TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

ELECTROSPINNING OF ELECTRICALLY CONDUCTIVE POLYETHYLENE OXIDE NANOFIBERS WITH IONIC LIQUIDS

POLÜETÜLEENOKSIIDIST ELEKTRIT JUHTIVATE NANOKIUDUDE ELEKTROKETRUS KOOS IOONSETE VEDELIKEGA

MASTER THESIS

Student: Ljudmila Solovjova
/name/

Student code 163495KVEM

Supervisor: Illia Krasnou, Research Scientist
/name, position/

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.

".....” ..... 201…..

Author: .....
/signature /

Thesis is in accordance with terms and requirements

".....” ..... 201….

Supervisor: …….....
/signature/

Accepted for defense

".....”.....2018 .

Chairman of theses defense commission: .....
/name and signature/

Department of Materials and Environmental Technology

THESIS TASK

Student: ……..……..(name, student code)

Study programme, ……..……. (code and title)

main speciality:

Supervisor(s): ……..……..(position, name, phone)

Consultants: ……..……..(name, position)

……..……..…… (company, phone, e-mail)

Thesis topic:

(in English) Electrospinning of electrically conductive polyethylene oxide nanofibers with ionic liquids

(in Estonian) Polüetüleenoksiidist elektrit juhtivate nanokiudude elektroketrus koos ioonsete vedelikega

Thesis main objectives:

1. To obtain nanofibrous mat with diameter of fibers around 100 nm
2. To study influence of ILs on the electrical conductivity of mats
3. Studying methods covering mats by AC

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Influence of ionic liquids on electrospun mats	28.02.17
2.	Production of PEO fibers with diameter around 100nm	30.05.17
3.	Studying methods of electrospun mats production with AC high load	28.02.18

Language: …….. **Deadline for submission of thesis:** "....."..... 201….a

Student: …….. ..... "....."..... 201….a

/signature/

Supervisor: …… ..... "....."..... 201….a

/signature/

Consultant: …… ..... "....."..... 201….a

/signature/

Terms of thesis closed defence and/or restricted access conditions to be formulated on the reverse side

CONTENTS

PREFACE

The topic of my master thesis “Electrospinning of electrically conductive polyethylene oxide nanofibers with ionic liquids” was proposed by my supervisor research scientist Illia Krasnou, Tallinn University of Technology. My work is dedicated to investigation of electrically conductive polymeric nanofibers production by conventional and opposite electrospinning. Activated carbon and ionic liquids were used as conductive fillers for polymer composite materials. I was engaged in research activity and writing the thesis of research from September 2017 until Mai 2018. The investigation was completed in Laboratory of polymers and textile technology, Tallinn University of Technology.

This work would not have been possible without the help of many people within the past two years. I am deeply grateful to my parents, who gave me opportunity to devote time to my study. Special thanks to my brother, who supported me and pleased, said that he was proud of his sister. Also, I am in debt to my boyfriend, who didn't let me give up.

I would also like to express my gratitude to my supervisor Illia Krasnou for all his advice regarding my personal and professional life. At that moment when I started to doubt my choice, he aroused in me a love for experimentation as in science, so in life and taught to be calmly to failures.

I would like to say my special thanks to leaders of laboratory professors Andres Krumme and Jaan Kers for their understanding, support and interesting lectures. They also influenced my decision to go to magistrature and in the choice of further profession. Their interest and care about their students makes the faculty special.

My deepest appreciation goes to my friend Anastassia Kotova, student of Tallinn University of Technology, Technology of Polymers faculty, for her support, helps and evening walks that calmed the nerves and released the head. A fresh mind has allowed me to finish this year.

Keywords: polyethylene oxide, electrospinning, ionic liquids, activated carbon, electrical conductivity

Märksõnad : polüetüleenoksiid, elektroketrus, ioonsed vedelikud, aktiivsüsi, elektrijuhtivus

LIST OF ABBREVIATIONS

AC	Activated carbon
[BMIM][Cl]	1-Butyl-3 Methylimidazolium Chloride
[BMIM][Ac]	1-Butyl-3 Methylimidazolium Acetate
[EMIM][Br]	1-Ethyl-3 Methylimidazolium Bromide
[EMIM][Ac]	1-Ethyl-3 Methylimidazolium Acetate
ILs	Ionic liquids
MW	Molecular weight
PEO	Polyethylene oxide

LIST OF SYMBOLS

%	Percentage
µ	Micro
cm	Centimeter
g	Gram
kV	Kilovolt
h	Hour
m	Meter
nm	Nanometer
S	Siemens

1. INTRODUCTION

Electrically conductive fibers preparation methods are actively studied nowadays. The aim of my work is to study the electrospinning method of nanofibers with high electrical conductivity production. Polyethylene oxide (PEO) was studied as fiber generating polymer, iIonic liquids (ILs) and activated carbon (Kuraray YP-80F) (AC) powder were used as electrical conductive fillers. The method of electrospinning for thin fibers production firstly was patented in 1934, by 1990's for electrospinning a variety of polymers were used. This method gives opportunity to produce fibrous mats, which can be used for different application including electronic components and devices manufacturing. Different electrospinning technologies of production fibrous mats were found. In my work I used conventional and opposite or simultaneous electrospinning. My research is consists of few steps:

Firstly, we studied PEO fibers production from solutions of different concentrations of PEO and usage of different solvents to dissolution. We found out the optimal concentration of 10 wt.% of PEO with molecular weight of 200kg/mol in water solution, it is suitable to produce nanofibers with diameter around 200 nm. Unfortunately we could not achieve PEO fibers with diameter below 100nm.

Then we studied influence of different ILs, as [Bmim][Cl], [Bmim][Ac], [Emim][Br], [Emim][Ac], up to 30% content in solution on the diameter of electrospun fibers and their electrical conductivity. The best IL was found to produce nanofibers with high electrical conductivity and for usage as dispersant of AC. [Emim][Ac] was chosen for our work due to its a moderate viscosity, small diameter of fibers area, good conductivity and electrospinnability. Fiber diameter increases with the increasing of ionic liquid content in mat.

Finally, were studied two different electrospinning methods to reach high amount of AC loaded in fibrous mat that improve it's electrical properties and remain small diameter of PEO fibers. The research shows that content of AC in fibers significantly effects on the electrical conductivity of fibers.

The opposite electrospinning method gives mat with high AC load. Mats were prepared by simultaneous electrospinning of a PEO solution and electrospray of AC dispersion using two syringes and single collector placed between syringes. This method gives possibility to produce nanofibrous mats with high content of carbon particles what are evenly distributed in polymer matrix. The maximum PEO-to-AC ratio in mat was achieved as 5% to 95%. We have got the mat with fiber's diameter from 200 to 1700 nm. Electrical conductivity of mats also increases and

reaches 426,95 μS/cm when the content of ionic liquid is 75 wt.% - to 25wt.% PEO in fibers and total ratio of fibers to AC in mat is 5wt.% to 95 wt.%.

The conventional electrospinning method showed that content of AC with IL in solution can produced nanofibrous mats with electrical conductivity. We have got mat with fiber's diameter dawn to 95±20 nm and electrical conductivity up to 20 μS/cm, which contains 34wt.% of AC, 43wt.% PEO and 23wt.% content of [Emim][Ac]. Two methods of electrospinning have similarity: AC particles are not incorporated into fibers, but distributed in PEO fibers as in web. We have not got materials with high electrical conductivity, but we have got good nanofibers around 100 nm with electrical conductivity. Also we have got electrospray of AC with PEO particles with electrical conductivity up to 7000 μS/cm, the coating consists of 32wt.% of AC, 40wt.% of PEO and 28wt.% of EmimAc.

2. LITERATURE REVIEW

2.1 Electrically conductive electrospun materials

Electrically conductive fibers are found application in electronic components and devices. [27] Method of electrospinning is suitable to produce nanomaterials with porous structure, which have good electrical properties and mechanical strength. Polyacrylonitrile (PAN) and polyvinylidenedifluoride (PVDF) electrospun mats have porous structure that increases the ionic conductivity. Such materials can be used as battery separators. Due to porous structure that improves the penetration of electrolyte, electrospun LiCoO2 nanofibers can be used in Li-ion batteries and TiO2 nanofibers in dye-sensitized solar cells.

Traditional conductive polymer materials include compositions based on the different polymers and conductive fillers and finds different applications. Carbon nanotubes, grapheme and activated carbon, as conductive fillers, are used. Chitosan, DNA with single – walled nanotubes are used in investigation of conducting CNT biofibers. [28] PEI with single – walled nanotubes also produce conductive fibers. [28] Such electrospun composite materials have as good electrical conductivity, but also mechanical properties, as consists of elastic-substrate providing mechanical properties of the composite, and the conductive polymer acts as an active component.

2.2 Electrospinning method

Electrospinning is a method of producing thin fibers from polymer fluids under the influence of an electric field. There are many different methods, in which different collectors and spinnerets can be used. Collectors are the one of the main parts in electrospinning techniques. It effects on the fiber production. Type of collector have a significantly influence on the arrangement and the final structure of fibers. There are different types of collectors, for example, drum, plate, grid, mandrel and dish. It is known that using grid type collector is used fibers with a big diameter [3]. It is observed that fibers collected in the plate collector are not lie evenly. Drum collector is most suitable for fiber production, due to the rotation of the collector fiber lies evenly [3]. Since the 80-

ies, and especially in recent years, the process of electrospinning is attracted more and more attention, this is due to the increasing interest in nanotechnology. Ultrafine fibers or fibrous structures of various polymers with diameters down to submicron or nanometers can easily be manufactured by this process.

To start the process to occur, three components are required: a high voltage source, syringe and collector. The polymer solution is pumped out of the syringe. A high voltage (10-50kV) is applied to the needle. It is used to create electrically charged filaments of the polymer solution coming out of the needle. When the solution of polymer reaches the end of the needle, coming droplet get charged. Charged droplet is stretched by electrostatic field into so called Taylor cone. Solvent should be conductive to get charge on it, so some solvents are not applicable for electrospinning. Polymer chains polarize and form dipoles (polymer chains must be dielectric) in electric field. Polarization of macromolecules makes rather difficult electrospinning of conductive polymers. Under the influence of a high voltage a fine jet from this solution reaches to the collector, which is grounded electrode. During travel time polymer chains get stretched and oriented in electric field and solvent evaporates. The fibers are deposing onto collector. Before reaching a collecting collector, the solvent evaporates and the polymer solidifies into fibers [1].

Many different parameters influence on the electrospinning process. It depends on the (a) parameters of the polymer solution, (b) process and (c) ambience [2]. Polymer solutions parameters: concentration, viscosity, conductivity, molecular weight, surface tension. Process parameters: voltage, type of collector, distance and flow rate. Ambient parameters: the humidity, temperature in the chamber.

A device for conventional electrospinning consists of syringe pump, syringe with needle, solution that is in it, collector and high voltage supply. Under a high voltage applied to the needle, the droplet is formed and rapidly departs in the direction of the collector. A fine jet stretches from this drop and grounds in the drum collector, collector winds fibers on the foil.

In 2013 researchers Nicolas Lavielle and al. [4] described a simple method of composite material production by simultaneous, or opposite, electrospinning. This device consists of two syringe pumps with syringes, which are toward to each other, collector placed between syringes. In the article composed material consist of PEG particles and PLA fibers with diameter of 1.6 ± 0.4 μm and 200 ± 20 nm. Such technique gives the opportunity to prepare different structured composite membranes for variety applications.

2.3 PEO (Polyethylene oxide)

This chapter represents published studies describing the formation PEO (polyethylene oxide) fibers and their applications. Usability comes from its unique properties; PEO is biocompatible, water-soluble, and easy to produce higher molecular weights than other polymers and last but not least non-toxic. It is know that PEO solutions are usually prepared with such solvents as DMF, ethanol, chloroform and water for fiber production by electrospinning method [5]. It can be used as pure polymer or as a supporting material [8] for other polymers to improve electrospinnability. PEO composites with other polymers for fibers production are used for many different applications [9].

What we know about PEO fibers is largely based upon empirical studies of how concentration, viscosity, surface tension, conditions of fibers formation affect the fiber quality and diameter. Many factors affect the morphology of PEO fibers. It is known that at higher PEO concentrations uniform fibers are produced [5]. With increasing of PEO weigh percent in solution, surface tension decreases, which lead to smaller diameter of fibers [9]. The surface tension depends on the viscosity of the solution. The addition of alcohols in PEO aqueous solution leads to an increase of surface tension. Also with increasing of PEO amount mechanical properties and tensile strength is increased, that is also associated with an increase of fiber diameter.

Important part in fiber production plays also humidity control. In article of Tripatanasuwan, Zhong and Reneker (2007) the effect of humidity on fiber production by method of electrospinning was studied. In experiment 6 wt.% PEO (400 000 g/mol) aqueous solutions were used. The authors found that diameter of fiber and beads formation depend on humidity in chamber. With increasing of humidity, the fiber's diameter decreases, as the solvent evaporation is slower. In the article, optimal humidity for production of PEO fibers was found. Fibers by 144 nm of diameter obtained at relative humidity of 48,7 %. Higher humidity lead to smaller diameter with beads formation [13].

Much of the current studies on formation PEO fibers pay particular attention to usage of water as solvent. PEO is widely used for fibers production by electrospinning due to its relatively simple structure and good solubility in different solvents. Investigation of TENG Hong, ZHANG Chun-ling, DOU Yan-li and LI Yi [5] showed that optimal concentration of PEO (average molecular weight of 6.3×10^5) in water to obtain thin fibers without beads are 6.5% and 8% PEO in water and get fibrous mat with diameter of fibers around 100 nm and 200 nm. Electrospinning of all solutions were carried out at ca. 31 °C. They studied PEO solutions in ratio from 3% to 7% of PEO in water. Lower concentrations of PEO in water forms beaded fibers by electrospinning. However, with increasing of PEO weight percent in solution, the amount of beads is decreased [5]. Numerous studies have attempted to explain beads formation. So beads formation on the fiber's surface was studied by H. Fong, I. Chun, D.H. Reneker [10] , Yarin [11] and Entov [12]. They concluded that higher viscosity, low surface tension promote formation of fibers without beads and small diameter fibers. Produced fiber from solutions of PEO in water or ethanol is used for micro-electronic-wiring and interconnects.

Research of polymer materials for batteries and others electrochemical devices are very important in technology, due to it's good mechanical properties and opportunity to prepare a thin material with a suitable sizes for different devices. PEO is electrolytic polymer and also used in mixing with carbon black or carbon nanotubes to improve mechanical and electrical properties of formed materials. In article [6] prepared solution with 3% of PEO and from 0,1% to 4% of Carbon black in water - ethanol (60/40) mixture for electrospinning. All samples were dried at 45ºC during 12 hours. It is known that pure PEO fibers have the highest conductivity. Researchers found that adding of carbon black inclusion decrease the conductivity [6]. They concluded that nanofiberous material consists of a two phases: PEO and carbon black, which have different conducting mechanisms [6].

