3, H-1, H-2, H-6, H-6′, H-5 and H-4 of the AGU in pure cellulose. $CH_2<$ groups at H-8, H-9, and H-10–17 are characterised by signals at 2.32–1.93, 1.88–1.45, and 1.27 ppm. Signals at 0.98–0.79 ppm are attributable to $-CH_3$ protons at H-18.(figure 2.3.1.3)

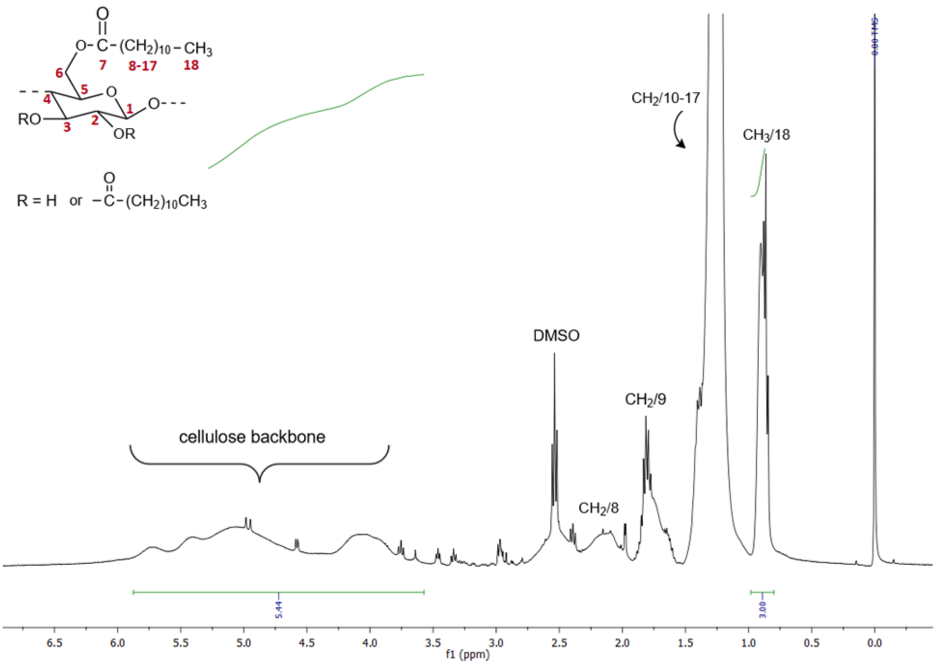


Figure 2.3.1.3 ^{1}H NMR spectra of CL obtained in 1:1 IL:DMSO

When analysing the ^{13}C NMR spectrum of the ester the carbons of on the aliphatic side chain C-8, C-16, C-9, C-17 and C-18 are characterised by peaks at 2.12, 25.82, 22.94 and 14.29 ppm, the carbons at C-10 to C-15 by signals ranging from 30.16 to 29.34 ppm and the carbons in the AGU at positions from C-1 to C-6 by signals at around 100 to 60 ppm. The last of the three confirms that the laurate ester was indeed formed onto the cellulose.(figure 2.3.1.3)

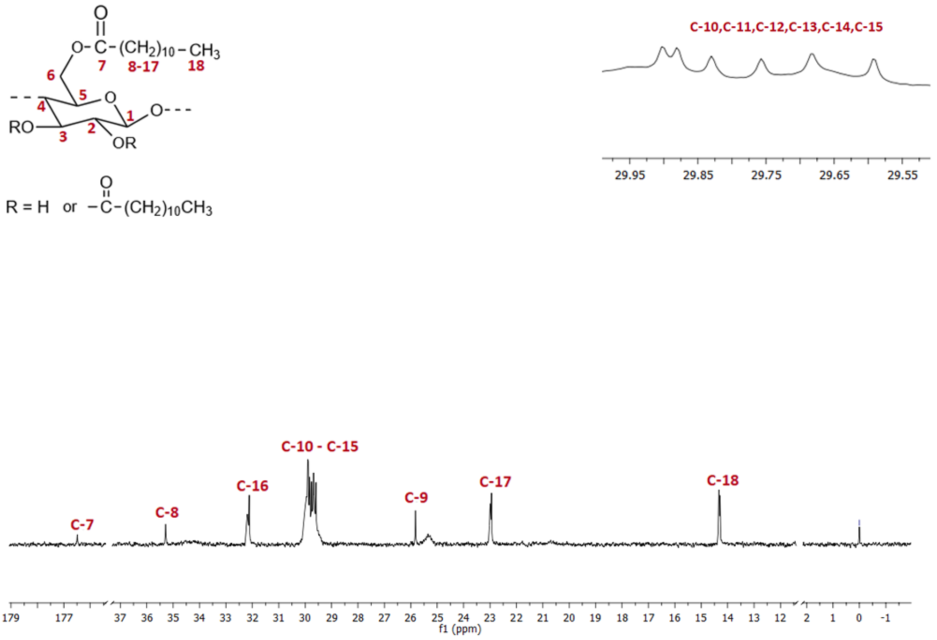


Figure 2.3.1.4 ^{13}C NMR spectra of CL obtained in 1:1 IL:DMSO

The product received had a DS of 1.55 according to calculations made based on NMR spectra analysis.

The relatively good DS was also corroborated by the FTIR spectra results (figure 2.3.1.6) which showed strong absorbance peaks at all the three relevant wavenumbers. There is, somewhat uncharacteristically, a very large peak at 1000-1100cm^{-1} though which could suggest COC bond stretching according to Nunes et. al 2020 and could be used as an indicator of DS as well.[55]

Synthesis of Cellulose Myristate

CM synthesis followed the described process and conditions but was done in two batches totalling 7 g of cellulose and 100 g of both IL and DMSO used.

When starting the synthesis itself the vinyl myristate needed to be poured in very slowly as there were previously issues with the ester staying unreacted as a layer on top of the dissolved cellulose, IL and DMSO mixture. The layer formed due to a big difference in viscosity between the two substances.

As the sample was, like cellulose laureate, soluble in DMSO, THF and pyridine NMR analysis was possible to be undertaken.

Figure 2.3.1.5 and figure 2.3.1.6 show the ^{1}H NMR and ^{13}C NMR spectra of CM with characteristic peaks similar to that of CL, with the caveat that myristate has a longer carbon chain.

