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

PREPARATION OF THERMOPLASTIC CELLULOSE IN IONIC LIQUID ENVIRONMENT

TERMOPLASTSE TSELLULOOSI VALMISTAMINE IOONSE VEDELIKU KESKKONNAS

MASTERS THESIS

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Tallinn 2021

(*On the reverse side of title page*)

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Department of Materials and Environmental Technology

PREPARATION OF THERMOPLASTIC CELLULOSE IN IONIC LIQUID ENVIRONMENT

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Study program: KVEM 12/18- Technology of Wood, Plastic and Textile.

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Thesis topic:

(in English) Preparation of thermoplastic cellulose in ionic liquid environment.

(in Estonian) Termoplastse tselluloosi valmistamine ioonse vedeliku keskkonnas.

.

Thesis main objectives:

1. To synthesize thermoplastic cellulose derivatives in ionic liquid environment.
2. To perform qualitative study of cellulose derivatization efficiency by infrared spectroscopy.
3. To perform quantitative evaluation of cellulose derivatives degree of substitution by infrared spectroscopy.
4. Validation of evaluated DS values with those measured by acid-base titration.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature overview, synthesis of [BMIM]Cl, synthesis of cellulose acetate for hands on practice.	May 2020
2.	Synthesis of cellulose stearate (CS), synthesis of cellulose laurate (Lauroyl chloride).	Oct 2020
3.	Titration and FTIR of CS and CL (Lauroyl Chloride).	Nov 2020
4.	Pre-treatment of alpha cellulose, Synthesis of cellulose laurate (Vinyl laurate)-CL(VL), Titration and FTIR of CL(VL).	March 2021
5.	Recycling of IL, Quantitative analysis of DS by FTIR from CL(VL), Solubility test, DSC analysis.	May 2021

Language: English **Deadline for submission of thesis:** 24.05.2021

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CONTENTS

PREFACE

The basic aim of this study is to prepare thermoplastic cellulose derivatives in ionic liquid environment. The idea is to utilize cellulose which is most widely available natural polymer for environment sustainability and growth of circular economy. This study comprises of learning of complete synthesis process and characterization of prepared cellulose derivative which are cellulose stearate and cellulose laurate along with quantitative evaluation of DS by using FTIR.

CS and CL are prepared by using green solvent, which is ionic liquid as reaction media. Acylation reagents such as stearoyl chloride, lauroyl chloride, and vinyl laurate are used for cellulose modification. Different reaction temperatures and reaction times are used during synthesis of cellulose laurate of different molar ratios to find out the reaction conditions needed for synthesis of derivative with demanded DS.

Degree of substitution of all prepared cellulose derivatives is determined by saponification reaction followed by back titration. The correlation between characteristic infrared light peaks intensity and integral area with DS determined by titration was established. Developed correlation formula allows evaluating DS of cellulose laurate by FTIR that is much faster and simpler than by titration and much cheaper by NMR.
Highly acylated commercial grade cellulose acetates purchased from Sigma-Aldridge and Esfil Tehno were also studied by titration and FTIR as reference materials.

I would like to thank specially to my supervisor Dr. Ilia Krasnov because without his supervision, guidance and focus I would not be able to complete this thesis. I also want to thank Tallinn University of Technology and Polymer department team for giving me opportunity to understand my thesis and use its resources. At last, I also want to thank my wife Hafsa Farzan for her understanding, motivation, and dedications during the period of my master studies.

Keywords: Cellulose derivative, ionic Liquid, reaction media, green solvent, degree of substitution.

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LIST OF ABBREVIATIONS AND SYMBOLS

ACP	Alpha cellulose Paper
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
[BMIM]BF$_4$	1-butyl-3-methylimidazolium tetrafluoroborate
Br$^-$	Bromide ion
[BF4]$^-$	Tetrafluoro bromide
CA	Cellulose acetate
CS	Cellulose stearate
CL	Cellulose laurate
CAS	Cellulose acetate stearate
CAL	Cellulose acetate laurate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
[CF3SO2]$^-$	Trifluoromethanesulfonic anion
Cl$^-$	Chloride ion
CL(VL)	Cellulose Laurate (Vinyl Laurate)
CPC	Craft Paper Cellulose
CF	Cotton fiber
DSC	Differential scanning calorimetry
DS	Degree of substitution
DP	Degree of polymerization
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
DS$_{Tit.}$	Degree of Substitution from titration
DS$_{FTIR}$	Degree of Substitution from FTIR by using intensity/area.
DAC	Di-acetate Cellulose
[EMIM]Cl	1-ethyl-3-methylimidazolium chloride
[EMIM]Ac	1-butyl-3-methylimidazoliumaccetate
EA	Ethyl Acetate
FTIR	Fourier transform infrared spectroscopy.
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
IL	Ionic liquid
ILs	Ionic liquids
[N(CN)2]$^-$	Dicyanamide anion
NMR	Nuclear Magnetic Resonance
NaOH	Sodium Hydroxide

OM	Optical Microscopy
$[PF6]^-$	Tetrafluoro phosphide
R-[BMIM]Cl	Recycled 1-butyl-3-methylimidazolium chloride.
R-[EMIM]Cl	Recycled 1-ethyl-3-methylimidazolium chloride.
R-Alcohol	Recycled Alcohol
R_I	Intensity Ratio
R_A	Area Ratio
SEM	Scanning electron microscopy
Synt.	Synthesis
Tit.	Titration
Tm	Melting Temperature
Tc	Crystallization Temperature
Tg	Glass Transition Temperature
VOCs	Volatile organic compounds
VL	Vinyl Laurate
y	Constant of peak intensity and integral area with and without intercept
x	Constant of peak intensity and integral area without intercept

INTRODUCTION

Over the past decades, preparation of cellulose derivatives is one of the major fields of research for scientists to attain environmental sustainability and for balancing of planet's ecosystem.

As it is known that cellulose is the vastly available polymer in nature [1]. Because of its high crystallinity, it is hard to process cellulose directly. So, cellulose modification helps to obtain its derivatives for further processing instead of processing cellulose itself. Manageable properties and nature loving cellulose derivatives could be used in several applications [2].

Thermoplastic cellulose derivatives can be prepared in a reaction media which is ionic liquids (ILs) by using different reagents for example acyl chlorides. These reagents can be used to produce derivatives like cellulose stearate (CS), cellulose acetate (CA), cellulose laurate (CL) and mixed cellulose derivative like cellulose acetate stearate (CAS), cellulose acetate laurate (CAL), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). Synthesis of these short and long chain cellulose fatty acid esters could be done by homogenous and heterogenous acylation [3]. In homogenous acylation, properties of mixture remain same throughout the process, like in case of cellulose once it is dissolved in ionic liquid give uniform solution having property of substituting molecules of acylating agent in place of free hydroxyl molecules of cellulose. Once the substitution of acylating agent molecules into cellulose is done, the product obtained is called cellulose derivative with its own specific properties at that point molecules of cellulose and acylating agent molecules are inseparable. While in heterogenous acylation properties are change within the system for example if we use catalyst during acylation process of cellulose, the catalyst worked only to fasten up the reaction with its specific properties. The catalyst will not get substituted or diffused with cellulose molecules.

Previously, characterization techniques used for analysis of cellulose derivatives are differential scanning calorimetry (DSC), Fourier Transformed Infrared Spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), optical microscopy and scanning electron microscopy (SEM) [4], [1], [2]. These characterization techniques were used to analyse the thermal, structural, and surface properties of produced thermoplastic cellulose derivatives.

Determination of degree of substitution of acylated thermoplastic cellulose derivatives is another main step in the process. Degree of substitution (DS) which is number of substituent groups attached on a base, unit also plays an important role in defining nature and functionality of prepared cellulose derivatives. Cellulose degree of substitution is ranges from 1 to 3. There are different kinds of methods from which we could calculate degree of substitution, development in getting accuracy in determination of DS is needed anytime [3]. Liquid-state NMR and solid-state NMR are the two famous characterization techniques used to get different types of information about product such as morphology, Regio chemistry, tacticity, stereochemistry, structures, and geometry. Characterization from NMR is precise and less time-consuming process, but it is very expensive as compared to other methods [5].

Conventionally, titration is used for DS determination. The main disadvantage of this method is that it is time and material consuming [3]. The need of new scientific ways for fast, easy, and trustworthy quantitative analysis for obtaining DS is highly beneficial. Fourier transformed infrared spectroscopy is an indirect and non-destructive method for DS determination [3].

This thesis comprises on the study of two different thermoplastic cellulose derivatives such as CS and CL. At first four different types of ionic liquid were tested for dissolution of cellulose. 1-ethyl-3-methylimidazoliumchloride [EMIM]Cl, 1-butyl-3-methylimidazoliumaccetate [BIMIM]Ac, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF_4, 1-butyl-3-methylimidazolium chloride [BMIM]Cl. It was found that chloride-based IL showed better dissolution of cellulose so for further experimental work 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-ethyl-3- methyl imidazolium chloride [EMIM]Cl, were used as the reaction media.

The main aims of this thesis are to prepare thermoplastic cellulose (CS and CL) by dissolution of cellulose in IL and following modification along with quantitative analysis of product DS by titration and FTIR. The long chain fatty acid esters of cellulose with carbon chain lengths C_{12} (cellulose laurate) and C_{18} (cellulose stearate) obtained as product.

The IR absorption peak intensity and area ratios are calculated by using two peaks at wavenumbers 1758 cm^{-1} corresponding to C=O bond of ester bond, (present in cellulose esters) and at 1015 cm^{-1} of C-O-C bond, of cellulose back bone chain (present unchanged in both cellulose and its derivatives).

Different reaction conditions (time and temperature) tested to find out the conditions for synthesis of materials with demanded DS.

Moreover, in this work, we also recycled solution of ionic liquid and solvents by using rotary evaporator in which volatile solvents were evaporated at certain temperature and pressure and then collected separately. After evaporation, the obtained solution was tested for dissolution ability for cellulose. The collected solvents were used again in washing and precipitation of cellulose derivatives during synthesis.

Development of IR-absorption intensity ratios vs DS correlation equation for long chain fatty acid esters is a new and fast method for DS determination.

CHAPTER 1: LITERATURE OVERVIEW

1. Materials

1.1. Cellulose

Cellulose, a polysaccharide, is the main and basic component of plant cell walls. Cellulose is widely available as because of the main component of plant cell walls, over 90% present in pure cotton and 40% - 60% in woods [6], [7]. Formation of cellulose is due to β-glucose units which are presented as β (1→4). The excellence of structural and physical properties of cellulose is due to strong hydrogen bonding interactions which results in semicrystalline structure of its derivatives with remarkable tensile properties because of highly crystalline part of polymer [2].

Hydrogen bonding as well makes cellulose insoluble and not meltable. Thus, cellulose cannot be processed in the manner thermoplastic materials- it decomposes before it melts. But derivatization of cellulose allows transferring it into material that could be processed in dissolved or molten state.

Cellulose has different degree of polymerization (DP) depending on its source. For cellulose powder the number of glucose repeating units range from 100-300, 20,000 for cotton or even it will go up to 40,000 for some kinds of algae. High values of DPs could decrease to 2500 because of purification of cellulose [8].

1.1.1. Structure of cellulose

Figure 1 is showing the basic chemical structure of cellulose. It is shown that the structure formed of β-1,4-linked glucopyranose rings. In structure of cellulose there is a cellobiose unit, which is formed by the arrangement of adjacent monomer units in which the glucoside oxygens points in opposite direction and the repeating unit of chain of cellulose is composed of two β-D-glucopyranose rings rotated with respect to each other [9].

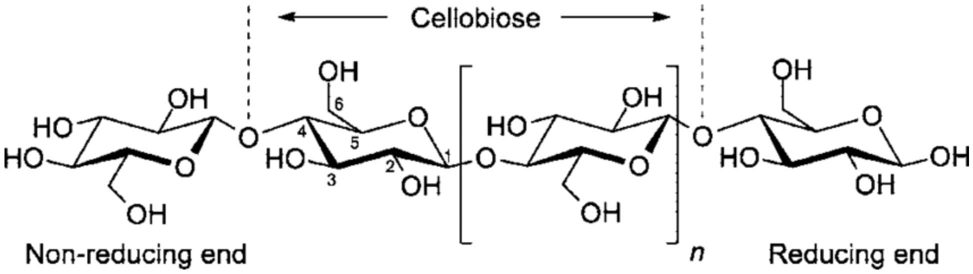


Figure 1. Chemical structure of cellulose and numbering system of carbon atom of anhydrous glucose units [47]

It is shown that carbon atom 2,3 and 6 is available for reaction as they carry free hydroxyls. The conformation shown in *figure 1* is called as chair conformation as it has lowest level of energy and is most stable one [10]. As it is shown in figure that carbon atom C_1 is attached with two oxygen atoms, C_2 and C_3 are attached with hydroxyl groups, C_4 attached with one Oxygen atom and the biggest substituent group hydroxyethyl is attached to C_5. The rings form by these carbon atoms are called as β-D-glucopyranose rings in which the C-O-C bond angle between two rings is 116° [9].

All the β-1,4-linked glucans have two ends, the first end is called reducing end which contains unsubstituted cyclic hemiacetal while other is non-reducing end contains addition hydroxyl group at C_4 [10].

1.1.2. Functional and reaction capabilities of cellulose

Reaction abilities of cellulose is basically attaining from the availability of free hydroxyl groups of D-glucopyranose units and the responsive behavior of β-1,4-glycosidic bonds between the glucose repeating unit to the hydrolytic breakage [8].

The modified chemical conversion is proposed by one primary (C_6) and two secondary (C_2 and C_3) hydroxyl groups inside each monomer unit. These primary and secondary groups take part in all types of alcoholic reactions such as esterification, etherification, and oxidation. The availability of these groups, due to spatial arrangements, in homogenous reaction media position 2 and 6 are most favorable as compared to position 3 but the reactivity of C_2 and C_6 hydroxyl groups mainly depends upon the type of reagent, reaction and reaction media in the synthesis. The reaction capabilities of C_2 are inherently higher as compared to C_6 as the protons can easily be removed from the group at position 2 [8].