Despite the fact that the polymer is a synthetic, PEO is a biocompatible and biodegradable polymer. It can be used in medicine and surgery. It is also used in various clinical products. This polymer has a good environmental stability and has the ability to dissolve easily in some solvents. In article [4] solution of 5% PEO in chloroform was prepared. This solution is electrospun under the different voltage from 9-12 kV. With increasing of voltage diameter of formed fibers are dicreased. Also studied the effect of distance between the needle and collector on fiber diameter. The greater the distance, the smaller the diameter. Good thin fibers were obtained, which find applications in medicine and surgery. [7]

PEO is electrospun with different biopolymers for biotechnological applications. Keratin with PEO in aqueous solution is used for filtration, for example, water purification, and air cleaning. [8] Chitosan with PEO in aqueous solution or in acetic acid is used in tissue engineering and drug delivery. [8] Silk in combination with PEO are used in production of proliferation of human marrow stroma cells. [8] And many others biopolymers are used in combination with PEO for fibers production used in biomedical and biotechnological applications. Many researches have shown that biopolymers without PEO are not able to produce fibers by electrospinning, as they have low molecular weight and low water solubility [8].

2.4 Ionic liquids and their electrical conductivity

Ionic liquids (ILs) are low-temperature molten salts with organic cations and inorganic anions [15] [17]. The first IL - ethyl ammonium nitrate was synthesized by Walden in 1914 [23]. In 1992, Wilkes and scientists Zaworotko were looking for new materials for electrolytic batteries, so air - and moisture-resistant compounds based on salts with anions imidazole BF4 - and CH3COO [25] were found. Active studies of ionic liquids restart since 2000. The unique properties of ionic liquids are related to their high electrochemical and thermal stability, the relatively high electrical conductivity, the practical absence of the vapor pressure [15]. Most of ILs possesses thermal stability but it significantly decreases with increasing hydrophilicity of anion [25]. Most ionic liquids have relatively high density, because of their ordered structure [26]. Density depends on the structure of the cation: decreases with increase of alkyl chain length, and varies in the interval of 1,1-1,5 g/cm3 [19]. Most of ILs is soluble in water. Halide-, ethanoate-, nitrate-, and trifluoroacetate-based ionic liquids are soluble in water at room temperature. However, ILs with anion [PF6] and [(CF3SO2)2N] are not soluble [26].

ILs are of strong interest to researchers as they could dissolve most of natural polymers, such as cellulose, collagen fibers, chitin and others and could be used for fiber production [21]. However, it is also used as a solvent for synthetic polymers, for example PAN [22], but such studies are much less. In the article of Wei Cheng and al. [22] studied the influence of different ionic liquids on the PAN fibers electrospinnability and morphology. Investigation showed that even the small amount adding of IL (0.1 - 1.0 wt %) can increases not only conductivity of the solution but also conductivity of fibers electrospun from solution. The adding of IL affect also diameter of fibers.

The significantly increase of IL content lead to production of fibers with diameter up to 1 μm. For different ILs , it was found limit of weight percent of IL in solution for minimum mean diameter of fibers production. Conductivity of solutions and electrospun fibers also depends on the IL's structure. For example, solution with content of (C2MIM)3PO4 has high electrical conductivity, but fibers with minimum mean diameter are produced with content of IL of 0,25 wt%. However, content of Cl12MIMCl in solution, which has low conductivity, can achieve 0,8 wt% for fibers production with minimum mean diameter. ILs has ability affect not only conductivity and morphology of electrospun fibers, but also electrospinning process. Adding of IL affects conductivity, viscosity and surface tension of solutions, which improve its electrospinnability. Except conductivity, viscosity and surface tension of solution have optimums for preparation of fibers by electrospinning method.

Well known, ILs can be used as solvent, additive, dispersant and polymer electrolyte [20]. They have higher conductivity compared with the other solvents due to the only ions what they consist of [20]. To conduct electrical current is a unique feature of ionic liquids. ILs have a wide range of conductivity from 0,1 to 20 mS/cm3. However, the electrical conductivity of various ionic liquids and their solutions are poorly studied. Among other ILs, imidazolium and pyridinium cations of ionic liquids are characterized by the highest ionic conductivity [18]. Electrical conductivity of about 10 uS/cm is typical of ionic liquids based on the cation 1-ethyl-3-methylimidazole. However, cations of tetraalkylammonium, pyrrolidine, piperidine and pyridine characterized by significantly lower values of electrical conductivity. Addition of IL into the aqueous solution leads to increasing of the conductivity due to dissociation of ions. The increasing of the conductivity occurs until 40 weight % of the IL's content in the solution and then begins to decrease [16]. This can be explained by the increase of the number of ions in solution due to dissociation, but above 40w.% there are no more water molecules could be involved in dissociation of IL at the same time increasing of the viscosity lowers ion mobility. The solution contained EmimCl has the higher conductivity between chloride ILs solutions. Then by decreasing in conductivity is the BmimCl, HmimCl and the smallest conductivity of solutions, containing DmimCl. The same behavior is observed in solutions contained tetrafluoroborates based ionic liquids. As we can see as the cations and anions of the ILs affect the conductivity [16]. Also we can say that conductivity depends on the viscosity of IL solutions. Increasing the solution temperature leads to reduce the viscosity of IL solutions and increasing of conductivity [20]. Since most organic solvents have relatively low viscosity that the dilution of the viscous IL-molecular solvent reduces the viscosity of the mixture, which also leads to an increase in conductivity. However, adding of chloride increase viscosity of IL solution [26]. The conductivity is affected by many factors: viscosity, density, size of ions and their mobility, the distribution of the charge on the anion. Applications ILs include

microwave organic synthesis, catalysis, biocatalysis, electrochemistry, synthesis of nanomaterials and others.

ILs could be used in the various research branches [19]. They are widely used in ecologically clean technologies, as they reduce environmental pollution in different reactions, but also accelerate the course of chemical reactions and reduce their temperature [1]. As an example, ILs are used in production of synthetic cellulose fibers. As a rule, a large number of chemicals that are toxic and dangerous for the environment usually applied to dissolving pulp, including in the production of cellulose fibers. Thanks to the use of ionic liquids, the entire production process can be greatly simplified. They allow replacing chemicals that are hazardous to health and the environment. Moreover, ionic liquids can be almost recovered completely and reused. So, the interest to ILs continues to grow.

3. EXPEREMENTAL PART

3.1 Materials

PEO – Polyethylene oxide –M_w=200kg/mol, medium, were purchased from Sigma Aldrich. Ionic liquids 1-Butyl-3 Methylimidazolium Chloride and 1-Ethyl-3 Methylimidazolium Bromide, 1-Butyl-3 Methylimidazolium Acetate and 1-Ethyl-3 Methylimidazolium Acetate were synthesized according to methods described in literature [29]. Synthesized IL was characterized by FTIR to prove the result of the synthesis. Solvents, as Acetone, Ethanol, Ethyl Acetate were obtained from Sigma Aldrich. Distilled water made in laboratory was used. Activated Carbon, Kuraray, YP – 80F (200g). All solutions and samples were stored at room temperature.

3.2 Preparation of solutions

Preparation PEO solutions in different solvents

The series of PEO solutions using different solvents were prepared. 10 wt% of Poly(ethylene oxide) (PEO) powder (having a molecular weight of 200,000 g/mol) purchased from Sigma-Aldrich were dissolved in distilled water/ethanol/acetone/ethyl acetate with different range. Each solution was stirred overnight at 60 - 72°C using a magnetic stirring plate to ensure a homogenous solution. All calculations were performed in grams (g) on the electrical scales. The total weight of each solution is 3 g.

All concentration were calculated by the formula :

$$C = \frac{\text{mass of polymer}}{\text{mass of full solution}} = \%$$

Preparation PEO solutions with ionic liquids

Poly(ethylene oxide) (PEO) solutions were prepared by first dissolution PEO powder (having a molecular weight of 200,000 g/mol) purchased from Sigma-Aldrich in distilled water. Then various ionic liquids [BMIM][Cl] /[BMIM][Ac] /[EMIM][Br] /[EMIM][Ac] were added in 10 wt % PEO/water solutions to attain ionic liquid concentrations in the range 7% - 30 wt %. Each solution was stirred

overnight at 72°C using a magnetic stirring plate to ensure a homogenous solution. All calculations were performed in grams (g) on the electrical scales. The total weight of each solution is 3 g.
All concentrations were calculated by the formula:

$$C = \frac{\text{mass of polymer}}{\text{mass of full solution}} = \%$$

Preparation PEO solutions with carbon filler for conventional electrospinning

PEO solutions were prepared with adding of ionic liquid (IL) [EMIM][Ac] and activated carbon (AC) - Kuraray. The content of ionic liquid in solutions were 3, 5 and 7 wt.% and content of carbon were from 3% - 8 wt.%. Were used PEO, as matrix polymer, AC, as conductive filler and IL, as dispersants for filler, to produce mats by electrospinning. Firstly, AC was dispersed with [EMIM][Ac] in ethanol. Then ethanol evaporated. 0.3 g PEO (10 wt.%) and distilled water were added into AC/[EMIM][Ac] blend. PEO was dissolved by stirring at 72°C. The total weight of each solution is 3 g.
All concentrations were calculated by the formula:

$$C = \frac{\text{mass of polymer}}{\text{mass of full solution}} = \%$$

Preparation PEO solutions with carbon filler for opposite electrospinning

AC dispersion prepared next way: [EMIM][Ac] dissolved in ethanol then AC dispersed in this solution. IL-to- AC ratio was 8/17, which amounted of concentration 25 wt% in ethanol.
Polymer solution prepared next way: PEO dissolved in water (10w. %); one solution was without IL and into three others IL were added 7, 17 and 30 wt.% to solution. Activated carbon solution was prepared by stirring (1 hour) and ultrasonication (15 x 2 min).
All concentrations were calculated by the formula:

$$C = \frac{\text{mass of polymer}}{\text{mass of full solution}} = \%$$

3.3 Methods of electrospinning

Conventional Electrospinning

The prepared solutions were put into the syringe. For electrospinning 1 ml syringe and 0,4 - 0,6 mm diameter of needle were used. Thanks to the forceps, removed the needle and grinded it to smooth corners. The collector was wrapped by foil. High voltage (10-20kV) was applied to the needle to create an electrically charged jet of polymer solution. A high voltage induces in the polymer solution by of the same name electric charges, which, as a result of the Coulomb electrostatic interaction, overcomes surface tension and leads to stretching of the polymer solution in continuous thinning jet. Collector is always grounded. Fibers were collected on an electrically grounded aluminum foil placed at 8 - 15 cm vertical distance to the needle tip. Pumping rate was used from 0,4 ml/hr. For conventional electrospinning syringe with the needle, syringe pump, high voltage supply and drum collector with the foil were used.

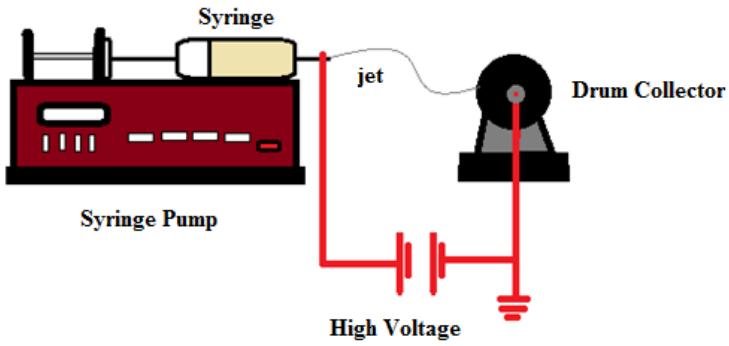


Figure 1 Scheme of conventional electrospinning equipment

Opposite Electrospinning

Mats were prepared by simultaneous electrospinning of a PEO solution and electrospray of AC dispersion using two syringes and collector placed between syringes. PEO nanofibers (kg/mol) were electrospun (Diameter of the Needle - 0,6 mm, ΔV = 17 kV, needle-collector distance = 12 cm, pump flow rate = 0,4 ml/h) from 1 ml syringe of PEO aqueous solution at the concentration of 10% (wt) 12 h after preparation of the solution. Activated Carbon microparticles were electrosprayed (Diameter of the Needle - 0,8 mm, ΔV = 17 kV, needle-collector distance = 15 cm, pump flow rate = 3,5 ml/h) from the solution of Ethanol / [EMIM][Ac] c 9:1 at the concentration of 25% (wt) 12 h after preparation of the solution and 30 min in ultrasonic bath. Suitable electrospinnig setups were found to obtain a homogeneous mixture of the particles within the fibers.

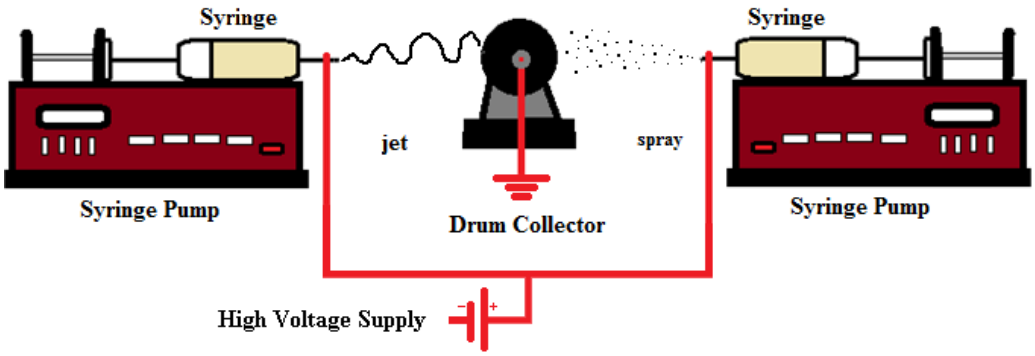


Figure 2 Scheme of opposite electrospinning equipment

3.4 Viscosity, Density and Contact angels measurements

Contact angles of PEO solutions with the different amount of ILs from 7 wt.% to 30 wt.% were measured by contact angle analyzer (Contact angel system OCA/DATEPHYSICS Tensiometer) using software SCA 20. Contact angles was measured at room temperature (T = 23°C).

Figure 3 Contact angle analyzer

Viscosity measurements were carried out using Anton Paar Physica MCR 501 rheometer with a constant speed of 750 rpm at 21°C. Measurements were repeated 3 times to ensure consistency and reproducibility.

Figure 4 Rheometer

3.5 Synthesis of [EMIM][Ac] - 1-Ethyl-3 Methylimidazolium Acetate

In laboratory of polymers and textile technology, Tallinn University of Technology, ionic liquid [EMIM][Ac] was synthesized according literature (N. Wang and al., Inc. J Appl Polym Sci, 2012).

First step: 54,82 g bromoethane and 32,8g 1-methylimidazole were stirred under 80°C per 24h.

Second step: 19,61 of dried potassium acetate was dissolved in 120 ml of ethanol. Then 43,81 g of [EMIM][Br] was added gradually.

Third step: This completed system was stirred at 40°C during 5h. Then it was placed into water bath at 0°C for 1h.

