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SYNTHESIS AND ELECTROSPINNING OF CELLULOSE STEARATE

MASTER THESIS

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Technology of Wood and Plastic, KVEM 12/13

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TSELLULOOSSTEARAADI SÜNTEES JA ELEKTROKETRUS

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Abbreviations and Acronyms

$[BF_4]$	Tetrafluorobromide
$[C_4min]Cl$	1-butyl-3-methylimidazolium chloride
$[CF_3SO_2]$	Trifluoromethanesulfonyl anion
CS	Cellulose Stearate
˚C	Degree Celsius
cP	Centipoise
DMAc	Dimetilacetone
DMF	N,N-dimetilfesamida
DCS	1,2-dichloroethane
DMSO	Dimetilsulfoxide
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared spectroscop
IL	Ionic liquid
ILs	Ionic liquids
MeOH	Methanol
T_m	Melting Point
PLA	Polylactic acid

T_g	Glass transition temperature
T_m	Melting temperature
T_c	Crystallization temperature
THF	Tetrahydrofuran
kV	Kilovolts
nm	Nanometer
T_b	Boiling point
ml/h	milliliter (unit of volume) per hour
SEM	Scanning electron microscopy
µm	micrometer (unit of length)

CONTENTS

Declaration

Hereby I declare that this master thesis, my original investigation and achievement, submitted for the master degree at Tallinn University of Technology has not been, submitted for any other degree or examination.

Ramkumar Jayapal

MASTER’S THESIS ASSIGNMENT

Name of the student: Ramkumar Jayapal **Student Code:** 131216 KVEM

Master’s thesis topic: SYNTHESIS AND ELECTROSPINNING OF CELLULOSE STEARATE

Supervisor: Dr. Illia Krasnou.

Aim of Master Thesis: The aim of the thesis is to develop technology for producing cellulose fatty acid esters that later will be used to produce fibrous materials by means of electrospinning.

ABSTRACT

In, this thesis work cellulose stearate (CS) is used to make fibres by means of electro spinning. To obtain cellulose stearate, cellulose is reacted with stearoyl chloride using 1-butyl-3-methylimidazolium chloride (an ionic liquid) as a reaction media. The length of its side chains is 18 carbons and the product obtained is a fatty acid ester. Before obtaining the polymer is necessary to synthesise the reaction media.

Electrospinning was tried with different concentration from 7% to 20 % of polymer. And best result was obtained at 15% of CS. CS is dissolved in mixed solvent toluene + Dimethylacetamide (DMAc) (volume ratio of 4:1) at concentration of 15%, we obtained a thin uniform coating. Even though the fibres were not obtained a thin uniform coating was obtained, which is quite positive result and can be taken to next level of research work.

Since electrospinning with CS was not successful to obtain fibres an alternative technic is performed by using CS as composite material with polylactic acid (PLA). With total concentration of 15 % PLA + CS (2 : 1) in mixed solvent toluene + DMAc (4 : 1) we successfully obtained fibers.

Keywords: cellulose stearate, Electrospinning, fibers, stearoyl chloride.

INTRODUCTION

Nowadays there is huge demand for Nano and Micro fibre material which is used in different application, and productizing these materials with natural available polymer like cellulose is more sustainable and environmental friendly. One of the popular technology and cost effective method to product nano and micro fibre is electro spinning [1]. The polymer material chosen for this research work is cellulose.

Cellulose is not an easy material to work because of its crystalline structure is very strong. Some cellulose derivatives have been tried to electro spin before, such as cellulose acetate (the most famous one), ethyl cellulose [2], methylcellulose [1, 2], etc. A lot of papers have been published about cellulose acetate and some of them talk about cellulose esters that come from cellulose substituted with long aliphatic chains from fatty acids [2]. And this is the topic that concerns this project, obtaining fibres from a cellulose derivative that comes from a fatty ester, which is quite innovative.

The characterization of the polymer is done with differential scanning calorimeter and FTIR. The degree of substitution (DS) was estimated by means of saponification method after the polymer is obtained. The degree of substitution (DS) should be as big as possible because the properties from the compound obtained are better than the ones with low DS. For electro spinning a high solubility in organic solvents is needed in order to prepare the mixtures. So, the DS has to be high. And, other important parameters for electro-spinning are solution parameters (concentration, molecular weight, viscosity, surface tension and type solvent) and processing parameters (voltage, flow rate, collector, distance between the tip of the needle and collector drum, parameters of ambient air) for obtaining the proper fibres [3].

Since, cellulose stearate is totally new cellulose derivative, which has not been tried before with electro spinning it’s really hard to find the perfect condition, concentration of polymer and perfect solvent for electro spinning. So the only way to find the all parameter is by intensive lab experiment.

To understand electro spinning process different know polymers are tried, which is very useful when we are working with new polymer like cellulose stearate. For this reason four different biopolymers (cellulose acetate, cellulose Di-acetate, cellulose Tri-cellulose acetate and polylactic acid are chosen and studied under different electro-spinning condition with different solvent .With 5% of Cellulose acetate mixed with Dicholoethane (DCE) : Methanol at a ratio of 4 : 1,and with Tri cellulose mixed with Dicholoethane : Methanol at a ratio of 4:1 no fibres was formed ,only droplet was formed on the collector drum. And, with 5% Di-Cellulose acetate mixed with Dicholoethane : Methanol at a ratio 4:1 un-continues lengthily fibres was obtained. And with 8% to 12% PLA mixed with DCE : Acetone at a ratio of 10 : 1 we obtained lengthy fibres obtained. This result gives us basic understanding of electro spinning process and its conditions.

1. Solution parameter plays a major role in electro spinning, like (viscosity, surface tension, solvent volatility, and solution phase transition of the polymer in Solvent. In our project our initial selection of solvent is based on solubility of the solvent with cellulose stearate in it. Solubility of the solvent is checked manually by mixing a small amount of CS in different solvents and by this test some good solvents are found: toluene, chlorofrom, dimethylformamide (DMF), and pure solvents were: Dimethyl sulfoxide (DMSO), DMAc, acetone and formic acid. Each of good solvent is mixed with pure solvent with different ratio as shown in Table 4.1 with CS for electrospinning. But the best result is with 15% of CS in mixture of toluene and DMAc (volume ratio of 4:1) were we obtained - a thin uniform coating was generated. One reason pure chloroform and DMF was not suitable for electro spinning with CS. Chloroform has very high volatility it means rapid evaporation leads to no fibre generation and with DMF solidification of the polymer at spinneret tip had happened.

2. Concentration is also another important factor that plays a major role to obtain fibres, at concentration from 7 % to 20 % electrospinning is tried and suitable concentration was 15 % of CS in mixed solvents. Concentration above 15 % of CS has very high viscosity and low surface tension which make electrospinning process difficult; because polymer solvent gets dried fast inside needle before it reaches the collector drum. At the concentration below 15 %, polymeric micro particles are obtained. At this time, electrospray occurs instead of electrospinning owing to

the low viscosity and high surface tensions of the solution, resulting in droplet and uneven droplet formation on the collector drum.

3. Ambient air parameters can also affect the formation of fibres, fibres diameter and morphology these are: humidity and temperature. As, mentioned above 15% of CS in toluene + DMAc (volume ratio of 4:1) has best result, but at room temperature the polymer is not soluble enough so to obtain good solution it has to be heated to (45 ºC - 60 ºC) for 1 hour with mechanical stirring. And, it has to maintain at this temperature (45ºC - 60ºC) during electrospinning process to get best result, low temperature increases the viscosity and it’s imposable to electro spin such system. On the contrary, high temperature decreases the viscosity but evaporates the solvent fast before it reaches the collector and result in no fibres.

4. Distance between the Collector and the Tip of the Syringe, It has been proven that the distance between the collector and the tip of the syringe can also affect the fibre diameter and morphologies [4] In brief, if the distance is too short, the fibre will not have enough time to solidify before reaching the collector, whereas if the distance is too long, bead fibre can be obtained. It is well known that one important physical aspect of the electro spun fibre is the dryness from the solvent, so optimum distance is recommended. And, the optimum distance, used to obtain the best result was 10 - 15 cm.

5. Applied voltage is the crucial factor. However, the voltage applied does not affect the formation of the fibre it only affect the diameter of fibre. This parameter is little controversial example Reneker and Chun [5] have demonstrated that there is not much effect of electric field on the diameter of electro spun polyethylene oxide (PEO) nanofibers. But, some studies have shown that higher voltages can increase the electrostatic repulsive force on the charged jet, favouring the narrowing of fibre diameter and high possibility of formation of fibre. For example, Yuan et al. [6] investigated the effect voltage on morphologies and fibre alignment with polysulfone (PSF) / DMAc / acetone. And, as far our investigation 15 kv to 30 kv does not make any different in result. And, we had the same result in between this voltage, more than voltage the significant factor for fibre formation is the concentration of the solution.

6. Flow rate, of the polymer solution within the syringe is another important process parameter. Generally, lower flow rate is more recommended as the polymer solution will get enough time

for polarization. [7] If the flow rate is very high, bead fibres with thick diameter will form rather than the smooth fibre with thin diameter owing to the short drying time prior to reaching the collector and low stretching forces [7] but in our investigation the lowest flow was 1.5 ml/hr and highest was 3.0 ml/hr which also does not make any difference in the formation of thin uniform coating. And, again this parameter does not make any difference in result. Below 1.5 ml/hr, the polymer solution was spared and droplet was formed in the collector drum.