1.1.3. Cellulose sources

In this work, pure cotton fibers and Hahnemuhle fine art alpha-cellulose paper fine powder were used.

1.2. Ionic Liquids (ILs)

The ionic liquids (ILs) are salt with melting point (Mp) below 100°C [11]. For hydrogen bonding ILs must have strong hydrogen bond donor which is a cation and strong hydrogen bond acceptor which is an anion. Commonly used cations are sulphonium, phosphonium, imidazolium, pyridinium and ammonium with several alkyl or aromatic substituents [12]. Cl^-, Br^-, $[BF_4]^-$, and $[PF_6]^-$ are the most common anions [13]. *Figure 2* is showing common cation ions and anions used for formation of ionic liquid.

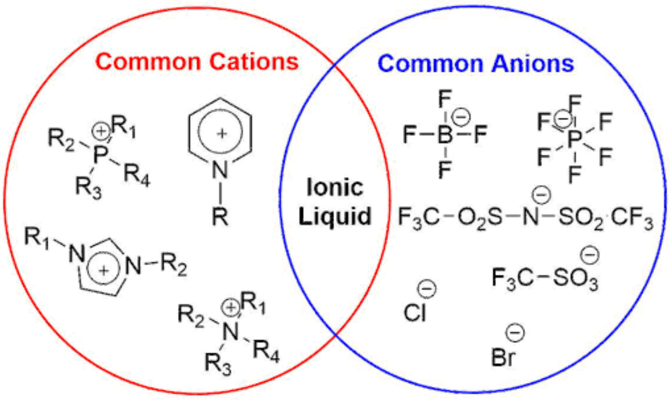


Figure 2. Common cations and anions used in ILs formation [49]

1.2.1. Synthesis of ionic liquids

ILs can be synthesized by two ways, alkylation or via protonation. The most common reaction of alkylation comprises of the usage of 1-methylimidazole with haloalkanes. This process is cheap because of the inexpensive price of haloalkanes, and they are also easily available. Ion’s reactivity increases with the usage of iodide, bromide and chloride, the most reactive ones are iodide [14].

The protonation reaction happens when the addition of nitric acid held in the aqueous solution of ethylamine. Later, excessive quantity of amine could be evaporated at temperature around 60^0C under vacuum conditions. Through quaternization, the obtaining of ions is simpler and easier as it is done by adding mixture of required alkylating agent amine during stirring and heating [15].

1.2.2. Purification of ionic liquids

Impurities in ILs can be classified into three major categories. One of the categories is the impurities that come from the source materials like contamination of dust, moisture, and other substances in source materials before synthesis. The second category is the impurities during reaction time like side product presence during alkylation reaction, degradation due to heating and unreacted source material presence and left-over products like alkali, metals, halide, or salts. Third category from which impurities occur in ionic liquid is unwanted solvents which were used in excess quantities [14].

Purification of ILs can be done by two ways, purification of finally produced ionic liquid or purification of ionic liquids at each step of synthesis [14]. For purification, all the starting materials must be dried under vacuum on required temperatures for removal of moisture contents from source materials. Stirring also helps in evaporation of unreacted substances at low temperatures under vacuum. Finally produced ionic liquid could be purified by washing it with solvents like, ethanol; ethyl acetate etc. and salts could be washed up by washing hydrophobic IL with distilled water at high-speed stirring.

1.2.3. Properties of Ionic Liquids

Ionic liquids are molten salts completely consists of ions. The characteristic properties include low melting point and ionicity. Because of their manageable properties such as polarity, solvent miscibility, and hydrophobicity they can be used as alternatives to other organic solvents. Other properties of ILs are thermal stability, their negligible vapor pressure in liquid state, coordination stability, solubility, and conductivity [16]. Density of ILs is less than 1 g/cm^3 that means they are less dense than water. Viscosity of ILs range from about 10-500 cP. Viscosity increases with increase in chain length and decreases on heating [17].

1.2.4. 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-ethyl-3- methyl imidazolium chloride [EMIM]Cl as reaction media

In this work, thermoplastic cellulose stearate and cellulose laurate were produced from cotton fibers and alpha-cellulose paper. [BMIM]Cl and [EMIM]Cl were used as reaction media.

The major factor in using ionic liquid as reaction media is the polarity of IL. If we need excellent dissolution of cellulose in ILs then we require high polarity ionic liquids like alky imidazolium-based liquids [18]. To do the quaternization reaction of [BMIM]Cl, n-methylimidazole and chlorobutane are used as reagents. The reaction shown in *figure 3*.

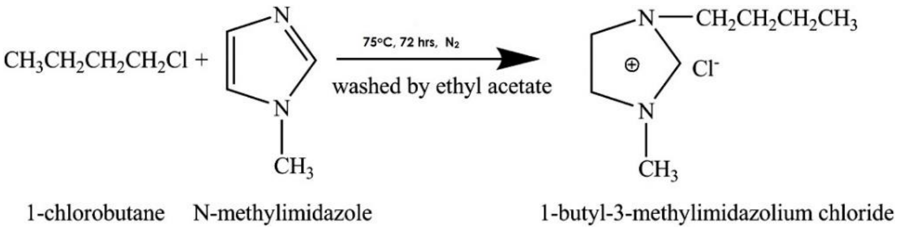


Figure 3. Chemical Reaction in preparation of [BMIM]Cl [51]

But it could also be synthesized by the reaction of 1-choloro ethane and 1-methyl immidazole in the presence of acetonitrile [19].

1.2.5. Drying of ionic liquid

Hygroscopic ionic liquids, after synthesis there could contain some quantity of moisture. To avoid any decomposition of product, ionic liquids must be dried. After washing with ethyl acetate, drying of ionic liquid must be done during continuous stirring and heating. Vacuum should be applied for accuracy and fast drying [14].

1.2.6. Recycling of ionic liquid for reuse

Different co-solvents and solvents could be used together with ionic liquid at synthesis of thermoplastic cellulose derivatives. Separation of these solutes and solvents could be done by distillation. Due to low volatility of ILs, low boiling point compounds can be separated from ILs easily [20].

1.3. Acylation reagents

In general, for modification of cellulose acidic halides are used. Some other reagents are also used like vinyl esters. Acyl chlorides have more reaction capabilities than sulfonyl chlorides [21]. Usually, acidic halides are formed by the reaction of carboxylic acid with reagents like thionyl chloride or oxalyl chloride [22].

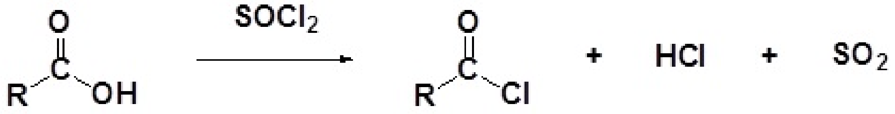


Figure 4. Chemical Reaction in preparation of Acid Halides [22]

1.3.1. Lauroyl Chloride [23]

Lauroyl chloride is an acylating agent could be used in the modification of cellulose with twelve carbon atoms in it. The molecular formula and molecular weight of lauroyl chloride is $C_{12}H_{23}ClO$ and 218.76 g/mol respectively, it can also be called as dodecanoyl chloride. The structural formula of lauroyl chloride is as below.

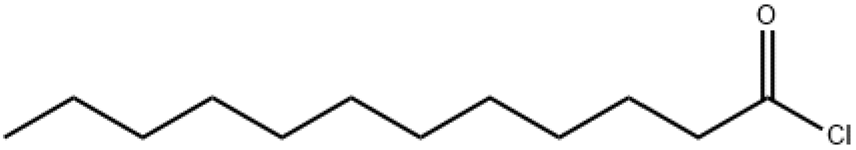


Figure 5. Structural formula of lauroyl chloride [23]

It is highly moisture sensitive and colorless liquid which do not allow to meet water. The density of lauroyl chloride is 0.946 g/mL and it could boil up at 134°C-137°C. Its solubility in methanol and ethanol is excellent.

1.3.2. Stearoyl Chloride [24]

Stearoyl chloride is a long chain fatty acid with eighteen carbon atoms in it. It is clear to yellowish liquid having density of 0.897 g/mL and its boiling point is 174°C-178°C. The molecular formula and molecular weight of stearoyl chloride is $C_{18}H_{35}ClO$ and 302.92 g/mol respectively, it can also be called as octadecanoyl chloride or stearic acid chloride. The structural formula of stearoyl chloride is as below.

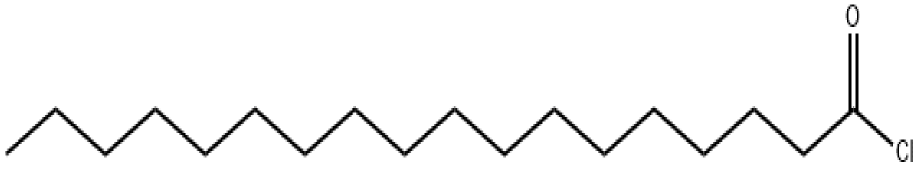


Figure 6. Structural formula of stearoyl chloride [24]

1.3.3. Vinyl Laurate [25]

The molecular formula and molecular weight of vinyl laurate is $C_{14}H_{26}O_2$ and 226.35 g/mol respectively, it can also be called as vinyl do-decanoate or lauric acid vinyl ester. The structural formula of vinyl laurate is as below.

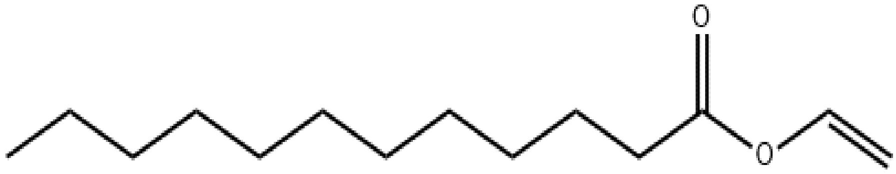


Figure 7. Structural formula of vinyl laurate [25]

VL is slightly soluble in water (1g/L). The density of vinyl laurate is 0.871 g/ml, and it could boil up at 254°C.

1.4. Solvents

Most of the chemical reactions happen between liquids phases in solution mixtures. Solvents are the liquids use to disintegrate solid reactants or dissolve liquids or gasses in the solution mixture. Solvents have great impact on rate of reaction. Their reactivity and functionality are under study since over a century. Selection of proper solvents for chemical reaction is also important for future physical processes [26].

Solvents are produced from crude oil while physical processes adopted by petrochemical industries are used to prepare aliphatic and aromatic hydrocarbons. [27]

1.5. Cellulose Derivatives

When a compound gone through chemical changes and converted into a new compound which have better and manageable properties to process and analyzation, the process called as derivatization [28]. Cellulose could also be derivatized by its chemical modification to form cellulose derivatives which are easy to process and have excellent manageable properties for different application.

The process of cellulose derivatization involves the reaction between 2,3, and 6 hydroxyl groups of cellulose with reagents used for modification [10]. The modified chemical conversion is proposed by one primary (C_6) and two secondary (C_2 and C_3) hydroxyl units inside each monomer unit [8]. These hydroxyl group consists of 32% by weight of cellulose. The chemical reactivity of cellulose is explained by its super molecular structure of its solid state [29]. Derivatizing cellulose involves the introduction of several functional groups into free hydroxyl groups of glucose units [30].

Cellulose is packed into crystalline and amorphous parts. Because of strong inter and intra molecular hydrogen bonding in crystalline part, the hydroxyl groups of this part are less accessible for reagents than the ones in amorphous part. So, the reaction of modification usually starts from hydroxyl groups of amorphous regions. For a uniform and balanced chemical modification, de-crystallization and swelling is needed [29].

To be sure of properties and functionality of cellulose derivatives, determination of degree of substitution could be done. DS values range from 0 to 3 which shown that how much hydroxyl groups are substituted with functional groups. Higher values of DS show that cellulose is mostly or fully converted to desired polymer and it could be soluble in organic solvents. Solubility of cellulose derivatives in water decrease with increase in DS and vice versa [29],

Most reactions of cellulose modification are esterification and etherification [10]. Films, filters, glasses, frames, toys, packaging, utensils etc., could be made from thermoplastic cellulose derivatives [31].

1.5.1. Esterification

Esterification is a chemical process in which dehydrating agent is present when reaction took place between cellulose and acid shown in *equation 1*. Or when cellulose is esterified with alkyl chlorides as shown in *equation 2*. Cellulose could also be esterified by reacting with acid anhydrides, shown in *equation 3* [10].

$$Cell - OH + HNO_3 \leftrightarrow Cell - O - NO_2 + H_2O \text{ -------- (eq. 1)}$$

$$Cell - OH + R - CO\,Cl \rightarrow Cell - CO - R + HCl \text{------- (eq. 2)}$$

$$Cell - OH + (CH_3CO)_2O \rightarrow Cell - CO - CH_3 + CH_3COOH \text{------- (eq. 3)}$$

From above reactions, we can get products like inorganic (cellulose nitrate, sulfate, or phosphate) and organic esters like cellulose acetate, aceto butyrate etc. [32]. Degree of substitution plays an important role in making cellulose derivatives thermally stable, as higher the degree of substitution higher will be the thermal stability [33].

Esters of short chain aliphatic acid and long chain fatty acid includes cellulose acetate, and cellulose stearate, cellulose laurate, respectively. Products like fibers, plastics, films, separation membranes and coating can be made from cellulose acetate. Mixed cellulose derivatives also prepared like cellulose acetate stearate (CAS) or cellulose acetate butyrate (CAB), their applications are in specialty plastics [10].