Forth step: Next step is filtration. The cold mixture is washed with ethanol by stirring, and then the top layer of ethanol with precipitation is removed.

Fifth step: Completed [EMIM][Ac] is dried by nitrogen inlet adapter overnight.

3.6 Scanning Electron Microscopy (SEM)

The surface morphology was examined using a field emission scanning electron microscope HITACHI, TM-1000 tabletop microscope (Japan) operating at 20 kV and a working distance (WD) of 8 mm and Gemini Zeiss Ultra 55 (Germany) for high resolution images. The mats were fixed on carbon tape and sputter coated with Au. The diameter of the fibers was measured with ImageJ software from the National Institutes of Health56 (Bethesda, MD), an open source image processing program designed for scientific multidimensional images. SEM was used for checking the surface morphology of the fibers with higher magnification. The fiber samples collected on the aluminum foil and are put on the adhesive conductive black „carbon tape". Samples were visualized under SEM at various magnifications. The average fiber diameter was evaluated by randomly selecting up to 5 different portions of the fibrous mat and averaging the diameter over the number of portion selected in each portion.

3.7 Conductivity tests

Conductivity of the solutions was measured using Mettler Toledo/Seven compact/Conductivity meter. The electrode was immersed into the solution and the measurement was carried out at 25°C.

Conductivity of electrospun mats were calculated from conductance measured by means of High resistance low conductance meter/HR2/Alphalab INC/Conductivity meter. Samples were prepared in size of 1cm x 1cm for conductance measurement. Each measurement was repeated five times and the average values were calculated. The conductivity was calculated according to the formula

$$A = \frac{\partial}{l * S} \quad ,$$

where

A – conductivity;

∂ – conductance;

l – thickness;

S – total area of sample = 1 cm^2

Figure 5 Conductivity meter of solutions (left) and electrospun mats (right)

4. RESULTS AND DISCUSSION

4.1 Effect of PEO different concentration on the fiber morphology

Influence of PEO concentration on the electrospun fiber's diameter

Were studied morphology of electrospun mats with different concentration of PEO from 8 wt.% to 12 wt.% and 18 wt% in pure water. More optimal concentration of PEO to produce thin fibers is 10 wt.% with diameter of fibers around 198 ± 74 nm. Fibers with high amount of beads, which are connected with fibers of small diameter around 93 ± 27 nm, were produced from solution with PEO concentration of 8 wt.% and 9 wt.%. Content of PEO more than 10 wt.% in solutions lead to production fibers with higher diameter around 221±27 nm with some beads on the fiber. And diameter of fibers reaches up to 335±33 nm with PEO concentration of 18 wt.%, as the viscosity of PEO solutions increases and charge density of solutions increases.

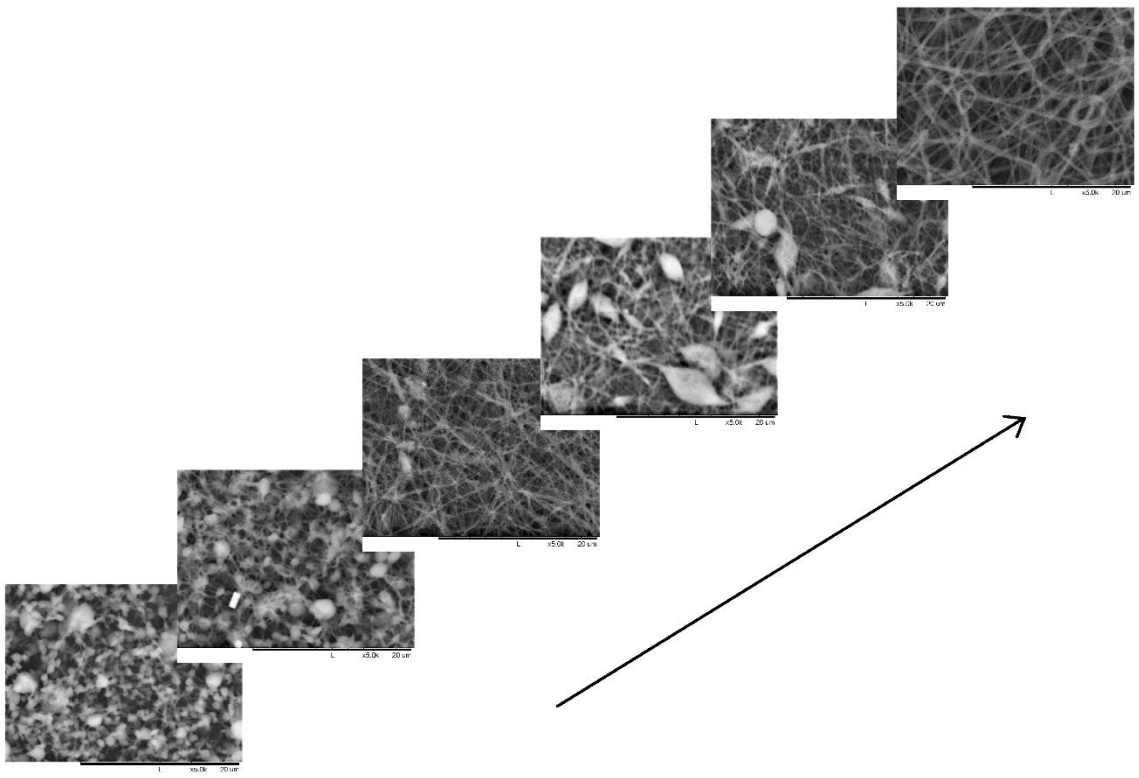
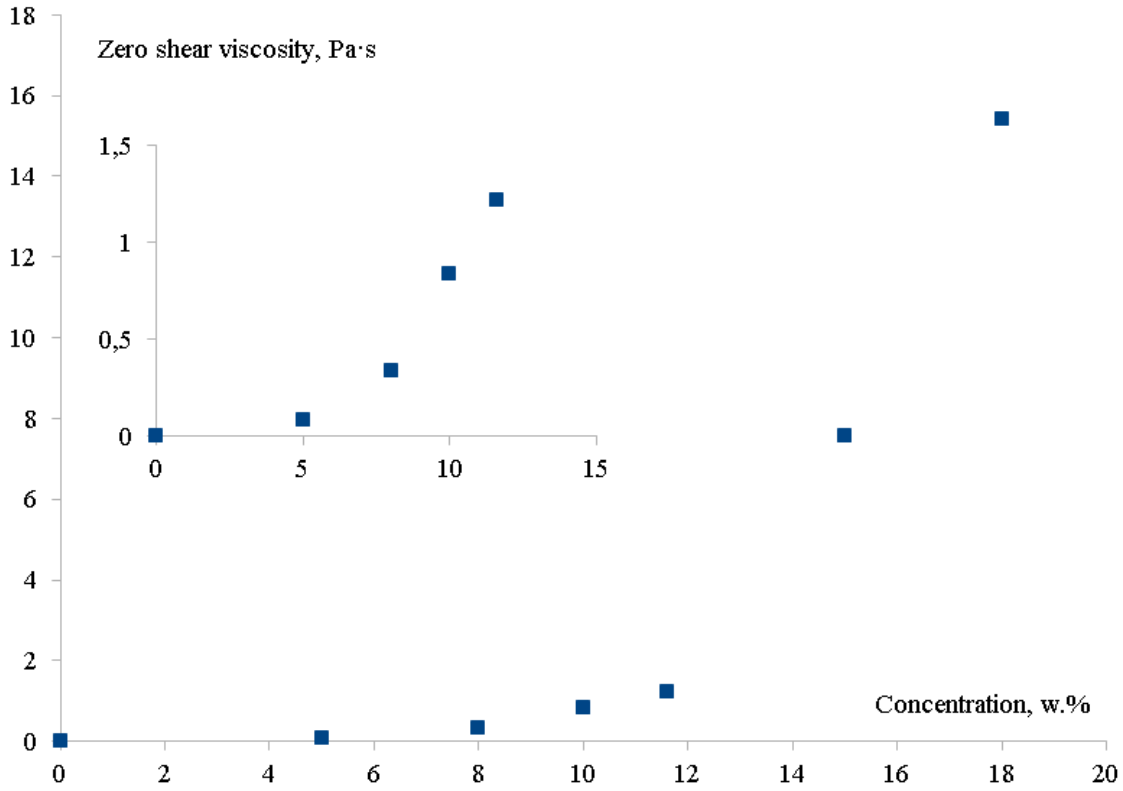


Figure 6 SEM images of dependence of structure and diameter of fibers on PEO content

Influence of PEO concentration on the viscosity of solutions

According to the graph 1 we can say that viscosity increases with increase of PEO concentration in distilled water. As it can be seen that viscosity of PEO solutions gradually grows up to 12 wt% concentration. The viscosity of more concentrated PEO solutions 15 wt% and 18 wt% increases dramatically what corresponds to power low dependence of viscosity on concentration, typical for linear polymer solutions.



Graph 1 Plot of viscosity of PEO in water as a function of concentration

4.2 Effect of different solvents on the PEO fiber morphology

The concentrations of the PEO and solvents were found for the nanofibers production by electrospinning process. In our experiments, 10 wt.% was considered to be the optimal concentration for the formation of uniform nanofibers. Were studied morphology of fibers electrospun from PEO solution with different solvents and the ratios of blend solvents, while the PEO concentration was constant. Selected solvents affect fiber's diameter and its structure, as it

depends on the viscosity, surface tension and rate of evaporation of the solvent during of electrospinning. Investigation showed that water and ethanol are more suitable for PEO fibers production by electrospinning method. The chart is divided into 4 parts, where influence of different solvents addition, as ethanol, acetone and ethylacetate, to the PEO aqueous solution on the fiber diameter produced by method of electrospinning is represented. The diameter of fibers electrospun from PEO/water solution is 198 ± 74 nm, consisting of some beads (Fig.7). Diameter of fibers electrospun from PEO/ethanol solution is 481±93 nm (Fig.7). The surface of the fibers was almost smooth without beads, but with big diameter, due to the rapid evaporation of the solvent.

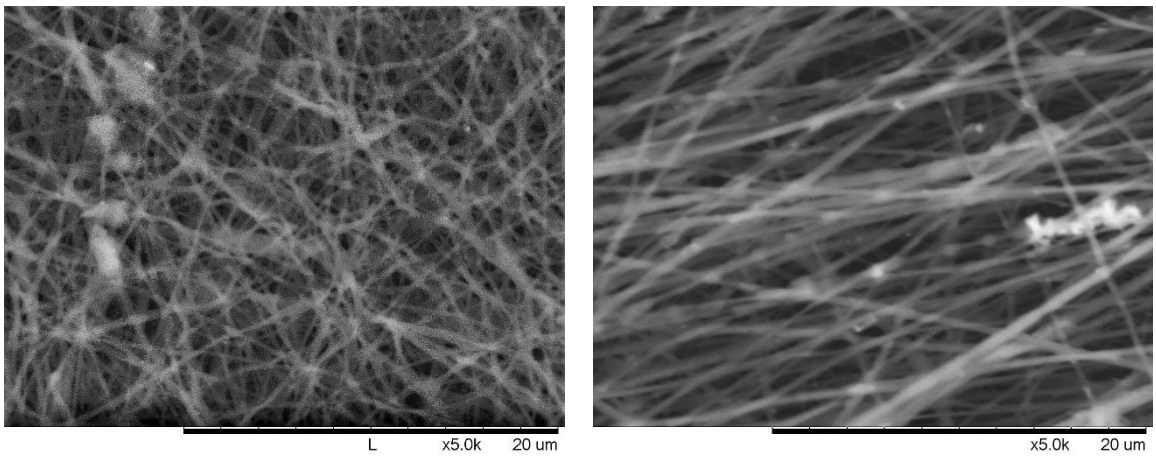


Figure 7 SEM images PEO in water (left) and PEO in Ethanol (right)

As it may be seen from the chart that adding of ethanol to PEO/water solution lead to increasing of fiber's diameter until 500 nm. Adding of acetone into water solution of PEO lead to fiber's diameter increase, but solutions with high acetone content dries too fast and disrupts electrospinning. The aim of the work was to achieve nanosized PEO fibers around 100 nm. Despite the fact that the fibers electrospun from PEO/water, ethyl acetate (9:1) and PEO/water, ethyl acetate (4:2) solutions has the smallest diameter of fibers around 164 ± 38 nm, electrospinnability of solutions worsens. Therefore, water, as a based solvent, was chosen and used in our work. The problem of beads formation on fiber surface can be solved by adding of ethanol or ethyl acetate to water by amount of 5 wt .% to solution (Fig.7). Diameter of fibers remains around 200 nm, namely, 205±77 nm electrospun from PEO/Water, ethanol (19:1) solution and 201±34 nm electrospun from PEO/Water, ethyl acetate (19:1) solution and surface of fibers are uniform. However, in case of our work adding of ILs leads not only to increasing of conductivity, but also

fibers production without beads (Paragraph 4.3). For our further work 10 wt.% PEO and pure water, as solvent, were used.

