TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

DEPARTMENT OF POLYMER MATERIALS

CHAIR OF POLYMER TECHNOLOGY

EFFECT OF IONIC LIQUIDS ON GRAPHENE OXIDE BASED ELECTROSPUN BIOPOLYMER

IOONVEDELIKE MÕJU GRAFEENOKSIIDI BAASIL ELEKTROKEDRATUD BIOPOLÜMEERILE

MASTER THESIS

Student:	Marco Oolo
Student code:	163383KVEM
Supervisor:	Kashif Javed, Chair of Polymer Technology, PhD student

Tallinn, 2018

AUTHOR'S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

"31" June 2018

Author: Marco Oolo

/signature /

Thesis is in accordance with terms and requirements

"......." 2018

Supervisor: Kashif Javed

/signature/

Accepted for defence

"......."....................2018

Chairman of theses defence commission: ....

/name and signature/

Department of Materials and Environmental Technology

THESIS TASK

Student: Marco Oolo, 163383KVEM

Study programme,   KVEM12/15 - Technology of Wood, Plastic and Textiles

main speciality: Technology of plastics and textiles

Supervisor: Kashif Javed, Chair of Polymer Technology, PhD student

Thesis topic:

(in English)   Effect of ionic liquids on graphene oxide based electrospun biopolymer

(in Estonian)   Ioonvedelike mõju grafeenoksiidi baasil elektrokedratud biopolümeerile

Thesis main objectives:

1. Study the effects of ionic liquids on graphene oxid ebased electrospun biopolymer.

2. Overview on tests composed with ionic liquid on graphene oxide based electrospun biopolymers and their results.

3. Spin an electroconductive mat using a biopolymer, ionic liquid and graphene oxide.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature overview and initial experiments with cellulose acetate and ionic liquid.	21.12.16
2.	Tests composed with BmimBr, BmimBF$_4$ ionic liquids.	20.05.17
3.	Tests composed with BmimCl and BmimAC ioni liquids.	22.12.17
4.	Compose master thesis in the right format and correction of mistakes.	30.05.18

Language: English **Deadline for submission of thesis:** "........"....................2018a

Student: Marco Oolo   ....….................   "........"....................2018a

/signature/

Supervisor: Kashif Javed   ………..............................   "........"......................2018a

/signature/

Contents

PREFACE

The aim of the thesis is to give a detailed overview on the effect of different ionic liquids on graphene oxide based electrospun biopolymer cellulose acetate. Give an overview about ionic liquids, graphene oxide and electrospinning. Author speculates that it is possible to make an electroconductive mat using graphene, ionic liquids and cellulose acetate. To achieve the end-goal the author will conduct experiments with the help of a supervisor, in the laboratories of TTU.

As a result it is noticed that not all of the ionic liquids could be used in the process of electrospinning with this particular biopolymer. Only one of the ionic liquids, BmimAc, used gives an end result that are suitable for final analysis and conductance measurements. The mats are examined and SEM images are analyzed.

Keywords: Electrospinning, graphene oxide, ionic liquid, biopolymer, cellulose acetate

LIST OF ABBREVIATIONS AND SYMBOLS

GO – graphene oxide

IL – ionic liquid

CA – cellulose acetate

BmimBr - 1-Butyl-3-methylimadzolium Bromide

$BmimBF_4$ - 1-butyl-3-methylimidazolium tetrafluoroborate

BmimCl - 1-Butyl-3-methylimidazolium chloride,

BmimAc - 1-Butyl-3-methylimidazolium acetate

DMAc – Dimethylacetamide

SEM – scanning electron microscope

Wt - weight

INTRODUCTION

In the past decade many research centers and big companies have invested a lot of time and money in research on developing biodegradable, biocompatible nanomaterials with different properties. This is one of the reasons why this particular area has gotten much interest and publications. The aim of the thesis is to investigate the effects of different ionic liquids on graphene oxide based biopolymer with the end goal to make a material that conducts electricity and in the same time degrades by itself in the nature. While having previous experience with graphene and electrospinning before as "Graphene based electrospun nanofibres" was the topic of my bachelor's thesis, keeping that in mind it was a very welcoming topic to choose. This topic was suggested to me by my supervisor.

This work mainly focuses on giving electrical properties to biopolymer nanofibres. With an implementation of highly conductive salts and graphene oxide (GO) it is possible to make cellulose fibres conduct electricity.

The main problem in todays world world are the lack of rare metals and elements. Cheaper alternatives are being search for to replace them. Why not replace the conductive materials in batteries or capacitors with conductive cellulose fibre. It can be used as a filler without replacing the whole material, but the save of rare metals and elements would be enormous. Different electronical devices could replace some parts with conductive cellulose fibres as well.

Cellulose acetate (CA), a biopolymer, has been widely used as an electrospun fibre. It is synthesized from ordinary wood, which is commonly found in not only trees, but in most of the plants. Since the base material is abundant and cheap, it makes a perfect alternative to rare metals used in electronic devices, if cellulose acetate fibres can be made electroconductive. The wide usage of the material comes from the fact that CA has very good properties, such as good chemical resistance, it is biodegradable, good biocompatibility, excellent thermal stability, easy electrospinning process. These properties make the material highly usable in a variety of applications. The material was chosen to test with because of the mentioned properties and since it is already widely used in the electrospinning field. Meaning the material is compatible with the electrospinning process.

Electrospinning technique has been widely used in the manufacturing process in a variety of different polymeric nanofibers. It is an efficient process for producing ultrathin fibres with sub-micrometer to nanometer scale diameters. This technique uses a high voltage electric field to create

a charged jet of polymer solution. By the effects of the high voltage on the solvent, electrostatic force will be formed which is equal to the surface tension. This forms a cone on the tip of the needle, called a Taylor cone. With the increase in the electrical field the the electrostatic force applied will get larger than the surface tension, thus the solution forms a fibre jet which is pulled onto the collector. While being pulled the solvent will be evaporated, leaving only fibres which are pulled to the collector. In a more simple form, electrospinning involves an application of a strong electrical field onto a needle which is attached to a syringe containing the electrospinnable liquid and a collector. The fibres produced by electrospinning have peculiar characteristics. Electrospinning process is purely a physical process in where the solvent is processed from liquid state into a fibre. These fibres have high porosity, high surface area to mass or volume ratio and a vast possibility for surface functionalization. The process is considered to be versatile and inexpensive.

Knowing there is a chance to make a conductive fibre while using cellulose as the main ingredient could mean a lot to the whole world. It can possibly help against the pollution that occurs in the making modern batteries and electronic devices.

1. LITERATURE OVERVIEW

For the subject to be easily understood there are some basics to be known. A brief overview will be given on each material and method which are implemented in the thesis.

1.1 Graphene

In 2010 the Nobel Prize in physics was given to Sir Professor Andrei Geim and Sir Professor Kostya Novoselov, from Manchester University. The award was given for ground-breaking discoveries in the experiments with graphene, a two-dimensional material. That was not the first time scientists acknowledged graphene as promising material. Since graphene production is very simple, effective and cheap, the Nobel Prize was the stepping stone of graphene to step into the light. Lots of researchers stepped in and started working with the material [1].

Graphene is a one atom-thick sheet of carbon atoms tightly packed into hexagonal structures. In simple terms, graphene is a thin layer of carbon. It is the thinnest compound known to man. Other than that graphene is the lightest material known, with $1m^2$ weighing around 0,77 milligrams, it is also the strongest compound discovered. This amterial is between 100-300 times stronger than steel[1].

Graphene is a material based on carbon that can be viewed as a one atom thick sheet of graphite. The material has been investigated intensely in recent years after a report by Novoselov was released about graphenes unique electronic properties [2]. After initial recovery the material was quickly put into use and various electronic devices were made for a variety of applications [3]. Very high quality graphene is often prepared by chemical vapor deposition (CVD), which requires expensive equipment [4,5], a lot of researchers turned their interest into graphene oxide as a better alternative for the preparation of graphene like materials[6,7,8].

Graphene is usable in a number of application fields varying from electronics, spintronics, photonics and optoelectronics sensors, flexible electronics, energy storage and generation, composites and biomedical applications [3]. These days graphene based electrospun nanofibers (GBEFs) have been promising and potential applications, including conducting fibers, energy-storing devices, and smart actuators.

Although graphene is a material with some of the best qualities there aren't many graphene-based products on the market yet, most of them like sporting equipment are an initial market entry, rather than the full commercial wave of graphene products. That indicates that scientists are still in a phase of research and development. That does not indicate that graphene is not used in different fields of study in science. The research on graphene has had a big rise in interest. The fast rise was not only fuelled by discoveries, it was also fuelled by European Comission and the Korean and UK governments. Even private investments like Samsung, IBM and Nokia had a great interest in graphene. That brought a big surge of different publications and patents which have led us to great discoveries. [9].

1.2 Graphene oxide

Graphene oxide (GO) can be viewed as a monomolecular layer of graphite. This unique material has various oxygen containing functionalities, like carbonyl, epoxide, carboxyl and hydroxyl groups [10, 11, 12]. The interest in GO was dramatically increased after the first single layer of graphite, graphene, was isolated and studied [13]. At first it was thought that GO was a synthetic precursor to graphene [14]. While having a moderately good conductivity and easy dispersion in water, this material was attractive to manufacturers to be used in electronic devices [15, 16, 17, 18, 19]. The usage was not limited to only electronic devices, GO can be used in nanocomposite materials [20], as an energy storage [21], in biomedical applications [22, 23, 24], composite materials [20], catalysis [25, 26, 27] and even as a surfactant [28].

Many of the procedures for GO synthesis are based on the first method reported by Hummers. By Hummers method graphite is oxidized by potassium permanganate in sulfuric acid [29]. Even reduction by hydrazine has been reported, but that is not recommended because hydrazine is highly toxic and can potentially functionalize the GO with nitrogen heteroatoms [30]. It is possible to

reduce GO as a thin film or in an aqueous solution. The different reduction methods are still being discovered.
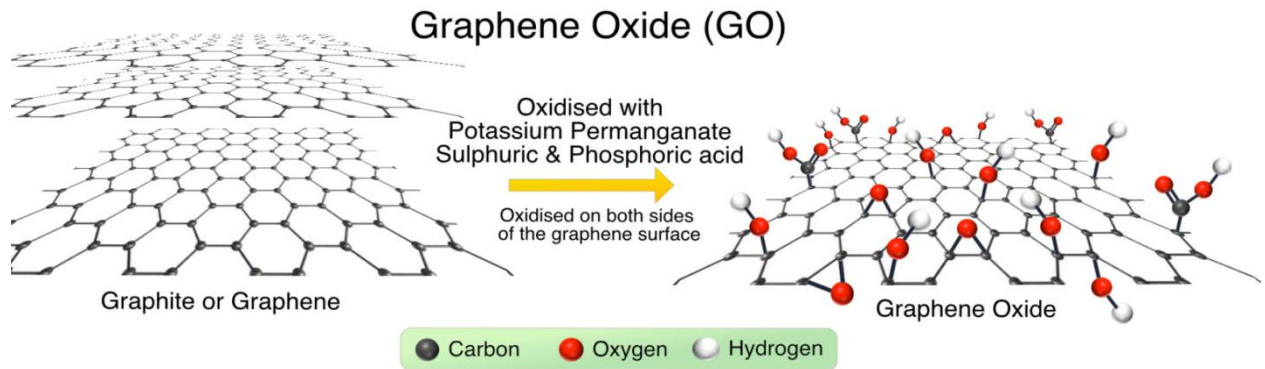

Figure 1. Synthesis of graphene oxide [31].

Different electronic devices have been composed using GO as the base material for atleast one of the components. One of those devices is a graphene based field effect transistor (GFET) [32, 33]. These transistors are used as a chemical or even biosensors. The usages in light emitting diodes (LEDs) and solar cells is quite common aswell. As a transparent electrode it is a good alternative because of the easy processing. Other than transparent electrode, GO can be used as a hole transport layer in LEDs and polymer solar cells [34, 35].

As it was mentioned, GO is used in nanocomposites. It is used for high capacity energy storage in lithium ion batteries. GO increases the performance of the materials used in batteries [36], for example it increases the energy storage capacity and the cycle stability [37]. These enhancing properties are seen because of the high surface area of the material, which is useful as an energy storage material in supercapacitors [38, 39].

1.3 Electrospinning

Electrospinning is a dry process which uses the force from the electrostatic field to draw fibres from a liquid solution or melt. This process where the solvent is processed from liquid state to fibres is entirely physical. It happens because of the loss of solvent via high voltage or the freezing of

melt. The method has become increasingly popular during the past years, because it is an easy method for manufacturing continuous nanoscale fibres.

The first records of electrostatic attractions of liquids were observed in the 17th century by William Gilbert. Gilbert was the Queen Elizabeths personal physician and the president of the Royal College of Physicians [40].

In the 18th century Georg Mathias Bose demonstrated his triboelectrical static electricity generating machine with the addition of a charge collector. Bose demonstrated the apparatus in a peculiar matter. Bose put a female subject standing on an insulating platform, while charging her up, then inviting the audience to kiss the girl. Both parties got an electric shock as a proof of charge collecting and releasing. As a well known scientist he was kidnaped during the Seven Years War with Prussia and died two years later as a hostage in Magdeburg [40].

In the 19th century George Audemars patented a collodion spinning method. The collodion was extracted from cellulose. The method was very easy, a needle was dipped into the solution and then pulled out, drawing a thin long rapidly hardening thread. Meanwhile, Charles Vernon Boys was conducting experiments on an apparatus which consisted of a small dish, insulated and connected with an electrical machine. Fibres could be pulled from the plate but it did not satisfy the researcher, so a new method for drawing a fibre was found. Boys attached a fused quartz to a crossbow bolt, heating the quartz and shooting the crossbow resulted in fibers wounding around a wooden former. These fibres had a length about 27 meters and thickness on 254nm [40].

During the 20th century Cooley filed the first electrospinning patent. In the patent there were four types of indirectly charged spinning head – a spinneret with a rotating distributor, an air assisted head, a coaxial head and a conventional head [40].