1.5.2. Etherification

Dehydration of commonly both aliphatic and aromatic alcohols to form ethers is known as etherification process. Cellulose could be etherified by reacting strong base with alkyl halides, the process adopted called as Williamson ether synthesis or weak basic medium is used for alkylene oxides. The reactions shown in *equation 4* and *5* respectively [10].

$$Cell - OH + R - Cl + NaOH \leftrightarrow Cell - O - R + HCl \text{ -------- (eq. 4)}$$

$$Cell - OH + (CH_2)_2O + NaOH \rightarrow Cell - O - CH_2CH_2OH \text{------- (eq. 5)}$$

The most common ethers formed by reaction with alkyl halides are ethyl cellulose, methyl cellulose, and carboxymethyl cellulose. Food, paints, cosmetics, textiles, detergents etc. industries are using these ethers as additives [10]. Furthermore, oxidation of three hydroxyl groups can form addition compounds in the presence of acids and bases [10].

2. Characterization techniques used for cellulose and its derivatives.

2.1. Optical Microscopy (OM)

For study of internal structure specifically shapes of any object can be done by several microscopic techniques, optical microscopy is one of them. An optical microscope is a knowledgeable equipment which can provide high resolution images of different samples [34].

Optical microscopy is a wise characterization technique which is used as problem solving, failure analysis, research and development of materials and their quality control. From an optical microscope micro and macro structures of material can be seen [35].

Nowadays most of the microscopes used are compound microscopes. In which a magnified image of an object is produced by the objective lens and this image is magnified by a second lens system for viewing [34].

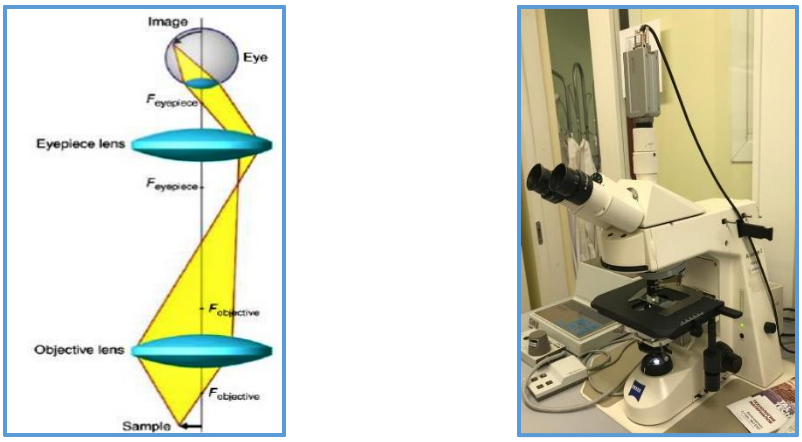


Figure 8. (a) Ray diagram of simple two lens microscope (left) [55] (b) Axioscope 3 optical microscope [57]

2.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a non-destructive technique [36] which is used for identification of organic and inorganic materials [37]. FTIR can be used to study inter and intra molecular forces between the molecules in the chain, material identification and used to study polymer morphology [38]. Very low amount of sample is used to provide fast results in the form of spectrum, the spectrum provides quantitative analytical knowledge.

A beam light falls on the sample, some part of it absorbed by the sample if the frequencies match with the vibrational frequencies of the molecules, the remaining light reflected. The detector in FTIR instrument detects the difference between light sent and light received.

The properties of molecular structure of polymer can be known by the wavelengths absorbed by the sample due to vibrations in molecules [37]. Because of these absorptions, peaks appear due to absorption intensities in the spectra showing presence of organic functional groups. Height of the peak indicate the amount of functional group presence with respect to molecular bond. The area under the peak and peak intensities can also be used to quantify the sample.

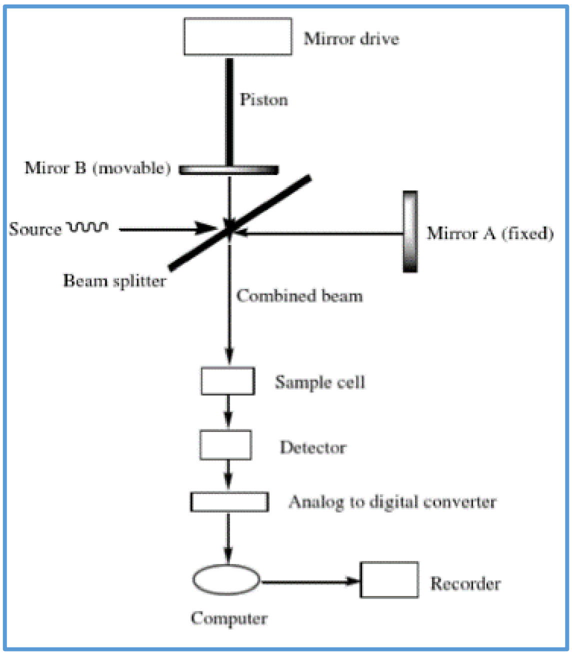


Figure 9. Schematic presentation of FTIR spectrometer [56]

2.3. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a technique for determination of properties like melting temperatures (Tm), glass transition temperature (Tg), heat changes like enthalpy and entropy, and crystallization of polymer [39].

Very small amount of material which is in milligrams is used in the process. In this study DSC is used to determine the purity of material and for the confirmation of thermoplastic behavior of prepared cellulose derivatives.

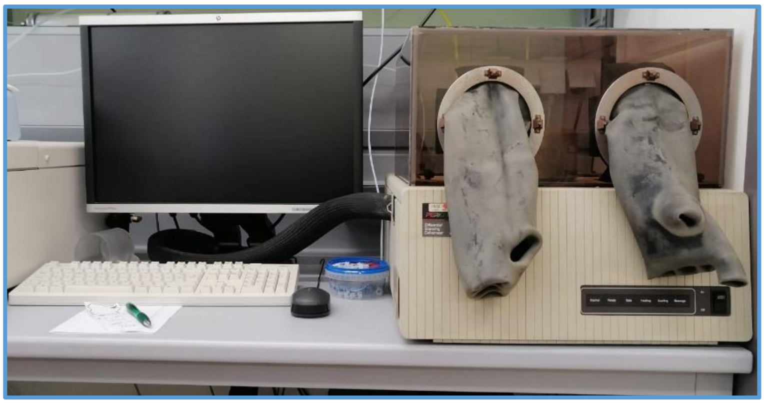


Figure 10. DSC instrument in Taltech laboratory

In *figure 11,* glass transition curve of amorphous polymers is shown. Around glass transition point, polymer comes in transition from solid to liquid.

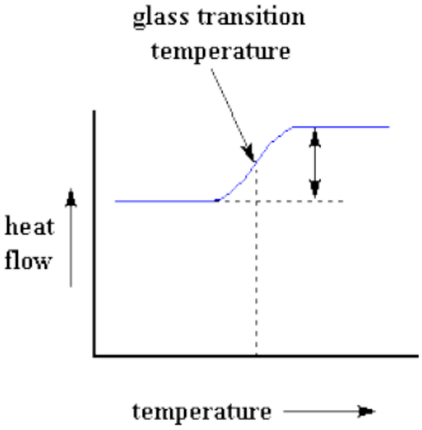


Figure 11. Graphical illustration of glass transition temperature (Tg) from DSC

In *figure 12*, melting curve of crystalline polymer is shown. Maximum temperature at which the polymer's crystallinity exists is called as melting temperature (Tm). After crossing Tm polymer becomes viscoelastic or high viscosity liquids [40]. The temperature at which polymer starts to solidify or the crystals formation starts upon cooling after melting is called as crystallization temperature (Tc).

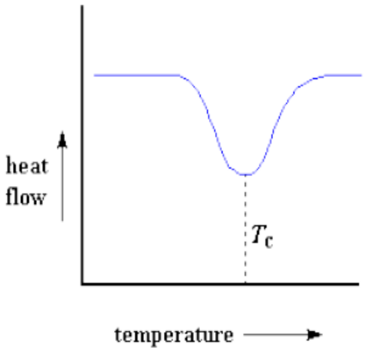


Figure 12. Graphic illustration of crystallization temperature (Tc) from DSC [63]

But at maximum set temperature, another physical transition occurs in polymer called as melting. In which formed crystals starts separating from each other. The rise of the heat is shown as peak in the graph as shown in *figure 13* below.

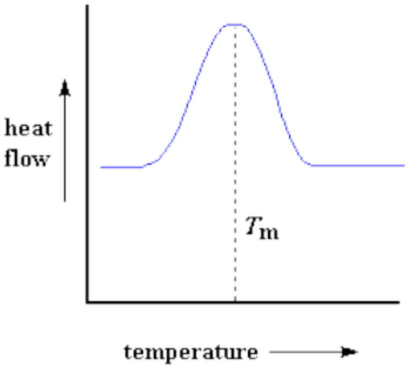


Figure 13. Graphic illustration of melting temperature (Tm) from DSC [63]

On summing up all the illustrations at the end we expected graph like shown in *figure 14* below showing Tg, Tc and Tm of the polymer. There is another phenomenon called as cold crystallization, it is done when heat is released by the system, means that the polymer sample which cooled down very quickly and do not got time to crystallize. Such polymer when heated again, forms crystals just after glass transition temperature. The process of formation of these crystals at very low temperature is called as cold crystallization [41].

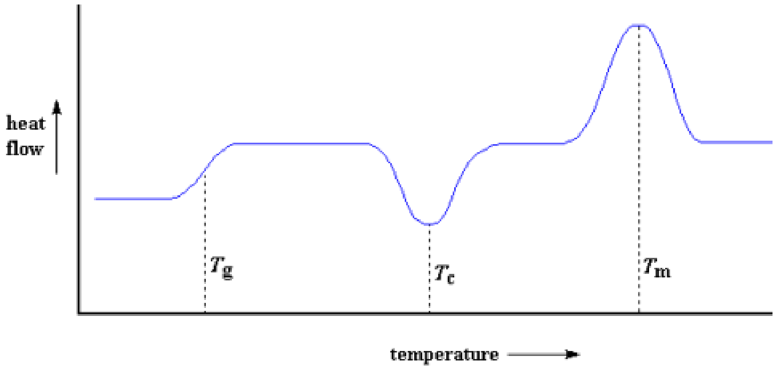


Figure 14. Graphic illustration of Tg, Tc and Tm from DSC [63]

2.4. Analysis for Degree of substitution (DS)

As discussed in introduction of this study, analysis of DS is important to find out to know how the reaction took place and how much anhydrous glucose units of cellulose are esterified. Several techniques are used for the determination of degree of substitution. Nuclear Magnetic Resonance spectroscopy (NMR) is one of the methods to find out the value of DS of any polymer directly via H-NMR spectra [42]. FTIR is also help for DS analysis [3].

Mathematical correlations are also used to convert data from element analysis (percentage of H, C, and O) for determination of DS [4]. Most conventional method to determine the value of DS is saponification method followed by back titration. NaOH is added in the mixture of polymer and alcohol then back titrated with HCl [3].

CHAPTER 2: EXPERIMENTAL PROCEDURES

1. Basic procedure for synthesis of cellulose derivatives

1.1. Introduction

In this work, cellulose is esterified by using acyl chlorides (alkyl halides) and vinyl ester. Generally, at first cellulose is dissolved in a reaction media which is ionic liquid along with co-solvent DMSO than esterified by the help of reagents like stearoyl chloride, lauroyl chloride, and vinyl laurate.

The esterification of cellulose with acyl chloride, the reaction scheme is shown in *figure 15.*

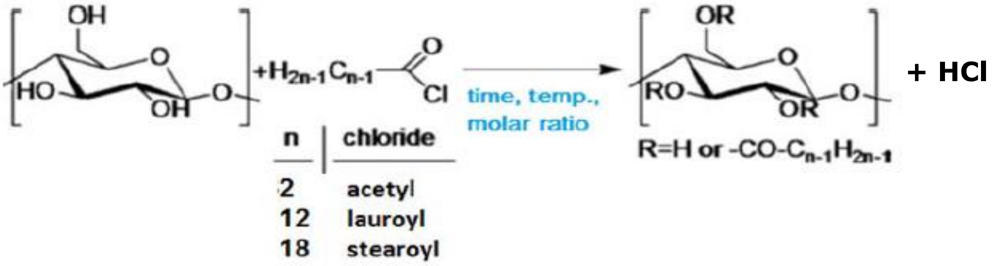


Figure 15. Esterification of cellulose by using acyl chlorides

The esterification of cellulose with vinyl laurate reaction scheme is shown in *figure 16* according to the method proposed in. [42].

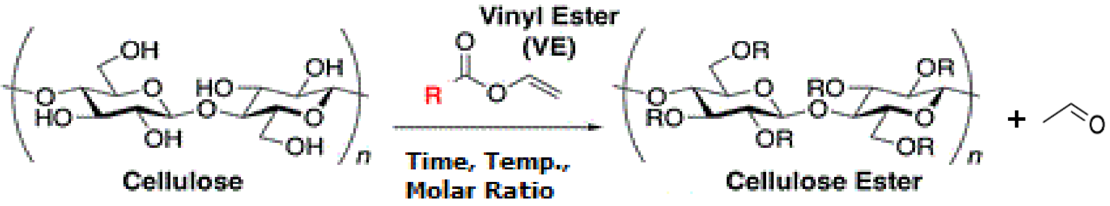


Figure 16. Reaction scheme of vinyl ester-based cellulose derivative [58]

In this study, at first stage, cellulose stearate and cellulose laurate were prepared to work out the synthesis procedure, materials handling and characterization techniques. At second stage, cellulose laurate was prepared by using vinyl laurate as acylating agent. Different molar ratios, temperatures of reaction and reaction time were tested to find out conditions for preparation of material with demanded degree of substitution of cellulose. The quantitative method of DS evaluation by FTIR was developed.

