TALLINNA TEHNIKAÜLIKOOL
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THE IMPACT OF CARBON NANOTUBES AND IONIC LIQUID ON THE PROPERTIES OF ELECTROSPINNING SOLUTIONS AND OBTAINED MEMBRANES

Master’s thesis

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Technology of Wood and Plastic curriculum KVEM12/13
Tallinn 2015

Declaration

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

All the work of other authors, important aspects from literature and data from elsewhere used in this thesis is cited or (in case of unpublished works) authorship is shown on the text.

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SÜSINIKNANOTORUDE JA IOONVEDELIKU MÕJU ELEKTROKEDRATAVATE LAHUSTE JA SAADUD MEMBRAANIDE OMADUSTELE

Magistritöö

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MASTER’S THESIS ASSIGNMENT

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The impact of carbon nanotubes and ionic liquid on the properties of electrospinning solutions and obtained membranes.

(in English)

Süsiniknanotorude ja ioonvedeliku mõju elektrokedratavate lahuste ja saadud membraanide omadustele.

(in Estonian)

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Aim and tasks of the master´s thesis:

The aim of the master’s thesis is to study how addition of multi-walled carbon nanotubes (MWCNTs) and ionic liquid (IL) 1-butyl-3-methylimidazolium choride ([Bmim]Cl) into copolymer of styrene and acrylonitrile (SAN) in dimethyl sulfoxide (DMSO) solution will affect electrospinning process, the morphology of obtained nanofibers, mechanical properties and electrical conductivity of obtained membranes. The main tasks during master’s thesis were to investigate:

1. The optimization of solution and process parameters for SAN in DMSO solution;
2. The impact of [Bmim]Cl on SAN in DMSO solution electrical conductivity, viscosity and morphology of obtained fibers;
3. The impact of MWCNTs on SAN in DMSO solution viscosity and electrical conductivity;
4. The impact of MWCNTs and [Bmim]Cl on SAN membrane electrical conductivity, mechanical properties and obtained fibers morphology.

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Abbreviations and acronyms

[Bmim]Cl	1-butyl-3-methylimidazolium chloride
$[C_4mim][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate
CNT	carbon nanotube
CVD	chemical vapor deposition
DCE	1,2-dichloroethane
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
DWCNT	double-walled carbon nanotube
EPDM	ethylene propylene diene monomer rubber
IL	ionic liquid
MEK	methyl ethyl ketone
MWCNT	multi-walled carbon nanotube
PC	polycarbonate
PCL	polycaprolactone
PMMA	polymethyl methacrylate
PPE	polyphenyl ether
PS	polystyrene
SAN	copolymer of styrene and acrylonitrile
SEM	scanning electron microscope
SWCNT	single-walled carbon nanotube
THF	tetrahydrofuran

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Introduction

Electrospinning is a fiber formation method for obtaining continuous fibers in micro- or nanoscale, by an electrically charged jet of polymer melt or polymer solution. The electrospinning process is one of the most common methods to prepare polymeric nanofibers nowadays. Mainly due to the high speed of the process and low cost, also for its simplicity, flexibility in the process parameters and the actuality in development of different nanomaterials for their implementation in various fields.

In recent years ionic liquids have attracted a lot of attention and have been widely used, as ILs are a promising class of green solvents. ILs are non-volatile, non-flammable, thermally and chemically stable, highly polar and with convertible physicochemical properties, therefore a good alternative for organic solvents. Moreover, it is known that, when ILs are used in electrospinning polymer solutions, an increase in electrical conductivity and viscosity of the solution and reduction of surface tension is seen. These parameters strongly affect the morphology of the obtained fiber.

Carbon nanotubes (CNTs) have drawn much attention all over the world, because of their remarkable properties, which make CNTs potential candidates to be used in numerous applications, although they are most often used in polymer composites as a reinforcing agent.

This research contains several parts. Theory is divided into 5 chapters, where in the first chapter are described different production methods and applications of nanofibers in general. The second and third chapter are devoted to explaining the process and describing the effect of different conditions. In the fourth and fifth chapter are presented production methods, properties and applications of ILs and CNTs. The theory part is followed by experimental part, where are described all the used methods and materials. After that comes results and discussion chapter, where is studied the impact of IL and CNTs on polymer solution and obtained fibers.

The aim of this research is to find out how the process of electrospinning, the morphology of the obtained nanofibers, and the mechanical properties and electrical conductivity of obtained materials is altered by the addition of MWCNTs and the IL [Bmim]Cl into the SAN in DMSO solution.

1. Production and applications of polymeric nanofibres

Nanomaterials are considered, by definition, to be materials, which have at least one dimension ≤100 nm. Therefore, nanofibres are such fibres, which have diameter of 100 nm or less, and an aspect ratio (length/diameter) larger than 100:1. The first known attempts of producing polymeric nanofibers were carried out in 1934 by A. Formhals, who published the first patent describing the exploratory creation of nanofibers. Since then, a lot of effort has been made to develop various production methods for polymeric nanofibers. The following five methods are the most common: (i) drawing, (ii) template synthesis, (iii) phase separation, (iv) self-assembly and (v) electrospinning. [1-3]

Nanofibers exhibit special properties mainly due to their extremely high surface to weight ratio in comparison to conventional nonwovens, and for that reason there are numerous fields, where nanofibers are used. [4] Figure 1 represents an overview of different applications of nanofibers.

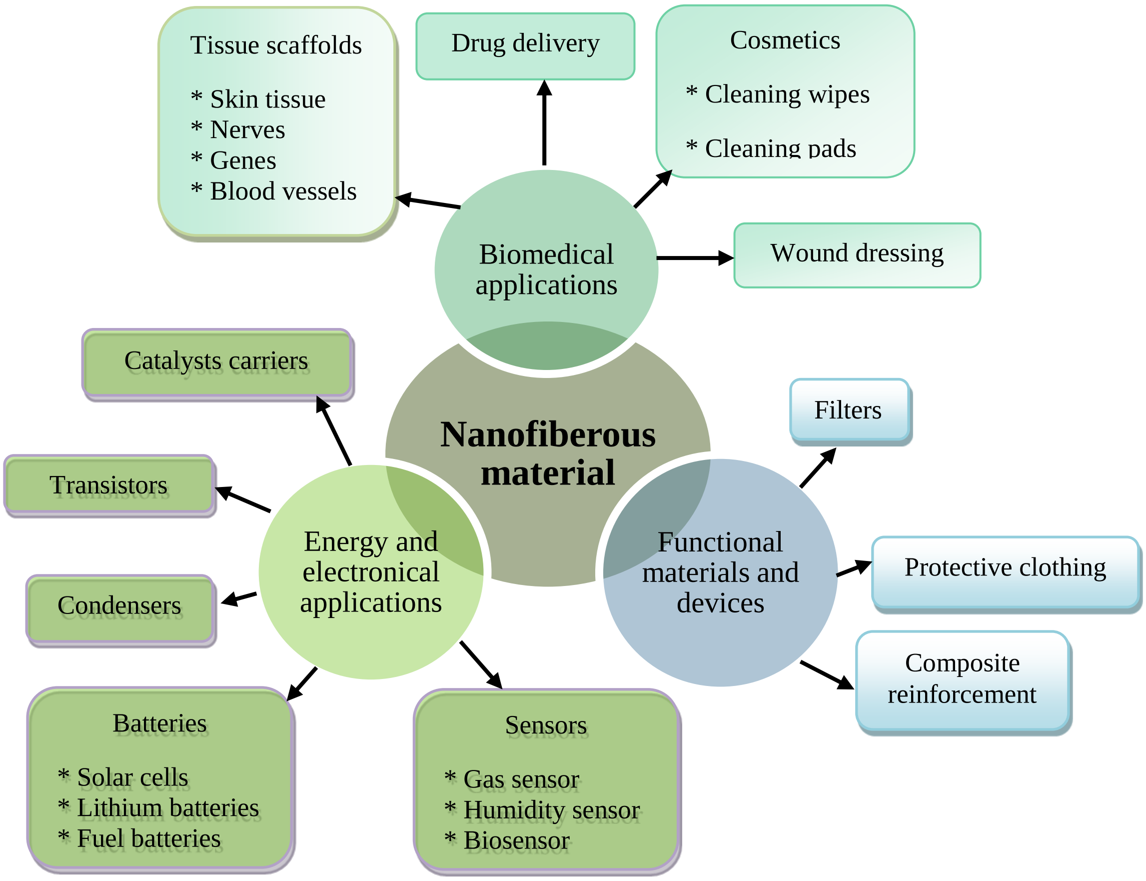


Figure 1: Applications of nanofibres. [5-8]

2. Electrospinning

The electrospinning process is known for more than a hundred years, and was first described by J. F. Cooley and W. J. Morton in 1902. However, it was not until the early 1990s, when the electrospinning process started to be more widely introduced by Dr. Darrell H. Reneker. [9]

Electrospinning provides a simple, versatile and inexpensive method, for the production of ultrathin fibers, ranging from 10µm to 10nm from a rich variety of materials that include polymers, composites and ceramics. The process is similar to conventional fiber spinning techniques (wet, dry, gel and melt spinning), but instead of using external mechanical force to push the the polymer melt or solution through the die, the electrospinning process uses an electrically charged polymer solution or melt and high voltage to produce the nanofibers. [10-11]