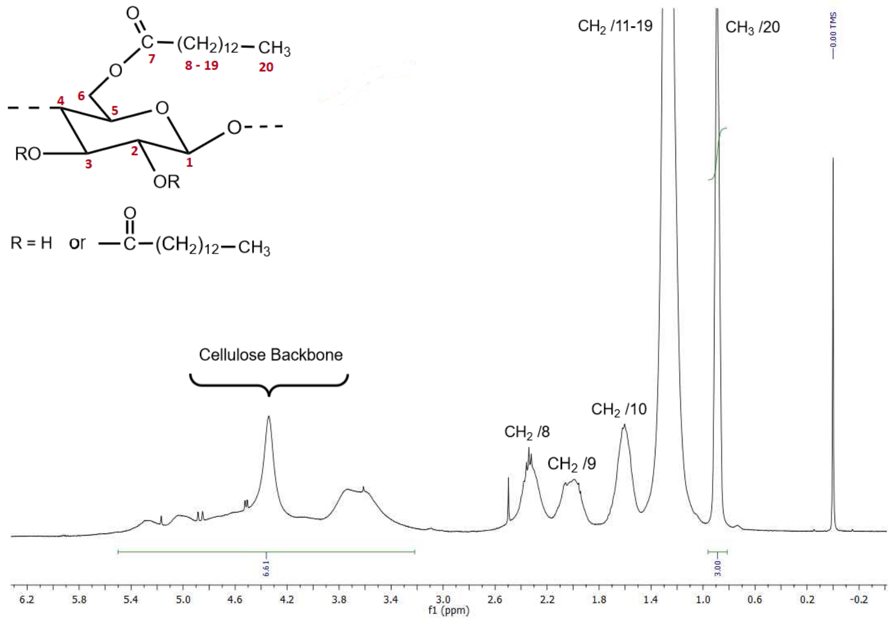


Figure 2.3.1.5 1H NMR spectra of CM obtained in 1:1 IL:DMSO

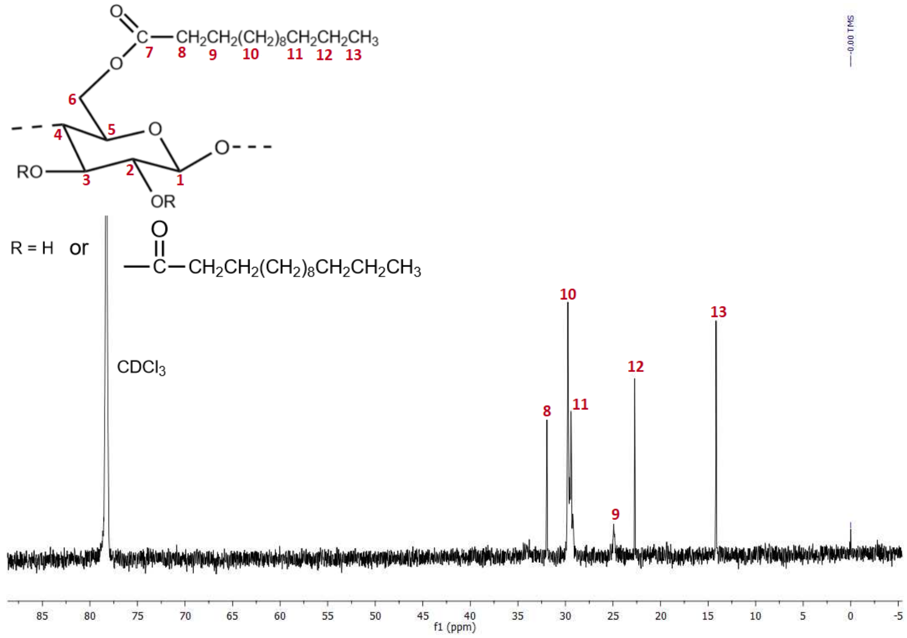


Figure 2.3.1.5 1H NMR spectra of CM obtained in 1:1 IL:DMSO

A DS of 1.31 was measured and was shown to be well substituted in the FTIR spectra (see figure 2.3.1.6) as well, as evidenced by high peaks at 2800-2900 cm^{-1} and a low gradual peak at 3300-3500 cm^{-1}.

Synthesis of cellulose stearate

Synthesis of cellulose stearate under chosen conditions turned out to not be optimal and the resulting sample was not soluble in any solvent.

Vinyl stearate was crystalline at room temperature so before adding it to the reactor it needed to be melted using a hot water bath. In the beginning, and throughout the first hour of synthesis, it seemed everything would go similarly to myristate. At some point during the reaction the solution became extremely viscous to the point that after opening the valve it would not pour out of the reactor and had to be manually scraped out.(Photo 2.3.1.1) The viscosity was probably due to the length of the stearate ester. Eventually though, most of the product got precipitated and the regular process could be followed to the end.

Photo 2.3.1.1 Photo of cellulose stearate stuck in reactor after synthesis, right before washing

The resulting sample was measured to have a relatively low DS of 0.23 which was obtained by titration.

Comparing cellulose esters synthesised

FTIR spectra from each of the synthesised samples and MCC as a control is shown in Figure 2.3.1.1 and shows that all have had some amount of esterification take place. The strongest tell of an alkyl chain having been added to the structure is the absorption peak at 1746 cm^{-1} that corresponds to a stretch in the esters carbonyl group (>C═O). Comparing the cellulose esters to pure MCC, there are a few other peaks that appear or change. Firstly, there are the sister peaks that show the asymmetric and symmetric stretching of a methylene group at 2950 cm^{-1} and 2847 cm^{-1}. The change in the 3300-3500cm^{-1} absorption band is indicative of a change in the amount of hydroxyl groups as well as they get substituted in the esterification.