2. Pre-synthesis procedures for preparation of cellulose derivatives

2.1. Cellulose

2.1.1. Introduction

Craft paper cellulose (CPC) and alpha-cellulose paper (ACP) in the form of sheets, also cotton fibers (CF) are used as sources of cellulose. All these materials were milled and converted into powder form. The main reason behind milling of cellulose is better and faster dissolution of cellulose in ionic liquid.

2.1.2. Pre-treatment of cellulose

Cellulose was washed with NaOH water solution in ultrasonic bath. Washing helps to remove impurities while ultrasonic bath helps to decrease degree of crystallinity of cellulose.

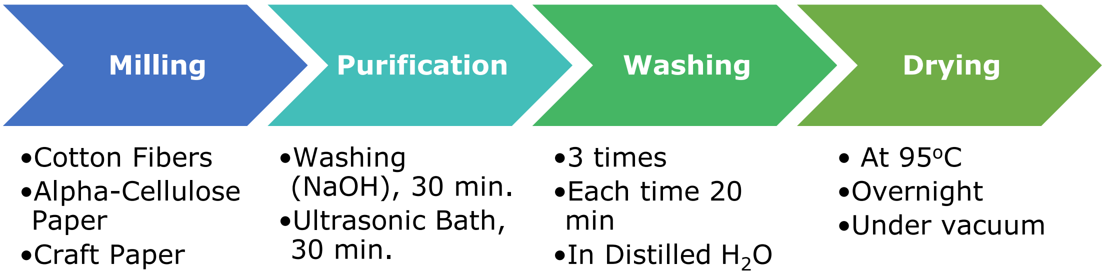
At first 5g of cellulose weighed with NaOH (5% weight of cellulose). Then distilled water is added in the flask containing cellulose and NaOH. The flask containing solution mixture placed on magnetic stirrer for high-speed mixing. The time for purification of cellulose with NaOH is 30 minutes. For next 30 minutes the solution mixture is placed in ultrasonic bath which helps to decrease degree of crystallinity of cellulose.

2.1.3. Washing and drying of cellulose

Washing of cellulose have been carried out by using distilled water. The flask containing solution mixture is placed on magnetic stirrer for 20 minutes. Then cellulose is filtered out on filter paper fixed in perforated funnel placed of flask. Vacuum suction helps in extracting the distilled water out from cellulose. The washing has been carried out three times from the same process.

For drying, cellulose material is placed in an oven at 95°C under vacuum for overnight. After drying cellulose is placed in desiccator to avoid contact with moisture from atmosphere.

2.1.4. An overview of procedure



Milling
- Cotton Fibers
- Alpha-Cellulose Paper
- Craft Paper

Purification
- Washing (NaOH), 30 min.
- Ultrasonic Bath, 30 min.

Washing
- 3 times
- Each time 20 min
- In Distilled H_2O

Drying
- At 95°C
- Overnight
- Under vacuum

2.2. Ionic Liquids (ILs)

2.2.1. Introduction

Two types of ionic liquids (ILs) are used for this thesis work, [EMIM]Cl is purchased and [BMIM]Cl is synthesized in laboratory.

[EMIM]Cl purchased and came in crystallized form, the bottle of [EMIM]Cl kept in bathtub of boiling water to convert it into liquid for further processing. To avoid process of liquification of [EMIM]Cl each time before synthesis, some of the ionic liquid transferred into zip lock bags and kept in glove box at N_2 atmosphere for future synthesis of cellulose derivatives and for ease of handling. The transfer of IL from bottle to zip lock bag have been carried out in gloves box as [EMIM]Cl is hygroscopic material; it can rapidly absorb moisture from environment.

2.2.2. Synthesis of ionic liquid (IL)

2.2.2.1. Materials used.

Chemicals and solvents used in the preparation of IL are as followed.

Table 1. Chemicals used in the synthesis of IL.

Material	Supplier
1-Methylimidazole	Merck KgaA (≥ 99%)
1-Chlorobutane	Merck KgaA (≥ 99%)
Ethyl acetate	Sigma-Aldrich (≥ 99.5%)
N_2 gas	Line gas

2.2.2.2. Procedure

1-butyl-3-methylimidazolium chloride [BMIM]Cl is synthesized in via the reaction between methylimidazole and chlorobutane at 75°C under nitrogen atmosphere. Moisture absorbent (silica gel in the form of small stones) is also present in glass funnel at the top of Erlenmeyer flask which is used to absorb any moisture in generated the reactor.

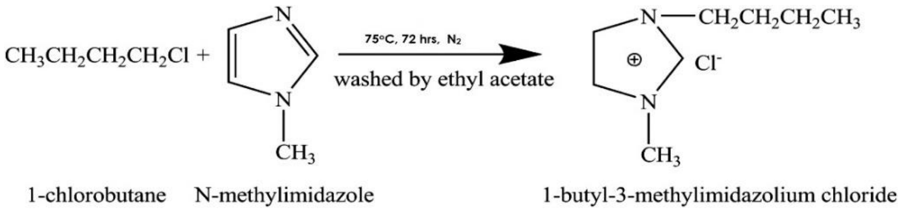


Figure 17. Reaction scheme of synthesis of IL according to [51]

The reaction continuously carried out for 3 days under high temperature. Reflux was used to avoid losing volatile 1-chlorobutane, reaction set is shown in *figure 18*.

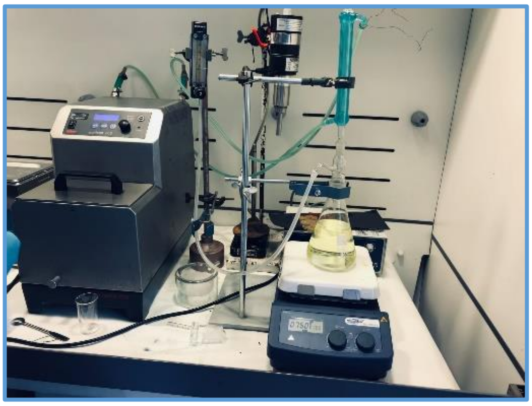


Figure 18. Synthesis of [BMIM]Cl

2.2.2.3. Calculations

1 mole of methylimidazole and 1.5 moles of chlorobutane were used.

1 mole of methylimidazole = 82.10 g: 1.5 moles of chlorobutane = 138.85 g
As we need to do several syntheses and the IL quantities required in each synthesis is from 70g to 100g, so we doubled the quantities of reactants in order to synthesize more IL.
So, we take.

- 1-methyl imidazole = 164 g
- 1-Chlorobutane = 260 g

From the reaction of above high purity reagents, the quantity of [BMIM]Cl produced was 248.40 g.

2.2.2.4. Washing of ionic liquid [BMIM]Cl

After completion of reaction, ionic liquid must be washed to remove all the impurities. For this purpose, ethyl acetate (EA) is used. After addition of EA, solution of ionic liquid stirred at high speed on magnetic stirrer for 10 minutes.

Stirrer stopped after 10 minutes and solution left for few minutes so that ionic liquid which is denser, settled down at the bottom of the flask. The interface appeared as shown in *figure 19* between IL and unreacted chlorobutane solution in ethyl acetate.

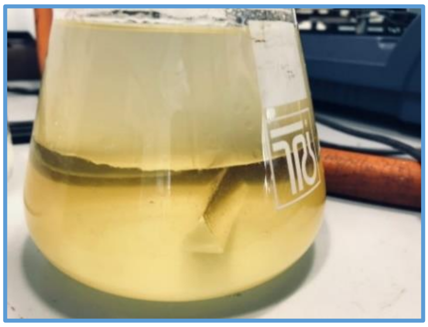


Figure 19. Interface between unreacted substances and IL during washing

Then, decanting of unreacted substance has been carried out carefully. This process is repeated three times for the complete removal of all impurities from the ionic liquid.

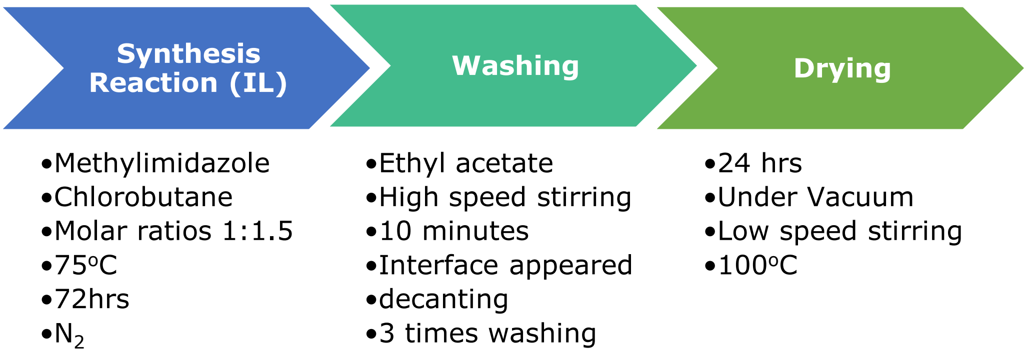
2.2.2.5. Drying of ionic liquid

Drying of ionic liquid has been carried out on heated plate on magnetic stirrer at 100°C for 24 hours. Vacuum is applied with heating and continuous stirring to evaporate all the solvents used for washing and impurities like highly volatile chlorobutane, water and ethyl acetate.

After this process ionic liquid [BMIM]Cl is ready to use. The process of drying must be followed each time when using IL for synthesis. To avoid humidity contact, IL is stored in a flask and the lid of flask is tightly close with the help of paraffin tape.

2.2.3. Overview of procedures

2.2.3.1. [BMIM]Cl



- Methylimidazole
- Chlorobutane
- Molar ratios 1:1.5
- 75°C
- 72hrs
- N_2

- Ethyl acetate
- High speed stirring
- 10 minutes
- Interface appeared
- decanting
- 3 times washing

- 24 hrs
- Under Vacuum
- Low speed stirring
- 100°C

2.3. Reagents used in the synthesis of cellulose derivatives.

Stearoyl chloride, lauroyl chloride and vinyl laurate are purchased from Sigma-Aldrich. It is important that the reagents used in the synthesis must be in liquid form and dried. In this work, all the reagents first filled in the syringe. Then they poured into reaction mixture through a rubber cork fixed as a lid on to the flask. This is done to avoid contacting with humidity and to keep the purity of reagents safe.

Table 2. Reagents used in the synthesis of cellulose Derivatives.

Material	**Supplier**
Acetyl chloride	Sigma-Aldrich
Stearoyl chloride	Sigma-Aldrich
Lauroyl chloride	Sigma-Aldrich
Vinyl laurate	Sigma-Aldrich

3. Procedures for the synthesis of cellulose derivatives

Before starting of synthesis process, all the reactants, reactors, and reaction media are dried and pure from impurities. Procedure for synthesis of cellulose consists of four steps, dissolution of cellulose, modification of cellulose, washing of cellulose derivatives, and drying of cellulose derivatives.

3.1. Procedures

Cellulose stearate and cellulose laurate are synthesized for this study. The procedure of each polymer is described separately.

3.1.1. Cellulose Stearate (CS)

Two synthesis reactions were carried out for the preparation of cellulose stearate with different reaction conditions. These syntheses comprise of same molar ratios of stearoyl chloride and same form of cellulose is used, that is milled cotton fibers, to prepare thermoplastic cellulose stearate. Toluene is also used in both syntheses to dilute the concentration of stearoyl chloride for homogenous reaction.

For modification of cotton fiber cellulose, Erlenmeyer flask of 250ml, vacuum suction lid, N_2 gas for purging and hot plate magnetic stirrer is used as reactor. All the materials and chemicals are mentioned in *table 5 below.* [BMIM]Cl is used as reaction media and DMSO is used as co-solvent of IL in which cellulose is dissolved at 100 ^{O}C for overnight under vacuum. For modification, the reaction has been carried out between stearoyl chloride and cellulose of molar ratio 3:1 (stearoyl chloride: cellulose) at temperature of 75^{O}C for overnight.
Molar ratios are calculated as per following formula 01.

$$\boldsymbol{Required\ weight\ of\ reagent} = (\boldsymbol{Molar\ mass\ of\ reagent} * \boldsymbol{Weight\ of\ cellulose\ used})/\boldsymbol{Molar\ mass\ of\ cellulose}\text{-------}\mathbf{(01)}$$

For calculation in volume, the formula 02 is used as.

$$\boldsymbol{Volume\ of\ reagent\ required} = \boldsymbol{Weight\ of\ reagent}/\ \boldsymbol{Density\ of\ reagent}\text{-----}\ \mathbf{(02)}$$

- 1 mole of cellulose = 162.14 g
- 1 mol of stearoyl chloride = 302.9 g
- Density of stearoyl chloride = 0.897 g/ml

From the above formulas, the calculated quantities of reagent used in the modification of cellulose are shown in *Table 4* below.

Table 3. Quantities of reagent used in the synthesis of cellulose stearate.

Ratio (Stearoyl chloride: Cellulose)	**Cellulose (g)**	**Stearoyl Chloride (ml)**	**Toluene (ml)**
3:1	1	6.24	3.12
3:1	1	6.24	3.12

3.1.1.1. Chemicals and materials used.

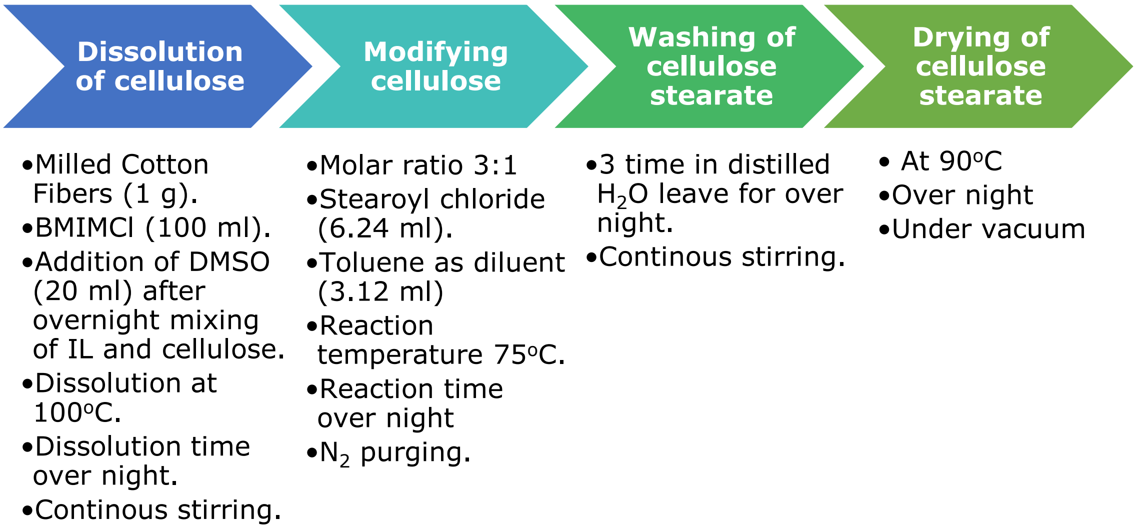
Following is the *Table 5* for complete list of materials and chemicals involved in the two-separate synthesis of cellulose stearate.