Compared to other fiber production methods, electrospinning is the most popular and preferred method to prepare nanofibres, mostly due to its cheapness, simplicity and quickness. Over the years the usage of the electrospinning method has increased, and consequently this approach of fiber preparation has expanded to new areas and overall consumption has been increased. It is hoped that further research and development of the electrospinning process can eventually make it the most important method in nanotechnology, which would extend the use of nanofibers to various industries. [5-6, 12]

The list of equipment needed for the electrospinning process is quite short, requiring only a syringe or a pipette to make a droplet of polymer solution; a pump, to control the feedrate of the polymer solution; a grounded collector for the deposition of newly obtained fibers; two electrodes and a high voltage source. One electrode is typically connected to the syringe needle, to give the electric charge to the polymer solution and the second electrode is connected to the collector to ground it. Figure 2 shows the typical scheme of the electrospinning setup. [10]

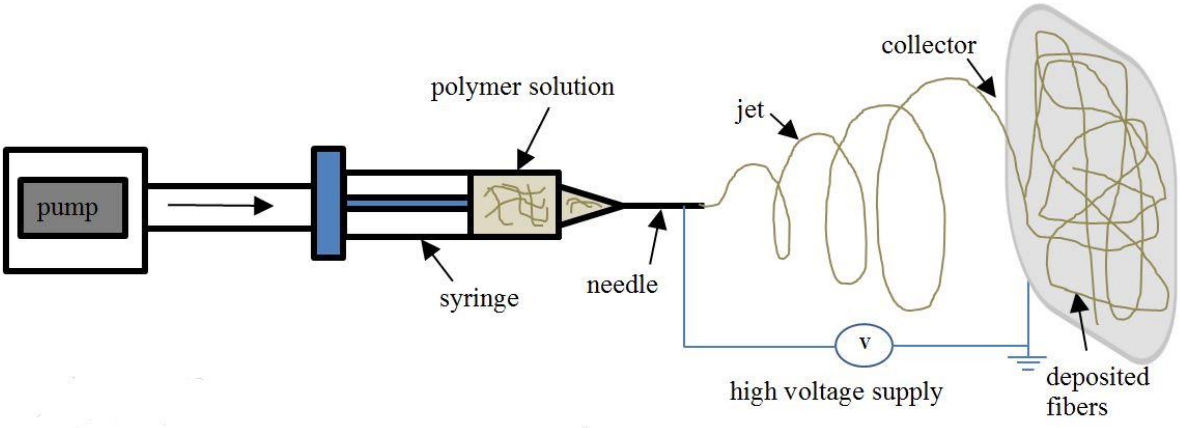


Figure 2: Typical scheme of electrospinning setup.

In order to start the fiber formation process, a high voltage is applied to the polymer solution in the syringe, which induces the charges in the solution. When the electric field is strong enough, the induced charges will start to hustle on the surface of the solution drop and develop shear stresses, which counteract the surface tension of the liquid. If the high voltage affecting the charges exceeds the intrinsic surface tension of the droplet, then the solution drop stretches, acquiring a conical shape, known as the Taylor cone (Figure 3). Increasing the voltage to a critical point, will impair the surface tension balance even more, because of the stetching forces exceed the surface tension of the solution drop, and as a result a charged jet erupts from the cone shaped drop. The ejected droplet jet moves towards lower potential, which is generally the grounded collector. During the jet movement from the needle tip to the collector, the jet stretches, and the solvent evaporates, resulting jet elongation and diameter decrease. Eventually forming a network of nanofibers on the collector. [10]

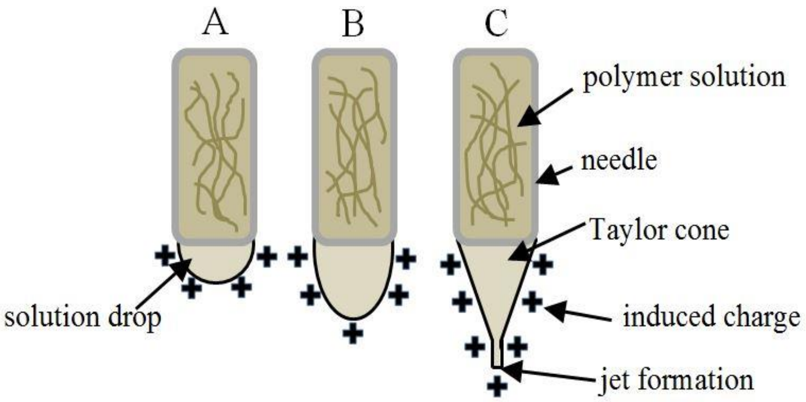


Figure 3: Formation of the Taylor cone: A – Induced charges on the solution drop on the tip of the needle; B – Elongation of solution droplet; C – Formation of Taylor cone and eruption of solution jet.

3. Parameters affecting the electrospinning process

There are many parameters, which affect the electrospinning process and the morphology of obtained nanofibers. These parameters can be roughly divided into three categories: (i) solution properties, (ii) electrospinning process conditions, and (iii) ambient parameters.

3.1 Properties of the solution

First of all, for the electrospinning process to even happen, the polymer must be in a liquid state, either as polymer solution or as polymer melt. In most cases polymer solutions are used, because the solvents increase the electrical conductivity of the solution. However, for polymer melts, there is a need for additives to get the solution electrically conductive. The parameters of the solution, such as the viscosity, surface tension, temperature and electrical conductivity can have a notable effect on the electrospinning process and morphology, as well on electrical conductivity, optical, thermal, chemical and mechanical properties of obtained fibers. Moreover, by changing different solution parameters, it is possible to get fibers with different morphologies. [8]

3.1.1 Polymer molecular weight, solution viscosity and surface tension

For the electrospinning process to start, the polymer solution must contain a sufficient amount of charged particles, and thereby the charges must be high enough to overcome the surface tension of the solution. [9]

The molecular weight of the polymer basically represents the length of the polymer chain and the chain length in turn will determine the amount of entanglement of the polymer chains in the solution. This has an effect on the viscosity of the solution, the higher the molecular weight of the polymer, the higher the viscosity of the solution. [13]

The solution’s viscosity is also very important, because during electrospinning, while the solution jet leaves the needle tip, the polymer solution is stretched as it travels towards the collector. During the stretching of the solution, the entanglement of the polymer chains prevents the electrically driven jet from breaking up, thus maintaining a continuous solution jet. Minimal viscosity is still necessary for electrospinning to happen, because if the viscosity of the solution is too low, electrospraying may occur and polymer particles are formed instead of fibers. [14]

The surface tension and viscosity of the solution are one of the reasons why solvent beads may be found in the fibers. Namely, the lower the viscosity of the solution, the more there will be free solvent molecules and due to surface tension, which decreases the polymer solution's surface area per unit mass, the more likely those solvent molecules will gather in one place and adopt a spherical shape. [9]

However, the gradual increase in viscosity will cause the shape of beads to change from a spherical shape to more of a cylinder one, until perfectly smooth bead-free fibers are formed. This happens, because polymer chains are more entangled at higher viscosities, which in turn means that the interaction between the polymer and solvent molecules is greater and therefore the solvent molecules are distributed throughout the chain. For that reason the effect of the surface tension is not that great at higher solution viscosities. Figure 4 shows how the polymer and solvent molecules are situated both at elevated and low viscosities. [15]

When the solution viscosity is too high, it is difficult to pump the solution out of the needle and the solution may dry on the needle tip before electrospinning can even begin, because the concentration of the solvent is too small. [14]

Another effect of higher viscosity is a smaller deposition area. This means that the viscosity of the solution is strong enough to discourage the jet bending. As a result, the jet path is reduced and the bending instability spreads over a smaller area. This reduced jet path also means that there is less stretching of the solution resulting in a larger fiber diameter. [15]

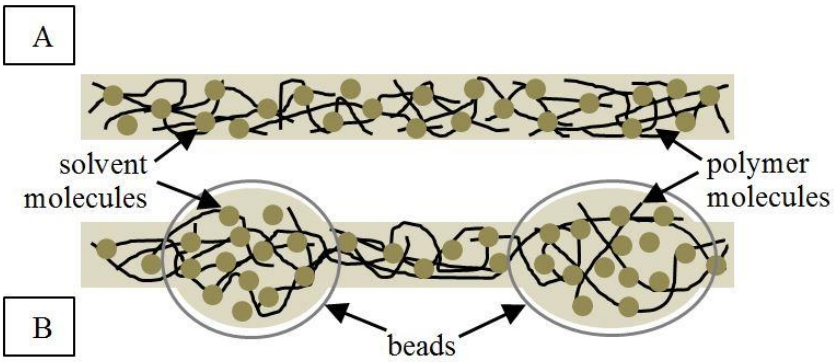


Figure 4: [A] At higher viscosities the solvent molecules are distributed all over the entangled polymer molecules; [B] At lower viscosities the solvent molecules gather in one place as an effect of surface tension of the solution.