These days nanofibers produced by number of methods by drawing polymers, template synthesis of nanostructured polymer, phase separation , self-assembly and electrospinning[41,42] . But the most popular technique is electrospinning - an unique and versatile method for the production of micro- and nanofibres [43] by jetting of polymer solution through an electric field to create nanofibers[44,45]. The machinery used during this thesis for electrospinning can be seen in Figure 2.
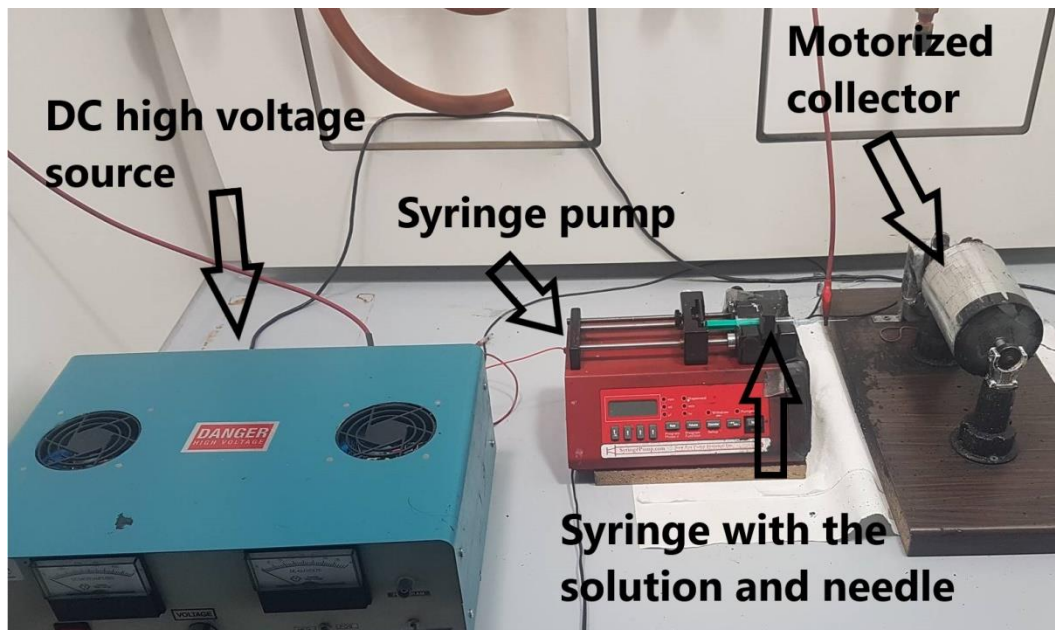
Figure 2. Electrospinning setup

Electrospinning is a process where electrical forces are utilized to produce polymer fibers. In short electrospinning is a process where a charged polymer jet is spun on a collector. It is the easiest way to produce nanofibers. Electrospinning technique is easy and robust way to make different polymer fibers. During the spinning process it is relatively easy to control the nanofiber composition. While maintaining control over the fibers spun you can achieve the desired results, by using different fillers it is possible to change its properties and functionality to your preference[46].

The term electrospinning is a relatively new word, the word came from electro static spinning which was used more than 60 years ago. The first description of a process recognizable as modern electrospinning was in 1902 when J.F.Cooley filed a United States patent entitled „Apparatus for electrically dispersing fibres". In his patent (US 692631) he describes a method of using high voltage power supplies to generate yarn[47].

The wide diversity of polymers that could be used in electrospinning results in a good variety of different fibers with different properties. More than 200 polymers have been electrospun over the years. Each of the fibers have different chemical and physical properties. They can be used in a lot of different fields in science, such as tissue engineering, scanning electron microscopy, transmission electron microscopy, X-ray diffractometry, nuclear magnetic resonance, differential scanning calorimeter etc. The amount of different applications for the fibre are increasing because of the fibers great properties and new means of usage are found every day. This simple, versatile and cost-effective technology has a bright future in the fields of science[46].

1.4 Ionic liquid

Ionic liquids (ILs) have been a topic of great interest since the mid-1990s [48]. Ionic liquids have attracted high attention as far as a decade ago, approximately 1800 papers were already published in the area of ILs in 2008 alone, documenting a variety of new IL applications [49].

Ionic liquids are generally defined as organic salts with melting points below 100 ^{0}C, many of the ILs are in a liquid state at room temperature, and composed entirely of ions[50, 51]. Despite the fact that ILs were first reported in the mid-1800s, widespread interest in this compound class has occurred only recently.

The room temperature ionic liquids (RTILs), also known as "designer solvents", named "designer solvents" because it is possible to give required properties to the ionic liquid, have served as greener alternatives to conventional toxic organic solvents[52, 53, 54]. RTILs have found to be useful in a other applications, and their development continues. The interest in RTILs is high because they have peculiar physical and chemical properties such as, high thermal and chemical stability, lack of inflammability, low volatility, and tunable solubility with several organic compounds. By taking advantage of their unique properties,[52, 55] several IL applications have been described, including reaction media for many organic transformations,[52, 56] in separations and extractions,[52, 57] as electrolytes for electrochemistry,[52, 58] in nanotechnology,[52, 59] in biotechnology,[52, 60] and in engineering processes,[52, 61] among others.

Taking account their properties and characteristics ILs can be grouped into three generations [62]. The first generation consists of ILs for which the accessible physical properties such as lowered vapor pressure and high thermal stability are often unique [63].

Second-generation of ILs have potential use as functional materials such as energetic materials, lubricants, and metal ion complexing agents. By taking advantage of their characteristic to change the physical and chemical properties, ILs can produce a remarkable platform on which the properties of both cation and anion can be modified separately and designed to enable the production of new materials while still having the main properties of an IL. Some RTILs have been used as reaction media to produce or improve the preparation of various pharmaceuticals [64, 65].

Recently, the third generation of ILs has been described using active pharmaceutical ingredients (APIs) to produce ILs with biological activity[65].

1.5 Ultrasonication

Ultrasound is known as acoustics frequencies between 16kHz and 1GHz. Ultrasonic is a term used in technical and industrial world and it means the same as ultrasound. Sound waves which frequencies are higher than the upper audible limit of human hearing, thus called ultrasonic. Ultrasonic sounds are regular soundwaves and their physical properties do not differ from normal sounds. The only exception is that humans cannot hear them.

Ultrasound has two different types of frequencies. Destructive frequencies which are between 20kHz to 2MHz and non-destructive diagnostics which are between 5MHz to 10 MHz. Nondestructive ultrasounds are mainly used in diagnostic applications [66]. In this thesis, destructive frequencies were used for its mechanical effects.

When ultrasonication is applied on the solution, the soundwaves compress and expand the liquid. The liquid will naturally follow the movement, but since the movement between the molecules can differ, cavitation can appear. These cavitations emerge because the distance between the molecules of the liquid are too large. These bubbles created will grow and the collapse, accelerating the liquid around it [66]. This mechanical effect, which is used to "stir" the solutions, used during this thesis is to make the solutions more homogeneous and assure that GO mixes well together with the biopolymer.

2. USED MATERIALS

In the course of this thesis, there are materials used that need to be discussed, why they were chosen and talk about some of their properties.

The biopolymer used in this thesis is called cellulose acetate (CA). CA has been a material of choice in a large variety of applications. Due to a common use in the electrical field of study and having an easy electrospinning process, it was a biopolymer that suited the end-goal of my thesis. The end goal is to spin an electroconductive mat.

Graphene oxide (GO) used in the thesis is ordered from the US. The graphene oxide powder consists of 15-20 sheets of 4-10% edge-oxidized graphene. The powder was ordered from Garmor Inc. The nominal particle size diameter is of 500nm. With 90% of the particles being under 800nm in diameter.

During the thesis there are four different ionic liquids (ILs) used for testing. All the the ILs were acquired from the schools laboratory. These ILs are:

1) BmimBr - 1-Ethyl-3-methylimadzolium Bromide

2) $BmimBF_4$ - 1-Butyl-3-methylimidazolium tetrafluoroborate

3) BmimCl - 1-Butyl-3-methylimidazolium chloride,

4) BmimAc - 1-Butyl-3-methylimidazolium acetate

The ionic liquids are numbered in the order of their use in the thesis.

3. INITIAL EXPERIMENT

The first part of the experiment started with mixing together solutions with different amounts of IL's in them. This was the part of the thesis that was always the first step when testing a new IL. Every ionic liquid that was taken into use was always tasted for its compatibility with the biopolymer cellulose acetate.

Adding ionic liquids to the solution can improve viscosity, conductivity, surface tension, electrospinnability and help control the fiber morphology. Since I lack experience in the electrospinning, tests needed to be done to find out what is the perfect amount of IL's in the solution for the fibers to start spinning at the best rate. That is the main discussion in the 1st experimental part.

The solution used in this work consisted on Acetone and DMAC in a ratio of 2:1. Then cellulose acetate was added to make the solution contain 17% of cellulose acetate.
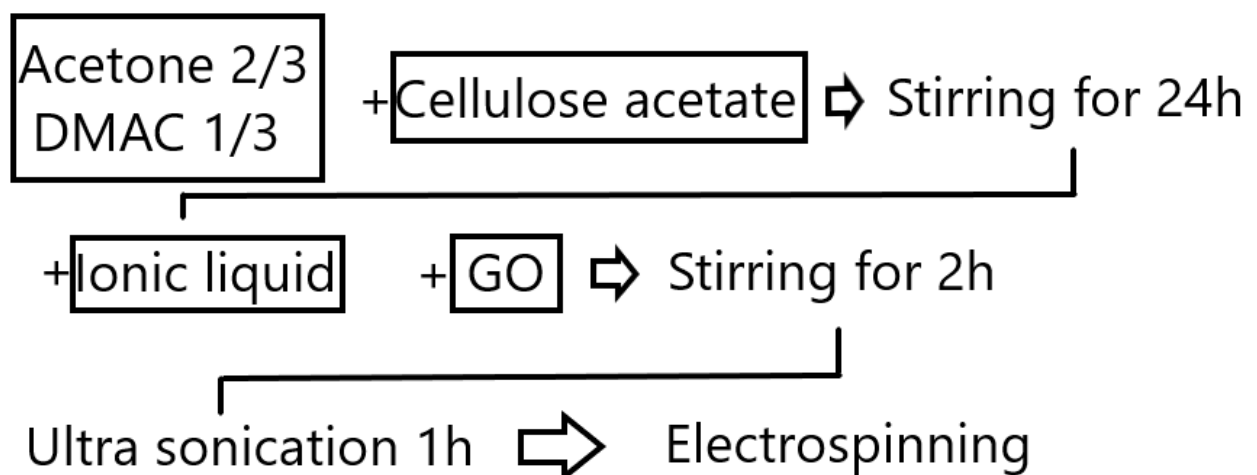

Figure 3. The procedure of making the electrospinnable solutions.

No graphene oxide additives were used in this experiment. For the first test procedure, solutions containing 17% Cellulose acetate and 1-Ethyl-3-methylimidazolium bromide ionic liquid in weight to weight ratios of 2%, 4%, 6%, 8%, 10%, 12% were used accordingly.

For the electrospinning process I used the setup shown on Figure 2. The flow rate was chosen 0,6 – 1,5 ml/h. The flow rates were chosen accordingly to the spinnability of the solutions used. Some of the solutions had higher viscosities or were not spinnable at higher rates. The diameter on the

pumping machine was chosen 4,5mm. Drum speed was turned to maximum. Distance between the collector and the tip of the needle was set to 10cm and the voltage used was 25kV.

3.1 Initial experimental results

The first experiment involves a solution containing 2% of EmimBr IL. The flow rate on the spinning process needed to be turned to 0,6 ml/h during electrospinning process because the solution started to agglomerate on the tip of the needle and the fibers did not form. That is why in some cases a lower flow rate was used. During the spinning process, forming of the fibers could not be visually seen. There were some lone fibers seen on the surface on the aluminum foil. On Figure 4 you can see a magnified picture of the fibers. Although they can be hardly seen with the naked eye they are still there.
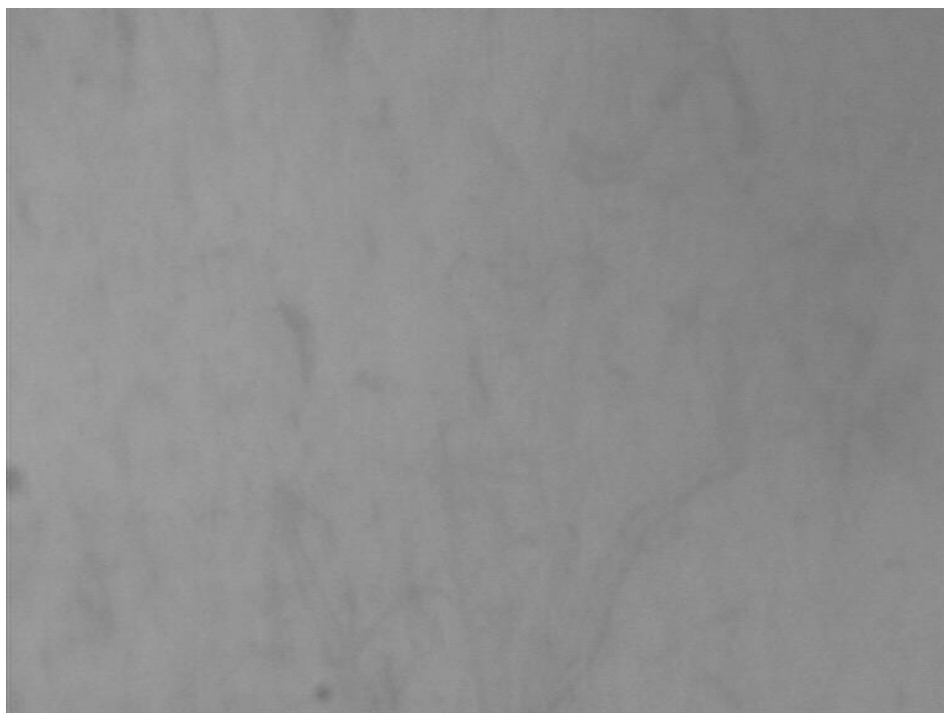

Figure 4. 2% EmimBr electrospun nanofibre from 17 wt % CA solution.