Table 4. Chemicals used in the synthesis of cellulose stearate.

Materials and chemicals	**Manufacturer**
Cellulose	ACP
[BMIM]Cl	Synthesized in lab
DMSO	Honeywell
Stearoyl chloride	Sigma-Aldridge
Toluene	Sigma-Aldridge

For washing distilled water is used three times. Filtration is done by using vacuum suction to filter out all the waste solution and then prepared cellulose laurate is placed on drying in oven at 90 °C under vacuum.

3.1.1.2. Overview of synthesis



Dissolution of cellulose
- Milled Cotton Fibers (1 g).
- BMIMCl (100 ml).
- Addition of DMSO (20 ml) after overnight mixing of IL and cellulose.
- Dissolution at 100°C.
- Dissolution time over night.
- Continous stirring.

Modifying cellulose
- Molar ratio 3:1
- Stearoyl chloride (6.24 ml).
- Toluene as diluent (3.12 ml)
- Reaction temperature 75°C.
- Reaction time over night
- N_2 purging.

Washing of cellulose stearate
- 3 time in distilled H_2O leave for over night.
- Continous stirring.

Drying of cellulose stearate
- At 90°C
- Over night
- Under vacuum

3.1.2. Cellulose Laurate (CL)

There are eleven separate syntheses reactions carried out for the preparation of cellulose laurate. These syntheses comprise of different molar ratios of reagents used, reagents are lauroyl chloride and vinyl laurate. Three different forms of cellulose are used, craft paper cellulose (CPC), milled cotton fibers cellulose (CF) and pre-treated powdered alpha cellulose paper (ACP). Two different reaction media (IL) [BMIM]Cl and [EMIM]Cl are also used in these reactions.

Erlenmeyer flask of 250ml, vacuum suction lid, N_2 gas for purging and hot plate magnetic stirrer is used as reactor. All the materials and chemical used are shown in *Table 07 below.* [BMIM]Cl and [EMIM]Cl are used as reaction media and DMSO is used as co-solvent of IL in which cellulose is dissolved at 60 ^{O}C for overnight under vacuum.

3.1.2.1. Modification of cellulose with lauroyl chloride

In the synthesis of cellulose with lauroyl chloride, cotton fiber was used as cellulose source which was dissolved in the mixture of ionic liquid [BMIM]Cl and DMSO (co-solvent of IL). The temperature used for dissolving cellulose was 100 ^{O}C, the dissolution was for overnight. The modification of cellulose was carried out by using lauroyl chloride in molar ratios of 3:1 and 5:1. Time of reaction was 6 hrs. at temperature of 110 ^{O}C. In one of the synthesis Tin (II) hexanoate is used as catalyst to see the affects in modification process and results.

3.1.2.2. Modification of cellulose with vinyl laurate

In the synthesis of cellulose with vinyl laurate, alpha-cellulose source first suspended in DMSO for 30 minutes at room temperature then the mixture was dissolved in [EMIM]Cl for 1 hour at different temperatures for several synthesis which are ranges from 60 ^{O}C to 95 ^{O}C. Then modification was carried out by using vinyl chloride in molar ratios of 3:1, 4.5:1, 6:1, 7:1, 7.5:1, and 9:1. There were different temperatures used for several synthesis in the range of 45 ^{O}C to 110 ^{O}C. The reaction time ranges from 1 to 3 hrs. in different synthesis and then the solution left at room temperature for overnight.

All the molar ratios were calculated by using same *formula 01* and *formula 02* mentioned in *section 3.1.1. Cellulose Stearate.*

- 1 mol of lauroyl chloride = 218.76 g
- Density of lauroyl chloride = 0.946 g/ml
- 1 mol of vinyl laurate = 226.36 g
- Density of vinyl laurate = 0.871 g/ml

From the above mathematical calculations, the calculated quantities of reagent used in the modification of cellulose are shown in *Table 06* below.

Table 5. Calculated quantities of reagent used in the synthesis of cellulose laurate.

Molar ratio	**Cellulose (g)**	**Lauroyl Chloride (ml)**	**Vinyl Laurate (ml)**
3:1 (CPC)	0.5	2.14	-
3:1 (CF)	0.5	2.14	-
5:1 (CF)	0.5	3.56	-
5:1 (CF)	0.0659	0.47	-
3:1 (ACP)	1	4.27	-
9:1 (ACP)	1	-	14.43
7.5:1 (ACP)	1	-	12.02
7:1 (ACP)	1	-	11.22
6:1 (ACP)	1	-	9.62
4.5:1 (ACP)	1	-	7.21
3:1 (ACP)	1	-	4.81

For washing ethanol, acetone, methanol, and distilled water are used in different syntheses. Filtration is done by using vacuum suction to filter out all the waste solution. At last, drying of every prepared cellulose laurate is done at different temperatures which ranges from 40 ^{O}C to 90 ^{O}C in oven or in ambient under vacuum for overnight.

3.1.2.3. Chemicals and materials used.

The list of materials and chemicals involved in synthesis of cellulose laurate are present in *Table 07.*

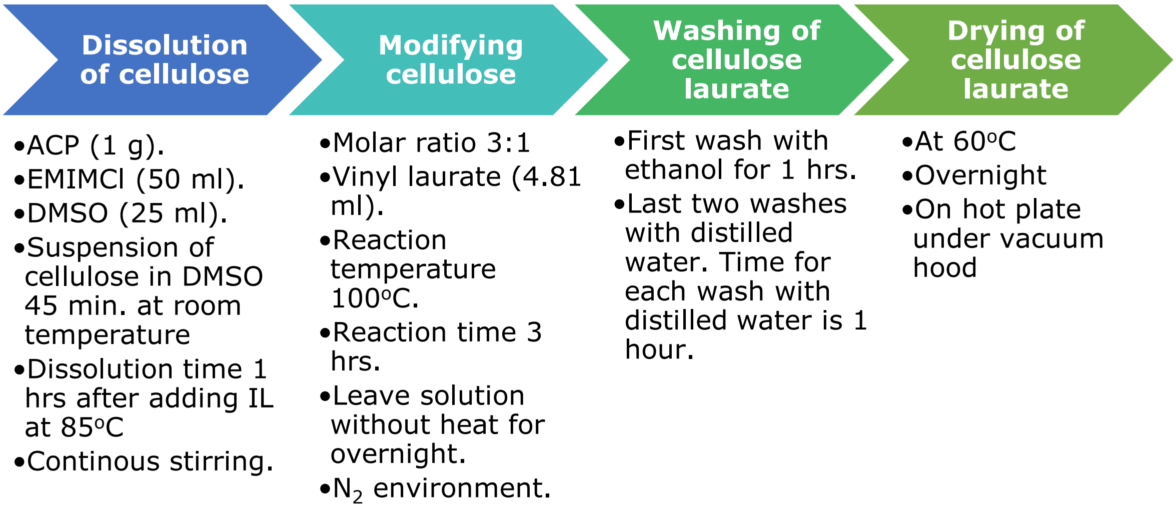
Table 6. Materials and chemicals used in the synthesis of cellulose laurate.

Materials and chemicals	**Manufacturer**
Cellulose	CF & ACP
[EMIM]Cl	Sigma-Aldridge
[BMIM]Cl	Synthesized in lab

DMSO	Honeywell
Lauroyl Chloride	Sigma-Aldridge
Vinyl Laurate	Sigma-Aldridge
Tin (II) ethyl hexanoate	Sigma-Aldridge
Methanol	Sigma-Aldridge
Ethanol	Sigma-Aldridge
Acetone	Sigma-Aldridge

3.1.2.4. Overviews of synthesis

For presenting overview of all CL(VL) synthesis, molar ratio 3:1 is presented below as reference.



Dissolution of cellulose

- ACP (1 g).
- EMIMCl (50 ml).
- DMSO (25 ml).
- Suspension of cellulose in DMSO 45 min. at room temperature
- Dissolution time 1 hrs after adding IL at 85°C
- Continous stirring.

Modifying cellulose

- Molar ratio 3:1
- Vinyl laurate (4.81 ml).
- Reaction temperature 100°C.
- Reaction time 3 hrs.
- Leave solution without heat for overnight.
- N_2 environment.

Washing of cellulose laurate

- First wash with ethanol for 1 hrs.
- Last two washes with distilled water. Time for each wash with distilled water is 1 hour.

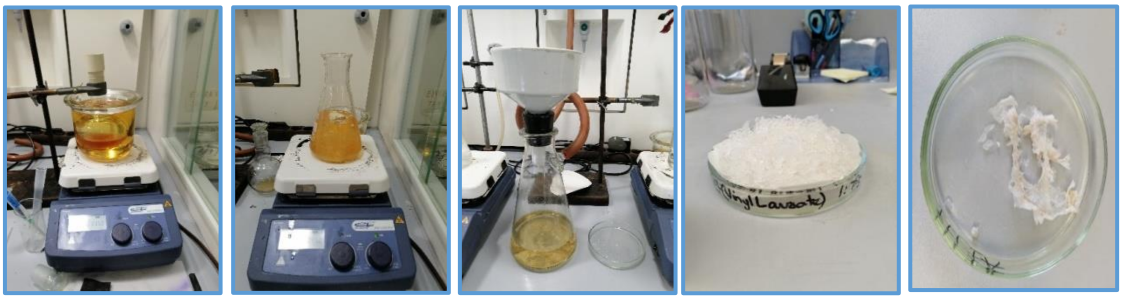
Drying of cellulose laurate

- At 60°C
- Overnight
- On hot plate under vacuum hood

3.1.3. Procedure scheme for cellulose derivatives

In *figure 20(a)* reaction set up is shown: round bottom flask in oil bath is used for uniform heating of reaction mixture. Rubber cork is fit on flask and acylating agent is transferred into the flask with the help of syringe to avoid penetration of moisture into reaction mixture. In *figure 20(b)*, washing solvent is placed into wide neck flask and kept on high-speed stirring with magnetic bar. The reaction stopped by pouring the reaction mixture into the flask with washing solvent.

Figure 20(c), showing filtration process under vacuum while in *figure 20(d)*, cellulose derivatives are obtained in the form of gel particles. After drying in vacuum oven cellulose derivatives are obtained in the form of flakes as shown in *figure 20(e).*



a b c d e

Figure 20. (a) Synthesis of Cellulose derivatives, (b) Washing of cellulose derivatives, (c) Filtration of cellulose derivatives, (d) Prepared cellulose derivative before drying in gel form, (e) Prepared cellulose derivative after drying.

4. Recycling of ionic liquid

In this work, rotary evaporator is used to remove volatile organic solvents of lower boiling point (alcohol and acetone) from IL under high vacuum and heating. Then IL placed on heating plate under vacuum for evaporation of DMSO co-solvent. Finally, IL washed with EA and dried at 100 ^{0}C under 10 mPa vacuum. Solvents separated from ionic liquid solution during distillation were used again for washing of cellulose derivatives.

Another way used for recycling of IL was just evaporate solvents with the help of rotary evaporator and mixture of IL and co-solvent (DMSO) collected and used without further distillation. The ratio of solution mixture of IL and DMSO was already calculated before so it could be used directly for dissolution of cellulose for further synthesis.

5. Analysis of degree of substitution

5.1. Back Titration

Degree of substitution is examined by Eberstadt saponification method followed by back titration. Cellulose derivatives have been swelled in 75% ethanol solution in water. Percentage of acyl contents is calculated from the formula mentioned in standard ASTM D 871-96 [43]. Degree of substitution was calculated from percentage of acyl content.

5.1.1. Chemicals used

Following are the chemicals mentioned in *Table 8*, involved in the process of saponification reaction followed by back titration.

Table 7. Chemicals used in determination of degree of substitution.

Chemicals	Properties
Ethanol	75%
HCl	0.5 M
NaOH	0.5 M
phenolphthalein	-

5.1.2. Procedure

Determination of degree of substitution comprises of three step, first step is the preparation of sample, in second step saponification is carried out and in the last step back titration is done.

Samples are prepared by drying of milled cellulose and cellulose derivatives in an oven at 105°C for 2 hours. All the flasks, stirrer and lid must be dried prior to the process. After drying sample and flasks placed in desiccator for cooling down under moisture free environment. After material become cool sample of required quantity transferred into Erlenmeyer flask.

Before the reaction started, 40 ml of 75 % ethanol is added into the flask containing 1 gram of cellulose and heated at 60°C for 30 minutes on continuous stirring. After 30 minutes, 40 ml 0.5M NaOH is added to the solution. The solution mixture again heated at 60°C but this time for 15 minutes only. Following is the saponification reaction.