3.1.2 Solution electrical conductivity

One of the most important solution parameters is its electrical conductivity, as electrospinning involves stretching of the solution caused by repulsion of the charges on its surface. If the solution is not electrically conductive, then no fibers are formed on the collector. The greater the electrical conductivity of the solution, the more charges it carries and the stronger the stretching, which leads to more uniform fibers are being formed. Moreover, the increased electrical conductivity of the solution influences the jet bending instability, which in turn means that depositing area is increased. This will also favor the formation of finer fibers since the jet path is now increased. [16]

The electrical conductivity of the solution can be increased by the addition of ions or by changing the solution pH. Substances, which increase the electrical conductivity are mineral salts and acids, carboxylic acids and stannic chloride for example. In some cases, the addition of ions enhances the viscosity of the solution and thereby increases the resistance of viscoelastic forces against the electrostatic force and at some point the reduction of the fiber diameter is suspended. Further, the morphology of the fiber can also be affected by the size of the ions added to the solution, as experiments have shown by electrospinning the same polymer solution, while adding ions with smaller atomic radius give fibers with smaller diameters and ions with greater atomic radius give fibers with larger diameters. [15, 17]

3.1.3 Solvent evaporation rate

As already said previously, the solvent evaporates during the jet movement from the needle tip to the collector. The evaporation rate is important, because when the solvent is completely evaporated before depositing on the collector, then only some individual fibers will be obtained. However, when the evaporation rate is too low, then the solvent might not evaporate completely before the jet reaches the collector, and for that reason fibers might not even form on the collector or a thin polymer solution film will form instead. Again, when the evaporation rate is too high, then the needle might clog, because the solvent evaporates too fast, which in turn decreases the number of charges and increases the viscosity of the solution. As a result, the voltage is not high enough to form the Taylor cone and start stretching the jet from the needle tip, which will eventually clog the needle. [17]

3.1.4 Solvent's dielectric properties

The dielectric properties of the solvent show a rough measure of whether the solvent is polar or non-polar. Polar solvents have large dipole moments, which means they have partial charges, and they contain bonds between atoms with very different electronegativities. While non-polar solvents contain bonds between atoms with similar electronegativities. Polarity in turn shows the ability of a solvent to dissolve common ionic compounds, such as salts. [18-19]

Therefore the solvent's dielectric properties are also of the more important solution properties, as they also influence the electrospinning process. The higher the polarizability of the solvent, the less solvent beads will form and the smaller is the obtained fiber's diameter during electrospinning process. Higher relative permittivity also increases the jet bending instability, leading to longer traveling time and stretching of the jet to the collector, resulting in fibers with smaller diameters and greater deposition areas. [15]

The dielectric properties of the solution, and thus the morphology of the fiber, can be improved by the addition of a solvent, which has good dielectric properties. If, however, the polymer does not dissolve in the solvent added to the solution, then the result is the opposite - fibers with more and larger beads are obtained. [15]

3.1.5 Solution temperature

A high solution temperature affects two characteristics, it increases the evaporation rate of the solvent and also reduces the viscosity of the solution. The reduced solution viscosity results in reduction of the fiber's diameter. Due to the increased temperature the mobility of the polymer molecules also increases, which allows the Columbic forces to stretch the solution further, resulting in fibers of a smaller diameter. [8]

3.1.6 Molecular forces

The molecular forces in the material have a strong influence on the flow properties of the material or solution. Viscosity increases with increasing intermolecular forces, which is the reason why it is important to know the binding forces of the solution before studying rheological properties of the solution (Table 1). Intramolecular forces include all the chemical bonds, which keep the molecules together. Intermolecular forces are attractive forces between neighboring molecules, which typically involve smaller charges that are farther apart and therefore make them relatively weak compared to intramolecular forces. [20-21]

Table 1. Molecular forces. [20]

Force	Bond formation	Energy (kJ/mol)
Primary or intramolecular forces		
Ionic	Cation-anion	400-4000
Covalent	Shared pair of electrons	150-1100
Metalic	Cation – delocalised electrons	75-1000
Secondary or intermolecular forces		
Ion-dipole	Ion charge – dipole charge	40-600
Hydrogen bond	Partially positive H is attracted to the partially negative charge molecule	10-40
Dipole-dipole	Dipole force	5-25
Ion-induced dipole	Ionic force - polarization of electron clouds	3-15
Dipole-induced dipole	Dipole force - polarization of electron clouds	2-10
Dispersion	Polarization of electron clouds	0.05-40

3.2 Electrospinning process conditions

The electrospinning process and fiber morphology, electrical conductivity, optical, thermal, chemical and mechanical properties of the membrane are affected by the conditions of the process itself or by the controllable parameters, such as voltage, distance, feedrate and collector type.

3.2.1 Voltage

The voltage is the most important condition for the to process function, because without a high voltage, no fiber will be formed. High voltage creates an electric field and induces charges in the polymer solution. If the solution’s surface tension is exceeded, the electrospinning process has begun. It is known that both positive and negative voltages can create Taylor cone on the tip of the needle. [12]

In most cases, the rising voltage causes greater stretching of the jet, because the number of charges trying to draw the jet also increases, which causes and decrease in obtained fiber’s diameter. However, a lower voltage, which indicates to a weaker electric field, reduces acceleration of the jet, thus increasing the flying time of the jet. A longer flight time enables the jet to stretch even more during electrospinning and therefore it is also possible to get finer fibers at a lower voltage. [17]

In some cases it has been also observed that high voltages cause bead formation in the fiber and by continuously increasing the voltage the bead shape changes from cylindrical to spherical. This is caused by the fact that at too high voltage the Taylor cone withdraws to the needle, which increases the instability of the jet, and this in turn increases the frequency of beads formation. It is also known that by further increasing the voltage, these beads may join to form large-diameter fibers. [17]

However, a high voltage does not only affect the fiber's morphology, but also the crystallinity of the fiber. Due to stretching, which is caused by a high voltage, polymer molecules are arranged more regularly during electrospinning, and this leads to an increase in the crystallinity of the fiber. Contrarily, above a certain voltage, the crystallinity of the fiber decreases instead, because rising voltages increase the acceleration of the jet towards the collector, which means that the flight time to the collector is shortened. As relocation of the molecules takes times and above a certain voltage the flight time of the jet is too short to be able to place the molecules more regularly, resulting in reduction of the fiber crystallinity. [15]

3.2.2 Feedrate

The feedrate determines the amount of solution which shall be given to the electrospinning process. Feedrate affects the formation of stable Taylor cone's (see Table 2) and the morphology of the obtained fibers. If the speed is too high, the diameter of the fiber is increased. This increase is due to a greater amount of solution on the needle tip, which decreases the evaporation rate of the solvent. Additionally, if the solvent does not evaporate quickly enough, then the result may be a fused fiber network. [7, 17]

3.2.3 Distance between the needle tip and the collector

The distance is also one of the most important parameters affecting the morphology of the fibers. Depending on the distance between the needle tip and the collector, the polymer solution jet's flight time is correspondingly shorter or longer. In addition, the distance has also direct effect on electric field strength. Table 2 describes the relationships between distance, flight time and voltage and the resulting fibers under these conditions. [15]

Table 2. Relationships between distance, flight time and voltage. [15]

Distance	Jet flight time	Electric field strength	RESULTS			
			Jet bending instability	Depositing area	Fiber diameter	Fiber morphology
short	short	strong	high	small	high	Fused together fibers
						high ↑
↕	↕	↕	↕	↕	↕	Amount of solvent beads
						↓ small
long	long	weak	small	high	small	Fibers do not form