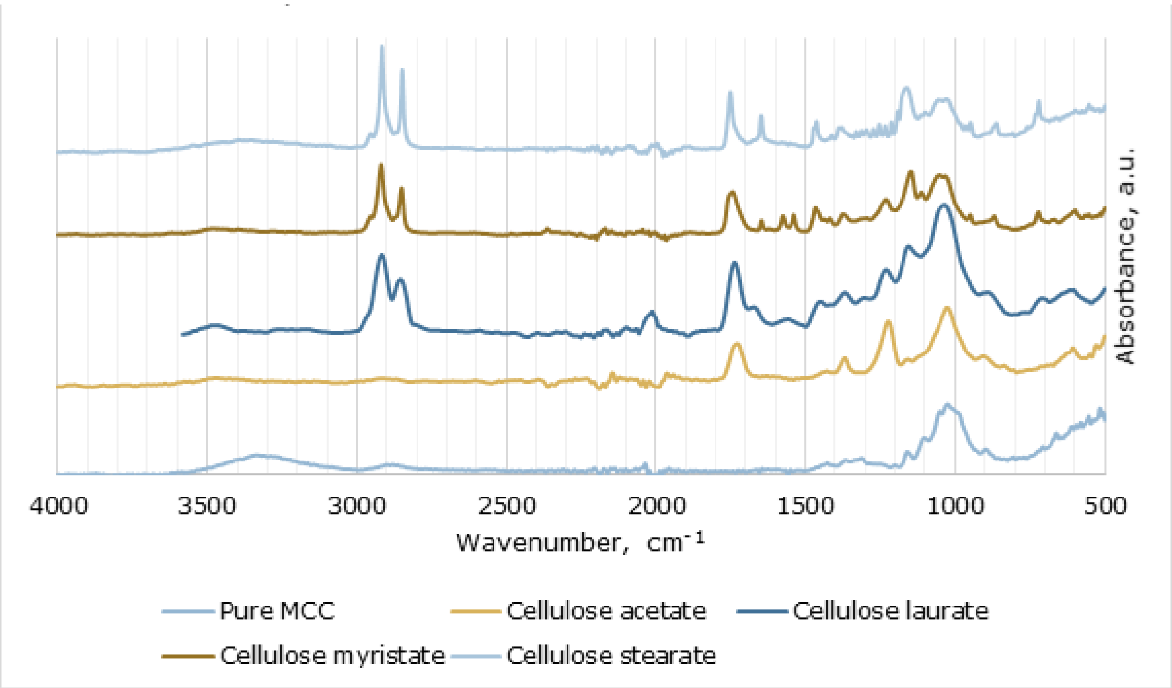


Figure 2.3.1.6 FTIR Spectra of different cellulose derivatives

Table 2.3.1.1 shows a pretty clear trend. With an increase in the ester carbon chain length, while keeping reaction conditions constant, there is a clear drop in DS values. Such results were expected as similar results were seen by Schenzel et al. 2014 as well, although it must be emphasised that the high DS values obtained with [mTBN][OAc] are very good.[18]

Table 2.3.1.1 Solubility and degree of substitution results of the cellulose esters synthesised

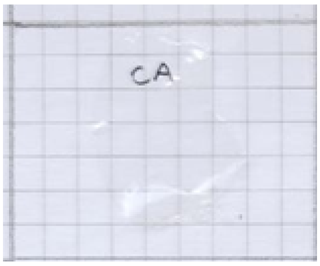
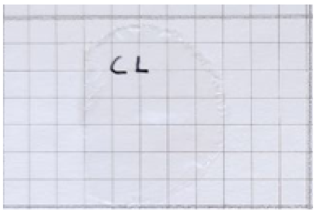
Sample	**Soluble in...**	**DS**
CA	DMSO,Pyridine	2.48
CL	DMSO, THF, Pyridine	1.55
CM	DMSO, THF, Pyridine	1.31
CS	none	0.23

It is evident that quite a high level of esterification was achieved. While no catalyst was used it has been found that the superbases DBN and DBU, which are somewhat analogous to the superbase mTBN, of which [mTBN][OAc] contains in small amounts, act as partial catalysts.[29], [56] Similar DS results for cellulose acetate and cellulose propionate were achieved by Kakko et al. using [DBN][OAc].[56]

With the fatty acid chains having higher steric hindrance, the DS values track with what was expected very well, seeing as CA has the highest DS, CL and CM a roughly similar DS and stearate, being the longest, having the lowest.

All of the obtained cellulose derivatives that were soluble in an pyridine made it possible to prepare casted films from them as well. As can be seen from table 2.3.1.2, it was possible to produce transparent films from pyridine and THF solutions for CA, CL and CM.

Table 2.3.1.2 Cellulose ester films prepared by dissolution in pyridine

Cellulose acetate	Cellulose laurate	Cellulose myristate	Cellulose stearate
			Not possible

Further work still needs to be done in analysing the physical properties of the samples produced and in increasing the percentage of cellulose used in the esterifications as 3.5% is relatively low still and not scalable in present conditions for industrial settings. The caveat being though, that usually temperatures and longer time are used in transesterification reactions, so receiving such high DS values is indeed a very good result. Potentially the use of different catalysts can be considered.

2.3.2 Cellulose Stearate Synthesis Optimisation

DS is the most important factor for predicting thermoplastic behaviour, as when it is close to or above 1.5 for cellulose esters, they have similar processing parameters as common polymers.[22] As producing a sample of CS with a high enough degree of substitution failed under the initially chosen parameters, parameter optimisation was undertaken to achieve a sample with a high enough DS.

The first test was to keep everything else the same but add the catalyst tin(II) 2-ethylhexanoate along with the vinyl stearate into the solution in the reactor. After adding only one drop of catalyst though, the solution became jelly-like in texture**.** After the passing of 2.5 hours it again needed to be scraped out, like the sample synthesised under the chosen constant parameters (CS-Co-261121), although less laboriously this time due to the aforementioned texture.

The produced sample (CS-Co-Tin-021221) was not soluble in any solvent. FTIR spectrum of the sample as presented in figure 2.3.2.1 shows no characteristic peaks at all.

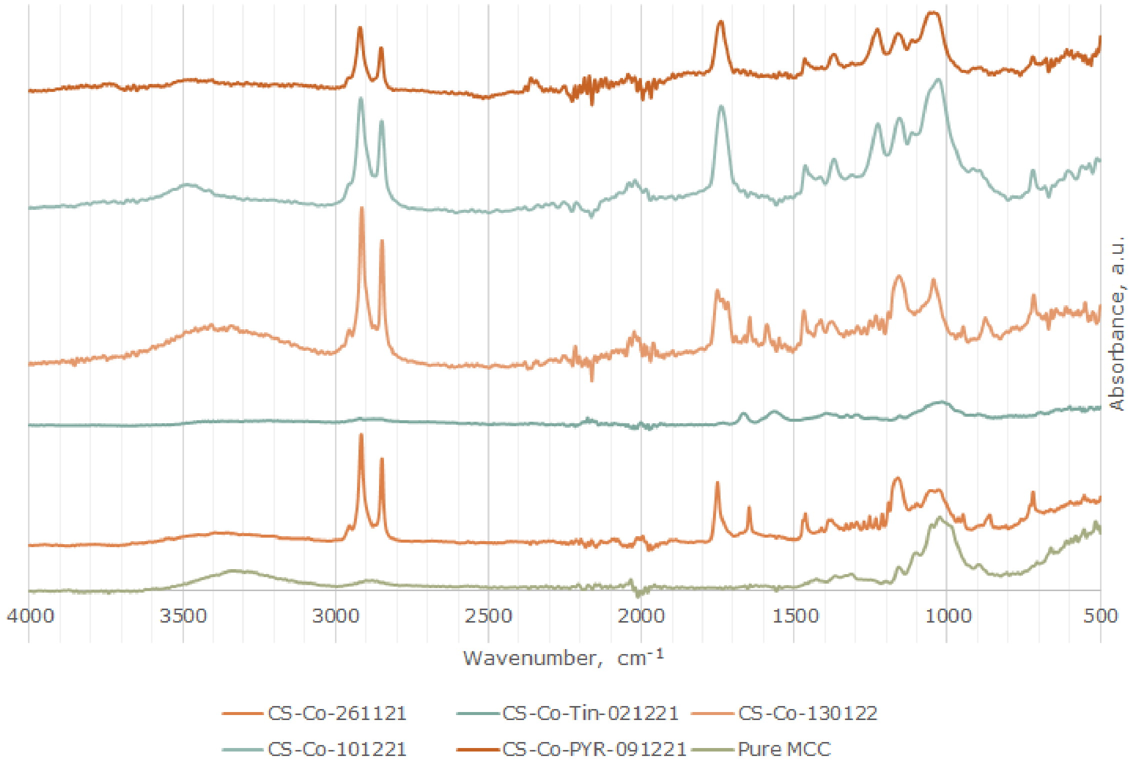


Figure 2.3.2.1 FTIR spectra of different cellulose stearate samples

As a catalyst did not affect the outcome positively a change was made in the cosolvent, the AGU:VS ratio and temperature. DMSO was replaced for pyridine to test whether the DMSO was interfering with the reaction somehow. Additionally, the AGU:VS ratio was raised from 1:3 to 1:6 with the intent of driving the reaction to the right by adding an excess of the limiting reagent. Temperature was raised with largely the same rationale behind it, but with the limitation that the reaction temperature could not be raised above 80°C as with anything above that there is a possibility that the IL starts to hydrolyze.