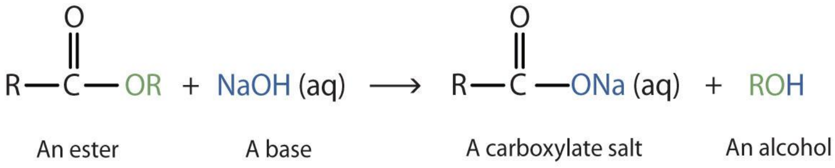


Figure 21. Saponification reaction [61]

After completion of reaction time, the Erlenmeyer flask is closed tightly and placed on stirring for 48 hrs. at room temperature.

Final step in determination of degree of substitution is titration, after 48 hrs excess NaOH is titrated with HCl of 0.5M. To check the neutralization of NaOH we use 5 drops of phenolphthalein as indicator. Once the indicator added to the flask the appeared color of solution is pink. Titration carried out continuously until the pink color vanished from the solution. The disappearance of pink color is the endpoint of titration.

1 ml of HCl is added to neutralize the remaining NaOH in the polymer and the solution mixture kept on stirring overnight at room temperature. Finally, excess of HCl is titrated with NaOH until the pink color appears again.

5.1.2.1. Calculation

Acyl contents can be calculated by using following formula as mentioned in ASTM D 871

$$Acetyl\,\% = [(D - C)Na + (A - B)Nb] * (F/W)$$

where

A = volume of NaOH (ml) added to the sample

B = volume of NaOH (ml) added to the blank

C = volume of HCl (ml) added to the sample

D = volume of HCl (ml) added to the blank

W = weight of the sample (g)

N_a = normality of HCl solution

N_b = normality of NaOH solution

F = Constant 4.305 for acetyl

The degree of substitution can be calculated by using following formula [3]

$$\boldsymbol{DS} = \frac{\mathbf{162} * \%\boldsymbol{A}}{(\mathbf{4305} - \mathbf{43} * \%\boldsymbol{A})}$$

5.2. Fourier Transformed Infrared spectroscopy (FTIR)

FTIR usually used to confirm qualitatively if the reaction of esterification the product obtained by the reaction of esterification was efficient. By observation of IR absorption bands characteristics to demanded functional group.

In this work, FTIR analysis of cellulose derivatives performed on *Interspectrum®* spectrometer. Range of wavelength used were from 4000 cm^{-1} to 500 cm^{-1} with resolution of 1 cm^{-1}.

5.2.1. Procedure

First step is the drying of samples, samples were dried at 90 ^{O}C for 3 hours to remove moisture.

As far as studied materials we obtained in powdered form attenuated total reflectance (ATR) attachment with diamond window to spectrometer was used.

Selection of characteristic peaks and base lines is done in the spectrum for the calculation of peak intensity and integral area ratios and will be discussed in results chapter.
The linear relationship between characteristic peaks area and intensity ratios versus degree of substitution determined by titration was developed. The obtained equation was further used for determination of DS by FTIR.

5.2.2. Calculations

Degree of substitution of cellulose laurate prepared by using vinyl laurate as reagent is calculated from FTIR by using following equations.
From peak intensity ratios below is the equation used for DS determination.

$$R_I = y * DS + x$$

From peak area ratios the equation used for DS determination is shown below.

$$R_A = y * DS + x$$

Where,

$I_{C=O}$ is the peak intensity of ester bond (1058 cm^{-1}) present in cellulose derivatives.

I_{C-O-C} is the peak intensity of reference bond (1015 cm^{-1}) present in both cellulose and its derivatives.

$A_{C=O}$ is the peak area of ester bond present in cellulose derivatives.

A_{C-O-C} is the peak area of reference bond present in both cellulose and its derivatives.

DS is the degree of substitution.

y is the constant for all the derivatives prepared by using different molar ratios.

x is the constant for all the derivatives prepared by using different molar ratios.

R_I is the intensity ratio of characteristic peak.

R_A is the area ratio of characteristic peak.

5.3. Differential Scanning Calorimetry (DSC)

The dynamic scanning calorimeter DSC7 (Perklin Elmer) was used to study thermal transitions in prepared cellulose derivatives.

5.3.1. Procedure

At first, sample is prepared in a way that 3 milligrams of cellulose derivative compressed into a flat flake then wrapped in aluminum foil.

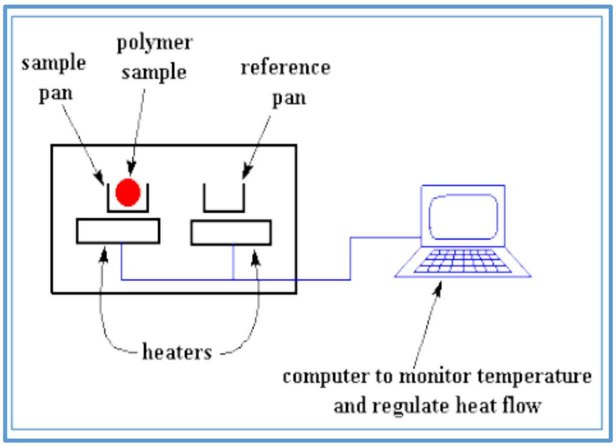


Figure 22. Illustration for sample placement in DSC instrument [63]

Following heating-cooling cycle was used.

1- Temperature held for 5 minutes at 0°C.

2- Heating from 0°C to 200°C with the speed of 120°C/min.

3- Temperature of 200°C held 5 minutes.

4- Cooling from 200°C to 0°C with the speed of 120°C/min.

5- Held 0°C for 1 minute.

CHAPTER 3: RESULTS AND DISCUSSION

1. Synthesis of Ionic Liquid (IL)

Ionic liquid [BMIM]Cl is synthesized by the reaction of 1-methylimidazole and 1-chlorobutane. Light yellowish color ionic liquid as shown in *figure 23*, is obtained.

Figure 23. Synthesized [BMIM]Cl

Optical microscope is used for the characterization and confirmation that the obtained ionic liquid is partially or fully capable of dissolving cellulose fiber. *Figure 24* is showing that almost all the fiber of cellulose has dissolved by synthesized ionic liquid [BMIM]Cl but some of the cellulose fiber particles are still present in the solution mixture.

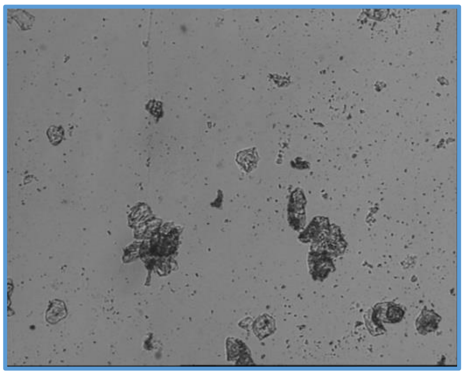


Figure 24. Optical microscopy of Alpha-cellulose paper after dissolution in [BMIM]Cl

In addition, the result of synthesized ionic liquid was good enough to dissolve maximum 2 wt.% of cellulose that is later undergo modification process.

2. Recycled ionic liquid (IL)

After all the synthesis, mixture of ionic liquid, DMSO and solvents were collected in flasks for recycling. Rotary evaporator was used for recycling of solution mixture. The collected mixture recycled ionic liquid and DMSO is used for further dissolution of cellulose. But it is observed from optical microscopy that the mixture of recycled ionic liquid and DMSO is unable to dissolve cellulose completely. Figure 34 is showing that cellulose fibers are still present in solution mixture.

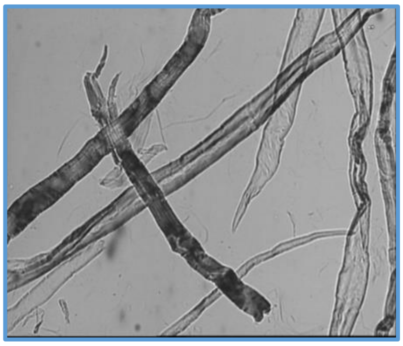


Figure 25. Presence of cellulose fiber in solution mixture after dissolution by using recycled IL.

3. Appearance of obtained cellulose derivatives.

All the cellulose derivatives (CS and CL) obtained by the modification of cellulose was in the form of gel like substance before drying. Before washing with suitable solvents like methanol, ethanol, acetone, and distilled water, cellulose derivatives obtained have yellowish tone, and some was even of brownish tone. This could be due to the presence of unreacted substances for example IL and reagents. After washing with alcohols and acetone, color disappeared, and the gel became whitish as shown in *figure 25* below.

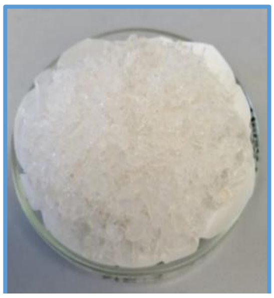


Figure 26. Gel like prepared thermoplastic cellulose before drying

After drying, some of the derivatives appeared like greyish white flakes and some of them appeared like brown flakes. Brown flakes could be the reason of degradation due to reaction temperatures; it could be due to the presence of unreacted substance in cellulose derivatives, or it could be due to the degradation of cellulose by hydrolysis.

Most of the brownish tone in cellulose derivative appeared which are prepared by reaction with acyl chloride. The reason for this could be presence of HCl, as the byproduct of reaction is HCl which could degrade the final product.

Following is the *figure 26* showing prepared cellulose derivatives, each sample has different molar ratio.

Figure 27. Prepared thermoplastic cellulose derivatives [CL 3:1, CL 5:1, CL(VL) 9:1, CL(VL) 7.5:1, CL(VL) 4.5:1, CS 3:1]

4. Solubility test of cellulose derivatives

Solubility test is performed for all the prepared cellulose derivatives. Chloroform and DMSO are used as solvents for cellulose derivatives.

Table 8. Solubility test of cellulose derivatives.

S. No.	Materials	Characteristics	Chloroform	DMSO
1	CS	3:1 (10/2020)	-	-
2	CS	3:1 (11/2020)	-	-
3	CL (VL)	9:1	-	-
4	CL (VL)	7.5:1	-	-
5	CL (VL)	7:1	+	+
6	CL (VL)	6:1	-	-
7	CL (VL)	4.5:1	+	-
8	CL (VL)	3:1	+	-
9	CL	3:1	-	-
10	CL	5:1	-	-

It is seen from *table 13* that prepared thermoplastic cellulose derivatives CL(VL) of molar ratios 3:1 and 4.5:1 is slightly soluble in chloroform, but they are not soluble in DMSO. While CL(VL) 7:1 is soluble in chloroform, but it is slightly soluble in DMSO. All the other prepared thermoplastic cellulose derivatives are not soluble in chloroform or DMSO.

The reason of no solubility in chloroform or DMSO could be due to very low DS of prepared cellulose derivatives. CL (VL) 7:1 is partially soluble in chloroform because it has DS highest value (DS=1.14) among prepared cellulose derivatives. However, the commercially prepared and pure CA and DAC having DS value 2.47 and 2.29 respectively are soluble in both the solvents.

5. Determination of degree of substitution by saponification reaction followed by back titration.

It was expected that the higher the quantity of molar ratios of reagent, higher would be the degree of substitution of prepared cellulose derivatives. But in real, it was not. When the molar ratio of vinyl laurate to cellulose increased, DS values of cellulose laurate found to be decreased. This makes us consider that the reaction temperature and time plays dominant role. The molar ratio should be kept 3:1 as far as each cellulose monomer unit has 3 sites available for substitution with 1 laurate chain.

Table 9. Results of acyl contents and degree of substitution with reaction conditions.

S. No.	Mater-ails	Cellulose	Charact-eristics	% A	DS	Reaction Tempera-true (°C)	React-ion Time (hrs.)
1	CS	CF	3:1	18.94	0.88	50	6
2	CS	CF	3:1	12.92	0.56	50	2
3	CL (VL)	ACP	9:1	4.31	0.17	65	3
4	CL (VL)	ACP	7.5:1	6.03	0.24	65	1.5
5	CL (VL)	ACP	7:1	23.25	1.14	100	3
6	CL (VL)	ACP	6:1	16.36	0.74	105	2
7	CL (VL)	ACP	4.5:1	18.08	0.83	100	3
8	CL (VL)	ACP	3:1	20.66	0.98	110	3
9	CL (VL)	ACP	3:1	12.05	0.52	95	1
10	CL (VL)	ACP	2:1	0.00	0.00	115	12
11	CL	CPC	3:1	0.00	0.00	50	6
12	CL	CF	5:1	0.00	0.00	45	8

The *table 9* represents materials and reaction conditions. It is observed that in order to obtain cellulose derivatives with higher degree of substitution temperature must kept between 100°C to 110°C while time of reaction should be from 3 hrs. to 6 hrs. At higher temperature and longer times hydrolysis of the product became evident.

Highest DS values obtained by the synthesis of CL(VL) 7:1 which is DS= 1.14. In this synthesis, the DS value could go above than the obtained DS if the time of reaction is increase up to 6 hrs. Same is for synthesis of CL(VL) 6:1, 4.5:1, and 3:1.

But if we see the DS values of CL(VL) 9:1 and 7.5:1, they are very low 0.17 and 0.24, respectively. This could be due to the use of low reaction temperatures and less reaction time.

Three syntheses of CL(VL) with ratio of 3:1 was performed at 110°C, 95 °C and 50 °C: at higher temperatures the time of reaction is 3 and 1 hour. So, the products obtained with DS of 0.98 and 0.52, respectively. But the product of low temperature was not substituted at all.

Synthesis of CL(VL) 2:1 *(shown in figure 27)* is not successful as the material kept on reaction for 12 hrs. at high temperature of 115ºC, so it completely degraded, and nothing was obtained after washing.

Another synthesis of CL with ratio of 3:1 was done by using craft paper cellulose (CPC), the material degraded probably due to moisture present in craft paper as see *figure 28.*

Figure 28. Degraded CL(VL) 2:1, due to high temperature and time

Figure 29. Degradation of CL 3:1 prepared by using craft paper cellulose by the presence of moisture.