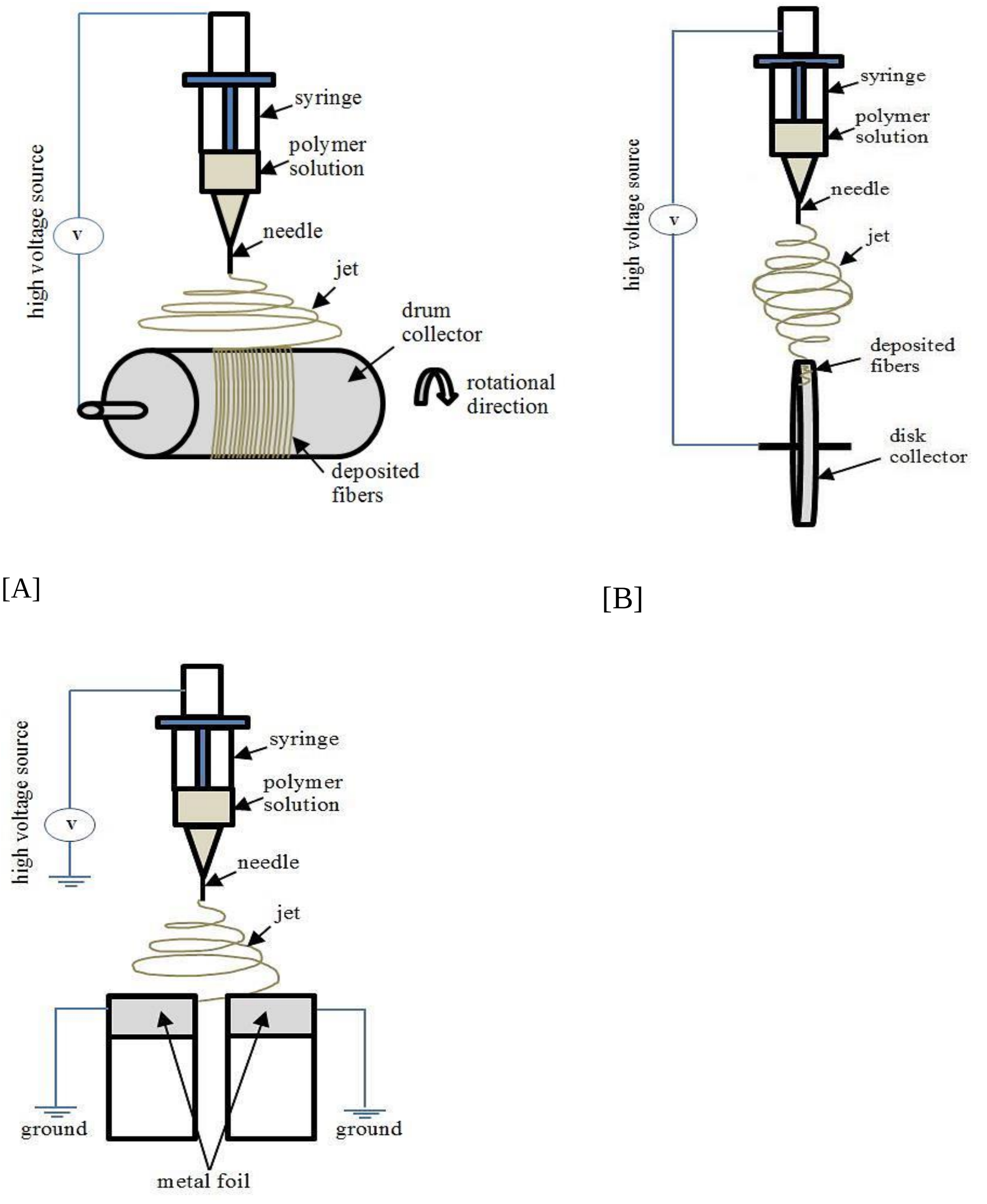
3.2.4 Effect of the collector

It has been determined that the collector material affects the morphology and the physical properties of obtained fibers. The most common collectors are metals, on which accumulated fibers are woven and randomly oriented. Conductive collectors determine also the fiber's location and packing density. Due to statical charges, the obtained fibers are more scattered, thereby allowing greater number of fibers to deposit on the collector. As a result the fibers are more closely packed together. In contrast, when the fibers are collected on the non-conductive collector, then the obtained fibers have a lower packing density. This is caused by poor dispersion of charges, which in turn creates repulsive forces resulting in sparsely packed fibers. [10]

In addition to conductive plate collectors, a rotating drum, a rotating disk and static parallel electrodes can be used. A rotating drum collector setup is schematically illustrated on Figure 5 [A]. This collector's main advantage is the opportunity to control the fiber's diameter and adapt it according to the drum's rotation speed. This method is mainly used to obtain aligned fiber membranes. [10]

Figure 5 [B] shows the rotating disk collector, which has a similar working principle as the rotating drum. However, the disk collector's advantage compared to the drum collector is that most of the fibers deposit on a sharp-edged disk, resulting in a network of patterned nanofibers. [10]

The main advantage of static parallel electrodes in comparison to other methods lies in its simplicity, because this technique enables to collect single fibers for mechanical testing. An air gap between the two electrodes helps to align the fibers, because it creates an electrostatic repulsion between the residual electrospun fibers. The apparatus of the parallel electrode method is schematically shown in Figure 5 [C]. [10]



[A]

[B]

[C]

Figure 5: Different types of collectors: [A] rotating drum; [B] rotating disk and [C] static parallel electrodes.

3.2.5 Needle inner diameter

It is known, that the smaller the size of the syringe needle or mouth of the pipette used in electrospinning, the lower the probability of blockage. The reason why less clogging occurs may be due the solution's smaller exposure to the air. It is also known that the orifice's inner diameter causes a reduction of the obtained fiber's diameter. This is due to the fact that the droplet size on the needle tip also decreases, therefore the surface tension of the droplet increases as the surface molecules start to influence each other with bigger tensile force, and thus requires greater electrostatic forces to create a solution jet and to begin pulling it towards the collector. The increased electrostatic force means that the acceleration and drawing of the jet increases and as the pulling force is stronger, resulting in smaller diameter fibers. However, the diameter of the orifice can not be too small, because then it may not be possible to push the solution droplet out of the needle orifice. [9]

3.3 Ambient parameters

The ambient parameters of electrospinning process include humidity, pressure and the composition of the environment. Unfortunately, the impact of environmental conditions on the electrospinning process is not very widely researched, still the impact of few parameters is determined. [15]

3.3.1 Humidity

Humidity can affect the electrospinning process. If the process is carried out in a normal atmosphere, but at high humidity, the water condenses on the fiber's surface, and it affects the morphology of the fiber, especially when the polymer is dissolved in a readily volatile solvent. Water condensation on the surface of the fiber slows the evaporation rate of the solvent, but the subsequent evaporation of water and the solvent will usually lead to pore formation in the fiber. The higher the humidity, the wider and deeper the pores. However, above a certain humidity the pores' diameter, depth and number will be satiated. One positive aspect of water is its ability to dissipate the static charges, making it possible to obtain more fibers on the collector. [14]

3.3.2 Pressure

The effect of pressure on the electrospinning process has been studied very little, but it is known that pressures, lower than the atmospheric pressure cause the polymer solution to flow out from the needle's tip faster and therefore resulting unstable jet formation. [15]

3.3.3 Environment

The electrospinning process is also affected by the composition of the surrounding environment, because different gases behave in the presence of electric field in different ways. For example, helium (He) breaks in the presence of a high electric field, in which electrospinning is not possible. However, if in the environment is a gas which has a high breakdown voltage, e.g. dichlorodifluoromethane, then the diameter of the obtained fibers is two times larger than fibers obtained just in the air environment at the same conditions. [15]

4. Ionic liquid [Bmim]Cl

ILs are generally described as molten salts, which are liquid at temperatures below 100^{o}C. ILs were first mentioned by Friedel and Crafts in a French scientific journal in 1877, where they described a reaction that resulted in a liquid that divided into two layers. The first synthesized IL was ammonium-based, which was reported by Gabriel in 1888. [22-23]

Until the late 1990s' ILs were mostly considered as rare. Nowadays ILs are not so uncommon anymore and the number of different ILs is increasing. Therefore the variety of methods and synthesis of ILs is also expanding. Some of the most common methods for IL preparation are: (i) alkylation, (ii) anion exchange, (iii) microwave and ultrasound-assisted synthesis, (iv) chiral synthesis and (v) halid-free synthesis. [23]

ILs are one of the fastest growing areas in recent years, with the aim to increase their use in various industries. The reason for the wide-spread interest in them, is mainly because of the unique physico-chemical properties of ILs and also due to their environmentally-friendly characteristics, which make them ideal canditates to replace volatile solvents. ILs are characterized by peculiar properties, such as high electrical conductivity, wide range of densities and viscosities, variable polarity and solubility, and high thermal and chemical stability. Moreover, ILs are good dispersants for fillers, soluble in most organic solvents, washable with water, reusable and non-volatile. They have a variety of uses in the nuclear industry, pharmaceuticals, petroleum industry, manufacturing of batteries and pulp processing. Despite the great number of uses, ILs are still not as widely used in industries as they could be, which is mainly due to their high price. [24-26]

Although ILs are not so extensively used in industries, they are still widely used at a laboratory level in different research and development projects. Therefore ILs are being used and studied also in the electrospinning process. It is known from the literature that the addition of an IL into the polymer solution, which is used in the electrospinning process, increases the solution's electrical conductivity, but does not decrease the obtained nanofiber's diameter. Instead it changes the fiber's structure from spindle-like to ribbon-like. The latter is formed, because ILs are non-volatile, thus some liquid component stays in the fiber after electrospinning, which causes the collapsing of the fiber's structure into a ribbon. [25]

Data of IL [Bmim]Cl, which was used in this research, can be seen in appendix 3.

5. Carbon nanotubes

CNTs are basically a tube-shaped materials of rolled graphene sheets, having a diameter in nanoscale and a length between 10 to 50µm. Formation of carbon filaments from the thermal decomposition of gaseous hydrocarbons was reported for the first time in 1889 and nowadays it is known that one step from the same production mechanism corresponds to the catalysed growth of a nanotube. However, the breakthrough came only in 1991, when Sumio Iijima wrote in his paper, that he has discovered CNTs. Since then CNTs have become one of the most studied materials in the world. [27]