CHAPTER 1. OVERVIEW

1.1. Components used for Cellulose Stearate synthesis

1.1.1 Cellulose

Cellulose is the most abundant natural polymer. It is of major commercial and scientific importance with a variety of natural properties that could be used for industrial purposes. With a perspective to improve its solubility and thermoplasticity, the production of cellulose fatty acid esters [1] is one of the most interesting aspects of its chemical modification. Since its one the abundant material and sustainable material present in market [1] it's a wise to use the material in industrial and other application where ever possible

For many centuries it has served mankind as a construction material, mainly in the form of intact wood and textile fibres such as cotton or flax, or in the form of paper and board. On the other hand, cellulose is a versatile starting material for chemical conversions, aiming at the production of artificial, cellulose-based threads and films as well as a variety of stable cellulose derivatives used in many areas of industry and domestic products. [2]

Cellulose is a polysaccharide the repeating unit in cellulose is actually made up of two glucose units with each glucose unit in the linear chain being “turned over”. Cellulose is the basic structural component of plants cell walls plants - 33%, cotton - 90% and wood - 50% of mass. [23]

1.1.2. Structure

Cellulose is a polymer made of repeating glucose molecules attached end to end (thus cellulose is an example of a polysaccharide). A cellulose molecule may be from several hundred to over 10,000 glucose units long. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibres have chain lengths ranging from 800 to 10,000 units [28].

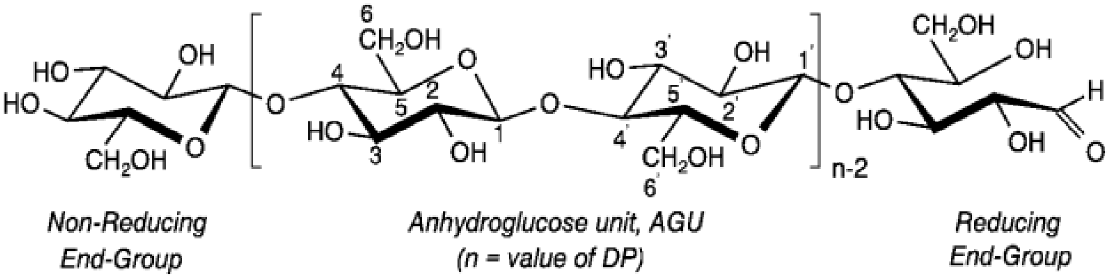
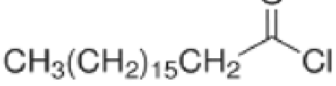


Figure 1 .Structure of Cellulose [9]

1.1.3. Stearate chloride

Generally, acid halides are obtained directly from the corresponding carboxylic acid with a variety of reagents. The two widely used reagents are thionyl chloride and oxalyl chloride. An important point is that the other halides (fluorides, bromides and iodides) are prepared with an exchange process between the acid chloride and another suitable source of halide. Specifically, stearoyl chloride is a halide obtained from a carboxylic acid, stearic acid, which is included in the huge group of fatty acids. [8]



$CH_3(CH_2)_{15}CH_2C(=O)Cl$

Figure 2.Molecular formula of stearoyl chloride [10]

The acid from which it comes has 18 carbons so it is an octadecanoic acid and it is a saturated fatty acid [26]. The only functional group that stearic acid has is the carboxylic group at the end of its chain. Referred to fatty acids, it is good to mention that are known more than 1000 natural acids but only around 50 are important. They can be found in milk fats and in some vegetable oils. [11].

1.1.4. IL used: 1-butyl-3-methylimidazolium chloride ([C4min]Cl)

Lots of simulations and experimental studies have been done about imidazolium based ILs [13] . This kind of systems has polar and non-polar domains. Besides that, using this kind of IL has some risks because of their toxicity (they can contaminate soil and water). ILs can become persistent pollutants and generate environmental risks. [12]

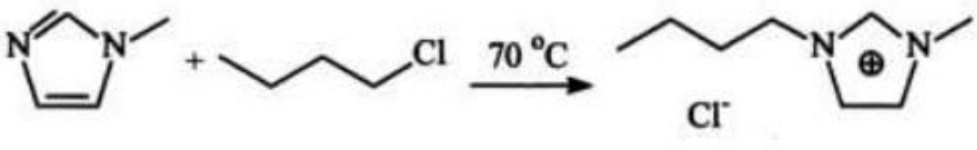


Figure 3.Reaction of [c4min]Cl obtained [13]p.219

Synthesis of 1-alkyl-3-alkylimidazolium chloride is well known. The reaction involves such reagents as N-alkylimidazole and alkyl chloride and it is called quaternization reaction [14]. Usually high pressure is used. [13] In order to obtain [C4min]Cl, the reagents that should be mixed are N-methylimidazole and chlorobutane.

1.1.5 Solvents used and their properties

Table 1.Solvents properties [29]

Solvent	**Density (g cm^{-3})**	**Boiling point (˚C)**	**Dipole Moment (Debye)**	**Dielectric Constant**	**Shear Viscosity (mPa s)**	**Surface Tension (mN m^{-}1) at 23˚C**
1-2-Dichloroethene(DCE)	0.86	85.00	1.25	10.36	1.02	38.75
Acetone	0.79	56.30	2.70	20.70	0.30	22.70
Chlorofrom	1.48	61.20	1.01	4.80	0.54	22.70
Ethyl Acetate	0.90	77.50	1.78	6.08	0.42	23.75
Dimethyl sulfoxide (DMSO)	1.09	189.00	4.09	46.70	1.99	43.54
Dimethylacetamide (DMAc)	0.94	165.00	3.72	37.80	0.95	32.43
Formic Acid	1.21	100.70	1.40	58.50	1.80	24.40
Methanol	0.79	66.70	1.60	32.60	0.55	22.10
Tetrahydrofuran (THF)	0.89	67.00	1.75	7.52	0.46	26.40
Toluene	0.86	110.62	0.30	2.38	0.56	28.53
Water	1.00	100.00	1.84	78.40	0.89	72.00

CHAPTER 2. LABORATORY PROCEDURES

2.1 Techniques for polymer characterisation

2.1.1. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC), is a thermal analysis technique that shows at how a material's heat capacity (C_p) is changed with temperature change. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions such as melts, glass transitions, phase changes, and curing. Because of this flexibility, since most materials exhibit some sort of transitions. In polymer science it's very important to understand the Glass transition temperature (T_g) because it's one of the most important property that can be implemented in particle and critical in production design.

Table 2 .Transition Point measured in polymer

Polymers	T_g	Indicator of material properties, effect of additives
	T_m	Polymer processing , heat history
	Exothermal	Reaction rate, curing of material, residual cure
	C_p	Energy need to process
	T_c	Recrystallization time, kinetics

2.1.2. Experiment

DSC was done on PerkinElmer Diamond DSC7 to analyse the data Pyris software were used. We have two pots; in one pot a polymer sample is placed. Another one issued for reference cup for comparison, it is empty. Each pot is placed on the furnace which is controlled by software from a computer and it warms both pots up at a certain rate, usually somewhere around 20°C per minute and the program is shown below. The computer monitors that the rate of heating remained the same during the whole experiment. And it is important to keep the two different pots with their respective heaters warming up exactly at the same rate Isothermal crystallization is performed using and the experiment is knows as time-to-event (TTE) experiments and also called as in isothermal crystallization, this process involves conditioning the test specimen at a temperature about 20 °C above the melting temperature, then cooling the specimen to the isothermal test temperature below the melting temperature. This test helps us to find the melting point, crystallization point of material and also quality of the material. [17, 30, 31, 32]

Time-to-event (TTE) experiments

- Hold for 1.0 min at 200.00°C
- Cool from 200.00° C to 0.00°C at 20.00°C/min
- Hold for 1.0 °C at 0.00°C
- Heat from 0.00°C to 200°C at 20.00°C/min
- Hold for 1.0 min at 200.00°C. And the DSC data collected with empty aluminium lid as references as shown below.

In this case the pot containing the polymer sample requires more heat to maintain the same rate of temperature rise as the empty (reference) pot. As the heater under the pot with the sample works harder than the heater under reference pot it must consume more energy. And by comparing the two pots in their entirety we can find out about thermal processes in the polymer sample.

2.1.3. FTIR spectroscopy

Analysing the sample with this technique is useful because it permits to confirm the product that is obtained with the reaction of esterification. In order to compare and be sure about the reaction has been successfully completed, cellulose is analysed too. The infrared spectroscopic analysis was performed on a spectrometer FT-IR with an ATR (Attenuated Total Reflectance) accessory. The brand of the spectrometer is Interspectrum® and the accessory is Specac. The range of wavelength used is from 500 cm^{-1} to 4500 cm^{-1} with spectral resolution of 2 cm^{-1}. The scans taken from each sample are 8 and from the background are 8 too. Those are overlapped forming a unique graph for each sample.