6. Fourier transformed infrared spectroscopy (FTIR)

6.1. Qualitative analysis of chemical structure by FTIR

To study the efficiency of cellulose modification FTIR was used. In figure 29 infrared absorption spectra are represented.

Peaks characteristic to bond and groups specific to cellulose and cellulose derivatives are shown in *table 10*.

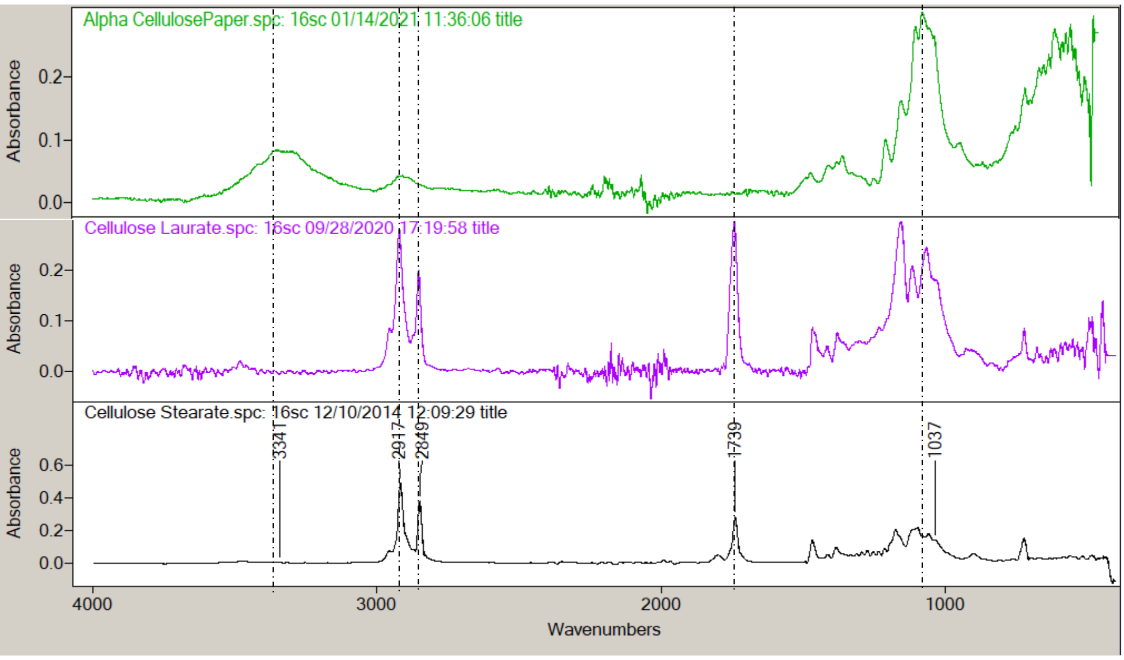


Figure 30. FTIR spectra of cellulose and its derivatives

Table 10. Characteristic peaks of FTIR spectra and their explanations.

Wave number (cm $^{-1}$)	**Description of peaks**
1000-1050	C-O-C of cellulose backbone in cellulose, CL, and CS
1210-1240	C-O stretching of acetyl group in CL and CS
1735-1750	C=O stretching of acetyl group in CL and CS
1350-1390	C-H_3 bending vibration of CH_3 group in aliphatic chain of CL and CS
2800-2950	C-H stretching of CH_2 or CH_3 in CL and CS aliphatic chain
3200-3500	O-H stretching in pure cellulose

Successful derivatization of cellulose is confirmed by appearance of two peaks in the range of 2800 cm^{-1} and 2950 cm^{-1} that represent symmetric and asymmetric stretching of C-H bond in aliphatic chain. As well the peak at 3200 cm^{-1} -3500 cm^{-1} range corresponding to O-H stretching in hydroxyl groups of cellulose will disappear from cellulose spectra.

The peak at 1750 cm^{-1} is characteristic to C=O stretching in acetyl group also evidences successful acetylation of cellulose. Special attention should be given to the peak at 1050 cm^{-1} that characteristics to C-O-C stretching in backbone of cellulose and its derivatives. This peak present in spectra of pure cellulose and derivatives and could be used for macromolecular chain stability. Also, it could be used as the signal of internal standard that could be applied for normalization of spectra.

6.2. Qualitative analysis of chemical structure by FTIR: Determination of degree of substitution by FTIR.

6.2.1. Selection of major peaks and the baseline

Intensity and area of the absorption peaks could be used to evaluate the amount of specific chemical group in tested compound.

Cellulose and cellulose derivatives contain equal number of C-O-C groups in the backbone, so the intensity and area of the peak (1000-1050 cm^{-1}) corresponding to this group could be used as reference values. Intensity (I) and area (A) of peak corresponding to C=O (1750 cm^{-1}) could be used for evaluation of amount of C=O groups in derivatized cellulose.

The C=O (1750 cm^{-1}) peak intensity $I_{C=O}$ and area $A_{C=O}$ in spectrum of cellulose, CL and CS should be the same, as amount of this group is constant in all materials. The C-O-C (1050 cm^{-1}) peak intensity I_{C-O-C} and area A_{C-O-C} should depend on the amount of acylated groups in a sample. Thus, if measure I_{C-O-C} and $I_{C=O}$ intensities of a sample and divide I_{1750} by I_{1050} we obtain relative intensity of C=O group absorption that is proportional to the amount of C=O group (degree of acylation) or degree of substitution of cellulose. It is called the intensity ratio (R_I):

$$R_I = \frac{I_{C=O}}{I_{C-O-C}}$$

The same true for area of 1750cm^{-1} peak, and the area ratio (R_A) could be introduced:

$$R_A = \frac{A_{C=O}}{A_{C-O-C}}$$

To make correct measurements of intensity and area proper position of peak and baseline should be done.

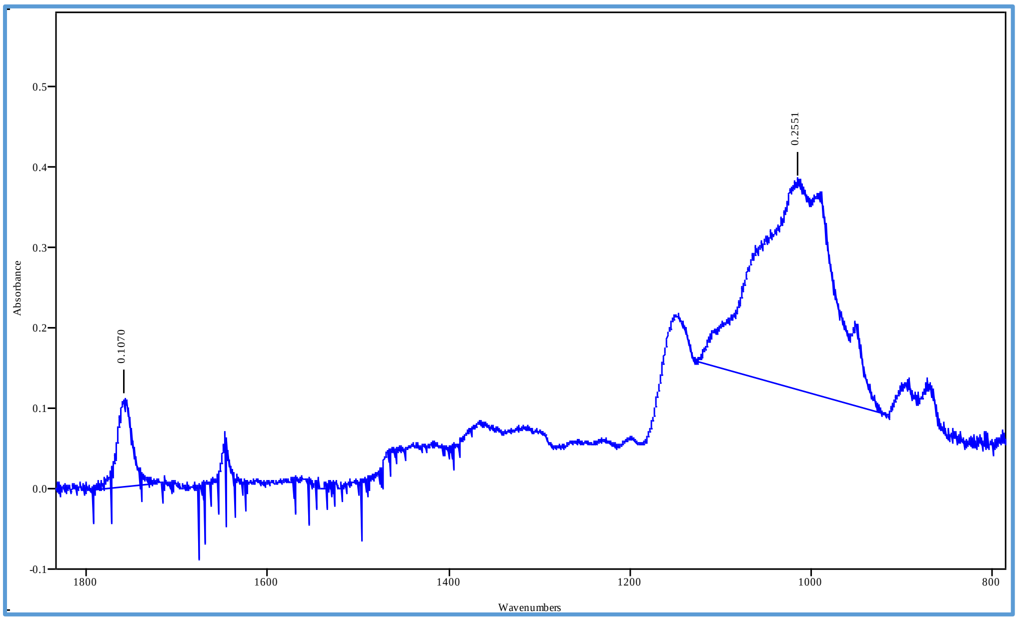


Figure 31. One of the prepared CL(VL) spectra showing two selected peaks at wavenumbers 1758 cm^{-1} and 1015 cm^{-1} and base lines for quantitative analysis of DS from Cellulose Laurate.

To do this a plot of R_I and R_A versus DS is made. A correct baseline gives the best linearity to these correlation curves. So, in this study for cellulose laurate peak related to C=O group localized at 1758 cm^{-1} and baseline was selected between 1790 cm^{-1} and 1736 cm^{-1}. The peak related to C-O-C group localized at 1015 cm^{-1} and baseline was selected between 1121 cm^{-1} and 958 cm^{-1} (*see Figure 30*).

To establish this method of DS evaluation several cellulose laurate samples were synthesized with different degree of substitution starting from 0.17 up to 1.14. Samples with different DS were obtained via synthesis using different molar ratios of cellulose and vinyl laurate (see Synthesis chapter). The DS values were obtained from back titration.

6.2.2. Quantitative analysis of cellulose laurate degree of substitution

As could be seen from the *Table 11* below that highest intensity of chosen characteristic peak obtained by using molar ratio of 3:1 while the lowest intensity is obtained by using molar ratio of 7.5:1. There is no increasing or decreasing trend shown in the obtained intensities of characteristic peaks of acyl group, although molar ratios used are in increasing trend.

Table 11. Results of characteristic peak intensity and integral area ratios

Materials	**Molar Ratios**	**Bonds**	**Peak Intensity (I)**	**Area (A)**	**Peak Intensity Ratio (R_I) ($I_{C=O}$/ I_{C-O-C})**	**Area Ratio (R_A) ($A_{C=O}$/ A_{C-O-C})**
Cellulose Laurate						
Alpha Cellulose	Blank	C=O	0,00	0,00	0,00	0,00
Alpha Cellulose	Blank	C-O-C	0,20	99,66		
CL (VL)	3:1	C=O	0,14	16,01	1,29	0,18
CL (VL)	3:1	C-O-C	0,11	89,72		
CL (VL)	3:1	C=O	0,06	16,85	1,35	0,20
CL (VL)	3:1	C-O-C	0,04	84,08		
CL (VL)	4.5:1	C=O	0,03	27,59	1,31	0,27
CL (VL)	4.5:1	C-O-C	0,02	102,28		
CL (VL)	6:1	C=O	0,13	16,27	0,69	0,19
CL (VL)	6:1	C-O-C	0,19	86,05		
CL (VL)	7:1	C=O	0,16	16,80	1,82	0,84
CL (VL)	7:1	C-O-C	0,09	20,12		
CL (VL)	7.5:1	C=O	0,02	17,75	0,06	0,20
CL (VL)	7.5:1	C-O-C	0,29	88,75		
CL (VL)	9:1	C=O	0,09	16,66	0,27	0,17
CL (VL)	9:1	C-O-C	0,35	95,38		

The expectation was the ratio of intensities of characteristic peaks of acyl group of each cellulose laurate would be increased by increasing the molar ratios but in real, values of intensity ratio and area ratios are not showing any trend. Most probably this is due to the different reaction conditions are used. This evidences that the reaction temperature and time play major role in synthesis.

6.2.3. Functional relationship between Ds obtained by titration and peak intensity/area ratio from FTIR.

The linear relationships between known DS obtained by titration and ratios of peak intensity and integral area are shown in figure 31 and 32, respectively. Two types of relations were under consideration: with and without intercepts.

However, the trend lines of intensities and areas are not coinciding, but they have same direction. It is seen in both figures that the functional relationship between peak intensity ratio and DS obtained by titration is more correlated.

The linear relationship between DS obtained by titration and R_A is not so good as expected, we should search better and precise baseline to get good correlation. Moreover, peak intensity of characteristic peak is more correlated as compared to integral area and it is more feasible for DS analysis from FTIR.

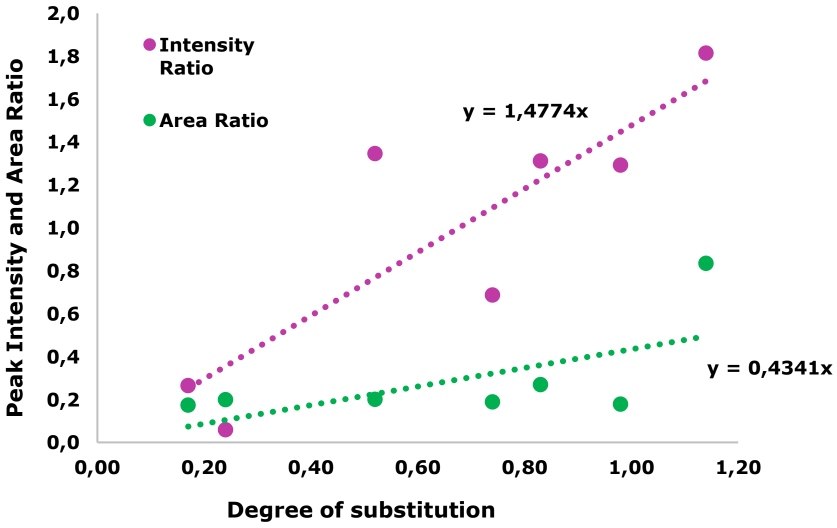


Figure 32. Relationship between DS by titration and FTIR intensity and area ratios. Trend lines with intercept.

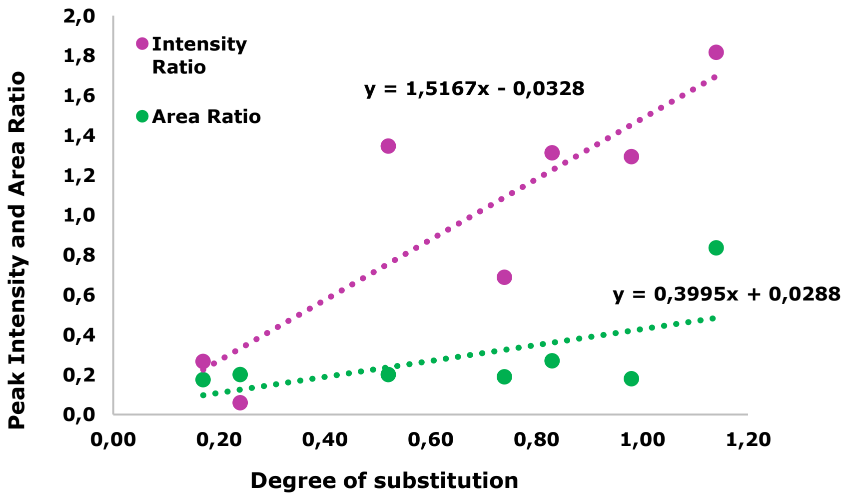


Figure 33. Relationship between DS by titration and FTIR intensity and area ratios
Trend lines without intercepts.