5.1.1.1 Production and purification

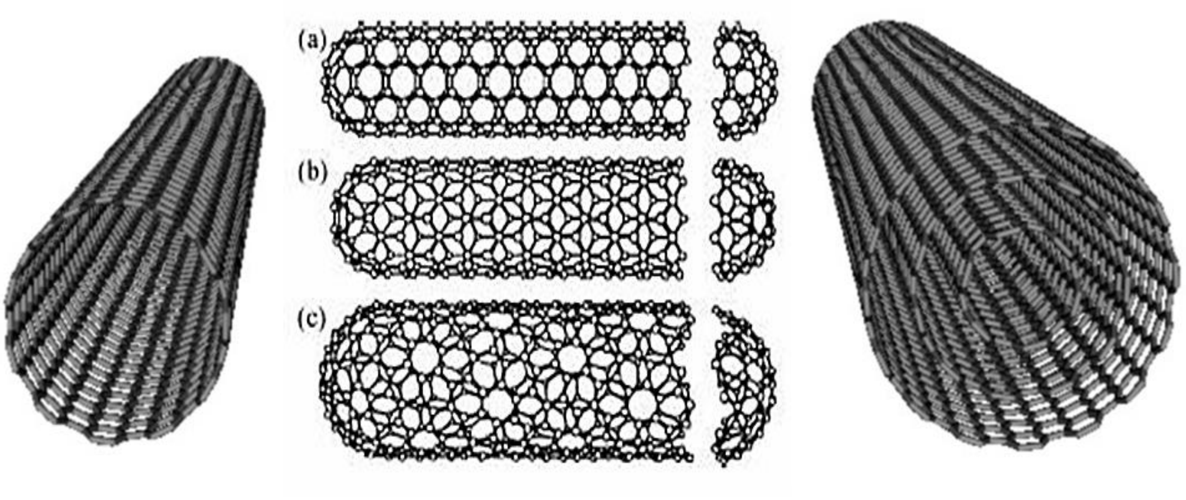
The production principle of CNTs is simple. All known production methods, such as carbon arc discharge, chemical vapor deposition (CVD), electrolysis, laser-vaporization and laser-ablation, involve carbon feedstock, metal catalysts and heat. The produced CNTs can be categorized by their structure as single-walled nanotubes (SWCNTs), multi-walled nanotubes (MWCNTs) and double-walled nanotubes (DWCNTs). [28]

The structure of a SWCNT can be envisioned as a layer of graphite, with a single atom thickness and coiled into a consistent chamber (see Figure 6 [A]). It is also possible to distinguish three different types of SWCNTs – armchair, zig-zag and chiral nanotubes (Figure 6 [B]). Most SWCNTs have a diameter close to 1 nm. [29-30]

MWCNT can look like either as a coaxial assembly of SWCNT or as a solitary sheet of graphite coiled into a roll (Figure 6 [C]). Due to the MWCNTs structure’s intricacy and diversity, its stucture is less well intelligible than the SWCNTs structure. However, the production of MWCNTs is simpler in higher quantities than the production of SWCNTs, which is also the reason why the price of SWCNTs is higher than MWCNTs. However, regions of structural defects may decrease the attractive properties of material. The diameters of MWCNTs are usually in the range of 5-50nm. [27, 31]

DWCNTs are an important sub-section of MWCNTs, similar morphology and properties of SWCNTs, implying that DWCNTs are a synthetic blend of both SWCNTs and MWCNTs. They exhibit the electrical and thermal stability of the MWCNTs and the flexibility of the SWCNTs. [32]

The production of CNTs usually involves catalytic particles, which means that produced CNTs are not entirely pure, containing some impurities like graphite nanoparticles, carbon black and fullerenes, depending on the production method. However, these impurities might be a problem for some applications. For instance impurities can change the electrical, chemical and electrochemical behavior of the tubes in technological applications, e.g those impurities might even cause cancer in biological applications. The solution to this problem is purfication and there are numerous techniques for that, such as oxidation, centrifugation, filtration, ultrasonication, microwave purification, annealing, acid-treatment and functionalization. [33-34]



[A] [B] [C]

Figure 6: [A] Structure of single-wall nanotube, [B] Different SWNT structures: (a) armchair, (b) zig-zig, (c) chiral, [C] Structure of multi-wall nanotube. [35-36]

5.1.1.2 Properties

CNTs demonstrate an exceptional blend of tenacity, stiffness and strength contrast to other fiber materials, which generally lack one or more of these properties. Tensile strength of CNTs is typically 11-63GPa and Young’s modulus 1TPa, which means that CNTs have remarkably good mechanical properties, being flexible and strong at the same time. However, these properties are still size-dependent and sensitive to the concentration of defects within the tube. The most common defects in the wall consist of pentagons or heptagons, which can induce elbows on a tube or allow junctions between tubes of different structures. [37-38]

Other significant characteristics of CNTs are its unique thermal and electrical properties. Electrical conductivity still depends strongly on the structure, which means that helicity of graphene sheet determines whether the CNT is a semiconductor or conductor. However, the electrical conductivity is higher in comparison to other conductive materials, like copper, aluminium, polyaniline or polypyrrole. [33, 39] Thermal conductivity of CNTs along its axis is very high, because vibrations of the carbon atoms propagate easily down the tube, making CNTs very good thermal conductors along the tube axis. Nonetheless, in the transverse direction of the tube axis, the nanotube is much less rigid and the thermal conductivity in that direction is about a factor of 100 smaller, making CNTs good insulators laterally to the tube axis. [40]

CNTs are also valued for their large surface area. A high diameter/length ratio gives CNTs a very good prospect to produce different composite structures in combination with polymers. Even when only small amounts of CNTs are applied, their exceptional properties are tranfered to the composite material. [41]

The main intrinsic drawback of CNTs is their insolubility, dispersion and poor compability with polymer matrix. Better dispersion of CNTs can be improved by using functionalizaton, ultrasonication, microfluidic processing, planetary shear mixing, a highly viscous solution/melt or choosing a compatible solvent or surfactant. [42-45]

5.1.1.3 Applications

Due to the good mechanical and conductive properties CNTs have a wide range of applications, which can be seen on Figure 7.

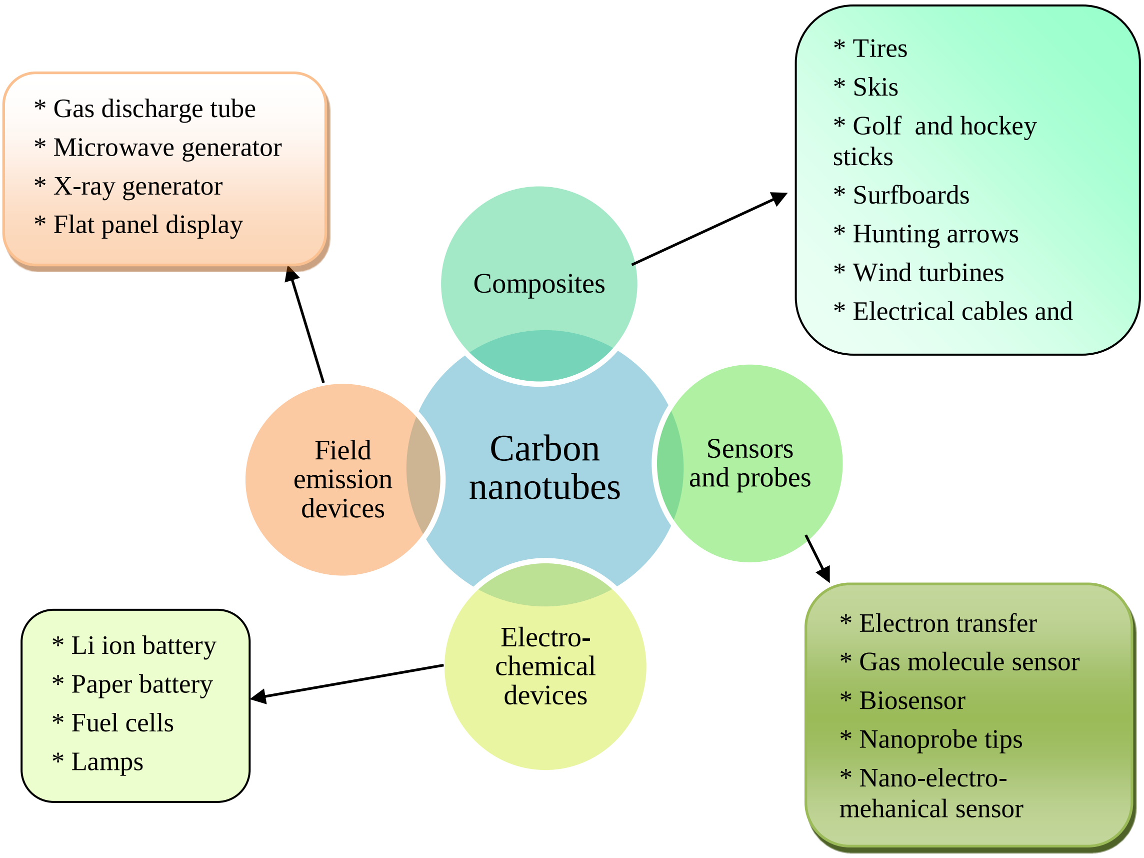


Figure 7: Applications of CNTs. [46-47]

6. Experimental part

6.1 Materials and methods

During this research the following solutions were investigated:

(i) Firstly, to find the best parameters for electrospinning SAN (Kostil B266, Polimeri Europe SRL, Italy) in DMSO (Emplura, Merck KGaA, Germany) solutions in different concentrations from 12.0 to 25.0% were made by mechanical mixing, with IKA Hotplate Stirrer C-MAG HS7 and magnetic stirring bar (length 50mm, diameter 12mm) (LaboChema, Estonia) at 50^{o}C for 8 hours.

(ii) Secondly, to investigate the impact of [Bmim]Cl on SAN in DMSO solution's properties, 20.0% SAN in DMSO solution with addition of 0.5 to 20.0% [Bmim]Cl were made. [Bmim]Cl concentration in the solution was calculated by weight of SAN in the solution. All solutions were prepared by mechanical mixing with an IKA Hotplate Stirrer C-MAG HS7 and magnetic stirring bar (length 10mm, diameter 6mm) (LaboChema, Estonia) at room temperature for 1 hour.