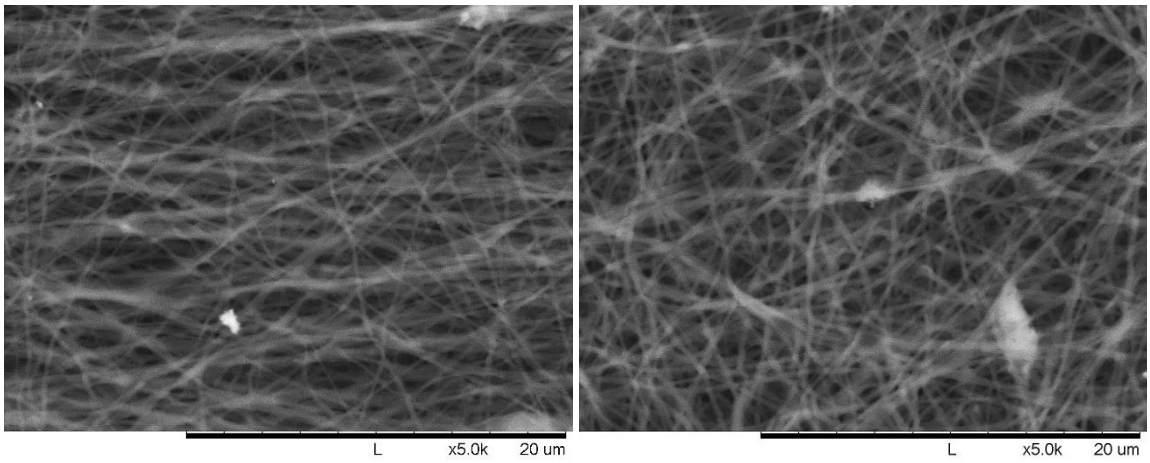
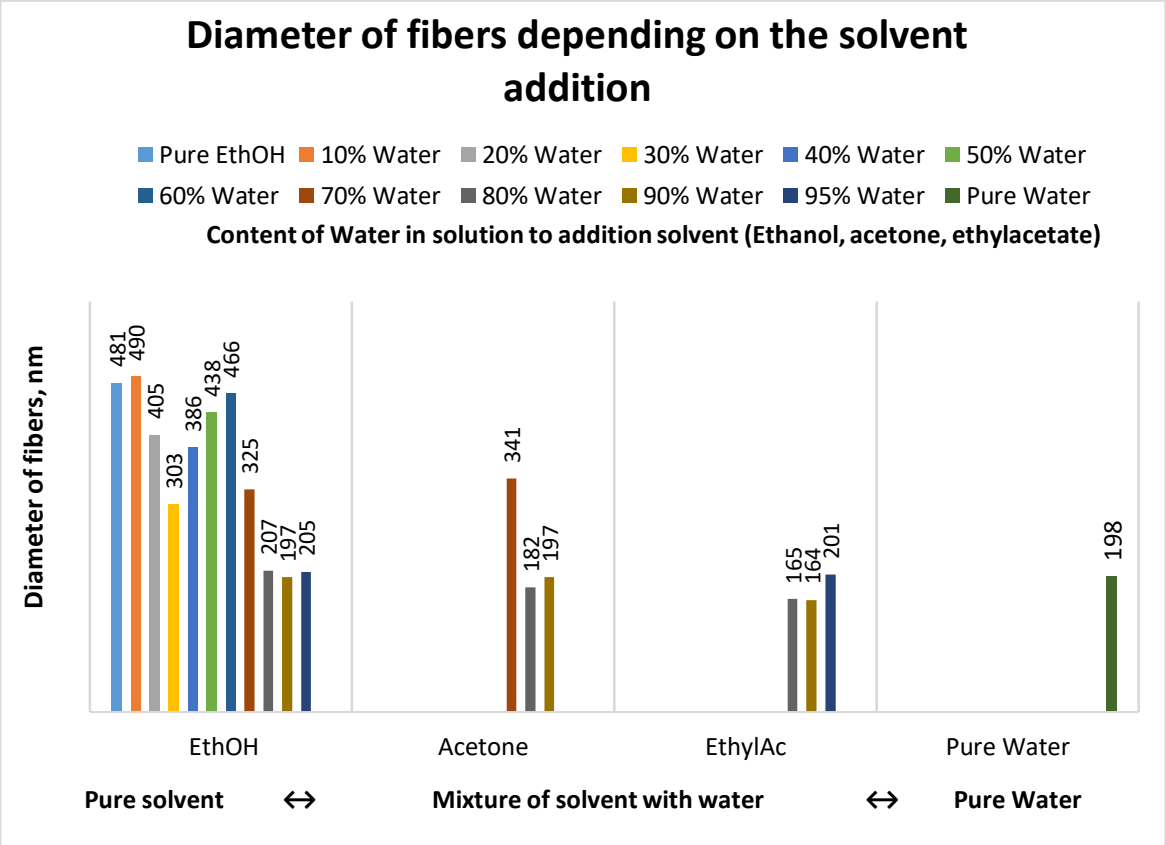


Figure 8 SEM images PEO in Water, ethylacetate 19:1 (left) and PEO in Water, ethanol 19:1 (right)



Graph 2 Diameter of fibers depending on the solvent addition

This study showed that solvents affect the viscosity and electrospinnability of solution and electrospun fiber's structure, amount of beads and its diameter. In case of solutions with IL content solvents also play role in electrical conductivity of mats. Adding of ethyl acetate into PEO/IL, water solution lead to production fibrous mats with electrical conductivity higher than mat electrospun from PEO/IL, water solution. It can be explained that adding of ethyl acetate impairs IL dissolution. IL settles on the surface of the fiber and covers fibers fully (Figure 10).

Solutions	**PEO/IL, water**	**PEO/IL,water, ethylacetate (9:1)**	**PEO/IL,water, ethylacetate (4:1)**
Electrical conductivity, µS/cm	80 µS/cm	145 µS/cm	153 µS/cm
Diameter of fibers, nm	194±36 nm	190±39 nm	243±26 nm

Table 1 Dates of electrospun mats with adding of ethyl acetate

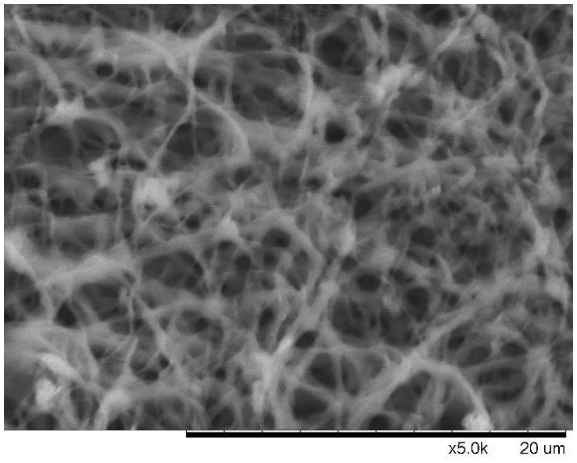


Figure 9 SEM image of fibers electrospun from PEO/IL, water solution

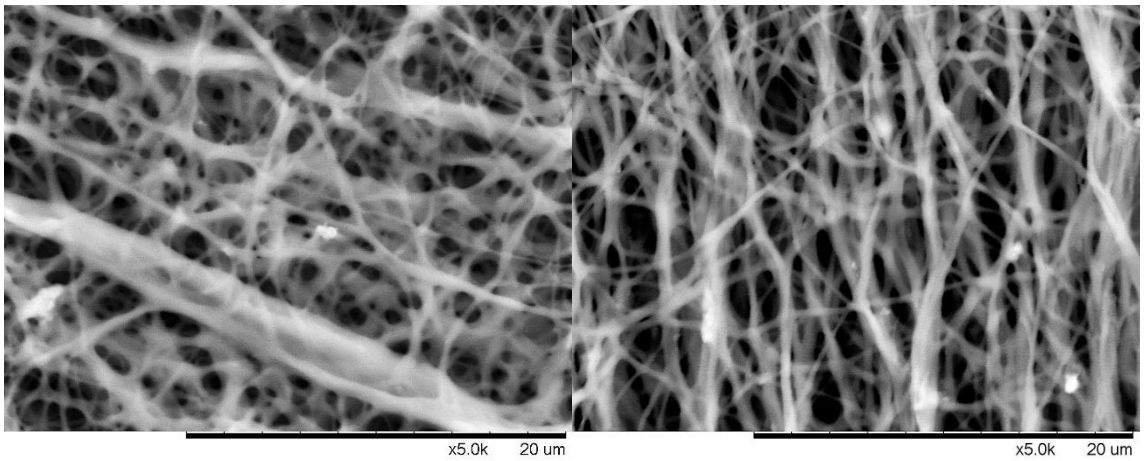
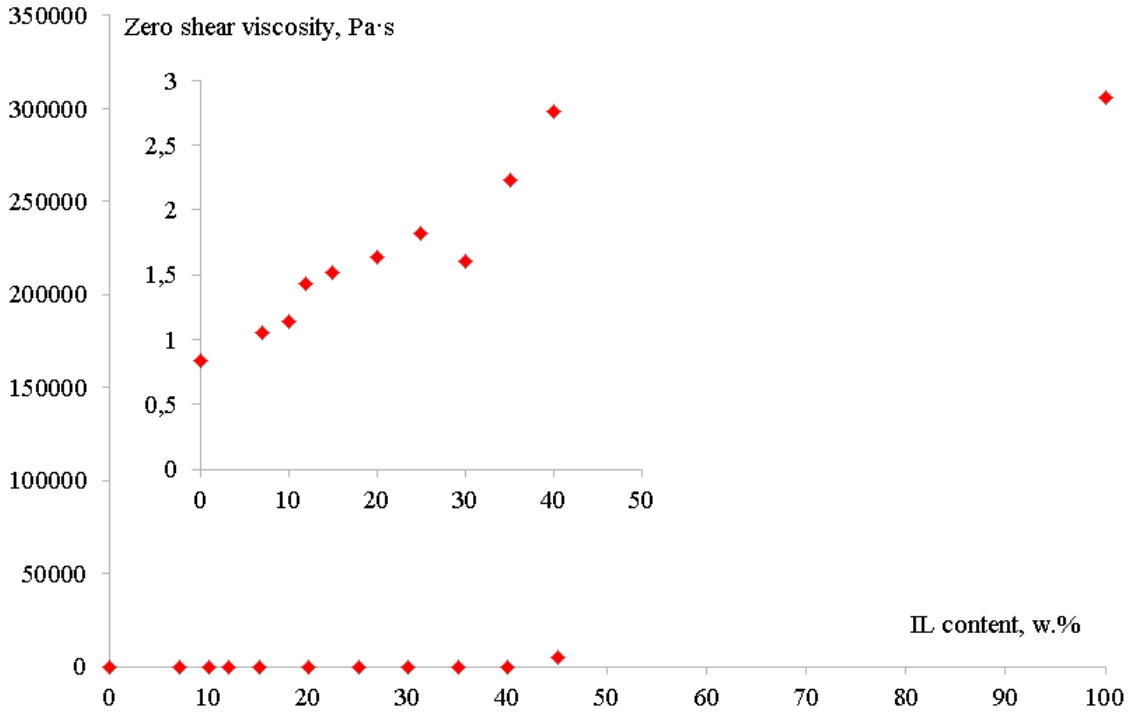


Figure 10 SEM image of fibers electrospun from PEO/IL, water+ethylacetate (9:1) left and (4:2) right

4.3 Effect of different ILs on the PEO fiber morphology and properties

Influence of ILs on the viscosity of PEO solutions in water

Viscosity is one of the important parameters affect electrospinnability. The diameter of fibers and the electrospinnability of solution depends on the viscosity. Were studied influence of [EMIM][Ac] on the solution viscosity.



Graph 3 Plot of viscosity of PEO with [EMIM][Ac] in water as a function of [EMIM][Ac] content

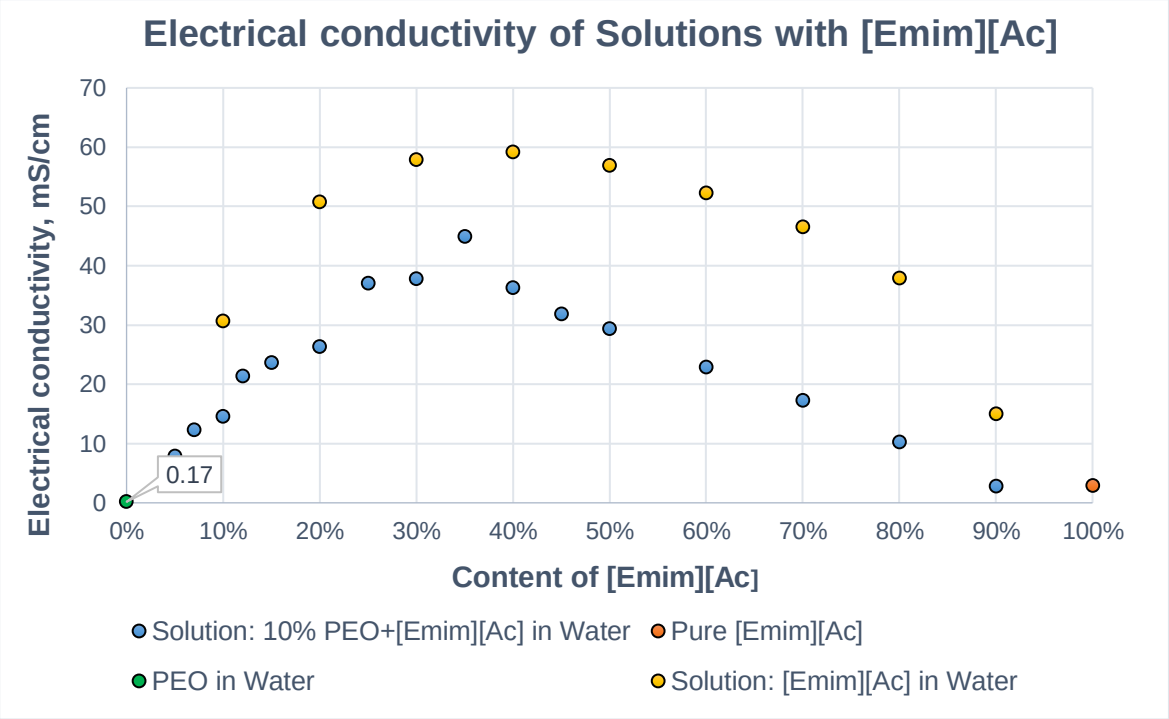
As could be seen from the plot, viscosity dependence on IL content is not uniform. Viscosity linearly grows in lower range of IL content probably IL decreases the solvent quality and polymer chain shrinks. At IL content near to 45% polymer precipitates from solution and no viscosity could be measured. Nevertheless, PEO is soluble in pure IL what is represented in the plot.

Influence of ILs on the electrical conductivity of PEO solutions in water

Conductivity of the polymer solution is important to overcome the surface tension and produce fibers by method of electrospinning. Conductivity of pure PEO with concentration of 10 wt.% in water is 168.6 µS/cm. With adding of [Emim][Ac], which electrical conductivity is 2.9 mS/cm, conductivity of PEO/water solution increases significantly. The Graph 4 presents data showing the conductivity measurement curve of PEO/[Emim][Ac] solutions, which has U – shaped. Conductivity of PEO in IL/water solutions grows with the growing of IL content up to 35 wt.% of the ionic liquid. At content near to 40 wt/% [Emim][Ac] in solution conductivity shows maximum. Similar to viscosity conductivity dependence changes drastically above 40% of IL content, probably addition of IL into solution stimulates aggregation processes in polymer chains and precipitation. As could be seen the electrical conductivity of solution gradually drops with further increase of IL content above 40%. That is unexpected. Probably this could be evidence of strong

interaction between PEO and IL and formation of PEO+IL aggregates what lowers the ion mobility and thus decreases the conductivity of solution.