In the case of 4% IL's electrospinning process, one could visually see some of the fibers forming and spinning around the collector. The flow rate used during this experiment was 0,8 ml/h because the solution still tends to agglomerate on the tip of the needle. You can see the magnified version of the fibers on Figure 5.
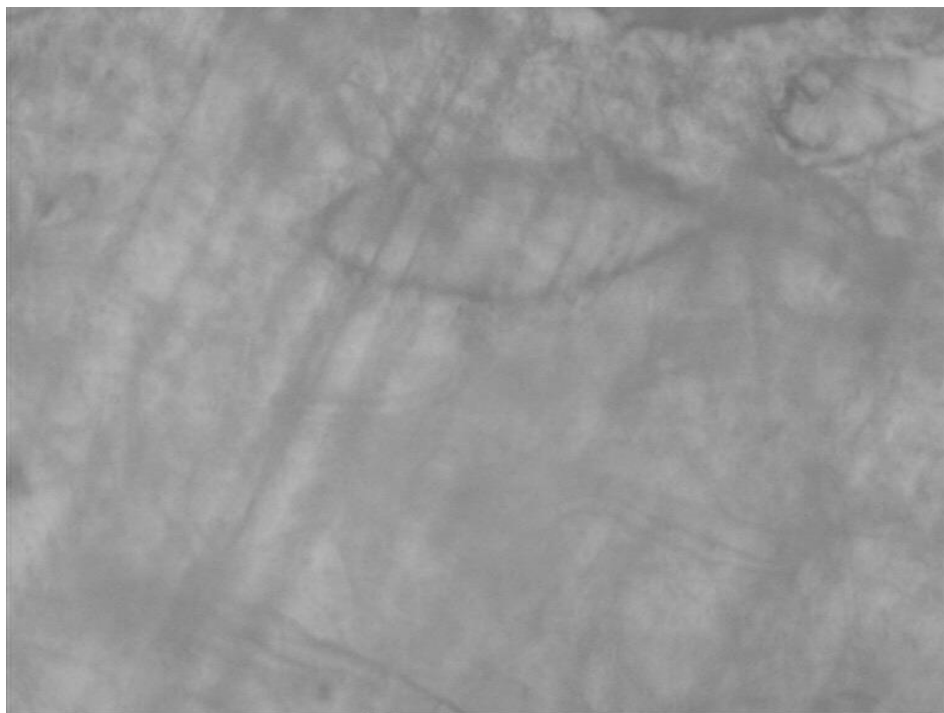

Figure 5. 4% EmimBr electrospun nanofibre from 17 wt % CA solution.

Using 6% IL's was boosting the ionic liquid forming during electrospinning and gave constant visually observable fibers. The fibers formed more frequently compared to the 2% and 4% solution. Flow rate used here was 0,8 ml/h because the agglomeration defect still affecting the spinning process. In this case you can see the fibres more clearly. Meaning the amount of fibres forming was much higher and we were reaching into an optimal point of quantities of ILs which can be used during electrospinning process. The magnified version of the fibers is presented on Figure 6.
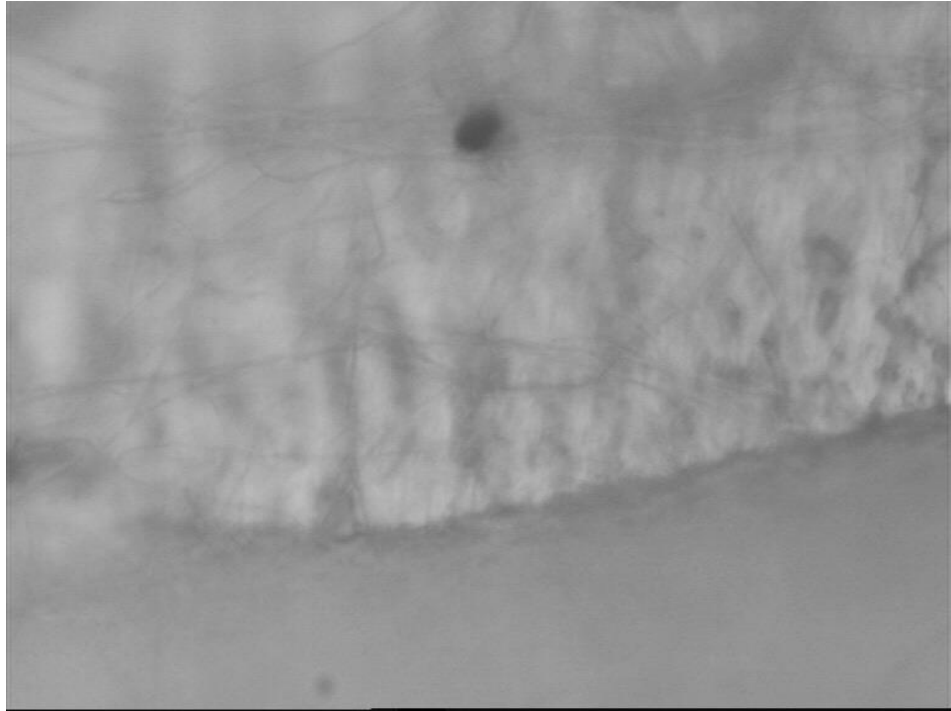
Figure 6. 6% EmimBr electrospun nanofibre from 17 wt % CA solution.

For the case of 8% EmimBr IL, the fibres are forming can be observed with the naked eye. Although there was no significant boost in the amount of fibres forming during the spinning process. It could be clearly seen on the foil that there were fibres, which could be torn of. Although the quantities of the fibres was very low, surely not fairly enough to get a piece to measure conductance or take any kind of samples.. The flow rate used in this experiment was 0,8 ml/h. The pictures of the magnified fibers can be seen on Figure 7.
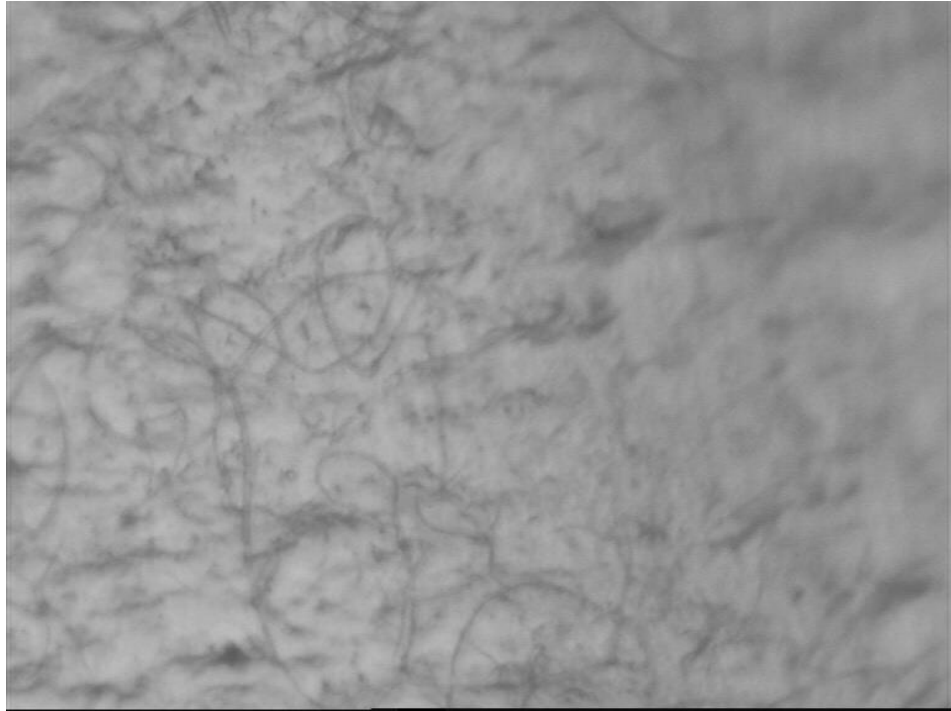
Figure 7. 8% EmimBr electrospun nanofibre from 17 wt % CA solution.

When using 10% of EmimBr there were visually observable long fibres forming. During other quantities of IL's the fibres were not forming persistently, occasional fibres were forming and pulled to the collector. Using 10% IL concentration clearly formed longer and more continuous fibres. The flow rate used here was 1,2-1,4 ml/h because there was less agglomeration appearing during the electrospinning. On rare occasions agglomeration could be seen on the tip of the needle but that only lasted for a couple of seconds, and then the agglomerated drop was pulled off from the tip. After removing the aluminum foil from the collector, fibers could be seen on the edge of the foil. The fibers formed a distinct layer on the surface of the foil and you could scrape them off. It must be mentioned that the amount of fibres that formed on the aluminum foil were not enough to perform for any kind of properties measuring. Magnified version of the created fibres could be seen on Figure 8.
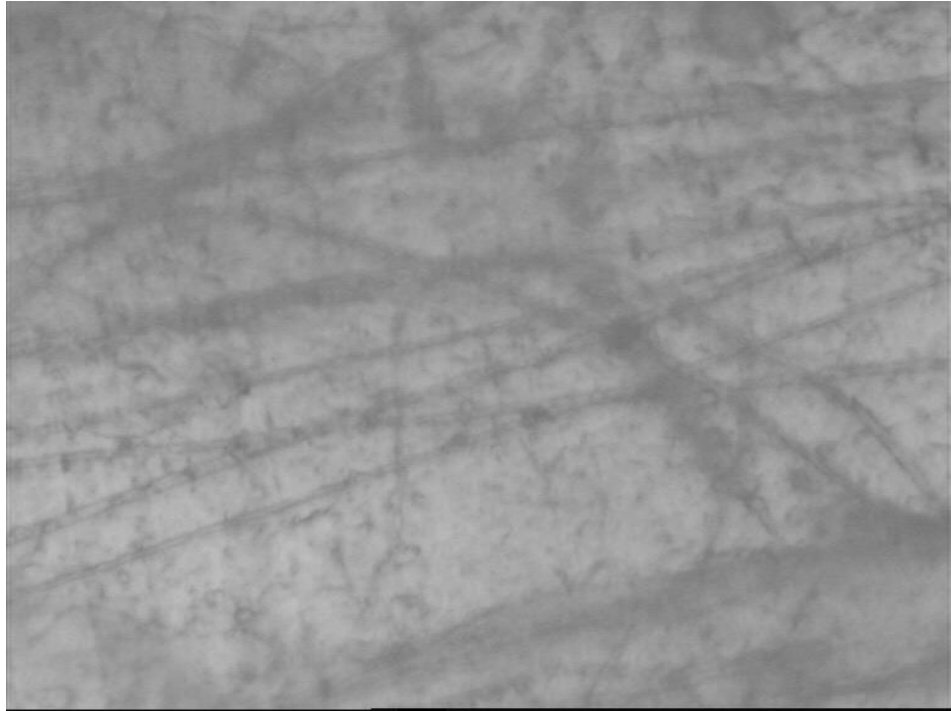
Figure 8. 10% EmimBr electrospun nanofibre from 17 wt % CA solution.

The 12% IL's solution formed a distinguishable layer of fibers on the foil. The process of spinning did not need a lot of "tinkering" and was considerably smooth prepared to lower concentrations of IL used. Flow rate used here was 1,5 ml/h. Agglomeration was barely visible, rarely a little droplet would form on the tip of the needle. It was clearly seen when the fibers formed and spun around the collector. The fibres were collectable from the aluminum foil because the quantity of the fibres was getting higher. The fibre forming was continuous as in the 10% IL solution. No distinct differences between the 10% and 12% solution only that the yield of fibres was forming was higher. On figure 9 you can see the fibres under magnification.

Figure 9. 12% EmimBr electrospun nanofibre from 17 wt % CA solution.

3.2 Conclusions on CA-BmimBr-nanofibres

Increasing the quantity of the IL to 14% or even higher did not improve the properties any further, since at that point the amount of IL was too high and the amount of cellulose in the solution was not enough to get a constant fibre spin. Since the base solution contains 17% of CA, which is the polymeric material that is formed in spinning process, adding a little too much IL can mean there is too much soluble material compared to the polymeric material in the solution. More polymeric material in the solution hypothetically means more material to electrospin, lowering the weight amount of polymeric material in the solution means that there is too much liquid evaporating during the electrospinning process, leaving us with lower amount of polymeric material. This causes a lack of polymeric material and the fibre forming is thus made harder. During the 1st experimental part 2 important points were made. Firstly, the visible boost in the spinning process started at 6% of IL and the maximum amount of IL that could be used in the 17% CA solution is 12%. Using more IL starts producing less fibres and the electrospinning process will downgrade. This preliminary process is the building block of all the other tests conducted. These tests showed us the maximum quantities of IL's which could be used during the process. Future tests will be done using the same parameters.

4. ELECTROSPINNING OF CA AND IL

The second experimental part consisted entirely of trying to spin a mat using biopolymer cellulose acetate and an ionic liquid. Since the main differences in the spinning processes appeared using quantities of 6%-12% of the IL in the solution, these quantities were used in the testing process of mat spinning.

This part of the thesis is necessary for the future tests. In this experimental part the capability of making a mat had to be tested. If a mat is forming there is a possibility to use other ionic liquid with this particular biopolymer to continue to my next step, which is adding graphene oxide to the solution and boosting the mats properties even further.

The electrospinning setup used during the electrospinning was the same as in the previous case. During spinning the flow rates were changed to keep and optimal rante during the process. The usage of a higher flow rate was needed to get longer fibers and a better constant flow.

For the mat spinning the spinning times were a lot longer. The mats were spun for up to 3-5 hours. The process of preparing a solution takes about 26 hours for it to be considered spinnable by electrospinning. Since the EmimBr IL used in this part was not a liquid but it was a solid at room temperature it was heated up and then added to the solution.

4.1 Results and discussion

Firstly the 6% IL containing solution was spun. Visually the fibers were spinning and there were no problems in the spinning process. Since experience was gathered with the previously spun fibres with those solutions, it was easier to use an optimal flow rates and detect problems during spinning. The spinning process was quite unproblematic, from time to time some agglomeration had to be cleared from the tip of the needle. This was nothing new in the process while using EmimBr.

The solution spun contained 12% of IL. Since previous experiments showed more constant fibres it was crucial to spin with this solution. In this pahse of experiment more continuous fibre forming was visually seen. Compared to the 6% solution the fibres quantity and fibres forming was visually higher. After cutting the aluminum foil from the drum long fibres hanging off from the side were

seen. In the 6% IL case the fibres seemed short and the foil did not seem "fuzzy". The 12% IL solution seems to be more efficient in the spinning process and seems to produce a lot more fibres.

After the spinning processes of both of the mats SEM pictures were taken by my supervisor. In these pictures you can clearly see the fibres and the build up of the spun material.