Thanks to ATR accessory, not only samples that are transparent and solid can be analysed. Liquid, powder, films, etc. samples could be tested directly because when a sample preparation is involved in between, some properties might change. So having this equipment allows to obtain of the spectra easier and it is a good way to ensure that the sample remains with the same chemical composition and how it is synthesized.

2.2. Electrospinning:

The electrospinning process has many variables to be discussed in the results section but the mechanics of the spinning is similar for every method practiced. The polymer solvent solution emerges from the nozzle and forms a droplet. The nozzle is charged which transfers its electrical charge to the droplet. At a characteristic voltage, the droplet will change shape and depart forming what is known the Taylor cone [19] Electrospinning, the polymer solution is subject to very high electrostatic force which causes the polymer solution or melts to being ejected a spray rapidly from a nozzle and deposited randomly on collector as fiber or matt. A straightforward, cheap and unique method to produce novel fibers with a diameter in the range of 100 nm and even less is related to electrospinning. For this goal, polymer solutions, liquid crystals, suspensions of solid particles and emulsions, are electro spun in the electric field of about 15 kV - 30 kV.

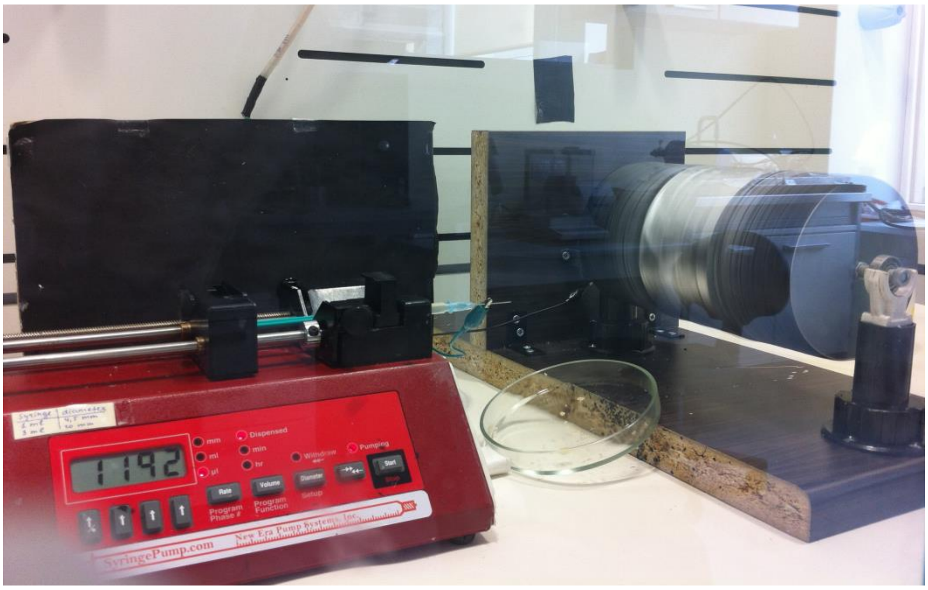


Figure 4. Single Syringe Electrospinning Setup

The electric force results in an electrically charged jet of polymer solution flowing out from a pendant or sessile droplet. After the jet flows away from the droplet in a nearly straight line, it bends into a complex path and other changes in shape occur, during which electrical forces stretch and thin it by very large ratios. After the solvent evaporates, fibres are left on the collector drum.

2.2.1 Selection of Solvents used for electrospinning

The Electrospinning process is control by many parameters, like solution parameters, process parameters, and ambient parameters. Solution parameters include viscosity, conductivity, molecular weight, and surface tension and process parameters include applied electric field, tip to collector distance and feeding or flow rate. [24] All this factor deepens on one another and significantly affects the output of the fibre morphology. And, all this affects has been discussed in the introduction.

The parameter mentioned above main factors the morphology of fibre, its diameter of the fibres. But, one of the foremost step in the electrospinning process is preparing polymer solution has greater influence on the formation of the fibre. Selection of Solvent depends on the solubility of solvent in the polymer; some of the other properties are good volatility, vapour pressure, boiling point and should maintain the integrity of the polymer solution. The intermolecular interaction in a polymer–solvent system (binary system) is either attractive or repulsive which depends solely on the type of solvent [24].

Table 3. Solubility check

Solvent	CS (1:5 IL and stearoyl chloride high purity)	CS(1:5) technical IL and stearoyl chloride high purity)	PLA
DCE	Turbulence	Soluble	Soluble
Acetone	Soluble	Soluble	Soluble
Chlorofrom	Soluble	Soluble	Soluble
Ethyl Acetate	Turbulence	Soluble	Turbulence
DMSO	No soluble	Turbulence	Soluble
Formic Acid	Turbulence	Soluble	Turbulence
Methanol	No soluble	No soluble	Turbulence
THF	Turbulence	Turbulence	Soluble
Toluene	Soluble	Soluble	Turbulence

2.2.2 Hot Electrospinning.

In, this work hot electro-spinning is used for two main reasons,

1. Solution is too viscous: Since, we are using higher polymer concentration in the solvent, the viscosity of the polymer solution is too high and, it is very difficult to pump solution during the electrospinning process. Especially spraying is very difficult due to high viscosity and also the polymer solution gets dried very fast before reaching the collector drum.

2. Avoid precipitation: Cellulose stearate is purely soluble in mixed solvents and solution is transparent at 65˚C as shown in Figure 5.A. At room temperature or below 65˚C it precipitates or looks like a dry solvent as shown in Figure 5.B. and it’s not suitable for electrospinning. So, the best solution to avoid this kind of problems is to use hot- electrospinning.

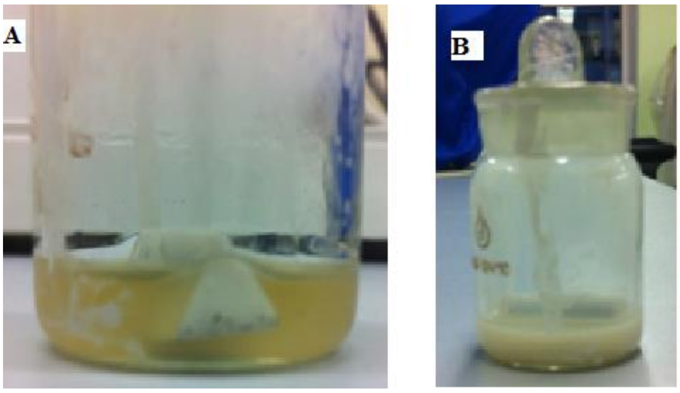


Figure 5 A. 12 % C.S of DCE : Accetone (10:1) soluble and Transparent at 65 C. B. 12 % of CS mixed with DCE : Acetone (10:1)

A small copper cylindrical coil is shown in the Figure 6. with central hole 0.8 mm (needle can be inserted) is used to restrain heat of the needle during electrospinning process. This helps the polymer solvent to flow continuously even with the high viscosity. Heating of the copper is done manually with candle for approximately 1 - 2 min. (approx. temperature 70-80 ˚C) during spinning process.

Figure 6. Needle with copper cylinder (with central hole of 0.8 mm)

Objective of this project:

- Study different biopolymers cellulose acetate, cellulose di-acetate, cellulose tri-acetate and polylactic acid and find suitable condition for electrospinning.
- Synthesize cellulose stearate with certain degree of substitution
- Purify the polymers obtained. Make sure of its purity carrying out DSC test and also
- Evaluation of the esterification reaction efficiency by FTIR.
- Test out the solubility of the polymers obtained in organic solvents.
- Find suitable solvent conditions for electrospinning mixtures.

CHAPTER 3. LABORATORY PROCEDURE

3.1. Steps involved in synthesis cellulose stearate

Synthesis Cellulose stearate and obtaining the polymer consists of three stage

- Stage one: dissolving cellulose into IL
- Stage two: one of reaction between cellulose and stearoyl chloride itself and
- Stage three: washing and drying the polymer obtained.

3.2. Dissolving cellulose into IL

Before dissolving the cellulose into IL, it should be dried because presence of moisture will decrease the solubility of cellulose in IL and may make second crystallization. Cellulose is dried at 105˚C in vacuum oven overnight.

IL of weight 150g is taken in an Erlenmeyer flask heated at 105˚C and stirred under vacuum. Cellulose of weight 150g is added to IL. But, one very important point should be noted while adding the cellulose is that it should be little by little to avoid lump formation.

After 150g of cellulose is completely added to the IL, it should be cooled down to 100˚C and kept stirred under nitrogen atmosphere for 24 hours or until it becomes transparent figure (see below).

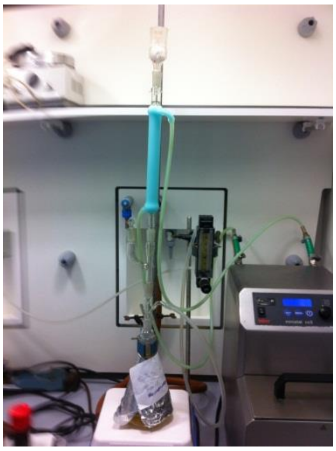


Figure 7 Setup cellulose stearate - process

3.3. Reaction

The reaction can be done with stearoyl chloride and cellulose in ratio 1:5 the aim of that is to test out the degree of substitution obtained and which are the best conditions for obtaining a good polymer. Stearoyl chloride is added drop by drop into the cellulose solution in IL, with temperature of 85˚C stirring with and nitrogen for 3 hours.