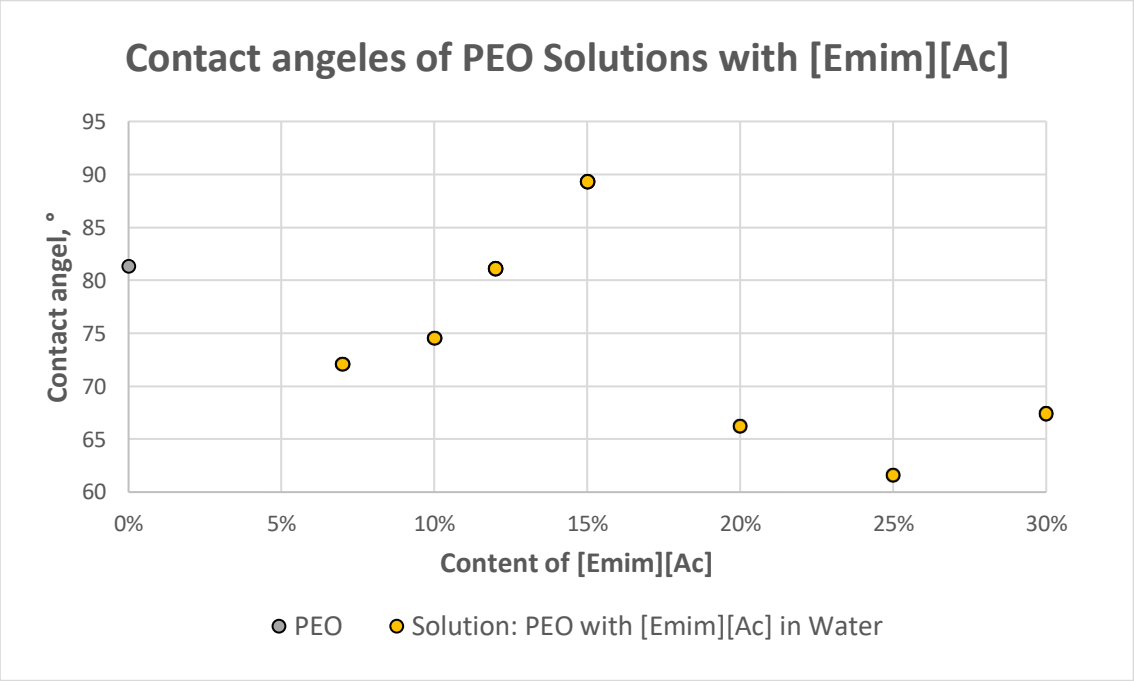
The graphs shows that effect of [Emim][Ac] addition on the electrical conductivity of PEO/water solution and only to water have the similar shape. So, we can say that PEO does not have specific influence on the electrical conductivity of solutions. However, conductivity of solution with PEO content is lower, as PEO content increase of solution viscosity and decrease ions mobility. Both types of solutions has maximum point in electrical conductivity by 40 wt.% of [Emim][Ac] content in solution. Further increasing of [Emim][Ac] content leads to decrease of electrical conductivity.



Graph 4 Plot of electrical conductivity of solutions as a function of [Emim][Ac] content

Influence of ILs on the contact angel of PEO solutions

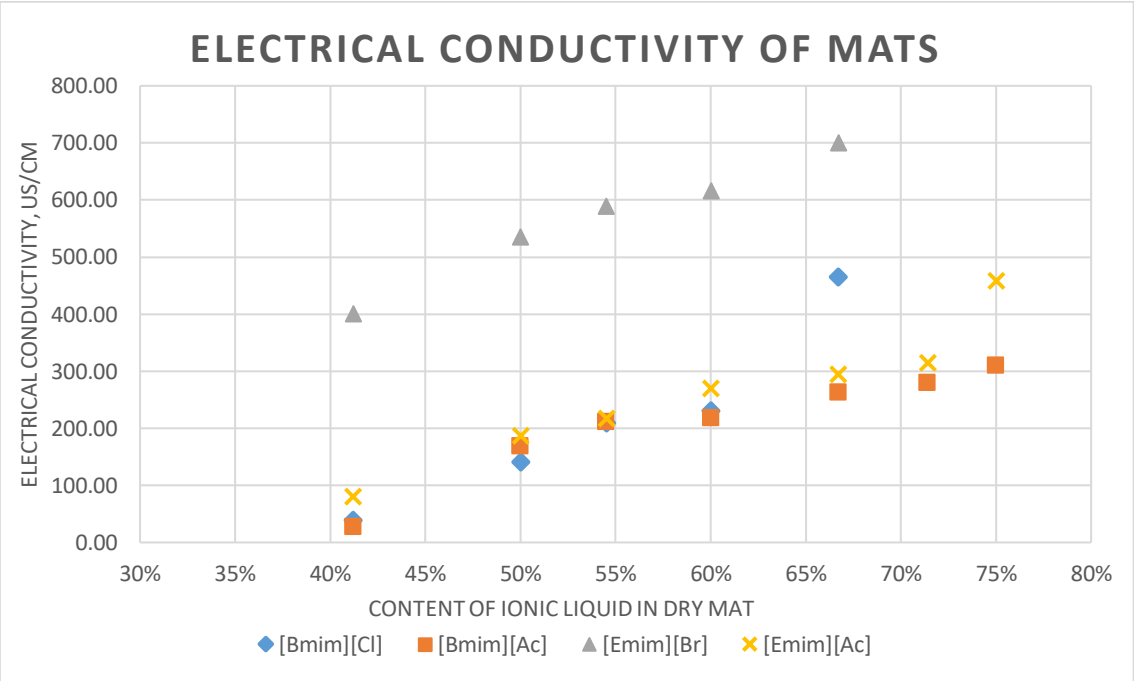
Contact angel of 10% PEO solution in pure water is 81°. With adding of 7 wt.% [Emim][Ac] into PEO/water solution lead to decreasing of contact angel to 72° From 7wt.% up to 15 wt.% addition of IL increases the contact angel. But after addition of IL more than 17wt.% contact angel drops and dependence show a plateau near to 60° for solutions with content of [Emim][Ac] within the range of concentrations from 25 wt.% to 30 wt.%.



Graph 5 Contact angeles of PEO solutions with [Emim][Ac]

Influence of ILs on the electrical conductivity of PEO electrospun mats

Conductivity measurement of PEO electrospun mats with the content of the ionic liquid from 41% - 75% showed increase in conductivity due to increase of the ionic liquid content in fibers. The conductivity measurement curve obtained is linear (Graph 6). Cations and anions also play important role in electrical conductivity of mats. Group of [Emim] ionic liquids showed higher conductivity than [Bmim]. Also, ILs with halogens anion showed conductivity higher than with acetate anion. Increase of IL content and electrical conductivity of solution lead to improve of its electrospinnability.



Graph 6 Electrical conductivity of PEO mats contained ILs

Morphology of electrospun mats

Figure 11 shows the SEM micrograph of the pure PEO fibers without IL. The fibers were relatively uniform with a diameter of 198 nm with a standard deviation (SD) of 74 nm. The fibers have an almost smooth surface. The irregularities mean that the solvent does not evaporate in a sufficient amount before the fiber was deposited onto the collector.

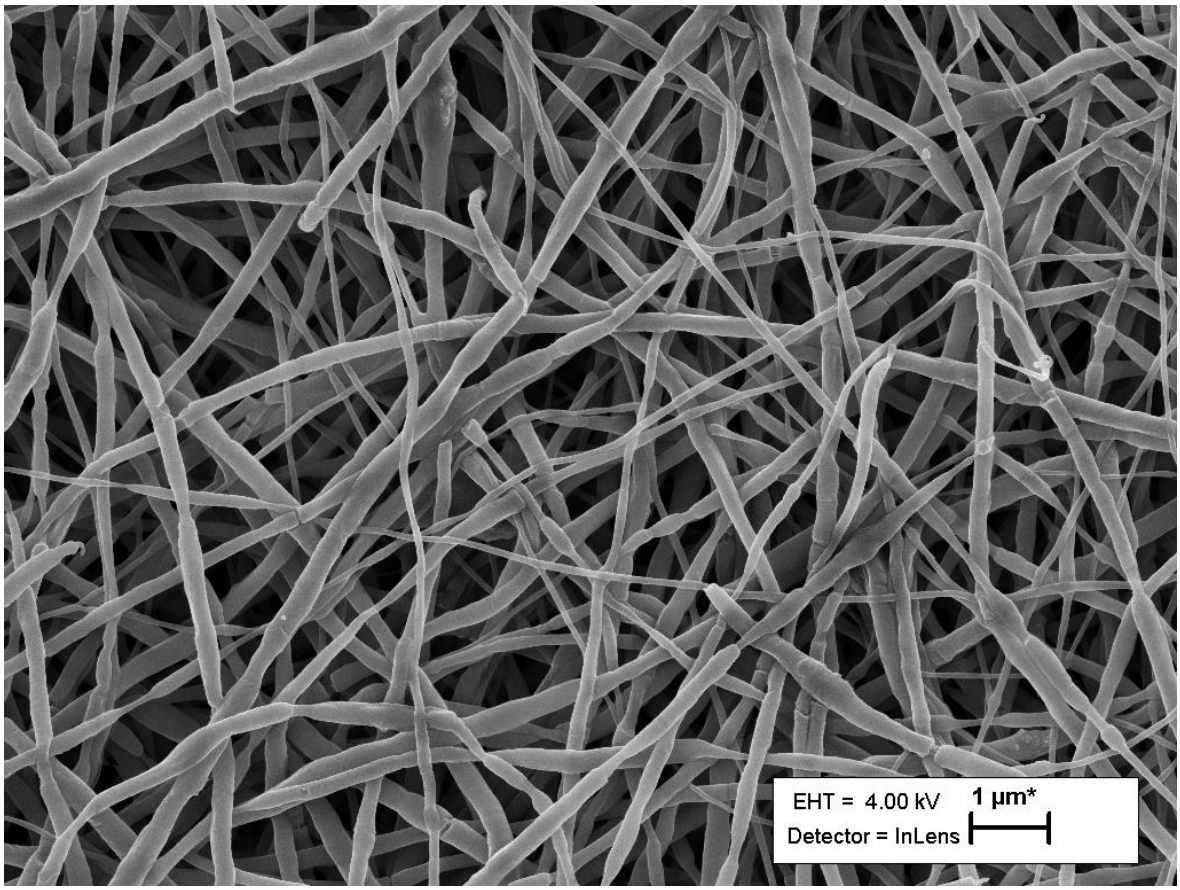


Figure 11 SEM image of PEO fibers

With adding of IL diameter of PEO fibers increase. Figure 11 – Figure 15 show the SEM images of PEO / ionic liquid nanofibers with a different content of ionic liquids. The diameters of PEO / IL fibers with different ILs in the range from 41 % - 67% contents in mats are given in Graph 7. So the most smallest diameter have mats with content of [Bmim] [Ac] и [Emim] [Ac] of 41 wt% , and the fiber distribution was more uniform. High content of IL ≥ content of 50% to PEO increases the diameter of the fibers, as covers the surface of the fibers fully. It is lead to partial or complete fiber fusion. Fibers contained [Bmim] [Cl] have the diameter higher than others around 1 µm. [Emim] [Ac] was chosen for our work due to it's a moderate viscosity, small diameter of fibers, good conductivity and electrospinnability.

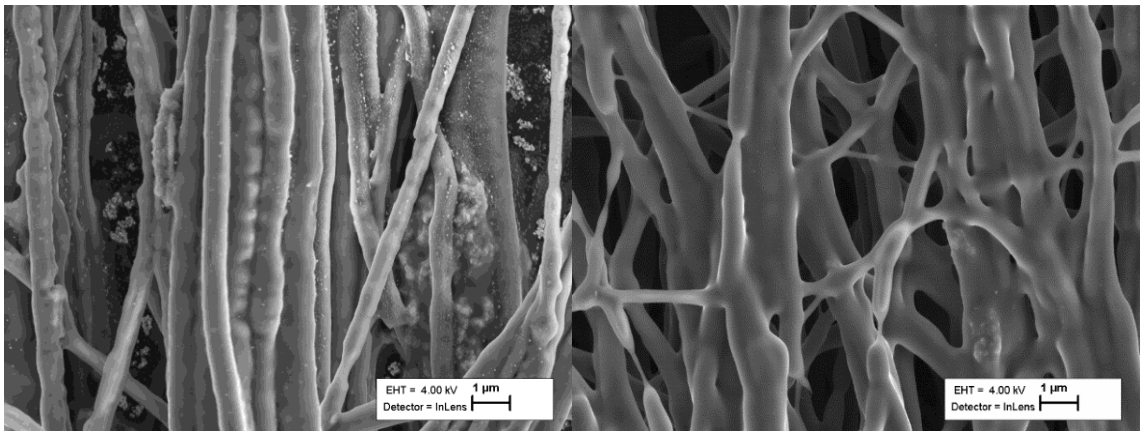


Figure 12 SEM image PEO + 41% BmimCl fibers (left) and PEO + 41% EmimBr fibers (right)

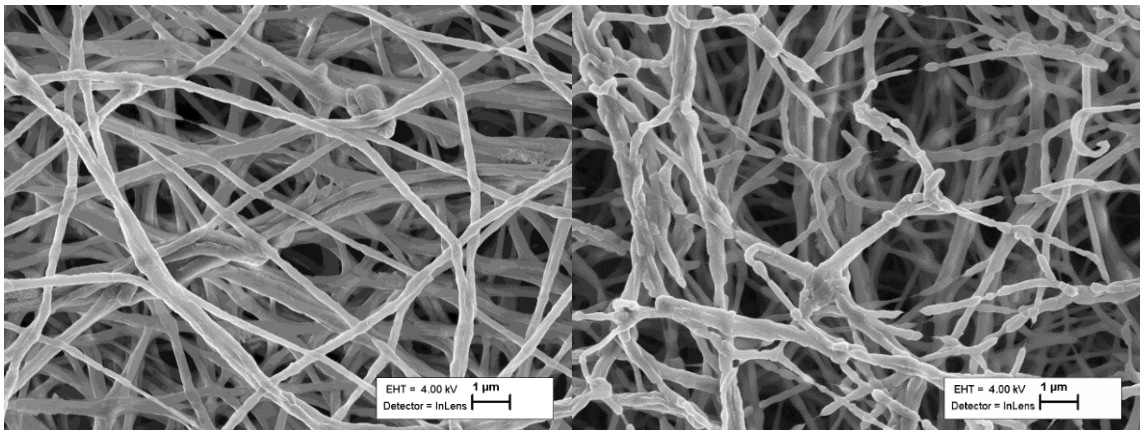


Figure 13 SEM image PEO + 41% BmimAc fibers (left) and PEO + 41% EmimAc fibers (right)

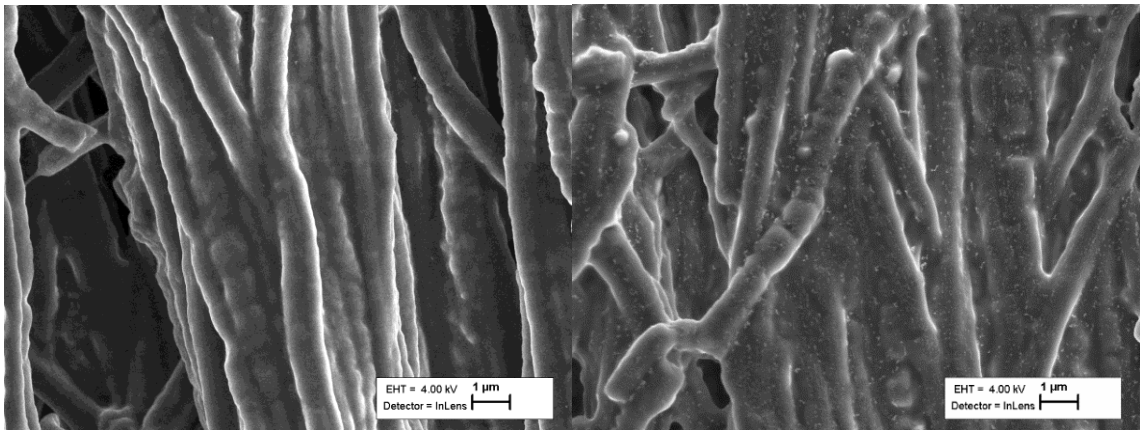


Figure 14 SEM image PEO + 67% BmimCl fibers (left) and PEO + 67% EmimBr fibers (right)