(iii) Thirdly, to study the impact of MWCNTs (NANOCYL^{TM} NC7000, Nanocyl s.a., Belgium) on the SAN solution's properties, solutions of 20.0% SAN in DMSO with 0.1-3.0% MWCNTs and 20.0% SAN in DMSO with 20.0% [Bmim]Cl and 0.1-3.0% MWCNTs were made. The amount of MWCNTs was taken by SAN weight in the solution. All solutions were mixed for 3 hours using an ultrasonicator BANDELIN SONOPULS HD 2070 (BANDELIN electronic GmbH & Co. KG, Germany) with a VS 70 probe, and for cooling, the solution flask was held in water during sonication. An illustative image of ultrasonicator can be seen on Figure 8 [A].

The ionic liquid [Bmim]Cl, used in this research, was synthesized in the laboratory of Tallinn Univesity of Technology, Department of Polymer Materials from 1 mole of 1-methyl imidazole (Merck Schuchardt OHG) and 1.5moles of 1-chlorobutane (Merck Schuchardt OHG) concentrations by mechanical mixing and flask fitted with a reflux condenser Hubner Ministat cc3 (Huber Kältemaschinenbau GmbH, Germany) at 80°C for three days. Afterwards two phases were formed, the upper phase, which contained reagents, was removed by washing it with ethyl acetate several times. The formed yellowish IL product of [Bmim]Cl was futher heated under vacuum at 50^{o}C, to remove all traces of ethyl actate solvent. [26, 48]

6.2 Electrospinning experiments

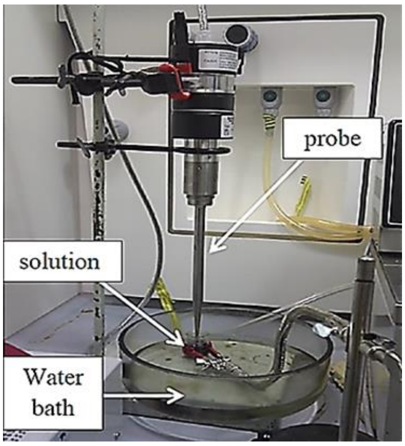
All prepared solutions were electrospun at an electrospinning setup (see Figure 8 [B]), that consisted of a high voltage device (Gamma High Voltage Research, Inc., USA), NE-1000 Single Syringe Pumping system (New Era Pump Systems, Inc., USA), 2ml syringe (Injekt®, B. Braun Melsungen AG, Germany) with needle of 15mm length and 0.6mm or 0.8mm outer diameter (Sterican®, B. Braun Melsungen AG, Germany). The obtained fibers were collected on a rotating drum, which was covered with aluminum foil with dimensions of 7x35cm. The distance between the needle tip and collector was 10 to 20cm and a high voltage of 20kV was used. All the equipment was placed under a fume hood.

6.3 Characterization

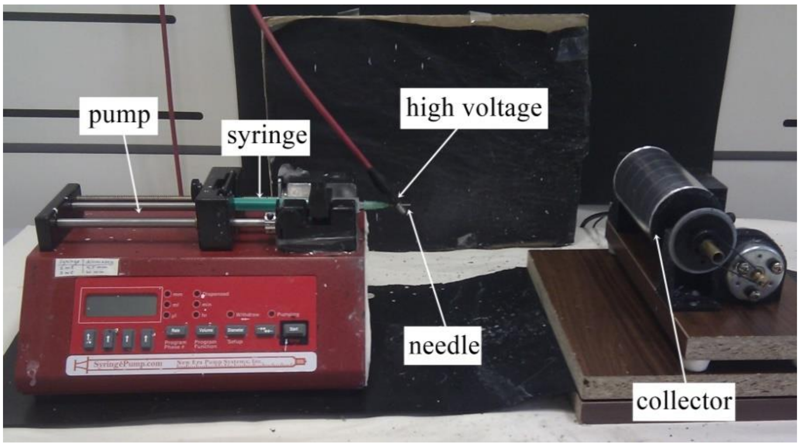
For each solution the viscosity was measured with concentric cylinder viscometer Brookfield RVDVII+ (Brookfield ENG LABS Inc., USA), using spindle nr 21 at 23.3°C. The temperature was held constant with a MGW Lauda C6 thermostat (Berner Osakyhtio, Finland). The solutions' electrical conductivities were measured with SevenCompact Conductivity S230 (Mettler Toledo, Switzerland) at room temperature.

The mechanical properties of membranes were measured at room temperature with Instron 5866 (Instron Corporation, USA) using the Bluehill™ 2 Version 2.17 software with a cross-head speed of 20mm/min and a clamps distance of 15mm. Th electrical conductivity of the membranes were measured with a High Resistance Meter Model HR2 (AlphaLab, Inc., USA) at room temperature. For both, the membrane's electrical conductivity and mechanical properties measurements were prepared six samples of each membrane with dimensions 5x25mm. The thickness of each sample was measured from three different places with a Sony U30-F Digital Indicator (Sony Magnescale Inc., Japan) and the average was calculated .

The morphology of the electrospun fibers was analyzed using a SEM microscope TM1000 (Hitachi High-Technologies Europe GmbH, Germany) and by a light microscope Axioskop 2 (Carl Zeiss AG, Germany). Illustrative images of all the used devices can be seen on Figure 8 [A]-[H].



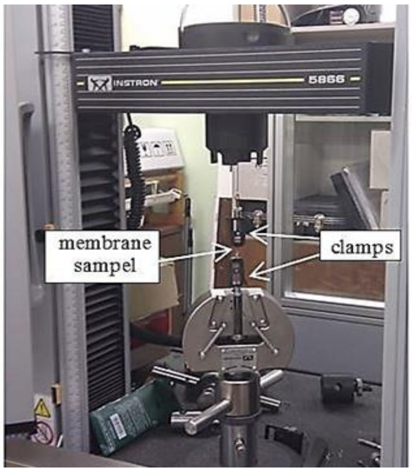
[A] Ultrasonication device Bandelin Sonopuls HD 2070 with probe configuration.



[B] Electrospinning setup.

[C] Concentric cylinder viscometer Brookfield RVDVII+.

[D] Electrical conductivity meter SevenCompact Conductivity S230.



[E] Instron 5866.

[F] Membrane electrical conductivity meter.

[G] Light microscope Axioskop 2.

[H] SEM microscope TM1000.

Figure 8: [A]-[H] Illustative images of used apparatus in research.

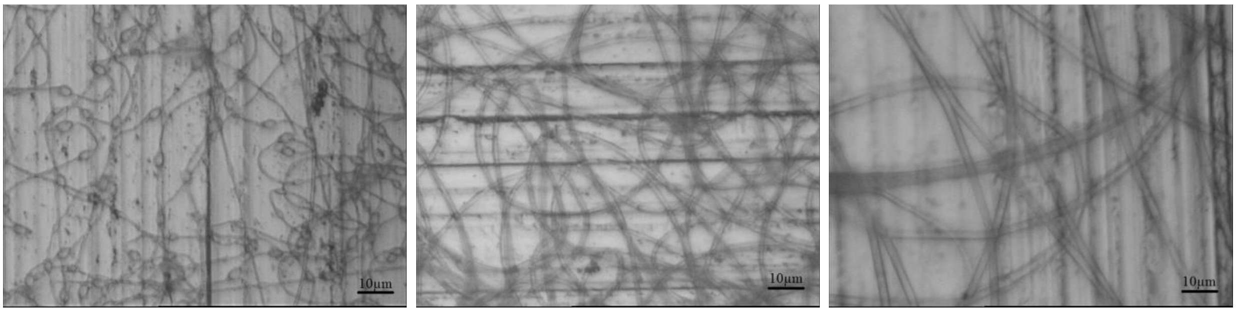
7. Results and discussion

7.1 Optimization of solution and process parameters for SAN in DMSO solution

To find out the most optimal SAN in DMSO solution concentration and electrospinning variables, solutions from 12.0 to 25.0% were prepared and electrospun at different parameters: at high voltages 10-20kV and distances 10-20cm. All the obtained fibers were investigated by optical microscopy (see Figure 9 and Figure 10).

7.1.1 Optimization of SAN solution concentration

While analyzing all the obtained fibers under a light microscope, it could be seen that for solution concentrations from 12.0 to 25.0%, the lower the concentration, the smaller the fiber diameter was, but at the same time the amount of solvent beads in the fibers increased as well (see Figure 9 [A]). The reason why fibers electrospun from lower concentration solutions have beads, is due to the fact that at lower concentrations higher amounts of solvent molecules and fewer chain entanglements of polymers are found, which also means that the surface tension of the solvent is higher than the interaction of solvent molecules with the polymer chains. This contributes to bead formation at lower solution concentrations. When the polymer’s concentration is increased, then the entanglement of polymer molecules during electrospinning also increases, resulting in higher diameter and smaller amount of beads, also changing the bead’s shape from spherical to spindle-like. Bead formation could not be seen, starting with a solution concentration of 20.0%. The increase in the average diameter of the fiber at higher concentrations (see Figure 9 [B]; [C]) is caused by the greater resistance of the solution to the stretching forces, as the amount of charged particles is decreased. Therefore, the solution’s concentration of 20.0% was chosen as the most optimal concentration for SAN in DMSO solution for further experiments.