3.4. Washing and drying of Polymers

After reaction is completed, the mixture is not homogeneous anymore because cellulose stearate, is not soluble in IL (it precipitates like powder). As it can be seen in the following pictures, at the end of the reaction the mixture becomes whiter (CS obtained is dispersed in the IL)

3.5. Saxhlet Extraction Setup

This method is used to separate the polymer from ionic liquid & stearoyl chloride. The solvent (methanol) is heated (125˚C) to reflux. The solvent vapour travels up thedistillation arm and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material as shown in the figure 7. This process is repeated until polymer become white or separated from ionic liquid approximately 12 hours. And, after this method the polymer is washed with 100 ml of methanol and filleted one time.

Figure 8. Soxhlet extractor setup (with 100ml of methanol at 125˚C)

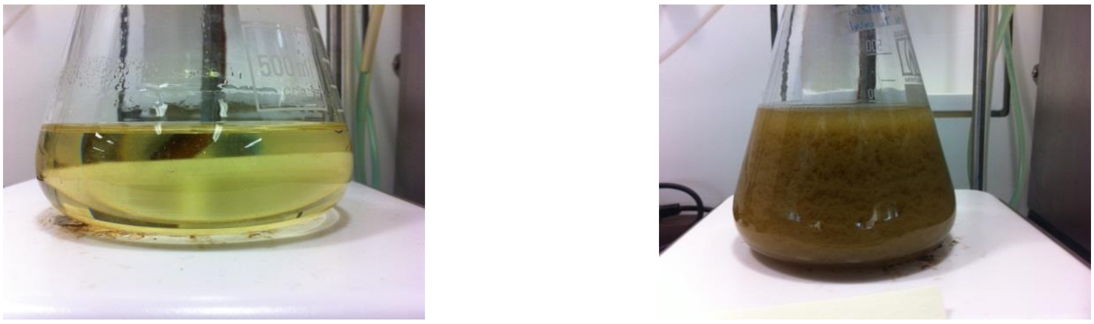


Figure 9. On the left IL with cellulose and stearate chloride and on the right polymer ready to wash

In, order to precipitate, methanol is added and left over night. As shown in the Figure 9 you can see the polymer is completely separated from IL. The filtration used is vacuum filtration because it makes the procedure faster and the polymer gets dry easily. And, second wash is also with methanol stirred for an hour and again filtration process is repeated. The procedure is repeated for one more times.

After the filtration process the polymer is dried at 60 ˚C under vacuum pressure for overnight to remove the solvents from the polymer.

3.6 Preparation of polymer solution for electrospinning process

The preparation of electrospinning solution as a single solvent or mixed solvent. The polymer is mixed with solvent by magnetic stirrer in room temperature for 30 - 180 min or either with temperature 35ºC - 45ºC for 30 - 180 min. This stirring process should be continued until the polymer solution became transparent as shown in the figure 10.B.below and this shown that the polymer is completely dissolved in solvent.

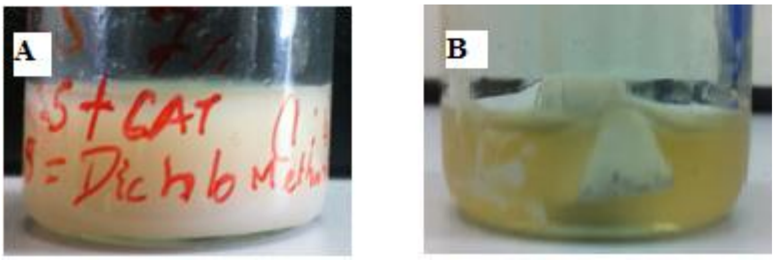


Figure 10.A. Precipitation of polymer in solvent B. Transparent Solution.

And on the other hand as shown in the Figure 10.A. that the polymer is not dissolved well in solvent. And, precipitated CS solution is not suitable for electrospinning process. Precipitation occurs in CS polymer for three reasons either the solvent is pure or mixed with pure solvent, or polymer solvent need more time to dissolve. At room temperature most of the CS solutions mentioned in the Table 4 are not good. But at 35ºC - 45ºC for 30-180 min all the solvent mentioned in the Table 4 dissolves CS.

CHAPTER 4. RESULT AND DISCUSSION:

4.1. Differential Scanning Calorimetry

DSC is very useful to determine phase transition of polymer, by heating and cooling. By this method we observe the melting peak (T_m) and in our case it should be only one peak, if it has more than one it means the polymer has impurities. If, it has more than one peak Tm it should be washed again to remove the organic solvent.

- Other compounds could present in CS
- Stearic acid: melting point (T_m) 69,8˚C [54]
- Stearoyl chloride: T_m 22˚C and boiling point (T_b) 178˚C [25]
- Water: T_m 0°C and T_b 100˚C.

Summarising, taking a quick view of the graphs, it can be seen that the polymer more purified. There is no stearoyl chloride remaining in the samples and water neither. The polymer melting temperature obtained in the range from 75˚C to 80˚C.

5.1.2. FTIR spectroscopy results

Two spectra have been obtained (one for each synthesis and one for cellulose). All of them are presented below. The results obtained from FTIR spectroscopy are presented in graphs (spectra). They are obtained directly from the instrument software used for examining the samples and they show the absorbance vs. wavenumber (cm^{-1}).

All peaks presented are referred to the bonds between the different atoms that shape cellulose stearate and other possible compounds that are remaining as impurities inside the polymer. Thus, it is really useful for detecting these impurities.

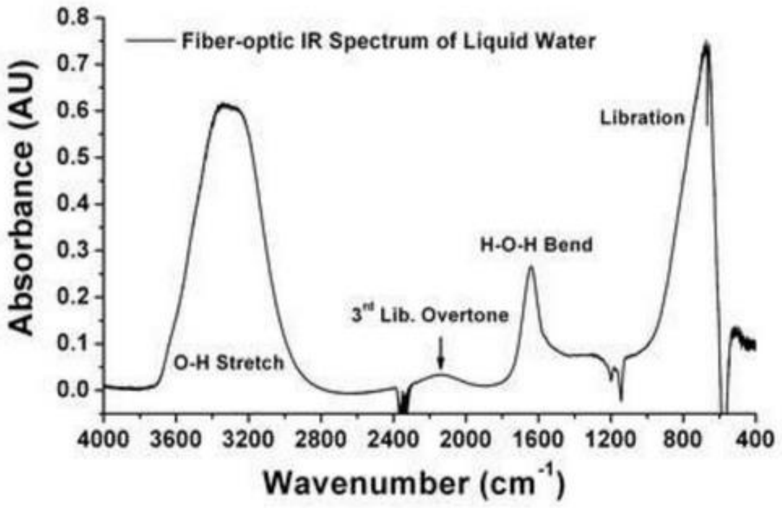


Figure 11 IR spectrum of liquid water [20].

To detect the obtained peak in Figure 13, there are two other spectra that are extremely important to compare: water in Figure 11 and steric acid Figure 12. The Figure 11 is important because it allows explain the shape of the polymer spectra in highest (over 3000 cm^{-1}) and in the lowest (under 1000 cm^{-1}) ranges. And, if the water spectrum and obtained spectra (cellulose and stearates) are compared carefully, it can be seen that they are similar. Hence, it can be said that there is water remains in the sample analyzed.

And from the figure 13 confirms the presence of carbon chain that come from the stearoly chloride, the reagent that provides the side chain in CS. They are formed from eighteen carbon and there are a lot of them so the intensity of the signal is sufficiently important for taking it into account. And this peaks referred to the presence of stearic acid in the mix,

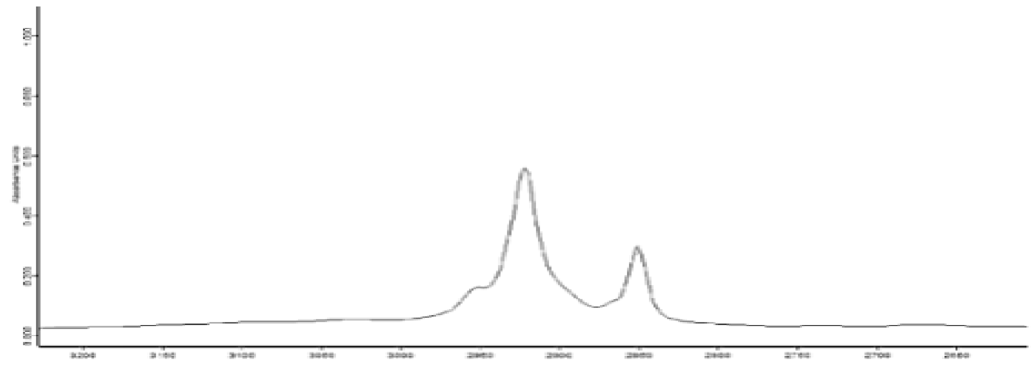


Figure 12 IR spectrum of stearic acid (peaks at 2900 and 2800 cm^{-1})[27]