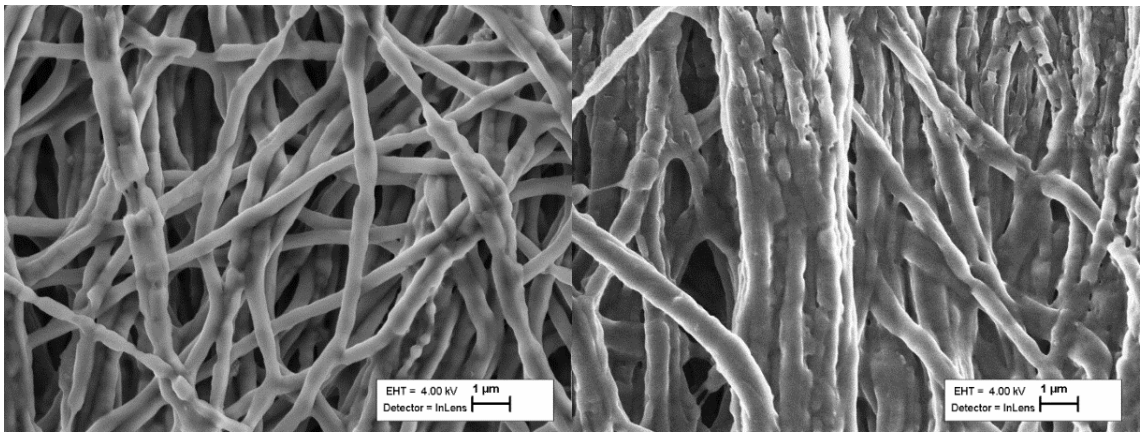
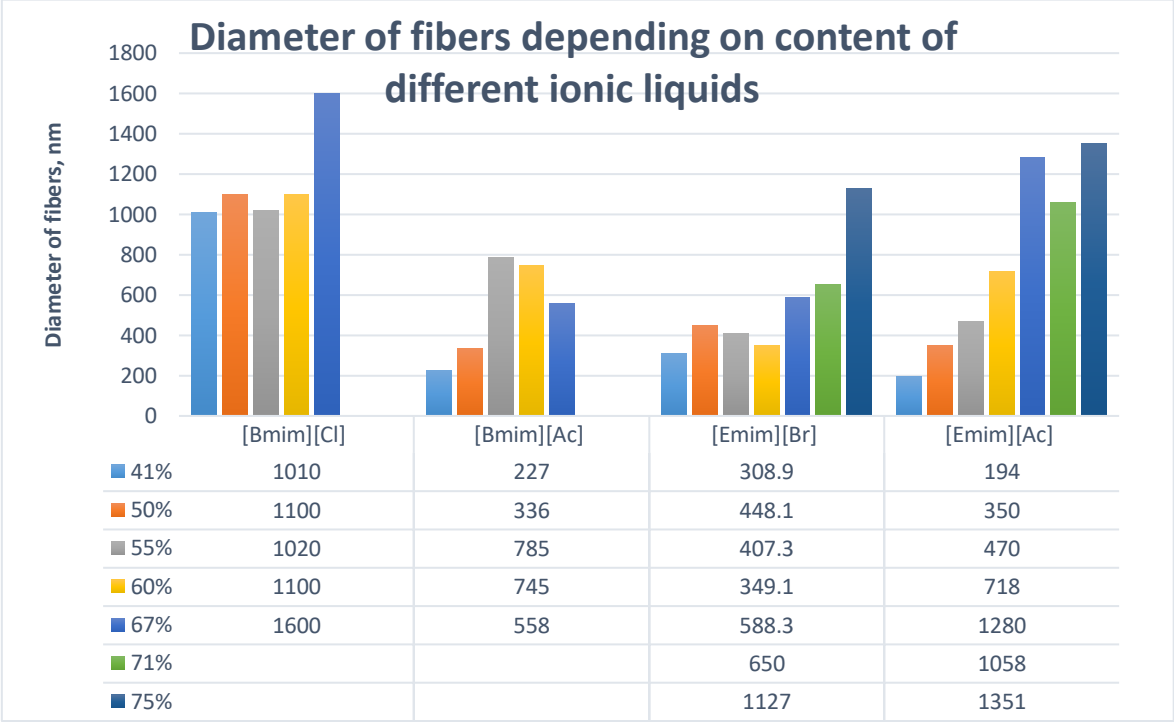


Figure 15 SEM image of PEO + 67% BmimAc fibers (left) and PEO + 67% EmimAc fibers (right)



	[Bmim][Cl]	[Bmim][Ac]	[Emim][Br]	[Emim][Ac]
41%	1010	227	308.9	194
50%	1100	336	448.1	350
55%	1020	785	407.3	470
60%	1100	745	349.1	718
67%	1600	558	588.3	1280
71%			650	1058
75%			1127	1351

Graph 7 Diameters of PEO fibers depending on IL content

As could be seen from Figure 16 fibers are partly destroyed after washing by acetone and ethanol (PEO is not soluble in acetone and purely soluble in ethanol). Also there are bright spots of IL remained on washed fibers. So we could conclude that ILs are not mixed with polymer in electrospun mats, but covers the surface of fibers. As far as PEO is soluble in studied ILs we could guess, that fibers partly swollen with IL and water.

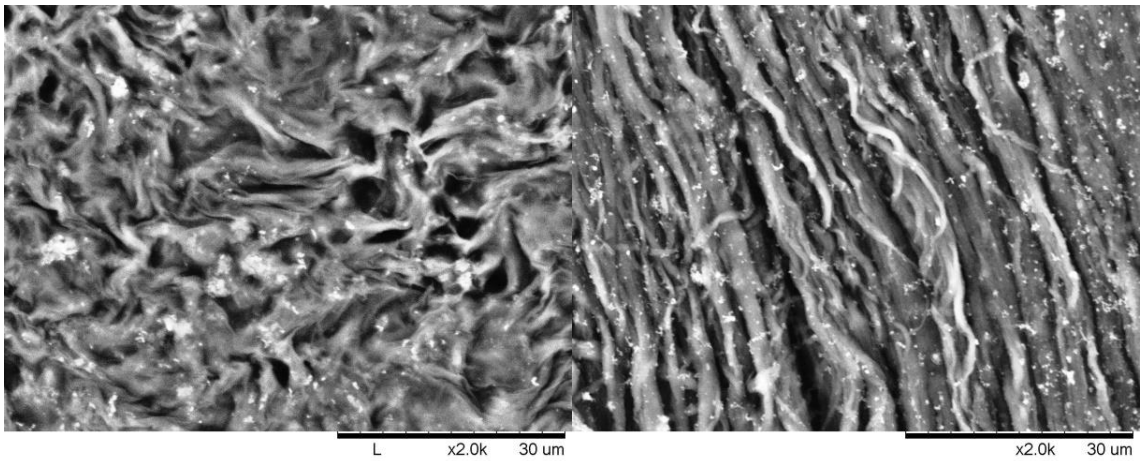


Figure 16 SEM image of PEO + 25% EmimAc fibers washed with acetone (left) and ethanol (right)

4.4 Effect of Activated Carbon on the PEO fiber morphology and properties

PEO fibrous mats with AC content electrospun by conventional electrospinning method

PEO electrospun mats with different contents of carbon filler and [Emim][Ac] dispersant were studied. As shown by previous experiment, fibers of diameter around 200 nm electrospun from PEO/water solution with 7 wt.% [Emim][Ac] content. Therefore, 3, 5 and 7 wt.% of [Emim][Ac] were used for AC dispersion. The Table 2 represents diameter of fibers, which I got. The diameters of fibers are not almost different. The presence of AC in the fiber does not affect the fiber diameter. The ratio of 5:4 PEO to AC lead to decrease of diameter. We got fibers with diameter of 92±21 nm with 23% content of [Emim][Ac] in mat. Increasing of IL content to 41% lead to a slight increase of fiber's diameter.

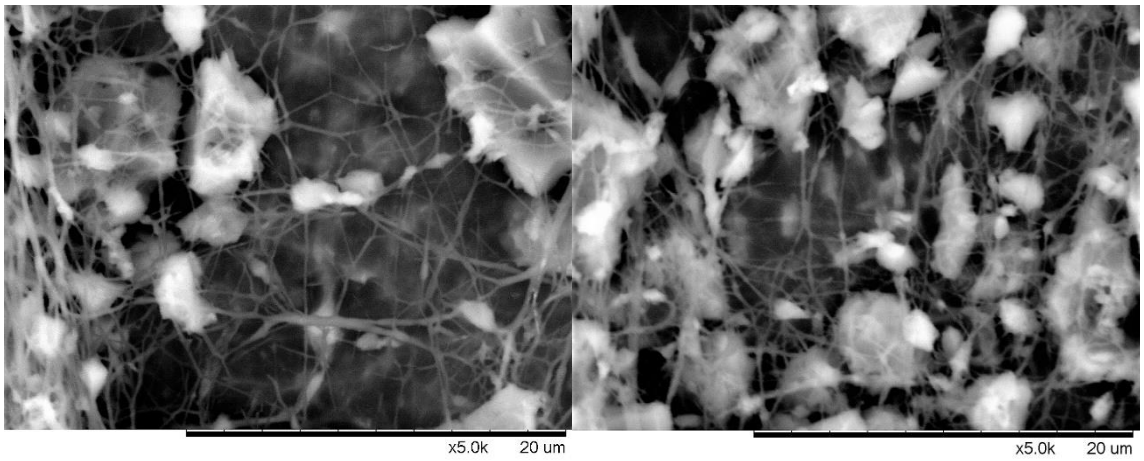
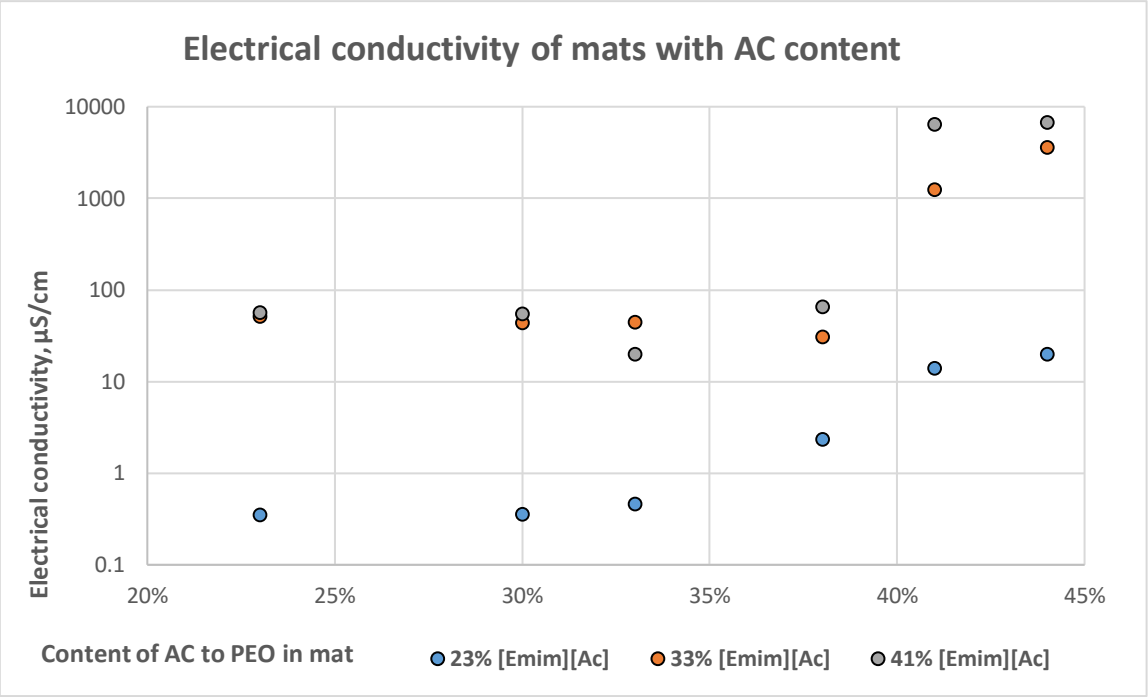


Figure 17 SEM image of 5:4 PEO to AC

PEO wt.% solution/mat	EmimAc, ratio of content to PEO	AC, ratio of content to PEO	Electrospun fiber diameter (nm)
10%	3% / 23%	3% / 23%	224±66
10%	5% / 33%	3% / 23%	243±95
10%	7% /41%	3% / 23%	511±82 / 155±38
10%	3% / 23%	4% / 30%	137±23
10%	5% / 33%	4% / 30%	335±80
10%	7% /41%	4% / 30%	263±59
10%	3% / 23%	5% / 33%	249±62
10%	5% / 33%	5% / 33%	244±74
10%	7% /41%	5% / 33%	232±33
10%	3% / 23%	6% / 38%	219±60
10%	5% / 33%	6% / 38%	157±33
10%	7% /41%	6% / 38%	428±104
10%	3% / 23%	7% / 41%	No fibers, spray
10%	5% / 33%	7% / 41%	No fibers, spray
10%	7% /41%	7% / 41%	No fibers, spray
10%	3% / 23%	8% / 47%	92±21
10%	5% / 33%	8%/ 47%	Spray
10%	7% /41%	8%	Spray, some visible fibers - 123±28

Table 2 Diameter of electrospun fibers with AC load

Determining diameter of fibers from SEM images one could notice that some of the mats contain two types of fibers by diameter; probably thick fibers are a bundles of thin fibers.



Graph 8 Electrical conductivity of AC containing PEO mats

The plot of electrical conductivity of electrospun mats is not linear. Up to 40% of AC ratio to PEO it does not show that with adding AC electrical conductivity increases. As, PEO mat with 41 wt.% [Emim][Ac] without AC, which is electrical conductivity is 80 µS/cm. Electrospun mat with AC content up to 40 wt. % has electrical conductivity lower than 60 µS/cm. Probably the amount of AC particles in fibers is not reaching the threshold concentration and thus has not established good electrical contact between each other. However, graph shows that with adding of [Emim][Ac] lead to increasing of conductivity, as covers of fiber's surface (Figure 20).