On Figure 10 a x2000 magnification of the 12% IL containing spun fibres can be seen. As noticed, there are some "beads" on the figure, it was determined to be the crystallized parts of the IL. Since the IL we used was a solid in room temperature it may have crystallized in the spinning process and formed "beads" onto the fibres spun.
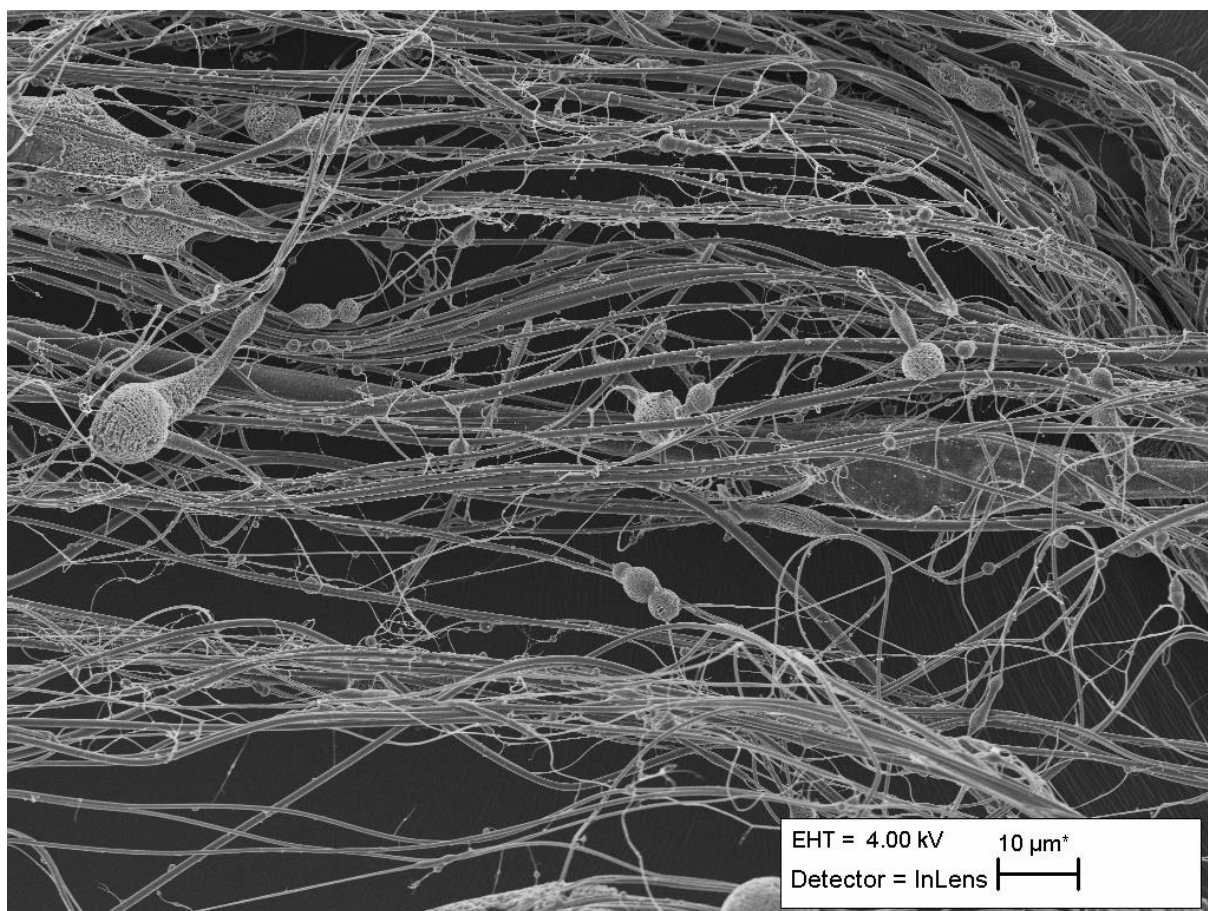

Figure 10. x2000 Magnification of 12% EmimBr electrospun nanofibre from 17 wt % CA solution.

The next picture, Figure 11, shows a 5000 times magnification. The little "beads" can even be seen on this level. You can almost see the material being cross-linked like a polymer. Cross-linking is a great thing to see during this thesis. Since our final goal is to get an electro conductive mat, cross-links help to make the material even more conductive.
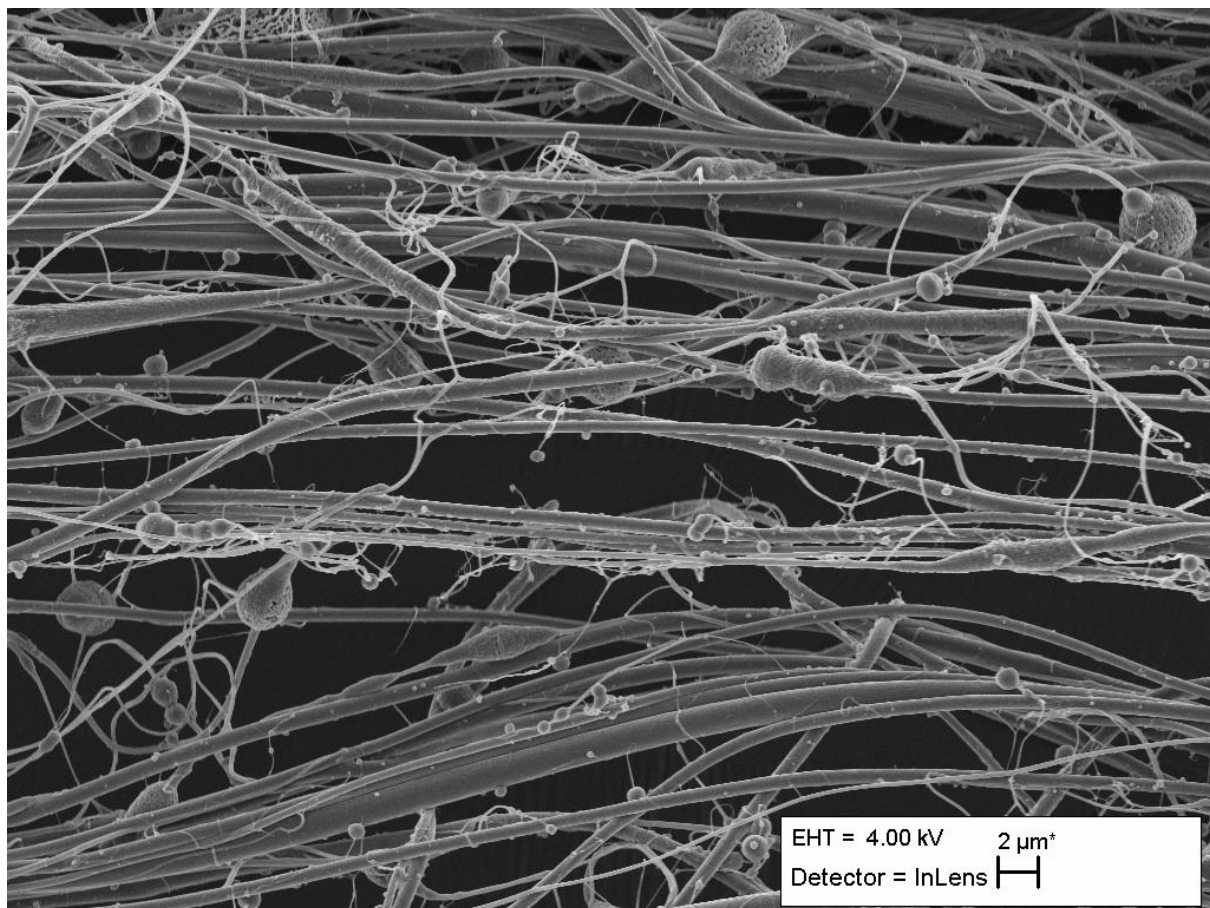
Figure 11. x5000 magnification of 12% EmimBr electrospun nanofibre from 17 wt % CA solution.

On Figure 12 a x20 000 zoom of the fibres can be seen, measurements are added in the picture. This gives a realization of how small the diametres of the fibres actually are. It can be seen that these fibres that have formed are in nanoscale, ranging from 370 nanometres to 1,5 micrometres.
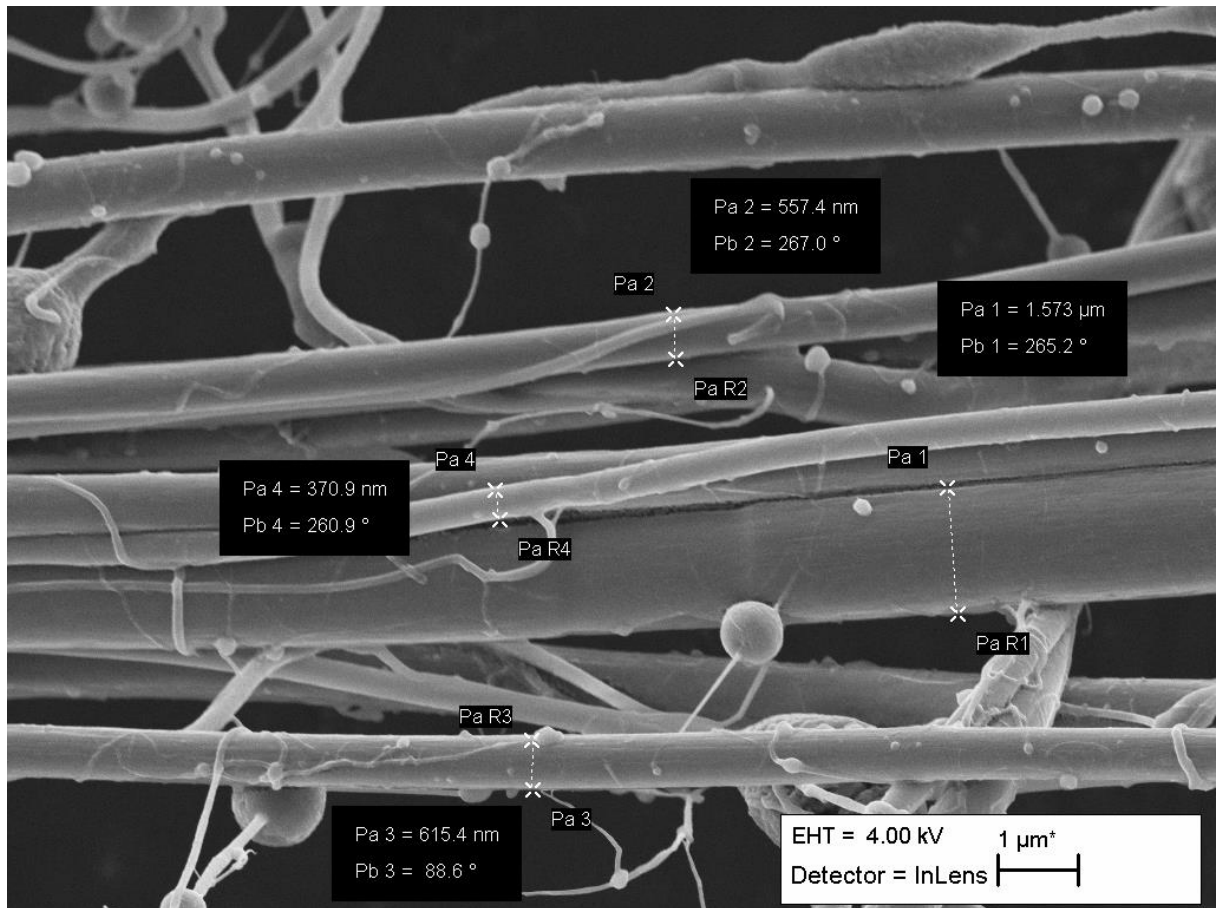
Figure 12. x10000 Magnification of 12% EmimBr electrospun nanofibre from 17 wt % CA solution.

4.2 Conlusions on CA-EmimBr electrospun nanofibres

The experimental part can be called a great success, not even was it possible to spin formidably good mats which we were able to take SEM pictures of, but we also saw cross-linkage between the biopolymer cellulose acetate fibres, with the help of ionic liquid EmimBr. This cross-linkage between the fibres is a good find in the hopes of making a biopolymer electrical conductive material.

The spinning process seems to be optimized for future tests. The higher amount of IL used in the solutions have stopped the solution from agglomerating on the tip of the needle. The learning curve of electrospinning has been very high during these tests alone. A lot of valuable information has been gathered to make future tests and electrospinning more optimal. It is noticed that using different amounts of ionic liquids in the solution can improve the spinning proves to a certain point. Using less

ionic liquid makes the solution unspinnable and using too much ionic liquids makes the solution unspinnable as well. A middle-ground has been found in the process of spinning, which will be used in future experiments.

5. ELECTROSPINNING OF CA-EMIMBR-GO NANOFIBRES

The third experimental part of my thesis involves adding graphene oxide to the previously tested solution. The main goal in this part is to see and learn about the effects of graphene oxide in the electrospinning process with the cellulose acetate. The solution must be compatible with GO used in this work or else there is no point in further testing.

5.1 Theoretical part

Gathering the theoretical part about this particular process was limited because previously there is no research done on this topic. The hypothesis is that adding the GO to the CA solution would improve the electrical conductivity of the solution, which would furthermore improve the spinning process on top of the IL additive added in last chapter. IL improved the conductivity of the spun fibers by giving more free electrons to the solution, but there was a certain limit of how much of the IL you could add to the mixture. Adding too much IL's would only start to work against the spinning process, since there is not enough cellulose to spin if we exceed the limit of IL in the solution.

Since graphene oxide has a good conductivity it was chosen as an extra additive to boost the electrospin process. Similar works on this topic show that adding graphene oxide particles to the spinning process will make the CA hybrid nanofibers thinner then before. Adding the graphene made the typical CA fibers ranging from 580±200 nm to 290±75 nm. In these experiments 4% wt of graphene was added.[26]

5.2 Experimental part

During this experimental part a solution was made that consisted of 6% EmimBr IL, 93,75% of CA solution and 0,25% of GO. 0,25% wt of GO was intentionally added to improve the spinning process. The solution was made as explained on Figure 3,.

During the spinning process the same parameters were used as with a solution without GO. This time the spinning process was very bad. The GO affected the solution so that the conductivity was higher but the spinning process was worse. The conductivity was better in the solution the but the solution did not want to evaporate. There were only agglomerations because the solution seemed to gather on the tip of the needle and then be pulled as a whole to the aluminum foil. This yielded in a no fibres and was worse than previous spinning processes. The yield of different specks was very high estimated to be a couple of times higher than in the case of pure 98% CA solution with 2% IL.

Since a hypothesis was set, it had to be tested. To prove that the GO and IL both affect the conductance of the solution individually, measurements were taken and could be seen in Table 1. It can be seen that the GO alone affects the solution only a little bit, but when it is mixed together with an IL, the change in conductance is exponential

Table 1. Proof of GO and IL conductance differences in the solution.

Solution (no)	Amount of IL (%)	Amount of GO (%)	17% CA solution (%)	Conductivity (mS/cm)
1	10	0	90	11,03
2	0	1	99	0,643
3	10	1	89	14,3
4	7	0,75	92,25	13,18

The process was unsuccessful and the spinning process did not yield in any fibres that could be extracted for future measurement of properties. No fibres were extractable from the foil. If there

had been any fibres present they would have been measured for their properties. If a conductance was found then the solution would have been further investigated and more research would have been conducted to optimize the quanitites of materials used to make a thicker and more conductive mat.