4.2. Peaks obtained and general comments

Apparently, by taking a quick look to two graphs of cellulose stearate they seem to be the same. This is a good point because it means that all reactions have been carried out in a similar way. [23, 24, 25, 26]

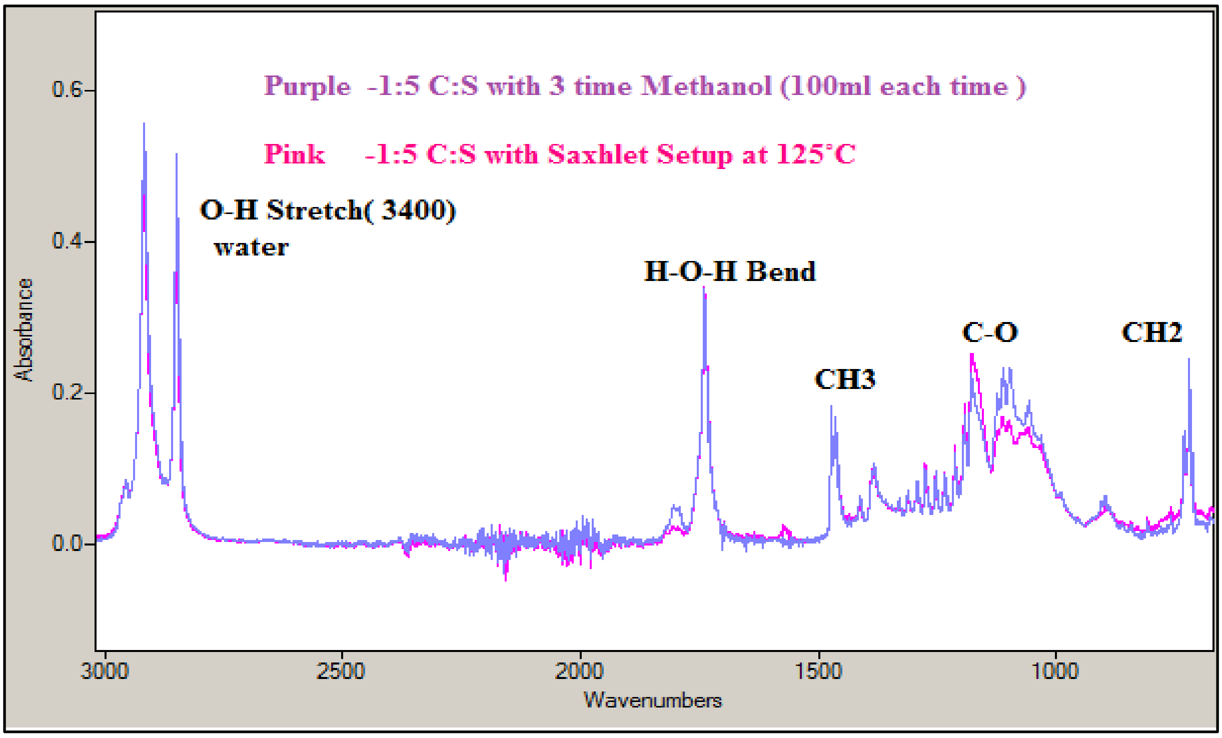


Figure 13 Purple is CS with 3 times methanol wash (100ml each time) and pink CS with Saxhlet Setup at 125

Table 4. Main peaks from the spectra and their meaning

Wavenumber(cm^{-1})	**Corresponding bond or group movement**	**Related Compound**
3400	O-H Stretch	Water
1600	H-O-H Bend	Cellulose OH
2800	C-H aliphatic	Aliphatic chain of 18 Carbons
2900		
1744	C=O	Ester
1237	C-O-C	
1000-1100	C-O	Ester and Cellulose C-OH
722	CH2 rocking	At least –CH2-CH2-CH2-CH2
1400	CH3	Last Carbon from Aliphatic Chain

4.3. Rheology

The electrospinning technique is controlled by several parameters, such as polymer solution and ambient parameters, being one of the most important parameters the solution viscosity, which allows defining the minimum viscosity needed to obtain fibres. The rheological analysis, allow us to estimate the molecular organization of the polymeric solutions and also to predict its dynamic properties, i.e. the viscosity. Temperature dependent test is performed, with different concentration as shown in figure below to understand does viscosity depends on temperature.

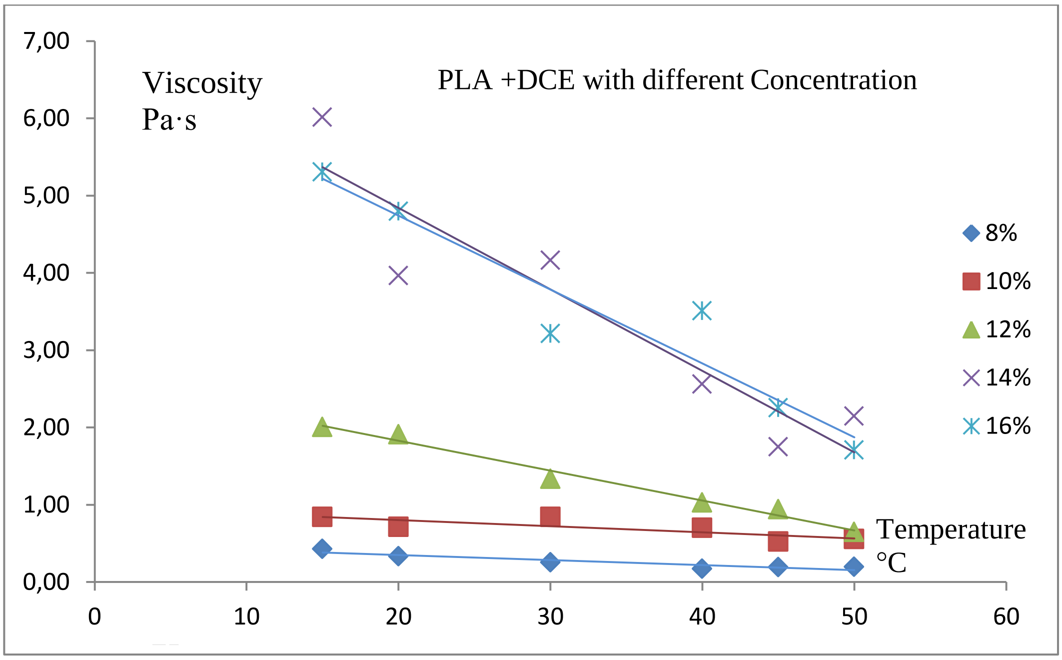


Figure 14. Dynamic viscosity vs. Temperature at different concentration of PLA in DCE

The viscosity of the solution has an effect on the electrospinning and the resultant fibre morphology. In general, the viscosity of the solution is connected to the extent of the entanglement of the polymer molecule chains within the solution. When the viscosity of the solution is too low, electro spraying may occur and polymer particles are formed instead of fibres. At a lower viscosity, where usually the polymer chain entanglements are lower, there is a higher similar that beaded fibres are obtained instead of smooth fibres. Therefore, factors that affect the viscosity of the solution will also affect the electrospinning process and the resultant fibres. [1]

By, observation of the (Figure 16) graph for 14% PLA solution in DCE between 20˚C and 30˚C there is increases in viscosity which means shear rate is not influenced by temperature and its same for 16% PLA in DCE between the temperature 30˚C - 40˚C and the viscosity is independent to temperature. And for 8%, 10% and 12 % PLA in DCE, when the temperature is increased, the shear rate is deceased. Which means viscosity is dependent on temperature.

4.4. Electrospinning

Since, we are dealing with new cellulose derivative; it was hard to find the suitable parameter (concentration of polymer in solvent, and electrospinning conditions). So, at first we tried with known cellulose derivatives and other known materials. Some of the materials were chosen as cellulose di-acetate, cellulose tri-acetate and PLA

Table 5.Electrospinning conditions and result

Sample	**Ratio of mixed Solvent (w/w)**	**Electrospinning Condition**	**Fiber Diameter**	**Observation**
5% Cellulose Acetate in Dichloroethane : methanol	4 : 1	15kV -0.6 ml/hr	No fibres	Dark patches obtained
5% Di-Cellulose Acetate Dichloroethane : Methanol-A Drop of Acetone)	4 : 1	15kV -0.6 ml/hr	Fibre Obtained 500 nm - 700 nm	Un-Continues Lengthily fibres Obtained
6% Tri-Cellulose in Acetate chloromethane : methanol-A Drop of Acetone)	4 : 1	15kV -0.6 ml/hr	No fibres	Unable to elerto-spary because of High Viscosity
7 % PLA in Dichloroethane : Methanol	4 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obtained 400nm -600 nm	Lengthy fibre obtained
8 % PLA in DCE : Accetone	10 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obtained 600nm -800 nm	Lengthy fibre obtained
9 % PLA in DCE : Accetone	10 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obtained 500 nm - 700 nm	Lengthy fibre obtained, But problem with electro spraying
10 % PLA in DCE : Accetone	10 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obtained 450 nm- 600 nm	Lengthy fibre obtained,But problem with electro spraying
12 % PLA in DCE : Accetone	10 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obtained 500 nm - 800 nm	Lengthy fibre obtained, But problem with electro spraying
15% PLA in Toluene+DMAc	04 : 1	15kV -30 kV ,0.6-3.0 ml/hr	Fibre Obationed 552 nm - 1300 nm	Lengthy fibre obtained

The objective of this is study is to try different material with electrospinning and find the idea condition and parameter for electrospinning and also to find out does temperature has any influent during electrospinning.