The resultant sample (CS-Co-Pyr-091221) was only partly soluble in DMSO but completely soluble in CHL, pyridine and THF and as such an NMR analysis was done. From the ^1H NMR spectra(figure 2.3.2.2) an integration was done to determine DS and ^{13}C NMR(figure 2.3.2.3) was done to confirm attachment of aliphatic side chains onto the cellulose backbone.

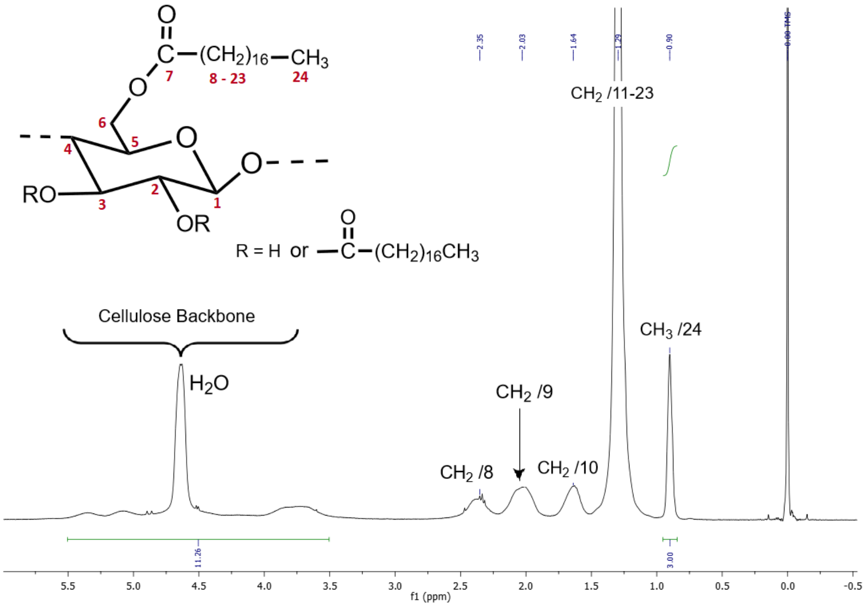


Figure 2.3.2.2 ^1H NMR spectra of CS-Co-Pyr-091221

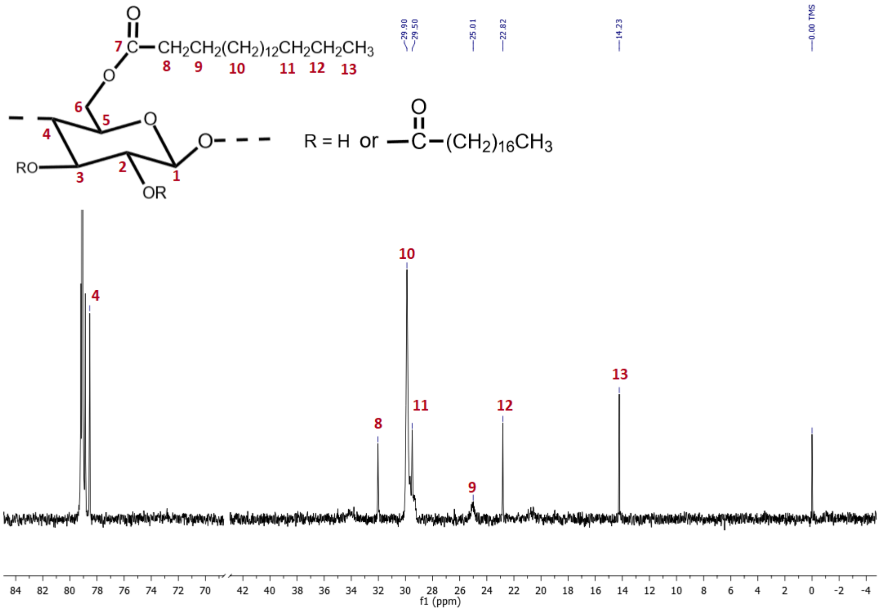


Figure 2.3.2.3 ^{13}C NMR spectra of CS-Co-Pyr-091221

As pyridine is very poisonous, and the DS of 0.83 that was calculated was still too low for us, additional work had to be done.

A switch back to DMSO was made and changes were made in the conditions once again, this time lowering the percentage of cellulose used from 3.5% to 2.5% with the goal of increasing the excess of vinyl stearate without increasing the volumes of reactants used.

The resulting sample (CS-Co-101221) was soluble in DMSO, CHL, THF and pyridine which solved the solubility issue and had a DS of 1.39 which was once again found by integration of the areas of the methyl groups and AGUs signals on the ^{1}H NMR spectra(figure 2.3.2.3).