Unfortunately these specks which were electrospinned could not be measured any way with our machinery. This means no further research will be conducted using EmimBr ionic liquid, since the final goal of this thesis would be examining the different effects of ionic liquids on our biopolymer and making an electroconductive mat. It is clear that the IL helped to improve the electrospinning process and it even formed cross-links, but there are no fibres forming when GO is added to the solution. The foil with specks can be seen on Figure 13.
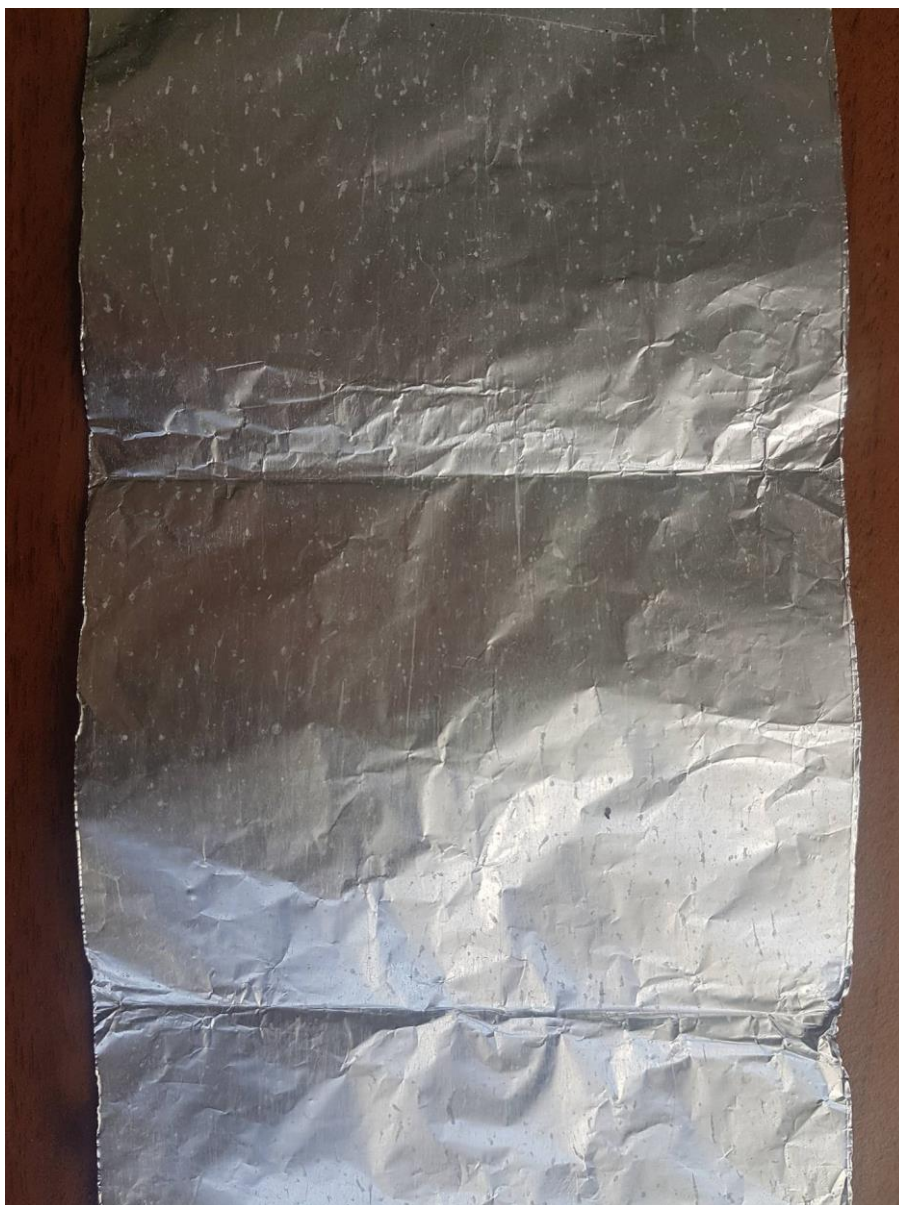

Figure 13. CA-EmimBr-GO solution aluminum foil after electrospinning.

5.3 Selecting a new IL

The previous ionic liquid EmimBr did not give any conductance and the effects on our biopolymer were clear there is no reason to continue working with the previously mentioned IL. Testing of new different IL's is the main topic during this part of the process.

Three new IL's were chosen and tested to find out the best one to add graphene oxide to. Those ionic liquids were BmimBF$_4$, BmimAC and BmimCl.

Firstly, new solutions were mixed together from fresh materials. New ILs were added to the solutions for testing. Solution conductivities were measured, These processes were performed as with the previously tested IL EmimBr. All of the ILs mentioned were added to the same concentration solution. These solutions were made to determine which of the ILs has the best conductance in our 17% CA solution. All of the solutions seen in Table 2 consist of 5% IL and 95% CA(17%), These amounts are wt/wt ratios.

According to Table 2 EmimBr had the lowest conductance out of all of them. This may explain why there was no conductivity when measuring properties of the fibres. As seen in the table, BmimBF4 has the highest solution conductivity, over 10 times higher than the previously tested ionic liquids.

Table 2. Conductivities of the solutions.

Ionic liquid	Solution conductivity(mS/cm)
EmimBr(1-Butyl-3-methylimidazolium Bromide)	0,8
BmimBF4(1-butyl-3-methyl imidazolium tetrafluoroborate)	8,1
BmimCl(1-Butyl-3-methylimidazolium chloride)	2,61
BmimAc(1-Butyl-3-methylimidazolium acetate)	1,5

Table 2 will be the most important table in deciding the next ionic liquids to be tested out. Since the conductivities of the ILs are known the highest conductance solution will be chosen for its good conductive properties for future tests.

5.4 Conclusion on electrospinning CA-EmimBr-Go nanofibres

It is clear that adding GO and IL into the same solution increases the conductivity exponentially. While being alone in the solution their summarized conductance is way lower than in a solution where they are in together. This proves that both of the materials assist each other in increasing the conductivity of the solutions.

Adding GO to EmimBr did no good to our solution and made the electrospinning process worse. The solution became unspinnable and only specs appeared, which could be seen on Figure 13. This concludes our research including EmimBr with our biopolymer because we will not be using this IL in the future.

New ionic liquids were chosen and their conductivities in our solution were measured to determine which of them will be used in future tests. These new ILs will be tested according to the solution conductivity values.

6. ELECTROSPINNING CA-BMIMBF$_4$-GO NANOFIBRES

BmimBF$_4$ was chosen as the 1st test subject of the new ILs for extensive testing in the making of a conductive mat. Because of the high conductivity of the solution BmimBF$_4$ is the best option, out of the four ILs mentioned in Table 2, to start the testing. The testing method uses previously made 17% CA solution mixed with BmimBF$_4$ IL in different quantities, and then graphene oxide will be added for increased conductivity. To make the testing process faster, lots of sample solutions will be made at once and they will all be tested accordingly.

6.1 BmimBF$_4$ IL experimental part

For the experimental part, solutions with different amounts of IL and graphene oxide were prepared for spinning, to determine the best possible ratios for conductive fibres. These could be seen in Table 3.

Table 3. Conductivities of different BmimBF4 solutions

Amount of ionic liquid	Amount of GO (%)	% CA solution used (%)	Solution conductivity (mS/cm)
10%	1	17	14,2
10%	0,5	17	12,42
7%	1	12	11,03
7%	0,5	12	8,64
5%	0,75	10	6,43
5%	0,5	10	6,02

In all the cases the solution conductivities were very high compared to EmimBr but there were no fibres forming during the spinning process. That is why the ratios of GO, IL and even the CA were changed in the process of making the solutions. The main problem seemed to be the thickness of the solution. The viscosity was so high that the solution kept agglomerating on the tip of the needle and the electrical forces were not strong enough to pull the fibres from the droplet. The concentration of CA was lowered to make the solution flow better and lower viscosity. To test the theory, later in the future viscosities were measured using a successfully spinnable and conductable mats solution and comparing it to the BmimBF4 solution. The results are seen in Table 4.

Table 4. Viscosities of the solutions made

Type of solution	GO(%)	IL (%)	17%CA (%)	Viscosity (mPa*s)
Pure solution	0	0	100	348,5
BmimAc solution	2	10	88	156,0
BmimBF4 solution	2	10	88	728,7

Changing the quantities of cellulose acetate to make the solutions less viscose did not change the outcome in any way. While this brought no results the amounts of ionic liquids and GO was changed to find the "perfect middle-ground" so the spinning would finally work. The amount of cellulose fibres possible to be drawn was lowered with the amounts of CA lowered from the solution, so the amount of IL couldn't get too high for the process. There was no middle-ground to find, the spinning processes did not work.

The only outcome from the electrospinning, were black specks on the aluminum foil, which can be seen on Figure 14.

Figure 14. CA-BmimBF4-GO aluminum foil after electrospinning.

6.2 Conclusion on electrospinning CA-BmimBF$_4$-GO nanofibres

The ionic liquid used in these experiments did not react with graphene oxide at all. Different amounts of GO and IL were tried out to find an optima quantity. Still the GO was agglomerating into little beads and even during the electrospinning process, the graphene oxide beads were pulled in

bulks to the folium so there was no fibre forming during this process. The BmimBF$_4$ did not mix with GO and it did not give any fibres during the electrospinning process. It was learned that using biopolymer CA in these certain quantities with GO and BmimBF4 yield no fibres and give no results.

BmimBF4 interacts badly with GO and CA, thus concludes our research on this IL. The IL had very good conductivity in the solution and even greater conductivity with graphene oxide, but the solution was no electrospinnable.

7. ELECTROSPINNING CA-BMIMCL-GO NANOFIBRES

BmimCl was chosen as the 2nd IL to work with, from Table 3, since the IL has moderately good conductivity. While having the 2nd best conductance out of the 3 new ILs taken to use it was a promising choice.

7.1 BmimCL IL experimental part

As with other solutions tested, many different wt % of GO and ionic liquids were added to the CA solution and the outcomes were tested. This time the spinning process was very smooth. No agglomerations were noticed. There were no defects appearing in the spinning process at all. The solution itself did not seem thick at all and since the spinning process was successful it did not require viscosity measurements.

The spinning did not give specks or little droplets of solution to the foil this time. The outcome of the spinning resulted in thick greyish mats. The grey color indicates that the GO added to the solution was well mixed and it attached to the fibres. The mats forming were enough to measure properties for future analysis.

The measurements of the mats showed that there was no conductivity in the fibres. Although the greyish color indicates the presence of GO in the mat it was not enough to form a porous cross-linked structure for the fibres to be capable of conducting electricity. The properties of BmimCl mats can be seen in Table 5.

Table 5. Conductivities of different BmimCl solutions

Amount of IL	Amount of GO (%)	%CA solution used (%)	Solution conductivity (mS/cm)	Fibre conductivity
10%	1	17	4,6	None
10%	0,5	17	3,8	None
7%	1	12	3,2	None
7%	0,5	12	2,2	None
5%	0,75	10	1,7	None
5%	0,5	10	1,5	None

7.2 Conclusion of spinning CA-BmimCl-GO nanofibres

Although the liquid had good conductivity and it seemed that GO particles were dispersed homogeneously throughout the solvent, the electrospun mats did not show any conductance. There were no indications of agglomeration during the spinning process. The main problem here was about compatibility. The biopolymer used with this certain IL and GO is spinnable, but during the forming of fibres, the electroconductive properties are non-existent. These experiments conclude my research on BmimCl because no conductive fibre was produced after spinning process.

8. ELECTROSPINNING CA-BMIMAC-GO NANOFIBRES

Testing of BmimAc ionic liquid will be the last IL tested in this thesis. The IL had the 2nd lowest conductivity of the solutions mentioned in Table 3. Although the conductivity is low, the ionic liquid is Ac based, the compatibility with our solution is very likely. Our 17% Ac solution is composed of Acetone and DMAC in 2:1 ratios with 17% cellulose acetate added into it. Since the solution is already based on Ac there should be no issues with the compatibility.

8.1 Solution preparation and electrospinning of CA-BmimAc-GO solution

During this part of the experiment, 3 solutions were made for testing, with different amounts of GO to find the best compatibility with our ionic liquid. To mention that the mixing of the solution has not changed. The electrospinning process was very smooth and the forming of fibres could be observed visually. The yield of fibres was very high. A thick mat was gathered in 3-4 hours with every solution prepared.

Since the mats came out very well, a lot of samples could be taken for testing and for SEM pictures aswell. The properties of the solutions made and mats were measured and are presented in Table 6.

Table 6. BmimCl solutions and mats conductivities.

Amount of IL	Amount of GO (%)	% CA solution used (%)	Solution conductivity (mS/cm)	Fibre conductivity (µS/cm)
10%	0,5	17	2,5	0,32
10%	1	17	2,55	0,36
10%	2	17	2,66	0,4

It could be seen in Table 6 that these mats have conductivity values as well. This electrospinning process was very successful giving the chance to further analyze the fibres formed. After mat spinning the fibres were cut from the mat and samples were made for conductivity measurements and for SEM analysis. All of the SEM pictures seen in this part are taken by the author of this thesis.

8.2 Analysis and results of CA-BmimAc-GO spun fibres SEM pictures

Every mat spun had a SEM picture taken with different magnifications, x1000, x3000, x10000. Only x1000 and x3000 magnification pictures will be presented in this chapter. The 10000 magnification pictures will be added to the appendixes because of the low quality they will not be presentable as valid data. On Appendixes 1-3 x10000 magnifications can be observed and the thicknesses of the fibres can be roughly estimated.

On figure 15 and Figure 16 a x1000 and a x3000 magnification of 0,5% GO 10% of IL and 89,5% solutions electrospun mat can be observed. The fibres are clearly distinguishable. There seem to be a hefty amount of beads appearing on the picture as well. The beads being white on the picture mean that they conduct electricity, meaning these parts can be residues of ILs or particles of GO. Same beads appear on every SEM image taken.

Figure 17 and Figure 18 show fibres of the 1% GO containing solution. It is clearly seen that the amount of fibres is higher and the structure seems denser. Data from Table 6 shows that the conductivity of the mat was higher aswell in this case. Meaning the extra GO added to the solution helped the biopolymer have better structure and increase the conductance as well.