And, by the scanning electron microscopy (SEM) result as shown in the Figure.15,16 & 17.we obtained fibres for 8%, 9% and 10 % PLA in DCE + Ethanol (10:1) and there is continues electrospinning process and temperature does influence the electrospinning process. At 12% of PLA in DCE + Ethanol (10:1) the electro spraying is not continues and but lengthy fibre obtained.

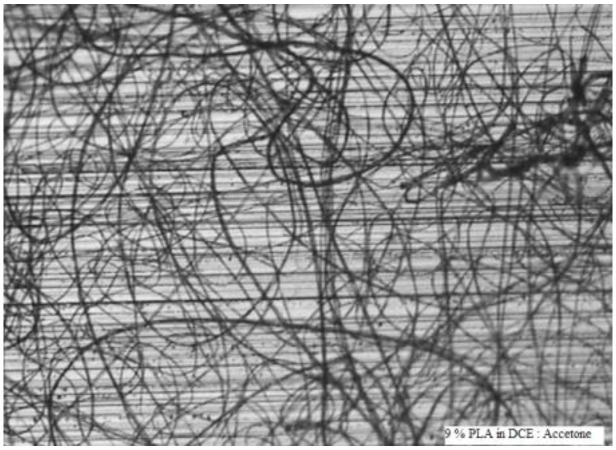
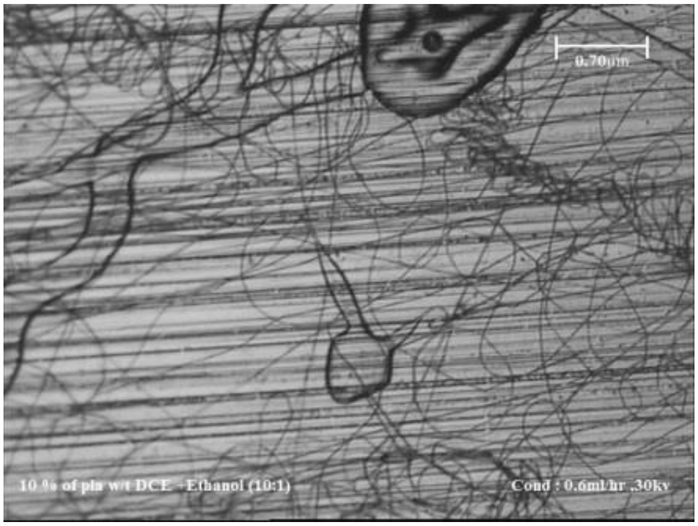


Figure 15 Microscopic image of PLA concentrations 8% in DCE+ Ethanol (10:1)



. Figure 16 Microscopic image of PLA Concentration 9% in DCE+ Ethanol (10:1)

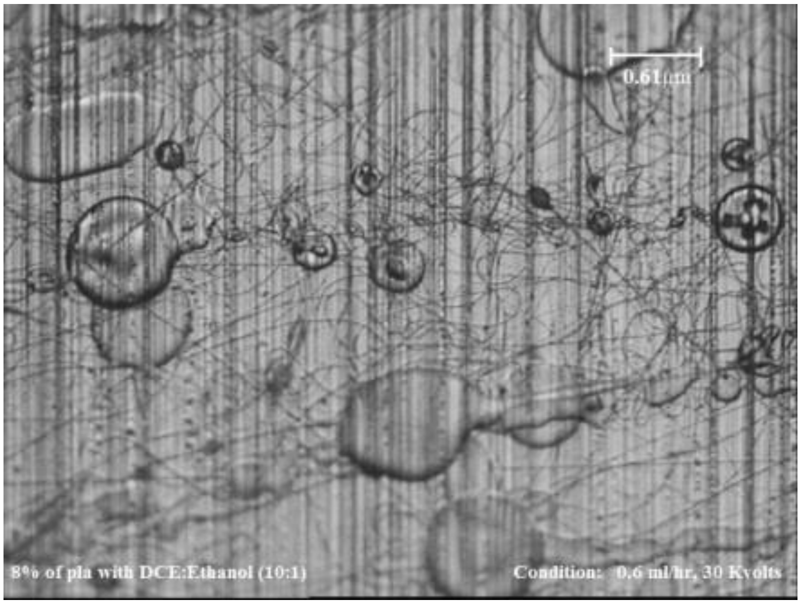


Figure 17 Microscopic image of PLA Concentration 10% with DCE+ Ethanol (10:1)

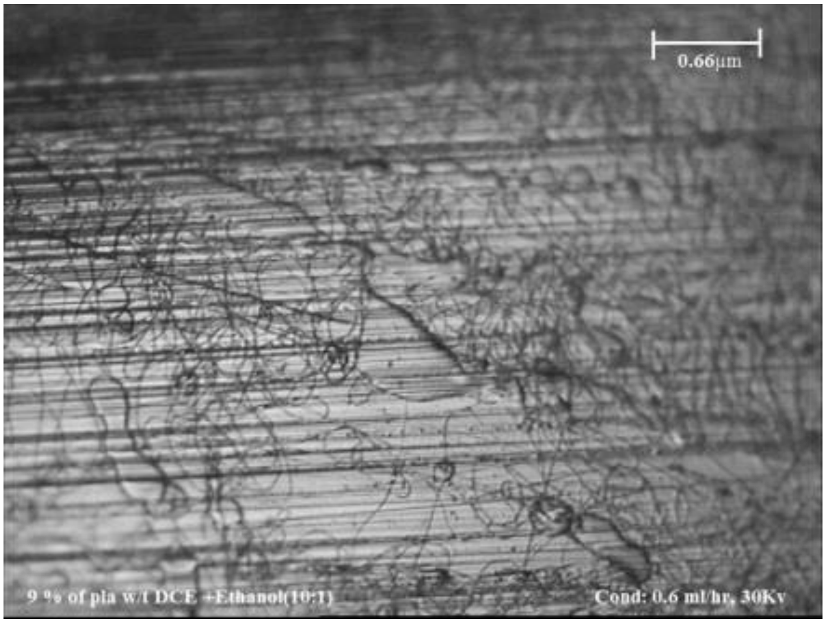


Figure 18. Microscopic 5% cellulose di-acetate in dichloroethane : methanol (4:1) with droplet of acetone

In Figure 18 is SEM image of 5% cellulose di-acetate where the fibre was obtained but the electro sparing was not continues, polymer solvent get dried faster before it reach the collector drum.

Sample	**Ratio of mixed Solvent (w/w)**	**Electrospinning Condition**	**Fiber Diameter (Nano Meter)nm**	**Observation**
7 % (w/w) CS Solution in Chlorofrom	1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
9 % (w/w) CS Solution in Chlorofrom	1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
11 % (w/w) CS Solution in Chlorofrom	1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
12 % (w/w) CS Solution in Chlorofrom	1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and elongated structure on the collector drum
20 % (w/w) CS Solution in Chlorofrom : THF	10 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and elongated structure on the collector drum
12 % (w/w) CS Solution in Chlorofrom : DMSO	4 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and elongated structure on the collector drum
12 % (w/w) CS Solution in Chlorofrom : MeOH	4 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
10 % (w/w) CS Solution in Toluene	1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
8 % (w/w) CS Solution in Toluene : MeOH	8 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
9 % (w/w) CS Solution in Toluene : DMSO	8 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
10 % (w/w) CS Solution in Toluene : THF	8 : 1	15kV 1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum
11 % (w/w) CS Solution in DCE : Acetone	10 : 1	15kV 30 kV -1.5- 3.0 ml/hr	No fibre obtained	Electro-sprays and Droplet formed on the collector drum

Cellulose stearates with all the soluble solvent with different concentration mentioned above in the table, electro spraying process was carried successful but only dark patches were collected in the collector drum. This because of very low concentration of CS in solvent and either the solvent mix is not suitable for CS.