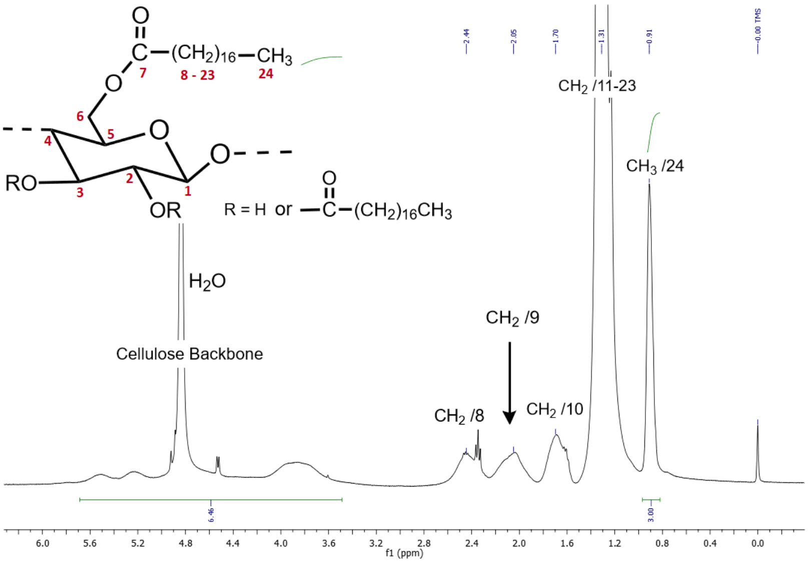


Figure 2.3.2.4 ^{1}H NMR spectra of CS-Co-101221

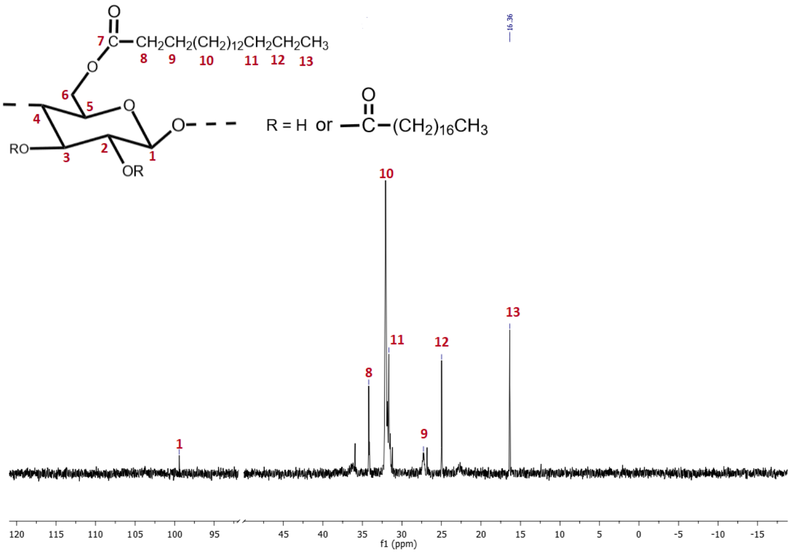


Figure 2.3.2.5 ^{13}C NMR spectra of CS-Co-101221

While lowering the percentage of cellulose worked, it is not favourable as obviously the industrial scalability argument diminishes the less cellulose per IL is used. In order to combat this, a sample with a cellulose percentage once more at 3.5% was synthesised. Still using a 1:6 AGU:VS ratio, 80°C and 1:1 IL:DMSO ratio, a change was made with increasing the reaction time from 2.5h to 3h. Doing this risked the structure of the IL breaking down, but a test had to be made to see whether DS could be increased substantially by doing this.

The resulting sample(CS-Co-131221) had a DS of 1.4 (calculated from the ^{1}H NMR spectra shown in figure 2.3.2.6) which was only marginally greater than that of the previous sample, due to a larger cellulose percentage more CS was created as the cellulose percentage was larger.

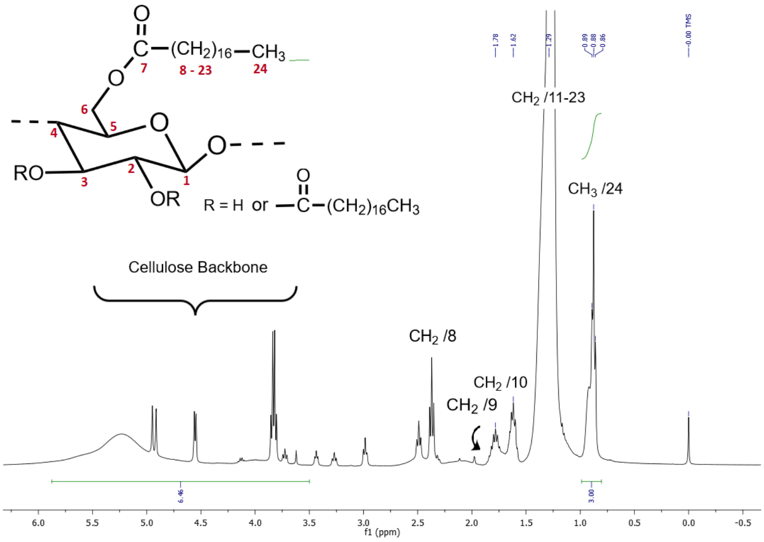


Figure 2.3.2.6 ^{1}H NMR spectra of CS-Co-131221

However, evidence of the IL having gotten hydrolyzed was present, as the solution had turned brown after the reaction, as opposed to the honey-like golden colour it usually has. Notwithstanding, in figure 2.3.2.3 showing the ^{13}C NMR spectra, a tiny peak confirming the O-C=O bond can be seen.(figure 2.3.2.7)

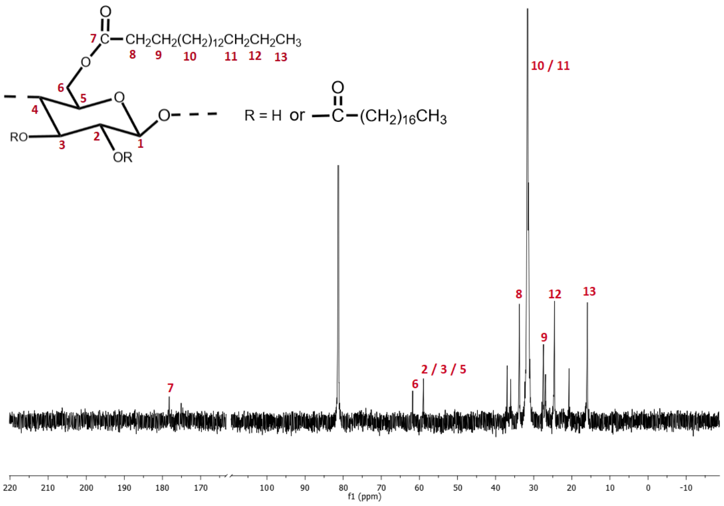


Figure 2.3.2.7 ^{13}C NMR spectra of CS-Co-131221

As can be seen from table 2.3.2.1, the degree of substitution of CS was improved significantly with the highest achieved value being 1.4. The FTIR results for all samples illustrate the effects of the decisions taken throughout the process as well, with the significant peaks at 1746 cm^{-1} and 2800-2900 cm^{-1} wavenumbers increasing gradually and the peak spanning from 3300 to 3500 cm^{-1} decreasing as the degree of substitution increases.

Table 2.3.2.1 Cellulose stearate samples shown together with their synthesis parameters and solubility and DS results

Sample	Solvent	C%	AGU:VS	T	t	Soluble in…	DS
CS-Co-261121	1:1 IL:DMSO	3.5	1:3	70°C	2.5 h	Pyridine (+/-)	0.23
CS-Co-Tin-021221	1:1 IL:DMSO	3.5	1:3	70°C	2.5 h	DMSO (gel)	NA
CS-Co-Pyr-091221	1:1 IL:Pyridine	3.5	1:6	80°C	2.5 h	CHL, PYR, THF	0.83
CS-Co-101221	1:1 IL:DMSO	2.5	1:6	80°C	2.5h	DMSO, CHL,THF, PYR	1.39
CS-Co-130122	1:1 IL:DMSO	3.5	1:6	80°C	3 h	THF, CHL, PYR, TOL, DMSO	1.4

2.3.3. Efficiency of Ionic Liquid Recycling

As ionic liquids are expensive, even [mTBN][OAc] costing around 1000€ per litre, it was paramount to develop recycling techniques to regenerate and reuse the solvent. The specific ILs recyclability has not been tested before and in this lab it was the first attempt as well.