On figure 19 and figure 20 2% of GO solution SEM images are seen. The fibres seem more chaotic and there appear to be a lot more white beads. While the GO amount was increased the amount of GO particles that may appear on the SEM was increased. The white beads can be a combination of IL or GO beads.
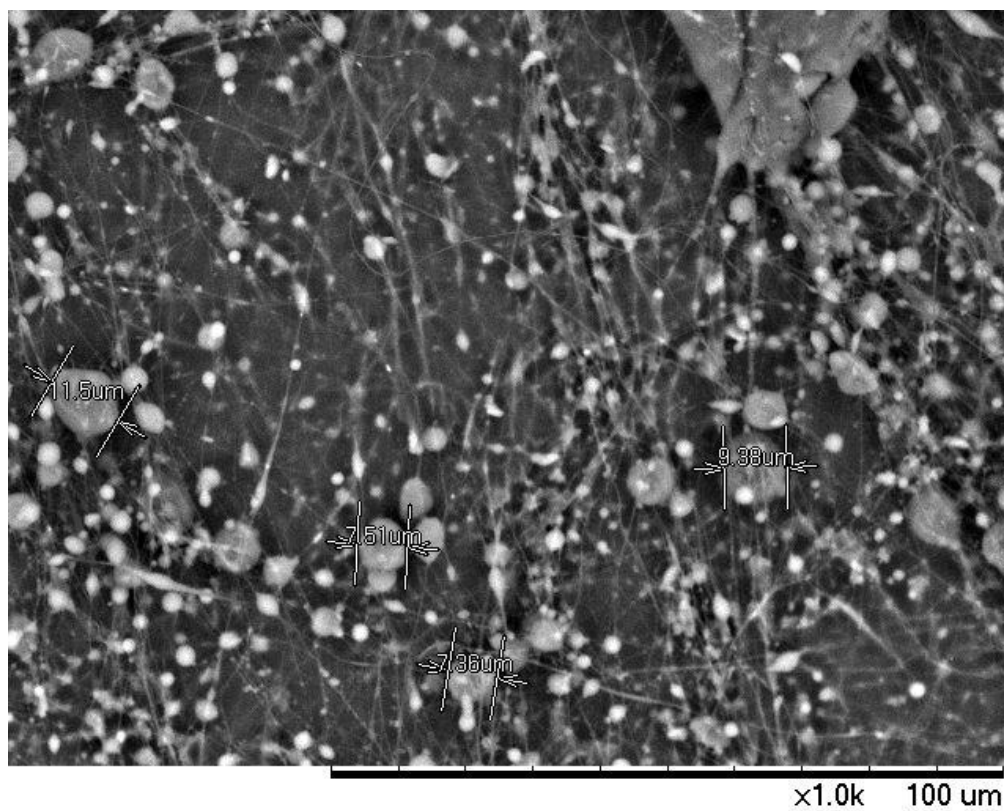
Figure 15. BmimaAc solution containing 0,5% GO under x1000 magnification
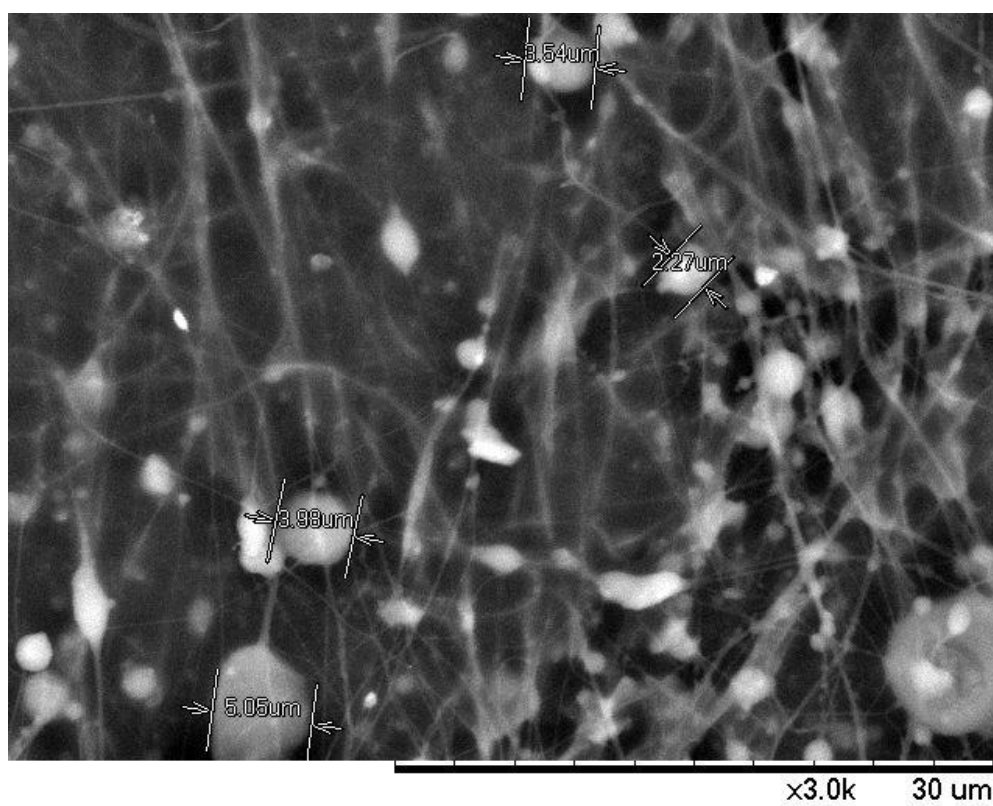

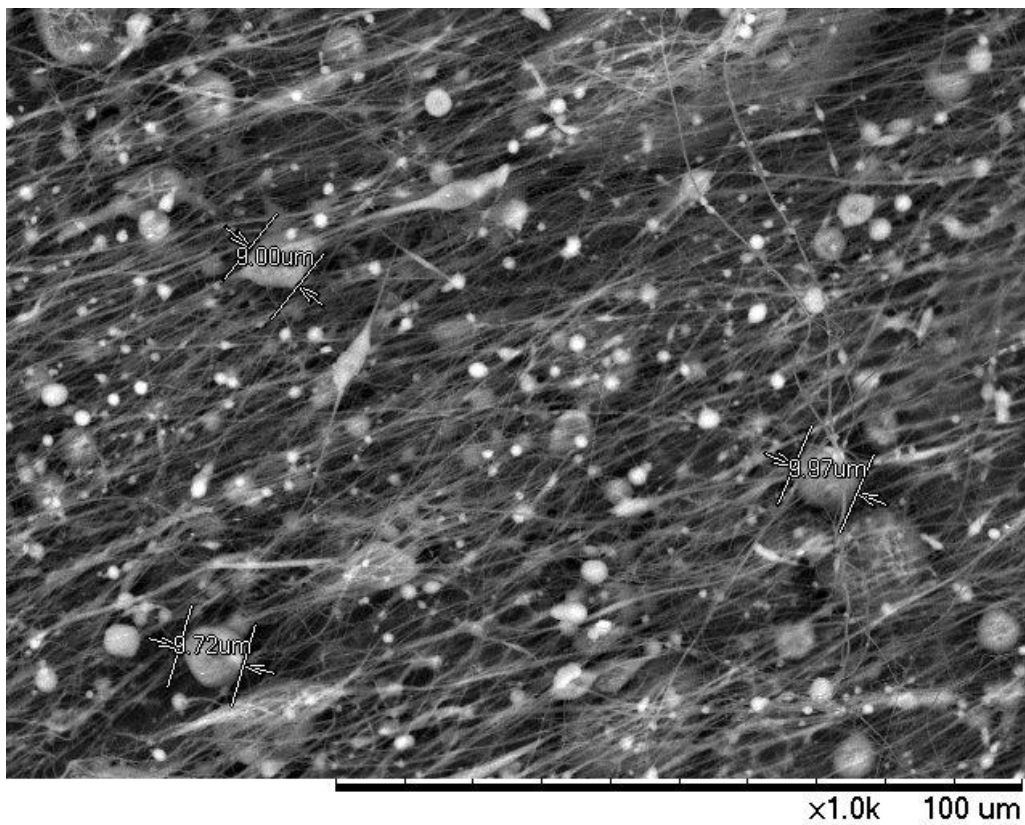Figure 16. BmimaAc solution containing 0,5% GO under x3000 magnification

Figure 17. BmimaAc solution containing 1% GO under x1000 magnification
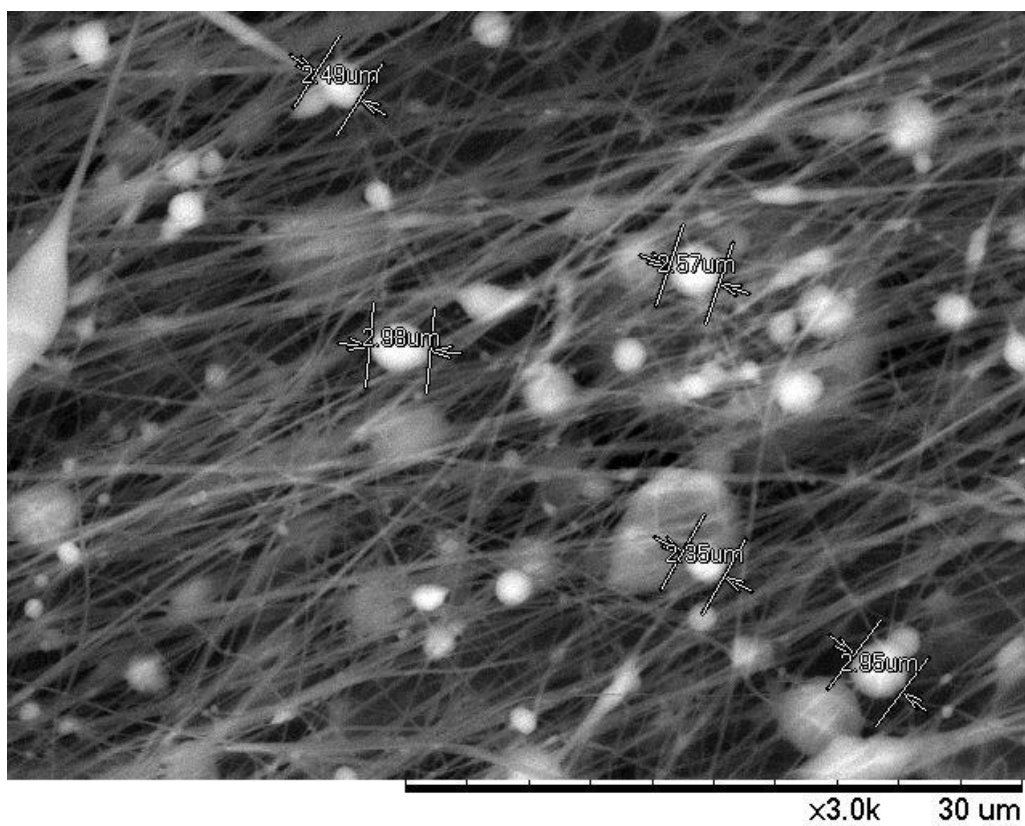

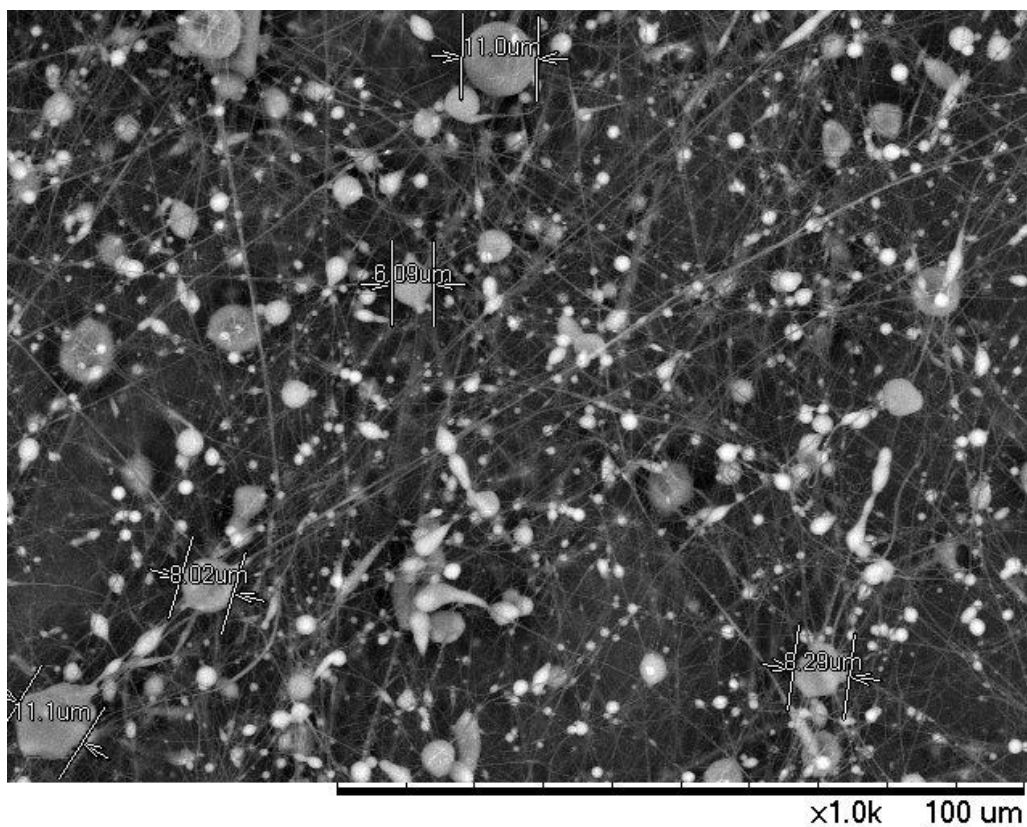Figure 18. BmimaAc solution containing 1% GO under x3000 magnification

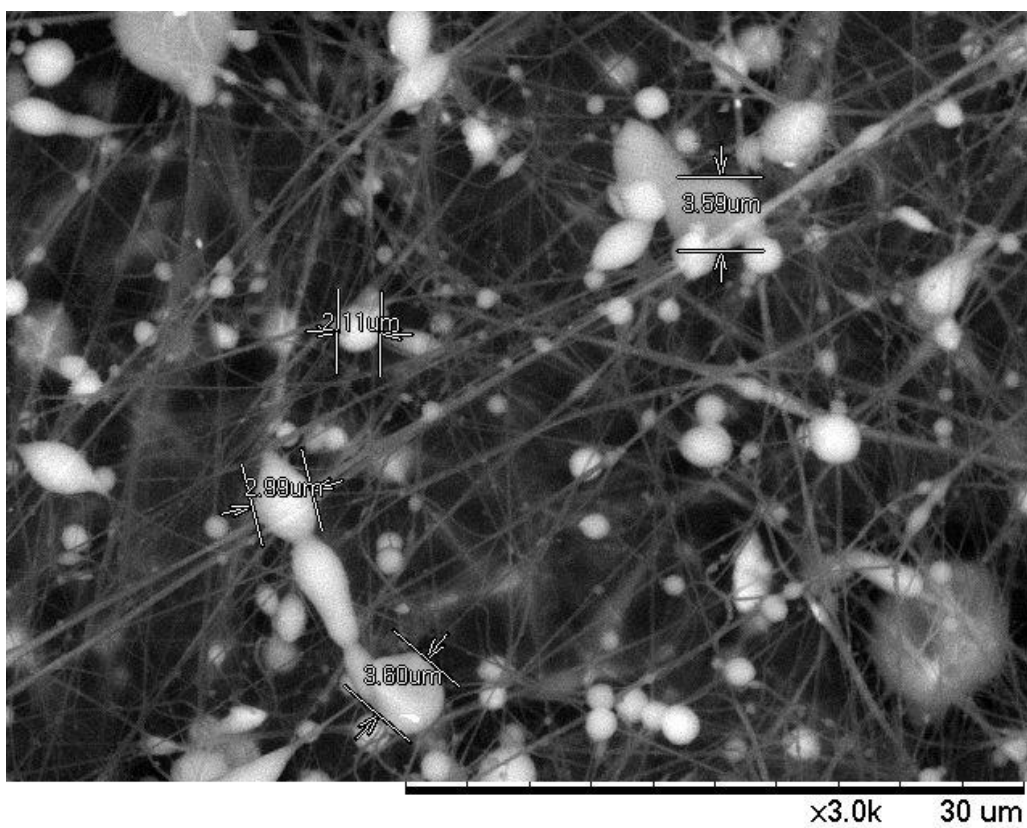Figure 19. BmimaAc solution containing 2% GO under x1000 magnification

Figure 20. BmimaAc solution containing 2% GO under x3000 magnification

8.3 Conclusions on electrospinning CA-BmimAC-GO solution

The usage of BmimAc with cellulose acetate biopolymer was a success. The solution was spinnable and a conductive mat was produced.