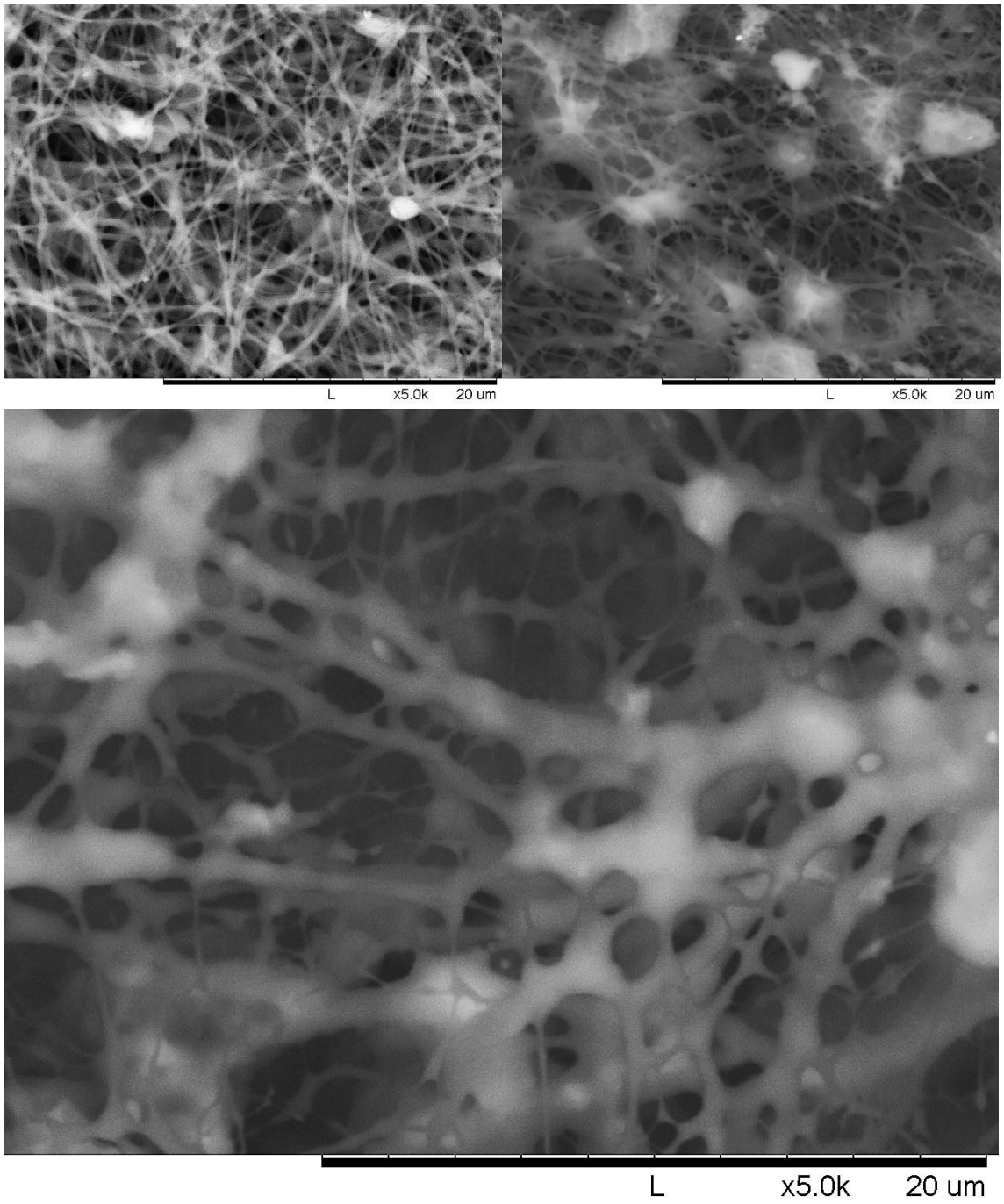


Figure 18 SEM of images of PEO fibers contained 23 wt.% AC and 23 wt.% (up left), 33 wt.% (up right) and 41 wt.% (bottom)

As could be seen from Figure 20 higher content of IL in mat has significant effect on SEM images quality, as IL gets charged in the electron beam of microscope and image became less sharp, what makes certain problems in determination of fiber diameter.

Some mats have a significantly high electrical conductivity in comparison with others. There are PEO mats with AC content of 41% with IL's content 33% and 41% have electrical conductivity 1257,69 and 6409,46 µS/cm (Figure 18). Also, there is PEO mat with AC content of 47% with IL's content 41% and electrical conductivity is 6826,32 µS/cm (Figure 19). Nevertheless, in those mats are not visible fibers, we got AC spray with PEO particles.

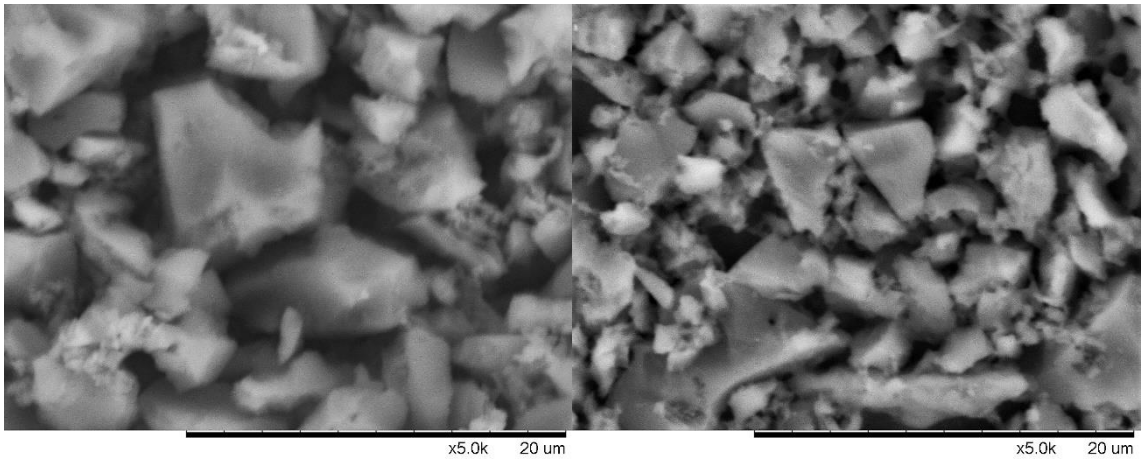


Figure 19 SEM images of are PEO mats with AC content of 41% with IL's content 33% (left) and 41% (right)

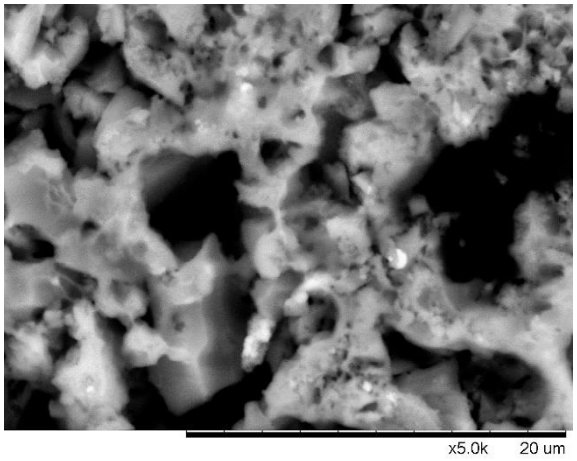


Figure 20 SEM images of PEO mat with AC content of 47% with IL's content 41%

As could be seen from the Graph 8 dependences of mat conductivity on AC concentration have typical S-shape, what corresponds to passing of percolation threshold in concentration range near to 40% of AC. What is interesting, that percolation threshold does not depends significantly on the concentration of IL in mat. Thus, we could conclude that electrical conductivity of activated carbon is dominating over ion conductivity of ionic liquid.

PEO fibrous mats with AC content electrospun by opposite electrospinning method

Mats were prepared by simultaneous electrospinning of a PEO solution and electrospray of AC dispersion using two syringes and collector placed between syringes. PEO dissolved in water (10w. %); one solution was without IL and into three others IL were added 7, 17 and 30 wt% to solution. Electrospray consist of 92% of AC and 8% [Emim][Ac] using as dispersant. EmimAc dissolved in ethanol then AC dispersed in this solution. This method gives opportunity to produce carbon highly filled fibrous composed material. PEO to AC ratio in mat was calculated as 5% to 95%, approximately.

Electrospinning of PEO	AC Electrospray	Electrical conductivity, µS/ cm	Diameter of fibers, nm
PEO 100%	92% AC + 8% [Emim][Ac]	0,85	200±13
59% PEO + 41%[Emim][Ac]	92% AC + 8%[Emim][Ac]	0,16	350 ±37
37% PEO + 63% [Emim][Ac]	92% AC + 8%[Emim][Ac]	189	565±145
25% PEO + 75% [Emim][Ac]	92% AC + 8%[Emim][Ac]	427	1691±145
37% PEO + 63% [Emim][Ac]	92% milled AC + 8%[Emim][Ac]	733	145±30

Table 3 Properties of electrospun mats obtained by opposite electrospinning

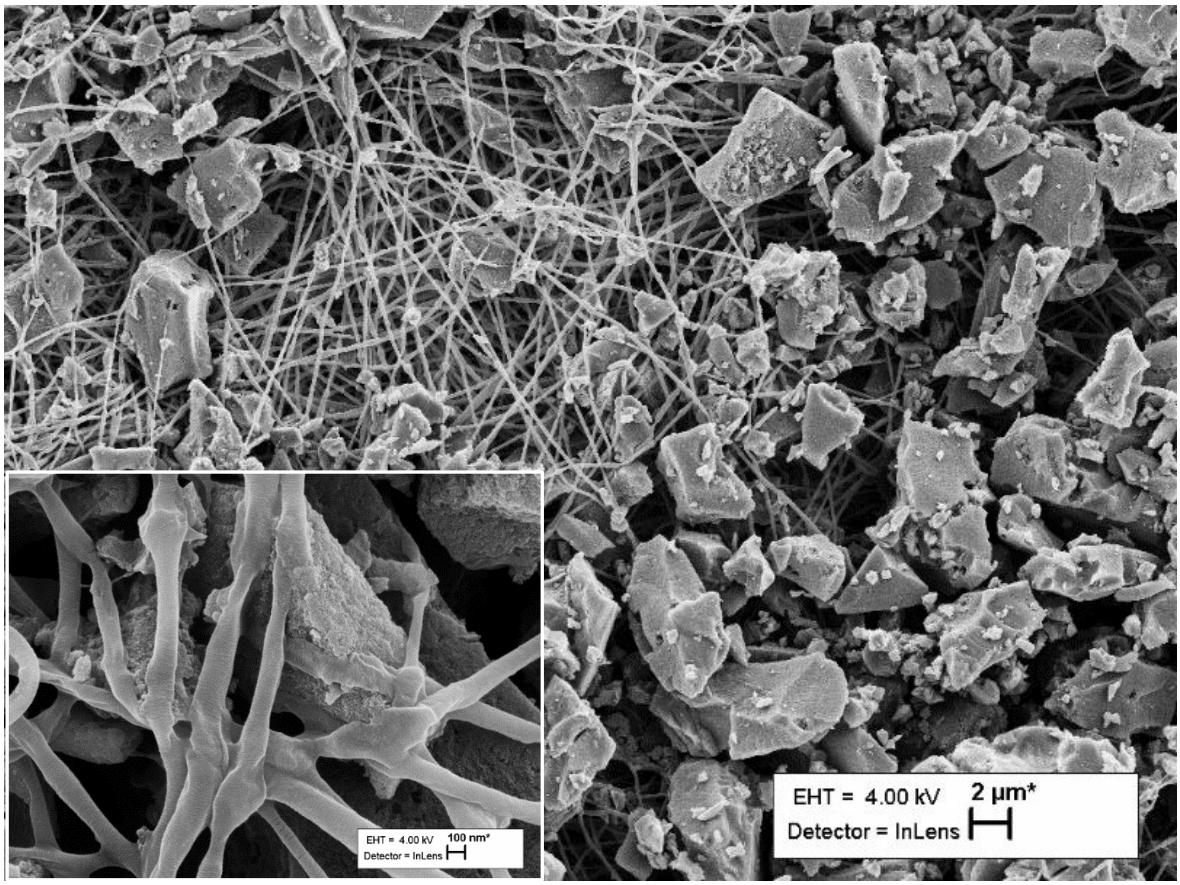


Figure 21 SEM image of PEO + 7% EmimAc + water opposite to 25% AC + 8% EmimAc + Ethanol electrospun fibers

As could be seen from Figure 21 opposite electrospinning gives mat with high AC load, but not uniform distribution of AC in the mat, because it is difficult to point the spinnerets directly on the same region of collector. One side is covered by fibers and other one by carbon particles, so electrical conductivity of the mat is significantly different at different ends of the foil. In our work we accounted the dates measured from center part of materials. The fibers of PEO and activated carbon particles deposited layer-by-layer center of the collector (Figure 22).

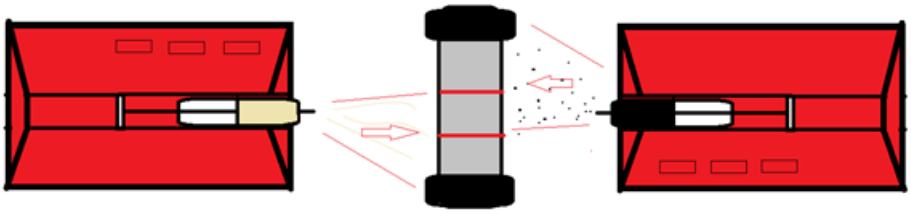


Figure 22 Scheme of foil's covering by PEO fibers and AC electrospray

At the same time AC particles are not covered with polymer, but distributed inside polymer fibers matrix. This provides good electrical contact between AC particles and keeps their surface open for absorption of charges or different substances.

PEO mats with content of [Emim][Ac] of 63 wt.% and 75 wt.% covered by AC uniform (Figure 23). Fibers are fully filled by ionic liquid, which strengthens the bond between the fiber and AC particles. However, the diameter of the fiber increases with a high content of ionic liquid. Diameter of PEO/ [Emim][Ac] fibers with carbon content corresponds to the diameter of fibers with ionic liquid without AC (Graph 7) . Therefore, we can say that opposite electrospinning method gives opportunity to prepare composite material filled by high load of AC with specific diameter of fibers.

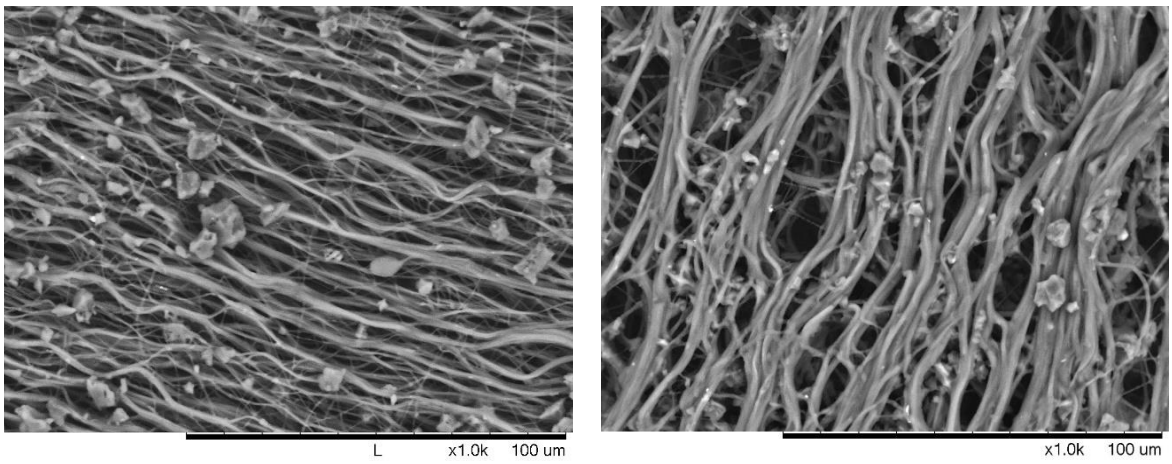


Figure 23 SEM image of PEO mats with IL content 63 wt.% (left) and 75 wt.% (right) covered by AC

PEO fibrous mats with crushed AC content electrospun by opposite electrospinning method

AC was crushed 1 hour. 1 ml of solution 10 wt.% PEO with 17 wt% [Emim][Ac] for fiber production was used, as we got a good results and uniform AC covering in previously experiment. 17 wt.% (of AC were dispersed in 8 wt.% [Emim][Ac] in ethanol (5 ml) for electrospray obtaining. We got fibrous mat with diameter of fibers of 145±30 nm and electrical conductivity of 733 μS/cm. Uniform AC covering have a good contact between particles that obtains mat with high electrical conductivity. The ratio PEO to AC in mat is 7 % to 93 %.