To evaluate efficiency of IL after recycling towards transesterification of cellulose, it was decided to make several cycles of distillation of IL collected from the washing process. After each cycle of distillation, IL was used for dissolution of cellulose and cellulose laurate synthesis once again.

In order to avoid additional variables in evaluation, it was decided to use pure IL without any co-solvent DMSO, although this did significantly increase the viscosity of the solutions.

Cellulose laurate was synthesised because there was extensive previous experience with the derivative in the lab and the synthesis does not have any extremely obvious hurdles like having to melt the vinyl ester beforehand or the washing liquid clogging up the filtration column filter papers as happens with longer carbon chain vinyl esters.

The percent of MCC was a constant 2%, the ratio of AGU:VL was chosen to be 1:3, the temperature 60°C and the time 2h. Such conditions were chosen as they were on the milder side to prevent hydrolysis of the IL.

In addition to the cellulose laurate samples synthesised using the recycled IL the IL itself was also analysed in between reactions. Namely, the viscosity of the liquid itself and the viscosity of the solution after MCC was attempted to dissolve in it. Shear rate as a controlled variable in figure 2.3.3.1 was chosen as it is an important factor to consider in talking about industrial use. Temperature dependence presented in figure 2.3.3.2 was chosen as the reaction temperatures for the synthesis vary.

In figure 2.3.3.1, which shows the viscosity versus shear rate plots of fresh [mTBNH][OAc], the once distilled (Dist-1) and the twice distilled (Dist-2) ionic liquid, there is a very clear difference between Dist-1 to Dist-2. While fresh IL and Dist-1 are quite similar, Dist-2 has a much higher viscosity at low shear rates. The difference levels off at higher shear rates, as all of the ILs act as non-Newtonian fluids due to the high viscosity.

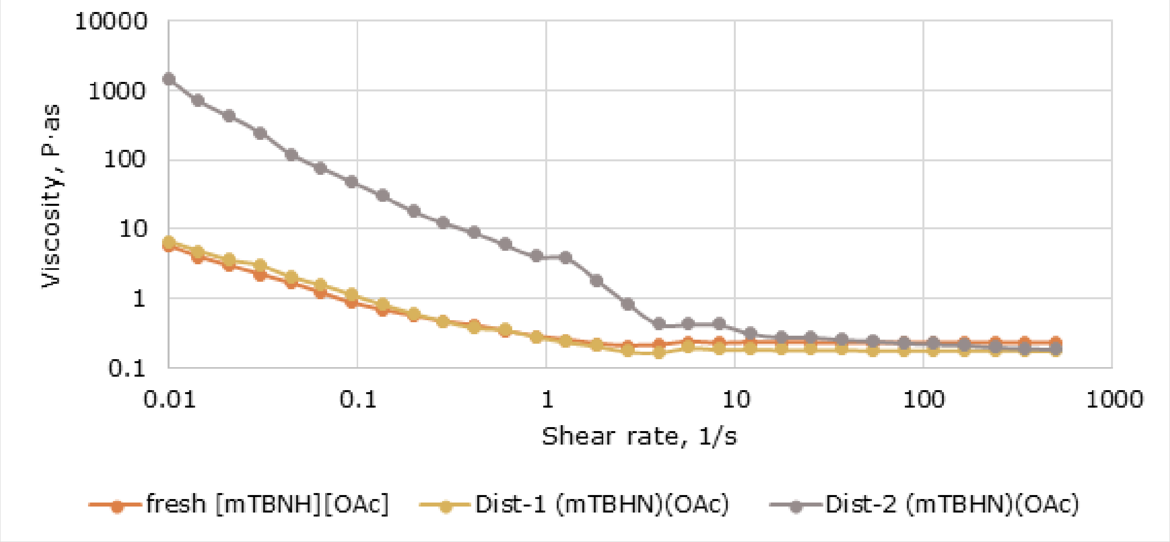


Figure 2.3.3.1 Shear rate dependence on viscosity of fresh and recycled IL

A very similar trend was seen with the viscosity temperature dependence graph (figure 2.3.3.2) of MCC dissolved in fresh IL, Dist-1 and Dist-2 as well. We see that, again, MCC in Fresh IL and Dist-1 are quite similar but there is a very sharp drop off of viscosity of the MCC dissolved in Dist-2. The MCC was dissolved in IL samples on the same day and at temperature around 70-80°C. The explanation of why the difference revealed is that there is a rapid degradation of MCC in Dist-2, probably due to hydrolysis.

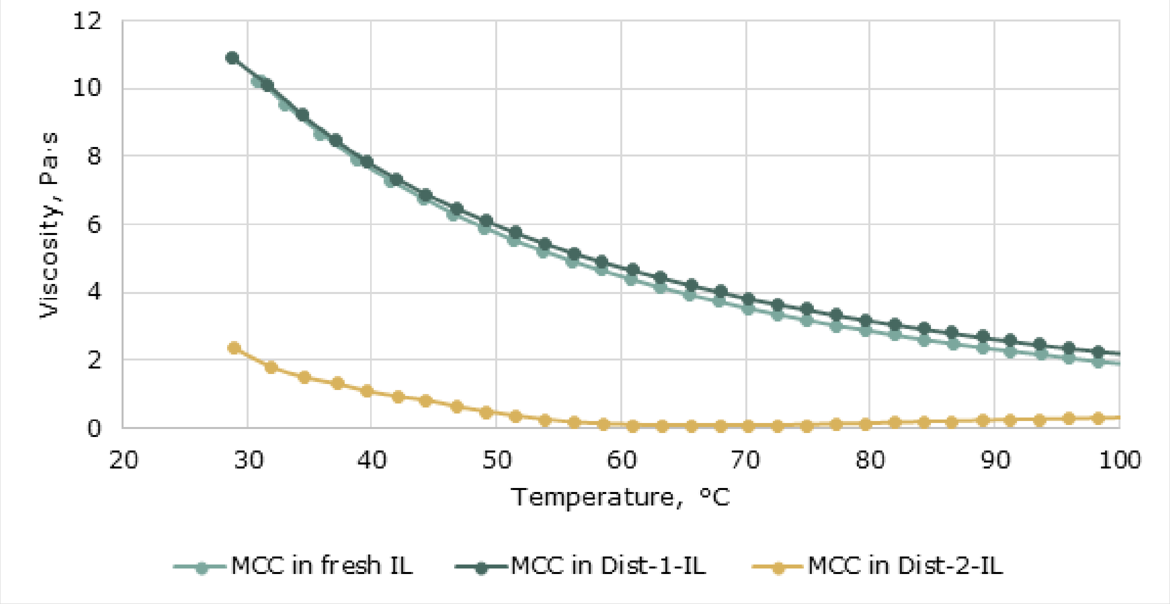


Figure 2.3.3.2 Temperature dependence on viscosity for MCC dissolved in fresh and recycled IL

In figure 2.3.3.1 the FTIR spectra for cellulose laureate samples prepared in fresh, Dist-1 and Dist-2 IL are shown together with a spectra of MCC for comparison. It is clearly visible that acylation has definitely taken place in CL-Re-0 and CL-Re-1 as evidenced by the characteristic peak at 1746 cm^{-1} indicative of a carbonyl group. However, a probable lower DS of CL-Re-1 is suspected because of the wide high peak at 3340 cm^{-1} which is correlated with a vibration in -OH groups. The more intense this peak the lower the DS probably is, as proportionally fewer ester groups have been formed.