Table 6. Electrospinning and results

Sample	**Ratio of mixed Solvent (w/w)**	**Electrospinning Condition**	**Fiber Diameter**	**Observation**
15 % of CS(1:5) Toluene : DMAc	1 : 1	15kV -30 kV ,0.6-3.0 ml/hr	No fiber obtained	Electro-sprays and Dark Patches on the collector drum
15 % of CS(1:5) Toluene : DMAc	2 : 1	15kV -30 kV ,0.6-3.0 ml/hr	No fiber obtained	Electro-sprays and Dark Patches on the collector drum
16 % of CS(1:5) Toluene : DMAc	3 : 1	15kV -30 kV ,0.6-3.0 ml/hr	No fiber obtained	Electro-sprays and Dark Patches on the collector drum
15 % of CS(1:5) Toluene : DMAc	4 : 1	15kV -30 kV ,0.6-3.0 ml/hr	No fiber obtained	Electro-sprays and Uniform Thin Sheet
15% PLA : CS (2:1) in Toluene+DMAc	4:1	15kV -30 kV ,0.6-3.0 ml/hr	Fiber Obtained 552 nm - 1300 nm	Lengthy fiber obtained

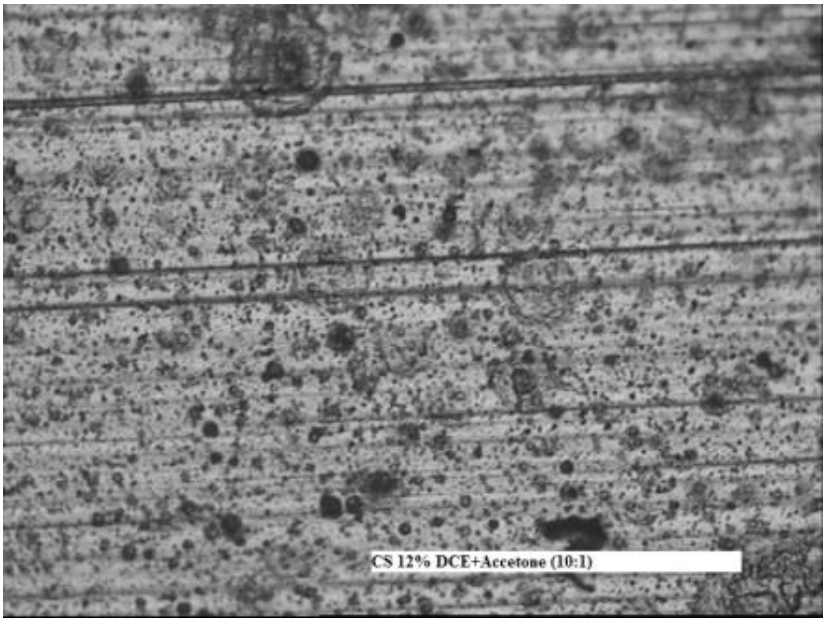


Figure 19. Microscopic image CS 12 % in DCE +acetone 10:1

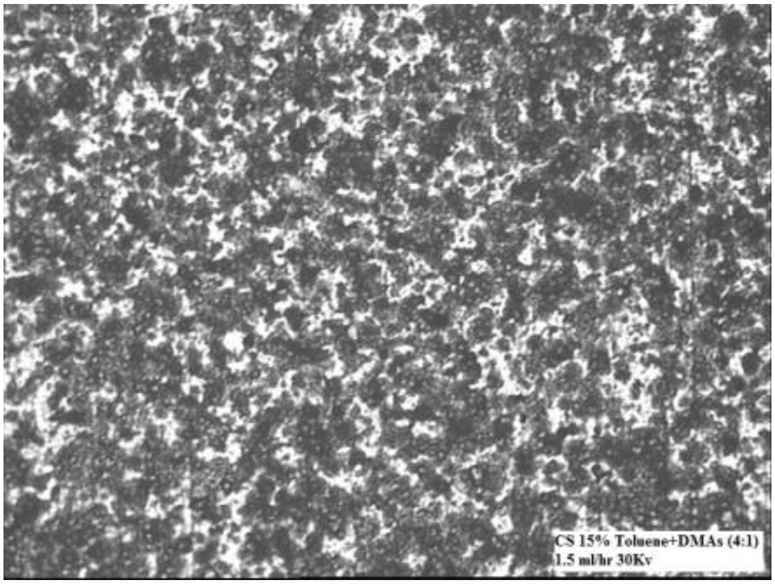


Figure 20. Microscopic image CS 15% toluene + DMA's(4:1)

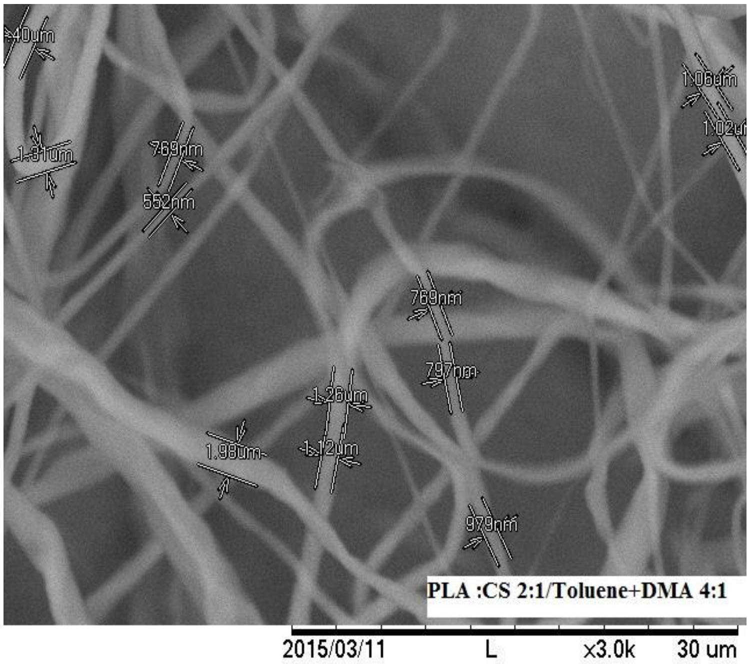


Figure 21. Microscopic image of 15 % of PLA + CS (2:1) in toluene + DMAc (4:1).

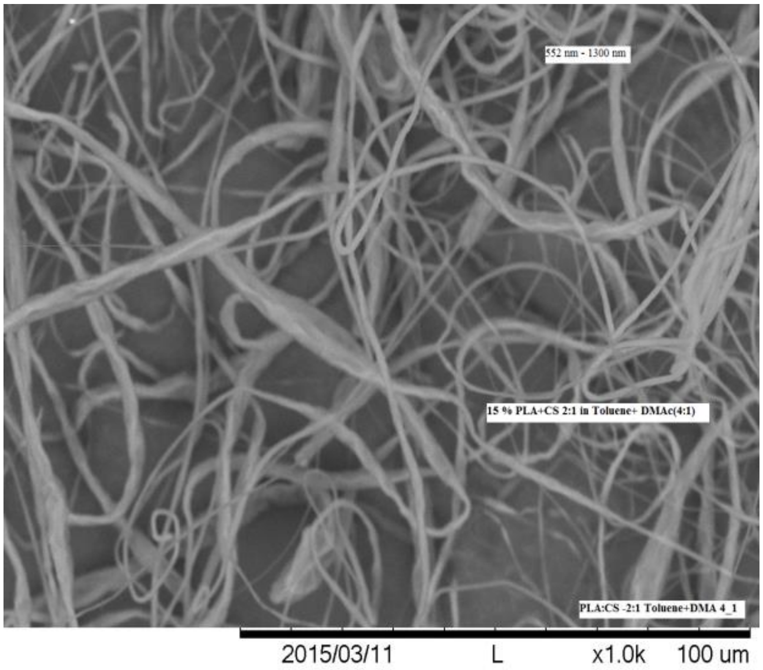


Figure 22. Microscopic image of 15 % of PLA + CS (2:1) in toluene + DMAc (4:1).

The Figure 22 and 23 shown the microscopic view of 15% of PLA+CS (2:1) in toluene : DMAc (4:1) at the electrospinning condition 15kV -30 kV, 0.6 - 3.0 ml/h, we obtained fiber diameter 552 nm - 1300 nm. To, achieve this result we used CS as composite material with PLA.

Conclusion

Synthesis of cellulose stearate was successfully done; it was obtained in powder form. The infrared spectra characterisation shows that fatty acid ester of cellulose was achieved. Using IL was very effective and simple method to modify cellulose when compared to other conventional methods. And, IL is also possible to recover and reuse, which makes it environmental friendly.

Saxhlet extraction setup and methanol wash is used to wash the polymer after the reaction with stearoyl chloride, but from FTIR result we can conclude that there is no difference in polymer structure. The only different is Saxhlet extraction setup is less time consuming than methanol washing.

From PLA study, we understood different electrospinning parameters needed to obtain fibres. It was really helpful before start working with a new polymer material like CS. Fibre is obtained from 8 % to 12 % of PLA in DCE : acetone without using hot electrospinning.

From rheology we understood that viscosity is not significantly depended on temperature below 12 % of PLA. And this is cause by interaction between polymer molecules and solvent and this interaction could determine the conformation of polymer molecules and better condition for creating fibres in electrospinning process.

Electrospinning of cellulose stearate alone was not successful with all tested solvents - it’s too viscous at high enough concentrations and because solution gets dried fast inside needle. At concentrations below 15% with all of the tested solvents solution is too fluid, and it just spays and only black patches is obtained as output. At concentration of 15% CS being dissolved in mixed solvent toluene + DMAc (volume ratio of 4:1) allows to obtain a thin uniform coating.

Using the CS to prepare composite material with PLA at ratio of (2:1), being dissolved in toluene + DMAc make successful electrospinning: we obtain lengthy fibres with diameter from 0.5 mm to 1.3 mm. This is simple, cost effective and very less time consuming combination of polymer material should be studied and more research work needed.

Further intensive research work is required to develop fibres generation from CS by electrospinning.