The spinning process was very smooth and a thick mat was gotten in a short period of time. There were no defects, agglomerations during the spinning process. The produced fibre was analyzed and properties were measured. The conductivity rose with the adding of more GO to the solution. Keep in mind that the amount of GO added to the solution is capped to a point. Adding a little too much GO makes the solution way too thick to electrospin. The process was optimized as much as possible. Researching the subject even further could give even better results on the subject.

White beads that appear on the SEM picture are considered to be conductive. SEM images show conductive elements in white color. These beads appear because something in the solution making or quantity is wrong. The beads could be solution residues that were not vaporized during the spinning process, or they could be particles of GO agglomerating into a bead. These beads may appear in the pictures when the quantities of the substances were not optimal or they did not interact 100% with each other.

The last experimental part discussed in this work was a success. The end goal was achieved and an electrospinnable conductive mat was achieved. Still there is room for improvements. Removing the beads from the structure while optimizing the solution and the conditions can be something for future researches.

9. SUMMARY

These days a lot of time and money is spent on researches on biodegradable and biocompatible materials which could possibly replace the current costly polymeric materials. Different solutions are found and researched on the daily basis. Finding a cheaper biodegradable material and infusing ionic liquid and graphene oxide into the material to observe the effects that appear was my main goal. As an extra goal I tried to find a suitable IL and GO in combination together with the biopolymer, to electrospin a mat which conducts electricity.

The thesis started with testing out if the biopolymer chosen for this work, cellulose acetate, would be spinnable in the lab conditions provided. After the positive initial experimental part, IL EmimBr was added in increasing quantities from 2-14%. This part of the experiment was important to find the maximum quantity of ILs that could be added to the mixture. Each test was observed carefully to notice any effects the IL could affect the biopolymer with. It was noticed that from 6% of IL used boosted the process and forming of fibres was noticed, The maximum amount of ILs that could be used was capped at 12% of wt%. Going over the limit would have a degrading effect in the electrospinning process.

The IL BmimBr was the 1st one to be tested with. Different solutions with different quantities of GO and IL were made but there were no fibres forming during electrospinning. Only specks of the solvent appeared on the aluminum foil. Since there were no fibres forming from the combination of CA solvent, GO and IL there was no point to continue working with this IL.

$BmimBF_4$ was the 2nd IL which was tested. As with the last IL, different solutions were made with different quantities of GO and IL. Since there appeared to be problems with the viscosities of the solution, and no fibres were forming, the amount of CA was lowered to lower the viscosity. Doing this did not help the electrospinning process and there were still no fibres appearing. The aluminum foil from the collector contained black specks of the solution. Since there were no fibres forming there was no point to continue working with $BmimBF_4$.

BmimCl was a more promising IL than the previous. Similarly to the previous experiments different solutions were made. The initial electrospinning process produced fibres. The fibre forming could be visually observed and a thick mat was achieved in a matter of hours. There were no noticeable defects in the spinning process. Enough fibres were formed for properties measurements. The fibres were collected from the aluminum foil and were folded together to make a mat for conductivity measurement. There was no conductance in the fibres, but at least the spinning process

worked this time. It is noticed that IL BmimCl works well with biopolymer cellulose acetate, but not with GO.

The last IL that was tested was BmimAc. Since the IL is acetone based just like our solvent which has 2 parts of acetone 1 part of DMAc and 17% wt % of cellulose acetate in it, it interacted well with each other. This time fibres were forming very fast and continuous yet of fibre was being pulled onto the collector. A thick mat formed in 3-4 hours. The fibres were more than enough to collect samples for SEM images and to measure conductance. The mat was indeed conductive and it could be noted that increasing the amount of GO increased the conductance of the fibres. SEM images show the presence of fibres and beads tended to appear on the SEM images. These beads can be explained as a residue of the solvent appearing because of wrong conditions or the quantities in the solvent were not optimized.

The end-goal was achieved, different IL effects were noticed, some of them made the the biopolymer solvent electrospinnable and some did not. Producing a conductive fibre was also achieved. This means that it is possible to make cellulose fibres conduct electricity. There seemed to be beads appearing on SEM images which means the solutions and the conditions are not perfect and further research must be conducted to optimize the fibre forming even further. This area needs more investigation and more experiments should be conducted using other ionic liquids.

10.   KOKKUVÕTE

Väga palju ressursse kasutatakse tänapäeval suurte ettevõtete ja uurimuskeskuste poolt, et leida võimalusi valmistamaks biolagunevat ja bioühilduvat materjali mis asendaksid tulevikus praegused polümeermaterjalid. Erinevaid lahendusi leitakse ja uuritakse igapäevaselt. Minu ülesandeks oli uurida võimalusi kuidas odavat biopolümeeri muuta elektrit juhtivaks, samal ajal uurides milliseid omadusi ioonvedelikud annavad antud materjalile. Biopolümeeriks sai valitud atsetüültselluloos, millele lisatakse erinevaid ioonvedelikke ja grafeen oksiidi, et muuta biopolümeeri kiud elektroketruse abil elektrit juhtivaks.

Esimeseks ülesandeks oli testida kas kasutusel olevate masinatega on võimalik elektrokedrata biopolümeerikiudu. Peale esimest õnnestunud elektroketrust lisati ioonvedelik EmimBr suurenevates kogustes lahusesse, 2-14%. Katsetuse mõtteks oli leida maksimaalne kogus ioonvedelikku mida on võimalik lisada lahusesse, et elektroketrus oleks veel võimalik. Igat katsetust jälgiti hoolega märkamaks millist mõju avaldab suurenev kogus ioonvedeliku elektrokedratavale lahusele. Tähtsamateks väärtusteks kujunesid 6% massist ioonvedeliku lisamine lahusesse. Sellest hetkest oli selgelt märgata elektroketruse protsessi hõlbustust. Maksimaalne kogus ioonvedeliku mida oli võimaliks lisada lahusesse oli 12%. Lisades üle testitud normi, ei olnud enam võimalik elektrokedrata kiude.

Esimeseks katsetuseks valiti BmimBr ioonvedelik. Erinevate massi protsentidega lisati lahustesse ioonvedelike ja grafeen oksiidi, et leida optimaalne kogus mil elektroketrus on edukaim. Antud katsetuses ei olnud võimalik saada ühtegi kiudu. Küll aga tekkisid lahuse piisad alumiiniumist paberile. Antud ioonvedelikuga ei olnud võimalik elektroketrust teostada ning liiguti edasi järgmise ioonvedeliku testimisele.

Teise ioonvedelikuna asuti testime $BmimBF_4$ ioonvedelikku. Antud ioonvedelikul oli suurim juhtivus võrreldes teistega. NImetatud juhul valmistati ka mitmeid lahuseid et leida optimaalne kogus elektroketrusele. Elektroketruse protsessi käigus ilmnes tõsine problem lahuse viskoossusega. Lahus oli liiga paks ning kiudu ei olnud võimalik kedrata. Atsetüültselluloosi kogust vähendades vähendati ka lahuse viskoossust kuid ka siis ei õnnestunud elektroketrus läbi viimine. Elektroketruse järgsel vaatlusel ilmes, et kiudude asemel oli alumiiniumist paber kaetud mustade lahuse piisakdega. Kiudude elektroketrus ei olnud võimalik ka konsentratsioonide muutmisega, seega võeti kasutusele uus ioonvedelik.

BmimCl oli kolmas ioonvedelik millega alustati katseid. Nagu ka eelmiste vedelikega valmistati mitmeid erinevaid lahuseid. Esimene elektroketrus oli juba edukas ning visuaalselt oli võimalik jälgida kiudude tekkimist ja nende liikumist poolile. Elektroketrus oli edukas ja probleeme ei esinenud. Piisavalt kiude sai elektrokedratud edasiste mõõtmiste ja testide jaoks. Kuigi juhtivust kiududel ei tuvastatud on siiski suureks positiivseks osaks kiudude elektroketruse õnnestumine.

Viimase ioonvedelikuna kasutati BmimAc ioonvedelikku. Antud vedelikul on sama baasaine mis ka biopolümeeri lahusel. Sellest võib järeldada, et antud materjalid on sarnased ja ühilduvad. Antud juhul toimus elektroketrus väga edukalt. Küllaltki tihke matt kiudu elektrokedrati vaid 3-4 tunni jooksul. Biopolümeerikiudu oli piisavalt katsetusteks, mõõtmisteks kui ka SEM piltide tegemiseks. Esmased mõõtmised näitasid, et elektrokedratud kiud juhivad edukalt elektrit. Täheldati, et tõstes grafeen oksiidi kogust lahuses, suurenes ka juhtivus. SEM piltidel on selgelt näha kiudude olemasolu ning oli märgata ka mõnda "pallikest". Antud defekti võib lugeda lahuse jääkideks mis ei reageerinud elektroketruse protsessil. Samuti võib probleemiks olla lahusesse lisatud ainete mitte optimaalsed kogused või hoopis valed elektroketruse tingimused.

Magistritöö alguses püsitatud ülesanded said saavutatud. Erinevaid ioonvedelike mõjusid uuriti, samuti suudeti valmistada elektrit juhtiv biopolümeerikiud. See tähendab, et on võimalik valmistada tselluloosibaasil elektrokedratud elektrit juhtivat kiudu. Antud katseid tuleks läbi viia ka teiste ioonvedelikega ning kindlasti vajaks antud ala intensiivsemat uuringut.

11.   REFERENCES

1. Jamie H. Warner, Chapter 1 - *Introduction, In Graphene*, *Elsevier*, 2013, Pages 1-4.

2. Dong, H.S. and S.J. Qi, *Realising the potential of graphene-based materials for biosurfaces – A future perspective. Biosurface and Biotribology*, 2015. 1(4): p. 229-248.

3. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Science 2004, 306, 666.

4. Allen, M. J.; Tung, V. C.; Kaner, R. B. Chem. Rev. 2010, 110, 132.

5. Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. R. Science 2009, 324, 1312.

6. Mattevi, C.; Kima, H.; Chhowalla, M. J. Mater. Chem. 2011, 21, 3324.

7. Compton, O. C.; Nguyen, S. T. Small 2010, 6, 711.

8. Ferrari, A.C., et al., *Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems.* Nanoscale, 2015. 7(11): p. 4598-4810.

9. Zurutuza, A. and C. Marinelli, *Challenges and opportunities in graphene commercialization.* Nat Nano, 2014. 9(10): p. 730-734.

10. Compton, O. C.; Nguyen, S. T. Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Material *Small* 2010, *6*, 711.

11. Mao, S.; Pu, H.; Chen, J. Graphene Oxide and its Reduction: Modeling and Experimental Progress *RSC Adv.*, 2012, *2*, 2643.

12. Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The Chemistry of Graphene Oxide *Chem. Soc. Rev.* 2010, *39*, 228.

13. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films *Science* 2004, *306*, 666.

14. Gilje, S.; Han, W.; Wang, M.; Wang, K. L.; Kaner, R. B. A Chemical Route to Graphene for Device Applications *Nano Lett.* 2007, *7*, 3394.

15. Chua, C. K.; Pumera, M. Chemical Reduction of Graphene Oxide: a Synthetic Chemistry Viewpoint *Chem. Soc. Rev.* 2014, *43*, 291.

16. Pei, S.; Cheng, H-M. The Reduction of Graphene Oxide *Carbon* 2012, *50*, 3210.

17. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and Graphene Oxide: Synthesis, Properties, and Applications *Adv. Mater.* 2010, *22*, 3906.

18. Chen, D.; Feng, H.; Li, J. Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications *Chem. Rev.* 2012, *112*, 6027.

19. Wan, X.; Huang, Y.; Chen, Y. Focusing on Energy and Optoelectronic Applications: A Journey for Graphene and Graphene Oxide at Large Scale *Acc. Chem. Res.* 2012, *45*, 598.

20. Eda, G.; Chhowalla, M. Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics *Adv. Mater.*2010, *22*, 2392.

21. Wan, X.; Long, G.; Huang, L.; Chen, Y. Graphene – A Promising Material for Organic Photovoltaic Cells *Adv. Mater.* 2011, *23*, 5342.

22. Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-Based Composites *Chem. Soc. Rev.* 2012, *41*, 666.

23. Lightcap, I.; Kamat, P. V. Graphitic Design: Prospects of Graphene-Based Nanocomposites for Solar Energy Conversion, Storage, and Sensing *Acc. Chem. Res.* 2013, *46*, 2235.

24. Chung, C.; Kim, Y-K.; Shin, D.; Ryoo, S-R.; Hong, B. H. Min, D-H. Biomedical Applications of Graphene and Graphene Oxide *Acc. Chem. Res.* 2013, *46*, 2211.

25. Wang, Y.; Li, Z.; Wang, J.; Li, J.; Lin, Y. Graphene and Graphene Oxide: Biofunctionalization and Applications in Biotechnology *Trends Biotechnol.* 2011, *29*, 205.

26. Pyun, J. Graphene Oxide as Catalyst: Application of Carbon Materials Beyond Nanotechnology *Angew. Chem. Int. Ed.* 2011, *50*, 46.