Looking at the CL-Re-2 spectra, we see even more evidence that Dist-2 IL is not usable anymore. The positions of peaks are practically identical to that of pure MCC which means that not any or a very low amount of esterification has taken place.

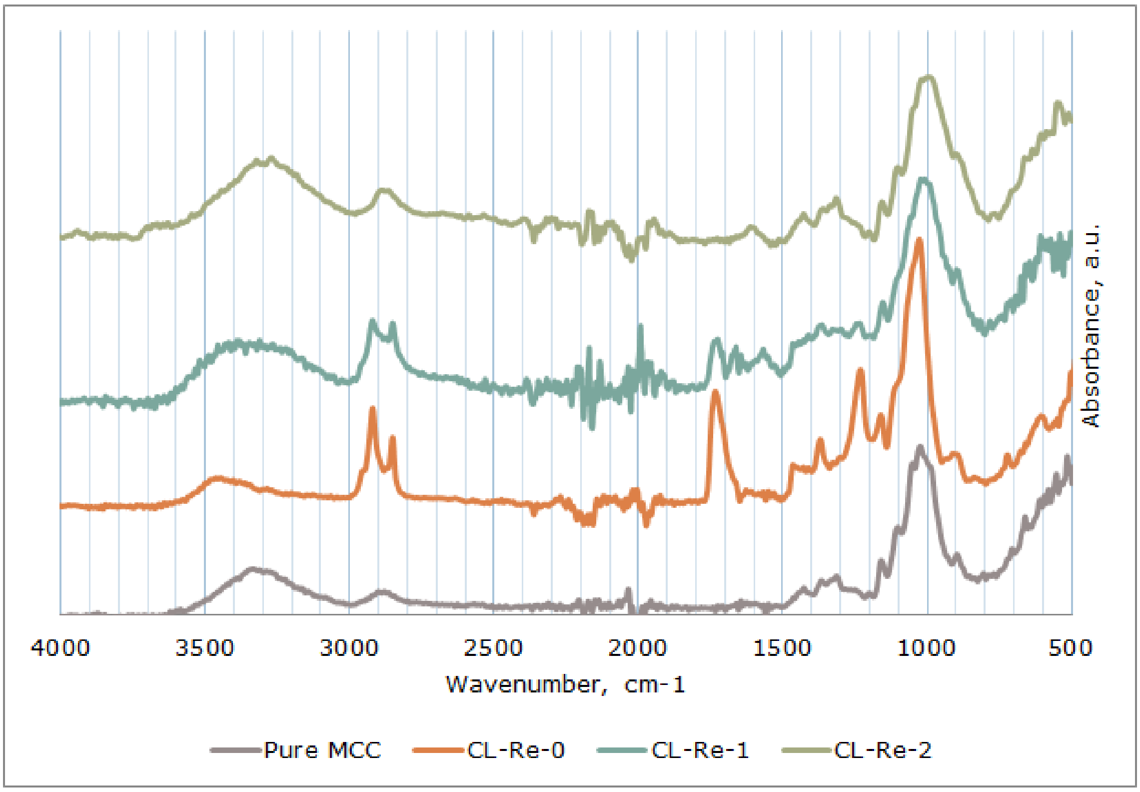


Figure 2.3.3.1 FTIR spectra of cellulose laureate samples synthesised in pure and recycled [mTBN][OAc] compared to pure MCC

The suspicions formed by FTIR analysis were confirmed when DS values were calculated from titration results. Table 2.3.3.1 shows what was already inferred previously. The CL-Re-0 sample had the greatest DS of 0.57, there was a drop in DS with Dist-1 and using Dist-2 for the synthesis was almost completely unfruitful. The DS values of CL-Re-0 being 0.57 and dropping down to 0.25 for CL-Re-1 is around a 43% loss. Going from that to only 0.08 for Re-2, which was basically equivalent to pure MCC at that point, was a very sharp drop in quality indeed.

Table 2.3.3.1 Table showing the DS values and solubility results for CL synthesised in pure and recycled [mTNBH][OAc]

Sample	**Soluble in…**	**DS**
CL-Re-0	DMSO	0.57
CL-Re-1	Not soluble	0.25
CL-Re-2	Not soluble	0.08

It can be concluded that while the first recycling cycle results in the IL possibly degrading and being polluted a little with the synthesis also resulting in a lower quality product, the second cycle of distillation contains some pollutants and hydrolyzing substances which cause cellulose degradation and prevent cellulose acylation entirely.

While a dropping quality was expected, it was especially interesting that the second distillation dropped it so steeply. One possible explanation for this could be the IL's thermal stability and its threshold for temperature changes. It could be that with the first evaporation the thermal stability threshold was being approached, but not exceeded so when considering extra stresses on the molecule throughout the second synthesis it was simply taken to its breaking point.

Another reason for the drop in quality could also be the compounding contamination from the substances involved in the synthesis process. It was expected that not all of the cellulose gets dissolved and even if it does, then not all of that dissolved cellulose will react with the vinyl ester. Having contaminants of cellulose, remnants of dissolved cellulose, the cellulose ester, and the vinyl ester itself in the solution was unavoidable and not all of it gets removed through distillation. Some amount of random contamination comes from the container the washing liquid was stored in and the distillation equipment as well, but this is likely so small as to not be substantial enough to account for the dramatic changes. Essentially, the compounding contamination of the IL is what partly leads to a lower quality product whereby its cellulose dissolving ability.

Further testing should be done for pinpointing the exact factors that lead to the IL breaking down. Possible areas of research could be distillation optimisation to minimise loss of favourable properties of the distillate and further development of the synthesis process by finding optimal parameters that prioritise for IL recovery right after synthesis.

CONCLUSIONS

To conclude, successful catalyst-free synthesis of cellulose acetate, -laurate, -myristate, and -stearate by homogenous transesterification of cellulose with vinyl esters has been conducted. The novel IL is very effective towards cellulose dissolution and transesterification, where traces of superbase mTBNH (from IL) possibly serve as an intrinsic catalyst.

Reaction conditions for cellulose esters have been optimised.

The recycling and reusing of [mTBNH][OAc] needs additional efforts for its purification.