[A] [B] [C]

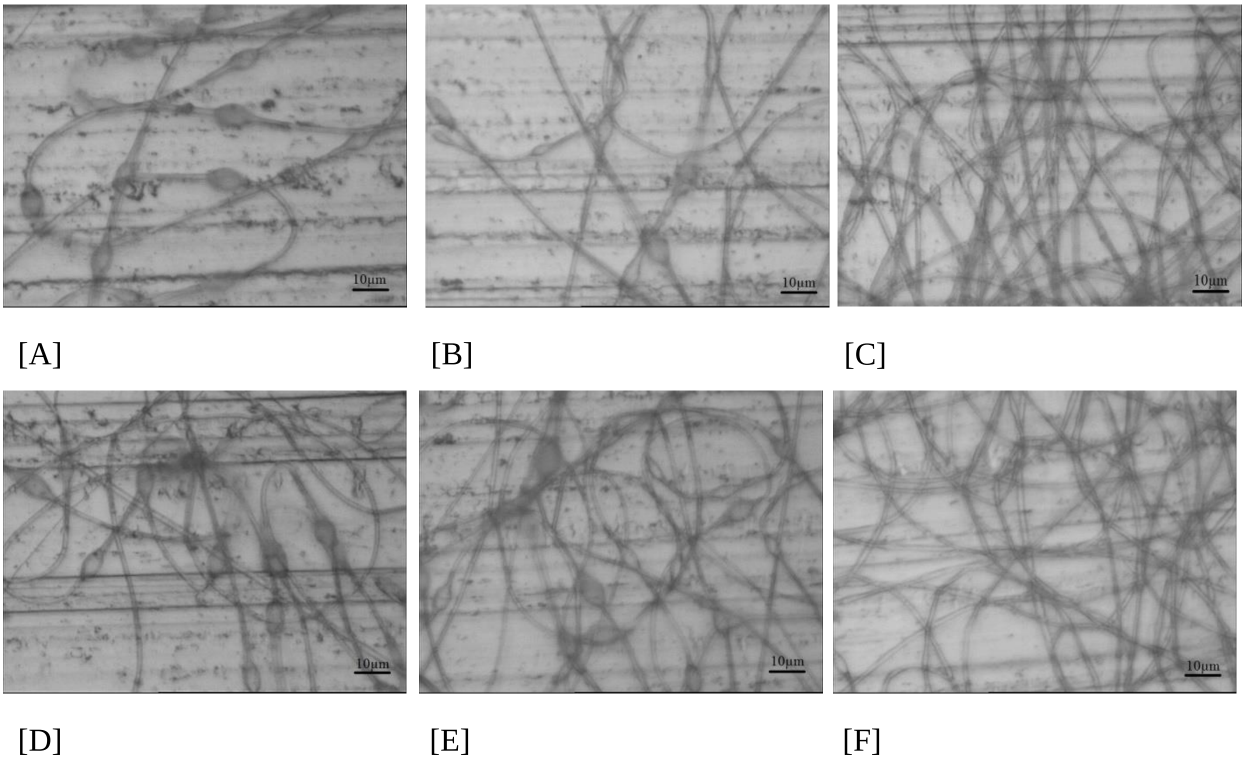
Figure 9: [A] 15.0% SAN in DMSO 20kV 20cm 0.07ml/h; [B] 20.0% SAN in DMSO 20kV 20cm 0.06ml/h; [C] 25.0% SAN in DMSO 20kV 20cm 0.07ml/h. Images are taken with a light microscope.

7.1.2 Optimization of SAN solution electrospinning variables

In order to find the most optimal electrospinning variables for 20.0% SAN in DMSO solution, the solution was electospun at 10-20kV, 10-20cm and 0.04-0.09ml/h (see Figure 10). It can be seen from the optical microscope images, that the solutions electrospun at 10 and 15kV gave fibers with beads, but fibers electrospun at 20kV were bead-free (Figure 10 [A]-[C]), which means that the most optimal electrospinning voltage is 20kV. Beads formation under 20kV is caused by too high pumping speeds and too low voltage, which both affect jet instability. As the feedrate is too high a lot of solution will be on the needle's tip, and as the voltage is not sufficiently high, then the stretching of the solution is not strong enough nor stable, leading to jet instability and in turn causing bead formation.

Electrospinned solutions at different distances can be seen on Figure 10 [D]-[F]. The most optimal distance is 20cm, because there were beads in the fibers at distances 10 and 15cm. The beads in the fibers can be caused by too small distances between the needle's tip and the collector, as decrease in distance has the same effect as increasing the high voltage. This in turn increases the electric field strength and also increases jet instability, which can cause bead formation. Moreover, the time for the solution jet to move towards the collector is also shorter and due to that, the solvent may not have enough time to evaporate entirely, therefore also contributing bead formation.

Therefore for further experiments 20kV and 20cm were chosen as the most optimal electrospinning variables for 20.0% SAN in DMSO solution.



[A] [B] [C]

[D] [E] [F]

Figure 10: 20.0% SAN in DMSO on different variables: [A] 10kV 20cm 0.9ml/h; [B] 15kV 20cm 0.09ml/h; [C] 20kV 20cm 0.06ml/h; [D] 20kV 10cm 0.04ml/h; [E] 20kV 15cm 0.06ml/h; [F] 20kV 20cm 0.06ml/h; Images are taken with a light microscope.

7.2 Impact of [Bmim]Cl on SAN in DMSO solution electrical conductivity, viscosity and morphology of obtained material

One way to avoid bead formation in the obtained fibers is by increasing the solution’s electrical conductivity, i.e by introducing new charged particles into the electrospinning solution, which as a consequense increases the stretching force of the electrospinning jet. As ILs consist of ions, then [Bmim]Cl was chosen for further experiments.

The solutions of 20.0% SAN in DMSO with 0-20.0% [Bmim]Cl were prepared and electrospun to investigate how different contents of [Bmim]Cl in the solution affect the solution’s properties and obtained nanofibers, and also find out what is the optimal content of [Bmim]Cl in the solution. Solutions viscosities, electrical conductivities and the electrospun fiber’s morphology were studied. All results are presented on Figure 11 and Figure 12.

7.2.1 Solution viscosity and electrical conductivity

As can be seen from the viscosity diagram, if the [Bmim]Cl content increases, then the solution’s viscosity decreases. This is related weak hydrogen bonds in DMSO, which in turn decreases the intermolecular interactions resulting from [Bmim]Cl dilution in DMSO. [49]

The same phenomena is also described in G. Yanfang et al’s article [50], where the authors studied viscosities and densities of 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) and N,N-dimethylformamide (DMF) binary mixtures.

The results of electrical conductivity measurements of 20.0% SAN in DMSO with 0-20.0% [Bmim]Cl solutions show that while increasing [Bmim]Cl concentrations from 0 up to 20.0%, an increase in the electrical conductivity of SAN solution from 0.854 up to 1698µS/cm could be seen. This can be explained with the fact that [Bmim]Cl is a salt and consist of a large $[Bmim]^+$ cation and small Cl^- anion. While introducing [Bmim]Cl into the SAN in DMSO solution, the ionic pairs dissociate in DMSO, therefore increasing the number of charge carriers. In brief, with increasing amount of [Bmim]Cl in the solution, the electrical conductivity of the solution also increases.

7.2.2 Morphology

The investigation of the obtained fibers with SEM microscopy showed that the addition of [Bmim]Cl into the solution, changes the fiber’s structure from spindle-like into ribbon-like. This can be explained by the fact that IL does not evaporate and due to that some liquid component remains inside the fiber after electrospinning. This causes the fiber’s walls stick together from inside and therefore changing the structure into ribbon-like. However, by increasing [Bmim]Cl content, a decreases in the average fiber diameter can be seen. This can be explained by the fact that addition of [Bmim]Cl increases the electrical conductivity of the solution, thus there are more free charge carriers and due to that, the stretching of the solution jet is stronger during electrospinning. Also with increasing [Bmim]Cl content the diameter also fluctuates less. For futher experiments the 20.0% [Bmim]Cl concentration was chosen to be the most optimal.