Based on the formula obtained from the graph at figure 32, the DS could be calculated. Peak intensity and integral area ratios with and without intercepts are shown in *table 12* and *table 13* below.

Standard equations used with intercepts:

$$R_I = y * DS$$

$$R_A = y * DS$$

Table 12. Determination of DS from FTIR by using standard equation and curve with intercept.

					Peak Intensity		Integral Area	
Material	Molar Ratio	R_I	R_A	$DS_{Tit.}$	y	DS_{FTIR}	y	DS_{FTIR}
CL (VL)	3:1	1,29	0,18	0,98	1,48	0,87	0,43	0,41
CL (VL)	3:1	1,35	0,20	0,52	1,48	0,91	0,43	0,46
CL (VL)	4.5:1	1,31	0,27	0,83	1,48	0,89	0,43	0,62
CL (VL)	6:1	0,69	0,19	0,74	1,48	0,47	0,43	0,44
CL (VL)	7:1	1,82	0,84	1,14	1,48	1,23	0,43	1,92
CL (VL)	7.5:1	0,06	0,20	0,24	1,48	0,04	0,43	0,46
CL (VL)	9:1	0,27	0,17	0,17	1,39	0,18	0,44	0,40

Standard equations used without intercepts:

$$R_I = y * DS + x$$
$$R_A = y * DS + x$$

Table 13. Determination of DS from FTIR by using standard equation and curve without intercept.

					Peak Intensity			Integral Area		
Material	Molar Ratio	R_I	R_A	$DS_{Tit.}$	x	y	DS_{FTIR}	x	y	DS_{FTIR}
CL (VL)	3:1	1,29	0,18	0,98	-0,03	1,52	0,87	0,03	0,40	0,37
CL (VL)	3:1	1,35	0,20	0,52	-0,03	1,52	0,91	0,03	0,40	0,43
CL (VL)	4.5:1	1,31	0,27	0,83	-0,03	1,52	0,89	0,03	0,40	0,60
CL (VL)	6:1	0,69	0,19	0,74	-0,03	1,52	0,47	0,03	0,40	0,40
CL (VL)	7:1	1,82	0,84	1,14	-0,03	1,52	1,22	0,03	0,40	2,02
CL (VL)	7.5:1	0,06	0,20	0,24	-0,03	1,52	0,06	0,03	0,40	0,43
CL (VL)	9:1	0,27	0,17	0,17	-0,03	1,52	0,20	0,03	0,40	0,37

It is seen from table 12 and table 13 that the value of DS obtained from FTIR by using standard equation without intercepts have closer values to values of DS obtained from titration. So we conclude that the formula without intercepts fits best for evaluation of DS by measurement of C=O intensity.

$$\boldsymbol{y = 1{,}5167x - 0{,}0328}$$

As the result of combination of two methods FTIR and titration we propose simple equation that could be used for evaluation of cellulose laurate degree of substitution from FTIR data.

$$\boldsymbol{DS_{FTIR} = \frac{R_I + 0.0328}{1.5167}}$$

7. Differential Scanning Calorimetry (DSC)

In this study, DSC is used to determine the thermal transition of all the prepared CL(VL). It is expected to obtain glass transition temperature and melting temperature of prepared CL(VL) (cellulose derivatives).

As it is shown in *figure 34*, that the first melting peak obtained is of [EMIM]Cl remained in CL, it has Tm = 74.18^{O}C. The second melting point of 86.66^{O}C is correspondent to laurate branches.

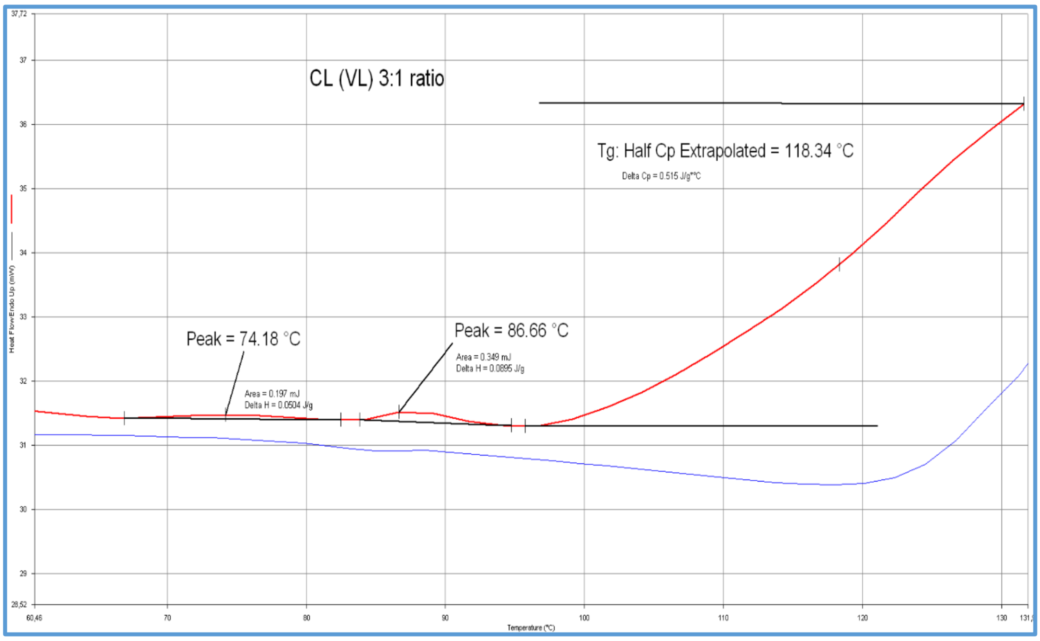


Figure 34. Calorimetry graph of CL(VL) 3:1

The glass transition temperature at 118.34^{O}C. This glass transition point is specific to cellulose laurates and it is in similar range as reported in literature [44].

Sample CL(VL) 3:1 has higher value of DS, so it is possible to determine Tm and Tg but for sample having low DS values, the signal of transition is so weak, and the curves have high noise level and weird shapes. For the reference, figure 35 and figure 36 is showing some experimental curves for low DS samples.

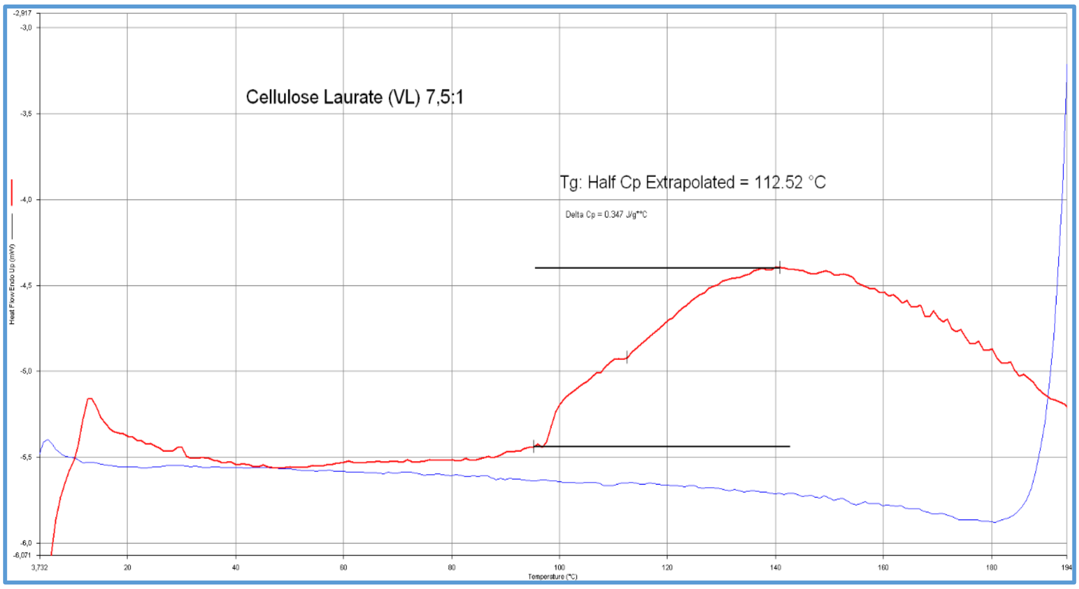


Figure 35. Calorimetry graph of CL(VL) 7.5:1

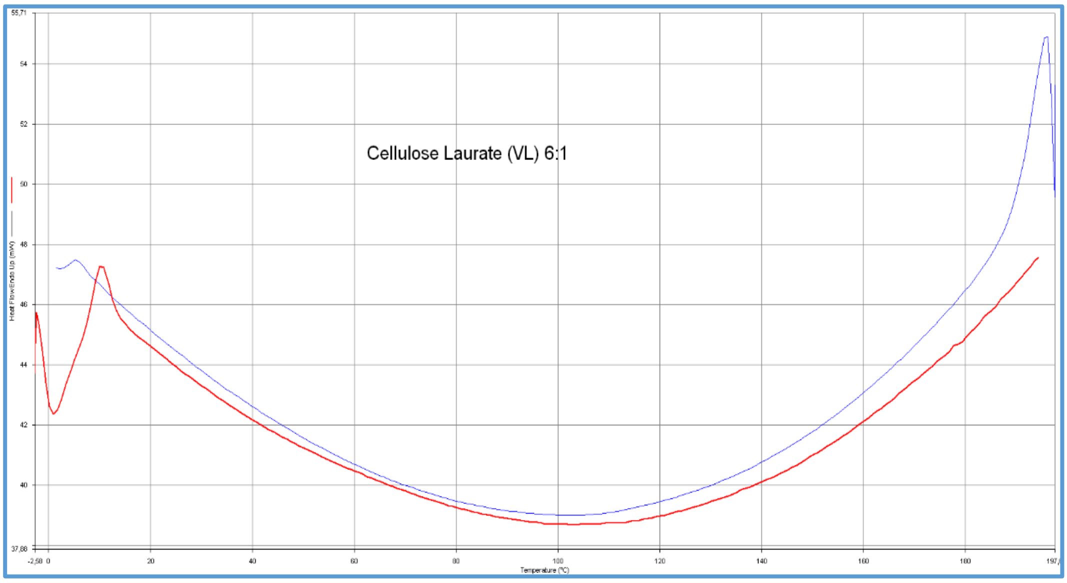


Figure 36. Calorimetry graph of CL(VL) 6:1

SUMMARY IN ENGLISH

Cellulose stearate and cellulose laurate were produced as thermoplastic cellulose derivatives by esterification reaction. Ionic liquid [BMIM]Cl was synthesized and used as reaction media, synthesized ionic liquid was good enough to dissolve maximum 2 wt.% of cellulose. [EMIM]Cl was also used as reaction media in the synthesis of cellulose laurate by using vinyl laurate as acylating agent.

Procedure was developed to synthesize cellulose derivatives. Cellulose laurate with different degree of substitution were prepared, highest DS value of cellulose laurate obtained was 1.22 by FTIR with molar ratio of CL(VL) 7:1 at optimum reaction condition (temperature 100°C and time 3 hrs.). Effect of time and temperature and molar ratio is also summarized.

Procedure for determination of DS by FTIR is established along with proposal of formula for DS evaluation by FTIR. Glass transition temperature (Tg) of CL obtained was near 120°C and melting point near 90°C.

KOKKUVÕTE EESTI KEELES

Tselluloosstearaat ja tselluloosilauraat toodeti tselluloosi termoplastsete derivaatidena esterdamisreaktsioonil. Ioonne vedelik [BMIM]Cl sünteesiti ja sede kasutati reaktsioonikeskkonnana. Sünteesitud ioone vedelik suutis lahustada maksimaalselt 2 massiprotsenti tselluloosi. [EMIM]Cl rakendeti kasutati reaktsioonikeskkonnana ka tselluloosilauraadi sünteesis, kasutades atsüüliva ainena vinüüllauraati.

Töötati välja protseduur tselluloosi derivaatide sünteesimiseks. Valmistati erineva asendusastmega tselluloosilauraat. Saadud tselluloosilauraadi suurim asendusastme (DS) optimaalsetes reaktsioonitingimustes (temperatuur 100^{o}C ja aeg 3 tundi) FTIR spektroskoopia põhjal väärtus oli 1,22, , kasutades vinüülestrit ja tselluloosi 7:1. Saadud tselluloosilauraadi klaasisiirdetemperatuur (Tg) oli ligikaudu 120°C ja sulamistemperatuur ligikaudu 90°C. Töö tulemusena on välja selgitatud reaktsiooni aja, temperatuuri ja moolsuhte mõju asendusastmele.

Töö tulemusena on loodud protseduur ja vastav arvutusmetoodika asendusastme määramiseks FTIR spektroskoopiat kasutades.

CONCLUSION

1. Titration is not reliable method for the calculation of DS as it is too sensitive.
2. Qualitative analysis by infrared spectroscopy showed that cellulose is derivatized.
3. The functional relationship between peak intensity ratio and $DS_{Tit.}$ is more correlated.
4. The best calculated results are from developed formula $\boldsymbol{DS_{FTIR} = \frac{R_I+0.0328}{1.5167}}$ that connects intensity and DS without intercept, this formula fits best evaluation of DS by measurement of **C=O** intensity.
5. Reaction condition plays vital role while increasing molar ratio of substituent.
6. Thermal transitions are more prominent in cellulose derivatives with high DS values.

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