SUMMARY

Within the thesis at hand, homogenous cellulose transesterification with the novel ionic liquid [mTBNH][OAc] was tested along with evaluating the efficiency of its recycling. Additionally, as not a high enough degree of substitution and solubility properties were received for cellulose stearate, synthesis optimisation was also undertaken.

The synthesis of cellulose acetate, cellulase laureate, cellulose myristate and cellulose stearate was done under a set of predetermined conditions of 3.5% microcrystalline cellulose by mass of solvent solution, a ratio of ionic liquid to dimethyl sulfoxide of 1:1, ratio of anhydroglucose units to vinyl ester of 1:3, the reaction temperature of 70°C and time of reaction of 2.5 h. This resulted in samples that all, apart from stearate, had a degree of substitution above 1.3. From cellulose acetate, -laurate and -myristate films could also be produced as they were solvent in pyridine. A trend, however, was evident as with the increasing of the aliphatic moieties of the esters used as the degree of substitution reacted inversely due to higher steric hindrance. The samples were compared with pure microcrystalline cellulose by way of Fourier transform infrared spectra and all samples showed specific peaks at relevant wavenumbers. An accurate degree of substitution value was obtained with nuclear magnetic resonance spectroscopy for samples that were soluble in either dimethyl sulfoxide or pyridine.

As the cellulose stearate sample synthesised under the initially chosen parameters was not soluble in dimethyl sulfoxide or pyridine its degree of substitution was determined by way of titration. The lack of solubility and the low degree of substitution, however, meant synthesis optimisation had to be done. Each of the already mentioned predetermined conditions was changed around and even a catalyst was tested until a sample with a degree of substitution of 1.4 was achieved. The optimal conditions were found to be 3.5% microcrystalline cellulose by mass of solvent solution, a ratio of ionic liquid to dimethyl sulfoxide of 1:1, ratio of anhydroglucose units to vinyl ester of 1:6, the reaction temperature of 80°C and time of reaction of 3 h.

As an objective of the thesis was also to test the efficiency of recycling [mTBNH][OAc], three samples of cellulose laurate were synthesised without a cosolvent. The degree of substitution for the samples had to be determined by way of titration. Fourier transform infrared spectroscopy was also performed on the samples and results were compared to pure microcrystalline cellulose. Additionally, between syntheses the

rheology properties of the ionic liquid itself and microcrystalline cellulose dissolved in the distilled ionic liquid were tested. The result echoed by all analysis methods points to the ionic liquid losing efficiency slightly after one round of recycling and having a sharp drop off after the second. The exact reason as to why and at what point the degradation in efficacy is happening has not been pinpointed yet and is the subject of another upcoming thesis. It is possible to hypothesise though, that probably the thermal load is too intense and that contamination from each subsequent synthesis compounds enough as to cause irreparable issues.

KOKKUVÕTE

Käesolevas lõputöös testiti tselluloosi homogeenset ümberesterdamist uudse ioonse vedelikuga [mTBNH][OAc] ja hinnati selle taaskasutamise efektiivsust. Lisaks, kuna tselluloosstearaadi asendus- ja lahustuvusomadused ei olnud piisavalt head, viidi läbi ka sünteesi optimeerimine.

Tselluloosatsetaadi, tselluloosilaureaadi, tselluloosimüristaadi ja tselluloosstearaadi süntees viidi läbi eelnevalt kindlaksmääratud tingimustes, mis olid järgmised: mikrokristalliline tselluloosi mass 3,5% lahustilahuse massist, ioonse vedeliku ja difmetüülsulfoksiidi suhe 1:1, anhüdroglükoosiühikute suhe vinüülestriga 1:3, reaktsioonitemperatuur 70°C ja reaktsiooniaeg 2,5 tundi. Nende tingimuste tulemusel saadi näidised, mille kõigi, välja arvatud stearaadi, asendusaste oli üle 1,3. Tselluloosatsetaadist, -lauraadist ja -müristaadist oli võimalik toota ka kilesid, kuna need lahustasid püridiinis. Siiski esines ilmselge trend, mille alusel sünteesitud estrite alifaatsete osade suurenemine oli kõrgemate steeriliste takistuste tõttu pöördvõrdeline asendusastmega. Proove võrreldi puhta mikrokristalliinse tselluloosiga Fourier' teisenduse infrapunaspektrite abil ja kõik proovid näitasid spetsiifilisi piike asjakohastel lainenumbritel. Täpne asendusastme väärtus saadi tuumamagnetresonantsspektroskoopia abil proovide puhul, mis lahustusid kas dimetüülsulfoksiidis või püridiinis.

Kuna algselt valitud parameetrite alusel sünteesitud tselluloosstearaadi proov ei lahustu dimetüülsulfoksiidis ega püridiinis, määrati selle asendusaste tiitrimise teel. Lahustuvuseomaduste puudumine ja madal asendusaste tähendasid sünteesi optimeerimise vajadust. Kõiki juba mainitud ettemääratud tingimusi muudeti ning testiti isegi katalüsaatorit, kuni saadi proov, mille asendusaste oli 1,4. Leiti, et optimaalsed tingimused on 3,5% mikrokristalliinset tselluloosi lahustilahuse massi kohta, ioonse vedeliku ja dimetüülsulfoksiidi suhe 1:1, anhüdroglükoosiühikute ja vinüülestri suhe 1:6, reaktsioonitemperatuur 80 °C ja reaktsiooniaeg 3 tundi.

Kuna lõputöö eesmärk oli ka testida [mTBNH][OAc] taaskasutuse efektiivsust, sünteesiti ilma kaaslahustita kolm tselluloosilauraadi näidist. Näidiste asendusaste määrati tiitrimise teel. Näidistele tehti ka Fourier' transformatsiooni infrapunaspektroskoopia ja tulemusi võrreldi puhta mikrokristalliinse tselluloosiga. Lisaks testiti sünteeside vahel ioonse vedeliku enda ja destilleeritud ioonses vedelikus lahustatud mikrokristalliinse tselluloosi reoloogilisi omadusi. Kõigi analüüsimeetodite poolt toetatud tulemused viitavad sellele, et ioonse vedeliku efektiivsus väheneb veidi pärast ühte taaskasutuse tsüklit ja järsult pärast teist. Täpset põhjust, miks ja millal efektiivsuse halvenemine toimub, ei ole veel täpselt välja selgitatud ja see on ühe teise töös oleva lõputöö teema. Siiski on oletatav, et tõenäoliselt on termiline koormus liiga intensiivne ja igast järgnevast sünteesist saastub iooniline vedelik piisavalt, et tekitada korvamatuid probleeme.

Kokkuvõtteks võib öelda, et tselluloosatsetaadi, -lauraadi, -müristaadi ja -stearaadi edukas katalüsaatorivaba süntees homogeense ümberesterdamise teel on [mTBNH][OAc] õigetel tingimustel võimalik ja väga tõhus.

[mTBNH][OAc] ringlussevõtt ja taaskasutamine aga osutus vähemalt testitud protsessi ja parameetrite puhul suhteliselt viljatuks.

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