27. Yeh, T-F.; Syu, J-M.; Cheng, C.; Chang, T-H.; Teng, H. Graphite Oxide as a Photocatalyst for Hydrogen Production from Water *Adv. Funct. Mater.* 2010, *20*, 2255.

28. Dreyer, D. R.; Jia, H-P.; Bielawski, C. W. Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions *Angew. Chem. Int. Ed.* 2010, *49*, 6813.

29. Kim, J.; Cote, L. J.; Franklin Kim, F.; Yuan, W.; Shull, K. R.; Huang, J. Graphene Oxide Sheets at Interfaces *J. Am. Chem. Soc.* 2010, *132*, 8180.

30. Shin,H-J.; Kim, K. K.; Benayad, A.; Yoon, S-M; Park, H. K.; Jung, I-S; Jin, M. H.; Jeong, H-K; Kim, J. M.; Choi, J-Y.; Lee, Y. H. Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance *Adv. Funct. Mater.* 2009, *19*, 1987.

31. Improved Synthesis of Graphene Oxide Daniela C. Marcano, Dmitry V. Kosynkin, Jacob M. Berlin, Alexander Sinitskii, Zhengzong Sun, Alexander Slesarev, Lawrence B. Alemany, Wei Lu, and James M. Tour ACS Nano 2010 4 (8), 4806-4814 DOI: 10.1021/nn1006368

32. Moon, K.; Lee, J.; Ruoff, R.S.; Lee, H. Reduced Graphene Oxide by Chemical Graphitization *Nat. Commun.* 2010, *1*, 73.

33. Pei, S.; Zhao, J.; Du, J.; Ren, W.; Cheng, H-M. Direct Reduction of Graphene Oxide Films into Highly Conductive and Flexible Graphene Films by Hydrohalic Acids *Carbon* 2010, *48*, 4466.

34. Su, C-Y.; Xu, Y.; Zhang, W.; Zhao, J.; Liu, A.; Tang, X.; Tsai, C-H.; Huang, Y.; Li, L-J. Highly Efficient Restoration of Graphitic Structure in Graphene Oxide Using Alcohol Vapors *ACS Nano* 2010, *4*, 5285.

35. Saha, S. K.; Bhaumik, S.; Maji, T.; Mandal, T. K.; Pal, A. J. Solution-Processed Reduced Graphene Oxide in Light-Emitting Diodes and Photovoltaic Devices with the Same Pair of Active Materials *RSC Adv.* 2014, *4*, 35493.

36. Li, S-S.; Tu, K-H.; Lin, C-C.; Chen, C-W.; Chhowalla, M. Solution-Processable Graphene Oxide as an Efficient Hole Transport Layer in Polymer Solar Cells *ACS Nano* 2010, *4*, 3169.

37. Wang, H.; Cui, L-F.; Yang, Y.; Casalongue, H. S.; Robinson, J. T.; Liang, Y.; Cui, Y.; Dai, H. Mn_3O_4-Graphene Hybrid as a High-Capacity Anode Material for Lithium Ion Batteries *J. Am. Chem. Soc.* 2010, *132*, 13978.

38. Zhou, G.; Wang, D-W.; Li, F.; Zhang, L.; Li, N.; Wu, Z-S.; Wen, L.; Lu, G. Q (M).; Cheng, H-M. Graphene-Wrapped Fe_3O_4 Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries *Chem. Mater.* 2010, *22*, 5306.

39. Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K.; J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. Carbon-Based Supercapacitors Produced by Activation of Graphene *Science* 2011, *332*, 1537.

40. Zhu, Y.; Murali, S.; Stoller, M. D.; Velamakanni, A.; Piner, R. D.; Ruoff, R. S. Microwave Assisted Exfoliation and Reduction of Graphite Oxide for Ultracapacitors *Carbon* 2010, *48*, 2118.

41. Nick Tucker, Ph.D., Jonathan J. Stanger, MSc, Mark P. Staiger, Ph.D., Hussam Razzaq, Ph.D., Kathleen Hofman*, Ph.D. Journal of Engineered Fibers and Fabrics SPECIAL ISSUE - July 2012 – FIBERS*

42. Ramakrishna, S., *An Introduction to Electrospinning and Nanofibers*. 2005: World Scientific.

43. Deka, A.K.a.M., *Nanofiber Reinforced Composite Polymer Electrolyte Membranes*. 2010: InTech.

44. Nain, A.S., et al., *Drawing suspended polymer micro-/nanofibers using glass micropipettes.* Applied Physics Letters, 2006. 89(18): p. 183105.

45. Almecija, D., et al., *Mechanical properties of individual electrospun polymer-nanotube composite nanofibers.* Carbon, 2009. 47(9): p. 2253-2258.

46. Jeong, J.S., et al., *Mechanical properties of electrospun PVA/MWNTs composite nanofibers.* Thin Solid Films, 2007. 515(12): p. 5136-5141.

47. Bhardwaj, N. and S.C. Kundu, *Electrospinning: A fascinating fiber fabrication technique.* Biotechnology Advances, 2010. 28(3): p. 325-347.

48. Zomer Volpato, F., *Composites for Biomedical Applications*. 2010, University of Trento.

49. S. Zhang, X. Lu, Q. Zhou, X. Li, X. Zang, S. Li, Ionic Liquids: Physicochemical Properties, Elsevier, Amsterdam, 2009.

50. S. Sowmiah, V. Srinivasadesikan, M.-C. Tseng, Y.-H. Chu, Molecules 2009, 14, 3780 – 3813.

51. T. Torimoto, T. Tsuda, K. Okazaki, S. Kuwabata, Adv. Mater. 2010, 22, 1196 – 1221.

52. P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2007.

53. D. B. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 2002, 74, 157 – 189

54. M. J. Earle, K. R. Seddon, Pure Appl. Chem. 2000, 72, 1391 – 1398

55. M. Haumann, A. Riisager, Chem. Rev. 2008, 108, 1474 – 1497; b) W. S. Miao, T. H. Chan, Acc. Chem. Res. 2006, 39, 897 – 908.

56. a) X. Han, D. W. Armstrong, Acc. Chem. Res. 2007, 40, 1079 – 1086; b) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, Chem. Commun. 1998, 1765 – 1766.

57. a) P. Hapiot, C. Lagrost, Chem. Rev. 2008, 108, 2238 – 2264; b) D. R. Macfarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil, E. I. Izgorodina, Acc. Chem. Res. 2007, 40, 1165 – 1173.

58. T. Ichikawa, M. Yoshio, A. Hamasaki, T. Mukai, H. Ohno, T. Kato, J. Am. Chem. Soc. 2007, 129, 10662 – 10663; b) K. Biswas, C. N. R. Rao, Chem. Eur. J. 2007, 13, 6123 – 6129.

59. F. van Rantwijk, R. A. Sheldon, Chem. Rev. 2007, 107, 2757 – 2785.

60. T. L. Greaves, C. J. Drummond, Chem. Rev. 2008, 108, 206 – 237; b) S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. Drake, Energy Fuels 2008, 22, 2871 – 2872.

61. W. L. Hough, M. Smiglak, H. Rodriguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. H. Davis, R. D. Rogers, New J. Chem. 2007, 31, 1429 – 1436.

62. M. Deetlefs, K. R. Seddon, M. Shara, Phys. Chem. Chem. Phys. 2006, 8, 642 – 649.

63. J. D. Holbrey, K. R. Seddon, Clean Technol. Environ. Policy 1999, 1, 223 – 236.

64. M. J. Earle, P. B. McCormac, K. R. Seddon, Green Chem. 2000, 2, 261 – 262.

65. Gopiraman et al. – eXPRESS Polymer Letters Vol.7, No.6 (2013) 554–563

66. Paulusse, J. M. and Sijbesma, R. P. (2006), Ultrasound in polymer chemistry: Revival of an established technique. J. Polym. Sci. A Polym. Chem., 44: 5445-5453.

12. APPENDICES

Appendix 1. BmimAc solution with 0,5% GO x10000 magnification
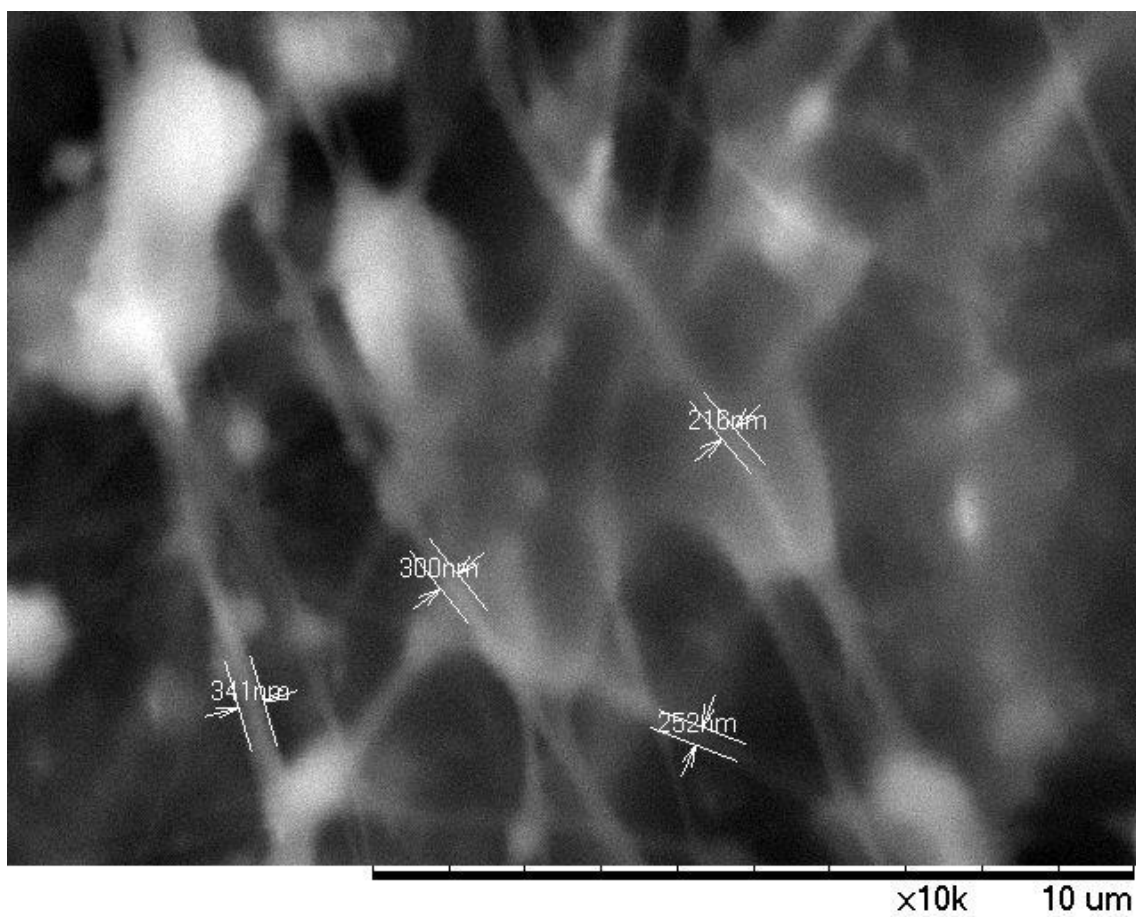
Appendix 2. BmimAc solution with 1% GO x10000 magnification
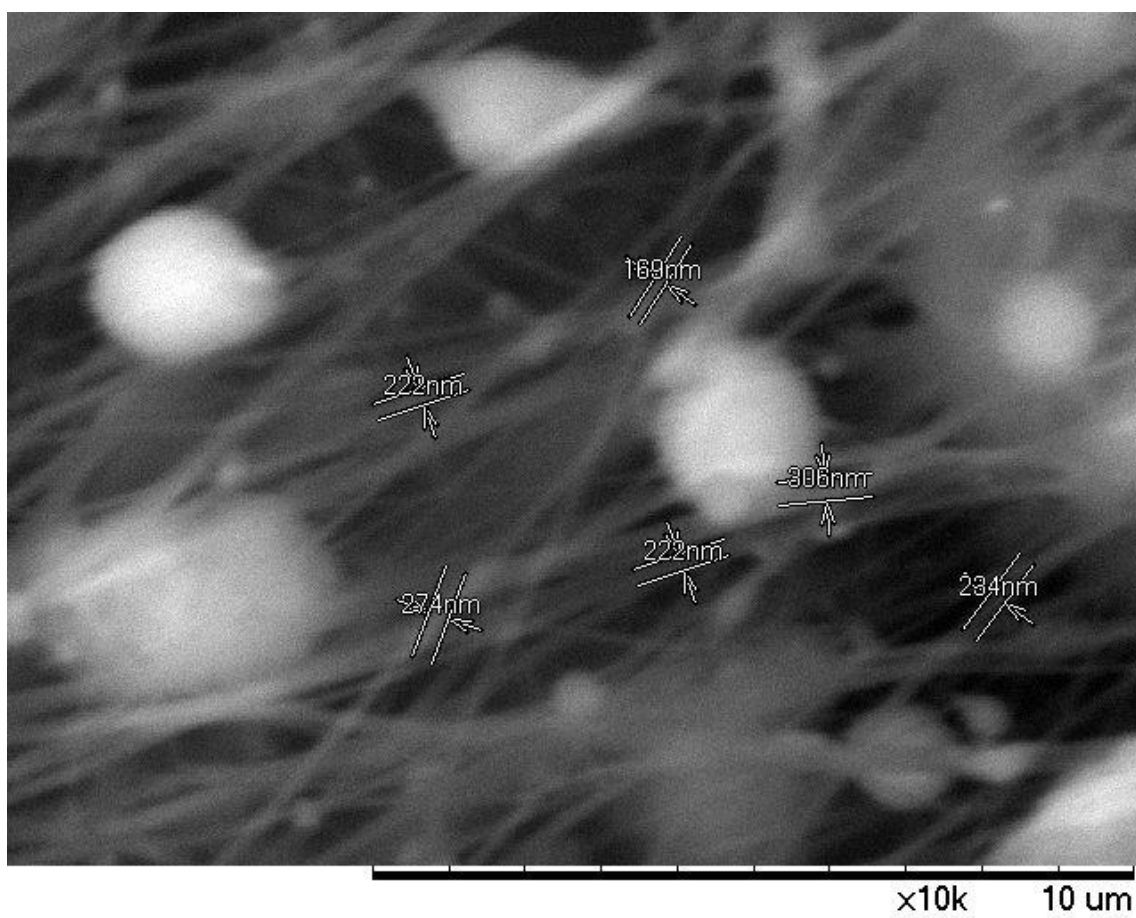
Appendix 3. BmimAc solution with 2% GO x10000 magnification