KOKKUVÕTE

Käesolevas töös kasutatakse tselluloosstearaati (CS) kiudude valmistamiseks elektroketruse teel. Tselluloosstearaadi saamiseks pannakse tselluloos reageerima stearoüülkloriidiga ioonvedeliku 1-butüül-3-metüülimidasooliumkloriidi keskkonnas. Tema külgahelates on 18 C-aatomit ja reaktsiooniproduktiks on rasvhappe ester. Enne polümeeri saamist on vaja sünteesida reaktsioonikeskkond.

Elektroketrust katsetati erinevatel polümeeri kontsentratsioonidel vahemikus 7% kuni 20%. Parim tulemus saadi 15% CS korral. Tolueeni ja dimetüülatsetamiidi (DMAc) 4:1 segus lahustati 15% CS, mis andis õhukese ühtlase kihi. Kuigi kiude ei saadud, oli õhukese ühtlase kihi saamine küllalt positiivne tulemus, mida saab järgmisel tasemel edasi uurida.

Kuivõrd CS elektroketrus ei olnud tulemuslik kiudude saamise seisukohalt, kasutati alternatiivseid võtteid valmistamaks tselluloosstearaadist komposiitmaterjali polüpiimhappega (PLA). Kiudude saamine õnnestus PLA+CS (2:1) lahusest tolueeni ja DMAc 4:1 segus polümeeri 15%-lise üldkontsentratsiooni korral.

Märksõnad : tselluloosstrearaat, elektroketrus, kiud, stearoyl kloriidi.

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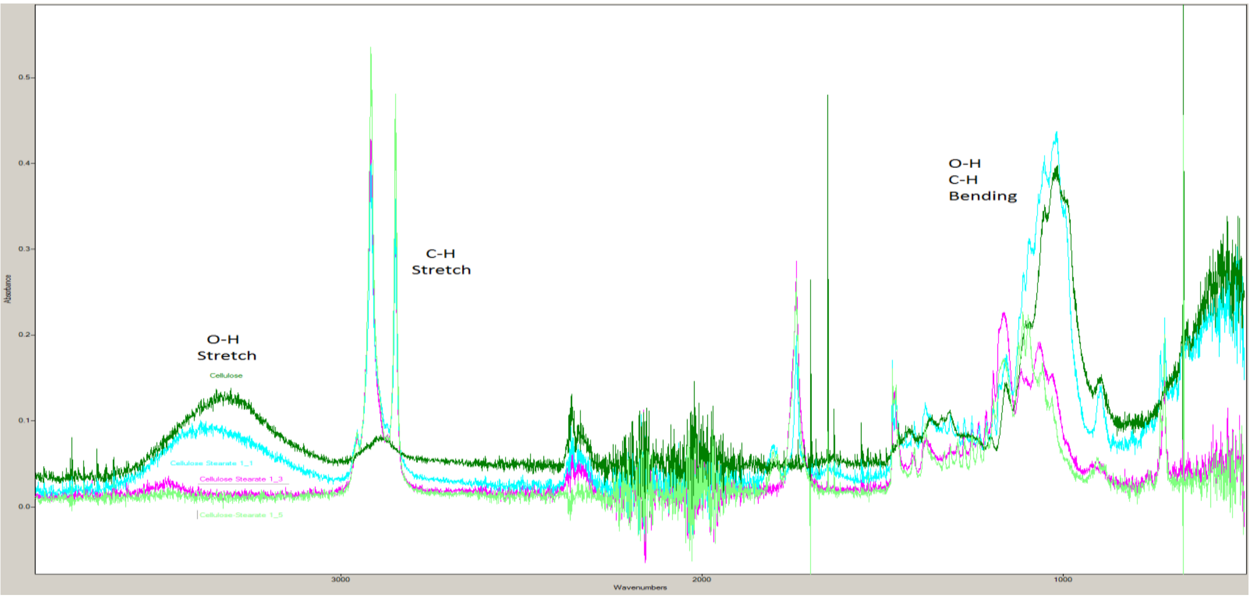
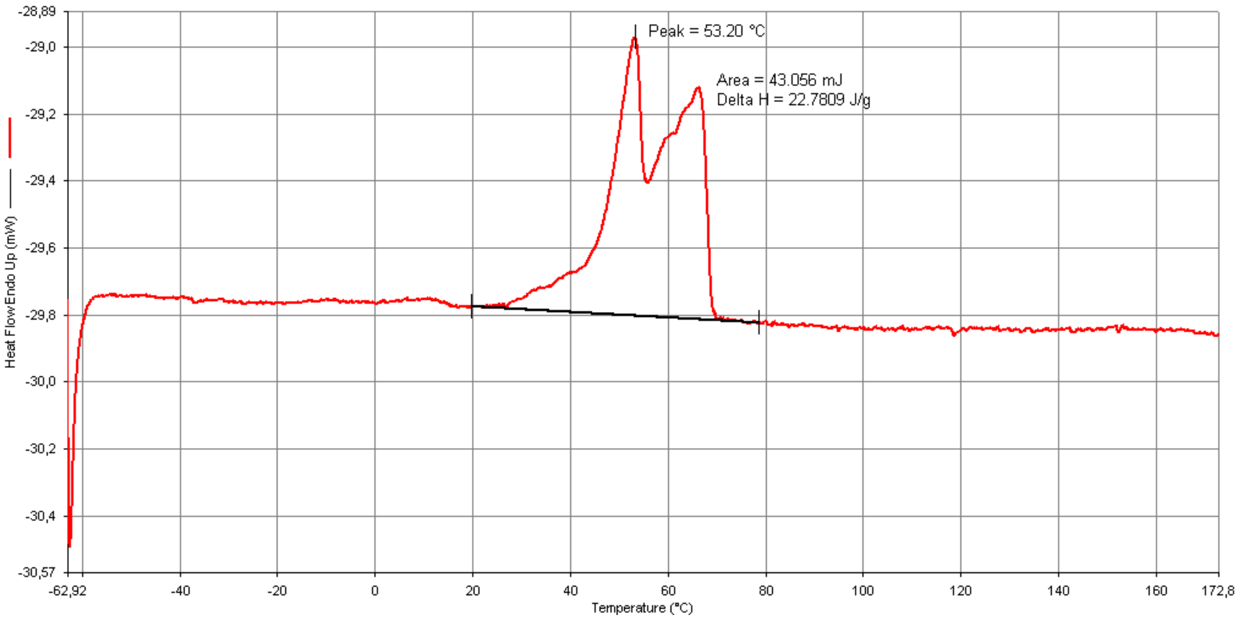
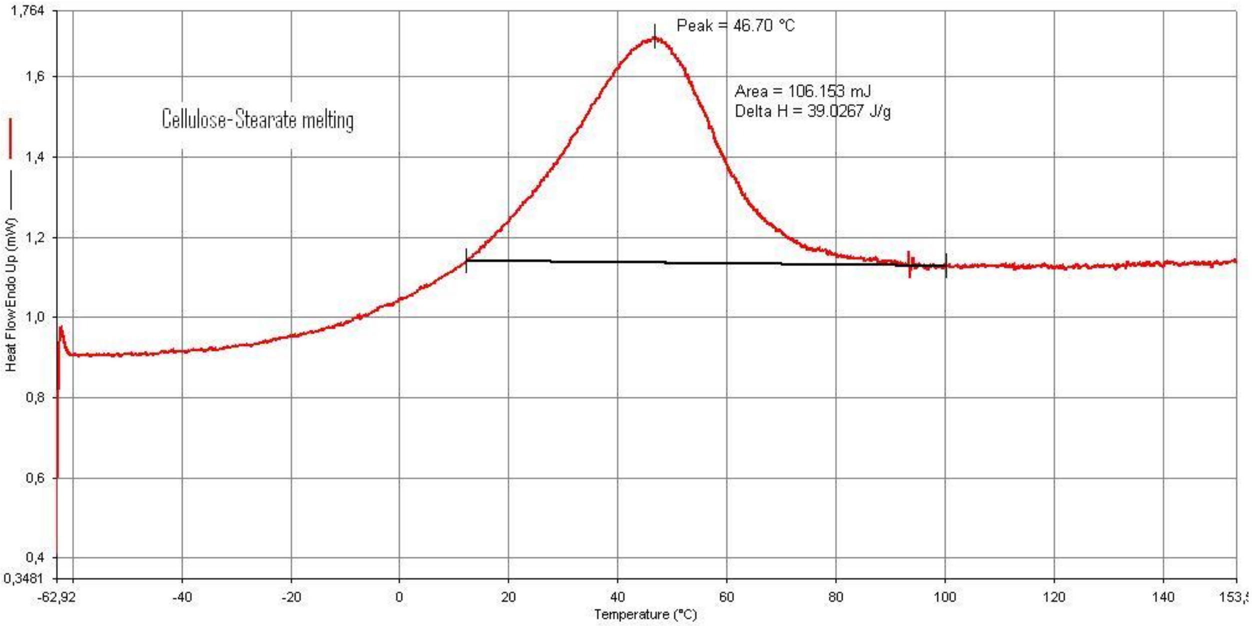
APPENDIX 1



FTIR spectra CS



DSC curve for cellulose stearate



DSC curve for cellulose stearate

Differential Scanning Calorimeter

Microscope used for evaluation of electrospinning results

FTIR spectrometer with ATR accessory.

METADATA

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Supervisor(s): Dr. Illia Krasnou

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Chair (in English): Chair of Wood and Plastic

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