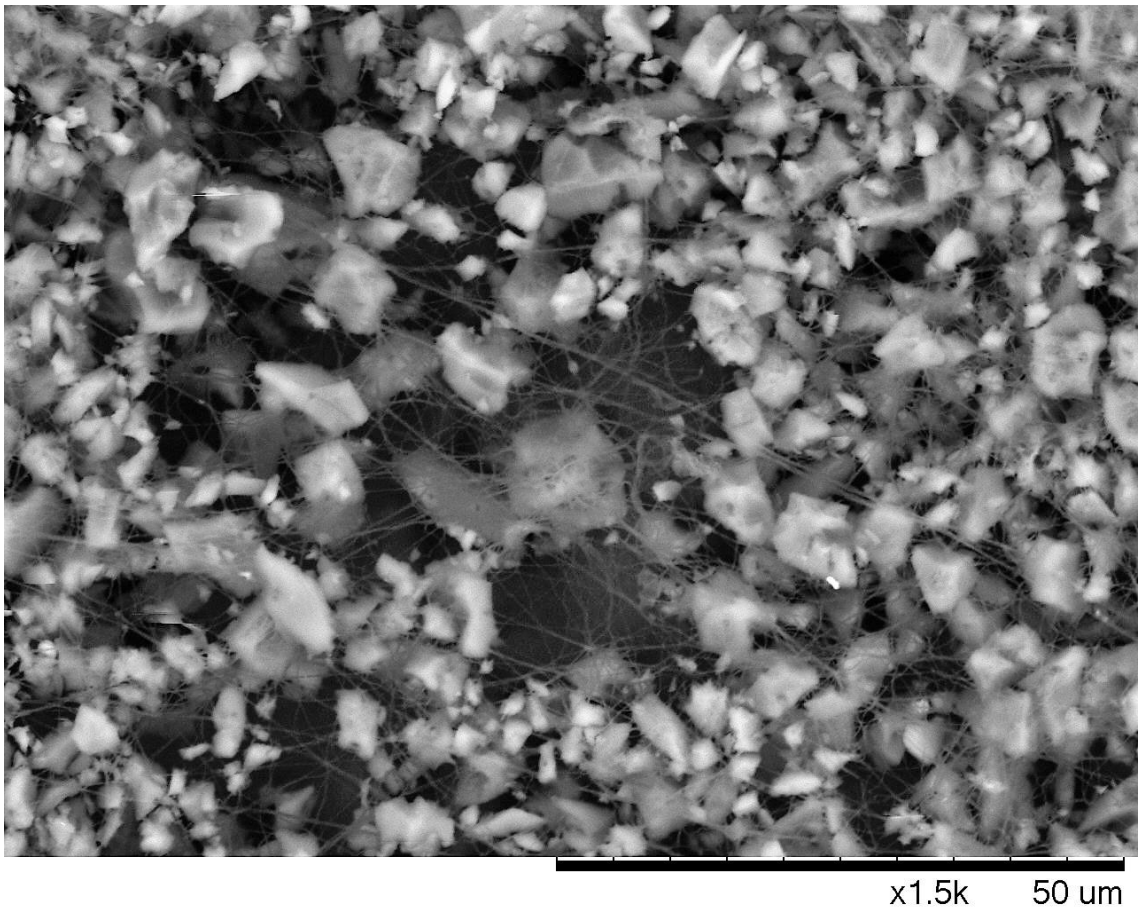


Figure 24 SEM image of PEO mat with 63% IL + content covered by milled AC

Comparison of conventional and opposite electrospinning

Both methods can be used for PEO mats production with AC content. Those methods give possibility to obtain fibrous mats with diameter of fibers around 100nm and good electrical conductivity. However, mats obtained by conventional electrospinning has a limit in AC content. Adding of AC from 41% content to PEO lead to electrospray of coating-like formation without fibers. Opposite electrospinning produce composite material layer by layer of PEO fibers and AC electrospray, which is not affect the fibers structure. Therefore, opposite electrospinning is a suitable method for nanofibrous mats production with high load of AC up to 95% to PEO ratio.

CONCLUSION

The effects of PEO concentration and solvent mixture on the morphology and diameter size distribution of electrospun fibers were investigated. The results show that 10 wt.% is the optimal PEO (Mw = 200kg/mol) concentration for fibers production with diameter near to 100 nm. Using distilled water for PEO dissolution were observed good fibers production by electrospinning with diameter of fibers around 198 ± 74 nm without beads. Addition of ILs into PEO aqueous solution leads to increase of viscosity and electrical conductivity solutions and electrical conductivity and as a result in increased diameter of electrospun fibers.

The aim of work was to study methods of PEO nanofibers with high electrical conductivity production by electrospinning method. After studying of ILs influence on the PEO fibers, [Emim][Ac] was chosen as the best for electrospinning. We obtain uniform nanofibrous PEO mats with IL content of 41 wt.% and with diameter of fibers 194 ± 36 nm; electrical conductivity of 80 μS/cm.

Mats with AC content were prepared by conventional and opposite electrospinning. Opposite electrospinning is suitable method for composite materials production with high load of AC up to 95% to PEO. It is also possible to maintain a specific fiber diameter. AC particles are not covered with polymer and have good contact between each other, what is an advantage for electrical conductivity or absorption properties. We obtain uniform nanofibrous mat with fibre diameter from 200 to 1700 nm. Electrical conductivity of mats also increases and reaches 426,95 μS/cm when the content of ionic liquid is 75 wt.% in mat covered by 95 wt.% AC. Unfortunately, distribution of AC in the mat is not uniform because it is difficult to point the spinnerets directly on the same region of collector. Electrospun PEO mat with 63% IL and covered by crushed AC of 93 % content have diameter of fibers 145±30 nm and electrical conductivity of 733 μS/cm.

REFERENCES

[1] Ljudmila Solovjova. Electrospinning of cellulose solutions in ionic liquid, Bachelor work, Tallinna University of Technology, Estonia, 2016

[2] Zhenyu Li, Ce Wang. Effects of Working Parameters on Electrospinning, Book - One-Dimensional nanostructures pp.15-28, USA, 2013

[3] Highlights of Interesting Scientific Applications. What is electrospinning? - Inwlowmation Chronicles Issue 1001 (2009)

[4] Nicolas Lavielle, Anne Hebraud, Guy Schlatter, Linda Thöny-Meyer, RenéM. Rossi, and Ana-Maria Popa. Simultaneous Electrospinning and Electrospraying: A Straightforward Approach for Fabricating Hierarchically Structured Composite Membranes, ACS Appl. Mater. Interfaces 5, 10090−10097, 2013

[5] SUN Guo-en, TENG Hong, ZHANG Chun-ling, DOU Yan-li and LI Yi. Preparation of Ultrafine Water-soluble Polymers Nanofiber Mats via Electrospinning, Chem. Res. Chinese Universities 2010, 26(2), 318—322, China

[6] Wai-Kit Li,Yuen-Wah Wong. Electrical properties of electrospun nanofibers of PEO/carbon black composite, Solid State Phenomena Vol. 151 (67-71), Hong Kong, 2009

[7] Saima N. Khan. Electrospinning Polymer Nanofibers - Electrical and Optical Characterization-Dissertation, College of Arts and Science of Ohio University, US, 2007

[8] Ana Cristina Vega Lugo. Understanding the Role of Poly(ethylene oxide) in the Electrospinning of Whey Protein Isolate Fibers, University of Guelph, Ontario, Canada, 2012

[9] Christopher Calvin Call. The study of electrospun nanofibers and the application of electrospinning in engineering education, Thesis, Virginia Commonwealth University , 2008

[10] H. Fong, I. Chun, D.H. Reneker. Beaded nanofibers formed during electrospinning, Polymer 40 (1999) 4585–4592, USA

[11] Yarin AL. Free liquid jets and films: hydrodynamics and rheology, Journal of Fluid Mechanics Volume 312 (1996), pp. 408-40, New York: Wiley

[12] Entov VM, Shmaryan LE. Numerical modeling of the capillary breakup of jets of polymer liquids. Fluid Dynamics 1997; 32(5):696–703

[13] Sureeporn Tripatanasuwan, Zhenxin Zhong, Darrell H. Reneker. Effect of evaporation and solidification of the charged jet in electrospinning of poly(ethylene oxide) aqueous solution, Polymer 48 (2007), 5742 – 5746, USA

[14] О.К. Лебедева, Д.Ю. Культин, Л.Ь Кустов, С.Ф. Дунаев. Ионные жидкости в электрохимических процессах. – Journal Российского химического общества имени Д.И Менделеева, XLVIII(6), 2004
[15] Короткова Екатерина Николаевна. Электропроводность и термодинамические характеристики ассоциации двух ионных жидкостей в ацетонитриле и диметилсульфоксиде и закономерности нагрева растворов микроволновым излучением. диссертация , Москва, 2014
[16] A. Panancea, S. Patachia, A. Porzsolt. Conductivity studies of imidazolium – based ionic liquids in aqueous solutions. Series I: Engineering Sciences, 8 (57), 2015
[17] Alexander Kokorin. Book: IONIC LIQUIDS: APPLICATIONS AND PERSPECTIVES. Croatia, 2011.
[18] Марина Максутовна Сейткалиева. Получение и структурное исследование биологически активных систем га основе имидазолиевых ионных жидкостей, Диссертация, Москва 2015
[19] Meli, Jianjun Miao, Jonathan S. Dordick, and Robert J. Linhardt. Electrospinning from room temperature ionic liquids for biopolymer fiber formation, GreenChem. 2010,12, 1883–1892 | 1887, Luciana
[20] Zhuojun Meng, Xuejing Zheng, Keyong Tang, Jie Liu, Shufa Qin. Dissolution of natural polymers in ionic liquids: A review/ e-Polymers 2012, no. 028 2012 China
[21] Wei Cheng, Qi Yu, Zhiming Qiu, Yurong Yan. Effects of Different Ionic Liquids on the Electrospinning of a Polyacrylonitrile Polymer Solution, J. APPL. POLYM. SCI. 2013, DOI: 10.1002/ APP.39275
[22] Walden P. Molecular weights and electrical conductivity of several fused salts, Bull. Acad. Sci. 1914 (P.405–422)
[23] Wilkes J.S., Zaworotko M.J. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, Chem. Commun. 1992. V.13. P.965–967
[24] Twu P., Zhao Q., Pitner W.R., Acree W.E., Jr., Baker G.A., Anderson J.L. Evaluating the solvation properties of functionalized ionic liquids with varied cation/anion composition using the solvation parameter model, J. Chromatogr. A. (2011) P.5311-5318
[25] Pringle J.M., Golding J., Baranyai K., Forsyth C.M., Deacon G.B., Scott J.L., MacFarlane D.R. The effect of anion fluorination in ionic liquids - physical properties of a range of bis(methanesulfonyl)amide salts, New J. Chem. 2003. V.27. P.1504-1510
[26] Seddon K.R., Stark A., Torres M-J. Influence of chloride, water and organic solvents on the physical properties of ionic liquids, Pure Appl.Chem. 2000. V.72. No. 12. P. 2275- 2287
[27] Jianjun Miao, Minoru Miyauchi, Trevor J. Simmons, Jonathan S. Dordick, Robert J. Linhardt. Electrospinning of Nanomaterials and Applications in Electronic Components and Devices, Journal of Nanoscience and Nanotechnology Vol. 10, 5507–5519, USA, 2010

[28] Byung Gil Min, Han Gi Chae, Marilyn L. Minus and Satish Kumar. Polymer/carbon nanotube composite fibers - An overview, Transworld Research Network 37/661 (2), Fort P.O., Trivandrum-695 023, Kerala, India, 2009

[29] Nanfang Wang, Yulin Jian, Suqin Liu, Younian Liu, Kelong Huang. Influence of acetated-based and bromo-based ionic liquids treatment on wool dyeing with acid blue 7, Wiley Periodicals, Inc. J Appl Polym Sci, Vol. 123, Issue 6, 2012

SUMMARY

The aim of my work is to study the electrospinning method of nanofibers with high electrical conductivity production. Polyethylene oxide (PEO) was studied as fiber generating polymer, iIonic liquids (ILs) and activated carbon (Kuraray YP-80F) (AC) powder were used as electrical conductive fillers. We found out the optimal concentration of 10 wt.% of PEO with molecular weight of 200kg/mol in water solution, it is suitable to produce nanofibers with diameter around 200 nm. Addition of ILs into PEO aqueous solution leads to increase of viscosity and electrical conductivity solutions and electrical conductivity and as a result in increased diameter of electrospun fibers. After studying of ILs, as [Bmim][Cl], [Bmim][Ac], [Emim][Br] [Emim][Ac], influence on the PEO fibers, [Emim][Ac] was chosen as the best for electrospinning. We obtain uniform nanofibrous PEO mats with IL content of 41 wt.% and with diameter of fibers 194 ± 36 nm; electrical conductivity of 80 μS/cm.

Mats with AC content were prepared by conventional and opposite electrospinning. Both methods can be used for PEO mats production with AC content. Those methods give opportunity to obtain fibrous mats with diameter of fibers around 100nm and good electrical conductivity. However, mats obtained by conventional electrospinning has a limit in AC addition. Adding of AC from 41% content to PEO lead to spray formation without fibers. Opposite electrospinning obtain composite material layer by layer by PEO fibers and AC electrospray, which is not affect the fibers structure. Therefore, opposite electrospinning is a suitable method for fibrous mats production with high load of AC up to 95% to PEO ratio. In both methods AC particles are not incorporated into fibers, but distributed in PEO fibers as in web.

We have not got materials with high electrical conductivity, but we have got good nanofibers around 100 nm with electrical conductivity. Also we have got electrospray of AC with PEO particles with electrical conductivity up to 7000 μS/cm, the coating consists of 32wt.% of AC, 40wt.% of PEO and 28wt.% of EmimAc.

GRAPHICAL MATERIAL

APPENDICES