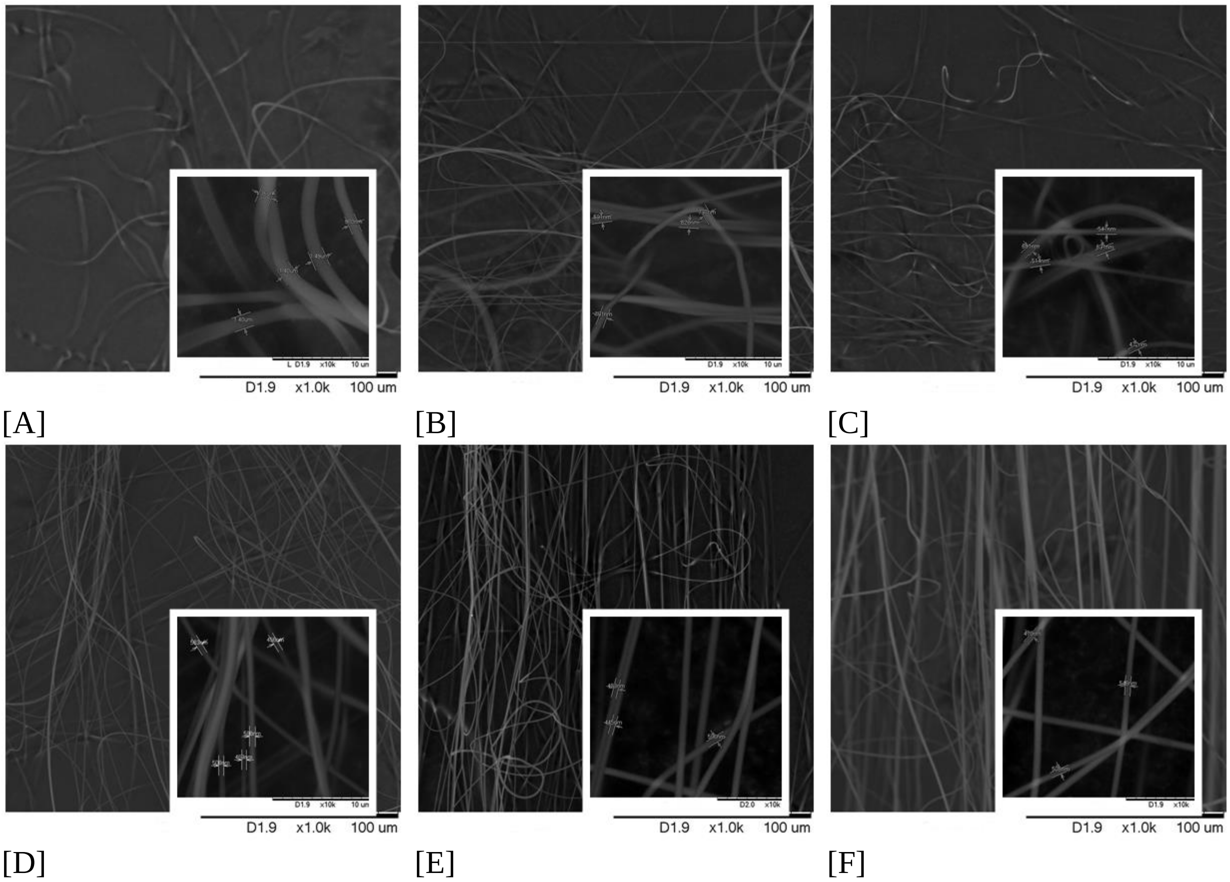


Figure 11: 20.0% SAN in DMSO with different [Bmim]Cl content: [A] - 0%; [B] – 2.0%; [C] – 5.0%; [D] – 10.0%; [E] – 15.0%; [F] - 20.0%. All fibers are obtained at the same variables 20kV, 20cm, 0.3ml/h and all images are taken with SEM.

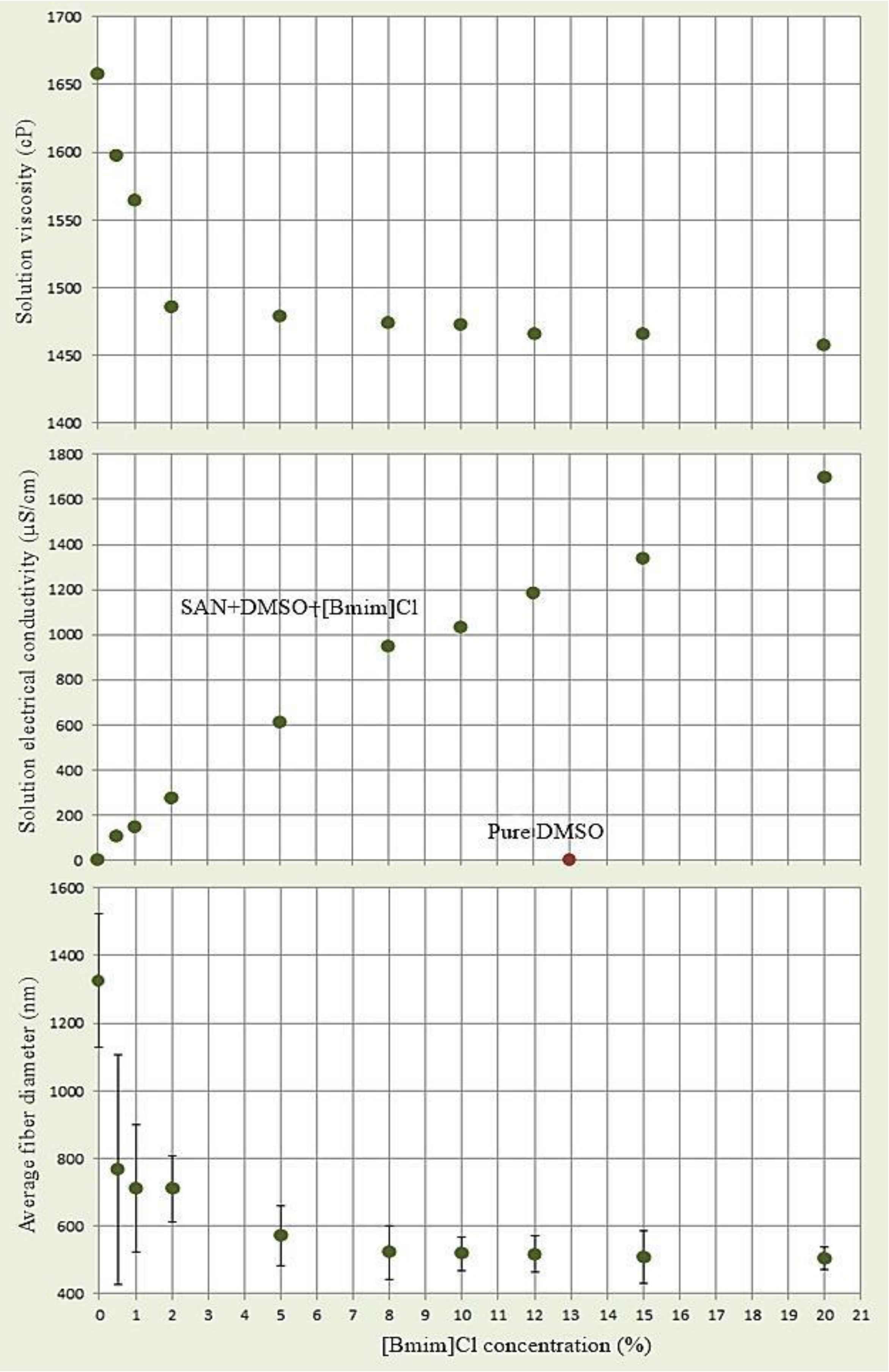


Figure 12: Viscosity, electrical conductivity and average fiber diameter dependence on [Bmim]Cl content in 20.0% SAN in DMSO solution.

7.3 Impact of MWCNTs on SAN in DMSO solution viscosity and electrical conductivity

To investigate the impact of MWCNTs and the role of [Bmim]Cl as dispersant for nanotubes, 20.0% SAN in DMSO with and without addition of 20.0% [Bmim]Cl were mixed with 0.1-3.0% MWCNTs. Viscosities and electrical conductivities of the prepared solutions were measured. All the results are presented on Figure 13.

7.3.1 Solution viscosity

It can be seen from the viscosity diagram that when the MWCNTs content increases in both solutions with and without [Bmim]Cl, then the viscosity also increases, which is caused by MWCNTs dispersion in the solution, because CNTs are entangled with the polymer chains. The higher the CNTs content, the higher the solution's viscosity. The same phenomena is described in C. Seoul et al's article [51], where the authors studied the viscosity of PVDF/DMF solutions with various CNT concentrations.

While comparing the solutions with and without [Bmim]Cl, it could be seen, that solutions with [Bmim]Cl have lower viscosities than solutions without [Bmim]Cl. Solution viscosity without [Bmim]Cl increased from 1537cP at 0% concentration up to 3436cP at 20.0% concentration, while viscosity of solutions containing [Bmim]Cl increased from 1184cP up to 1742cP at the same concentrations. The same phenomena was also found while investigating the impact of [Bmim]Cl on SAN in DMSO solution, where it could be seen that the higher the [Bmim]Cl content in the solution, the lower the viscosity.

7.3.2 Solution electrical conductivity

From the electrical conductivity diagram it can be seen that, for both solutions, with and without [Bmim]Cl, the higher the MWCNTs content, the higher to solution electrical conductivity. This can be explained by the conductive nature of CNTs, thus the higher the CNTs content in the solution, the higher the solution's electrical conductivity.

However, when comparing the electrical conductivities of solutions with and without [Bmim]Cl, it can be seen that the electrical conductivity without [Bmim]Cl increases from 0.854µS/cm at 0% up to 5.09µS/cm at 3.0% of MWCNTs. While the electrical conductivity of solutions with [Bmim]Cl increases from 178µS/cm at 0% up to 209µS/cm at 3.0% of MWCNTs. This marked difference between with and without [Bmim]Cl solutions is caused by the fact that [Bmim]Cl dissociates into ions in DMSO, and the amount of charge carriers increases accordingly.

Futhermore, the solutions with and without [Bmim]Cl at 0.1% MWCNTs content have basically the same conductivity as either the pure 20.0% SAN in DMSO or 20.0% SAN in DMSO with 20.0% [Bmim]Cl solution, which means that the CNTs content in the solution is not high enough to affect the solution’s electrical conductivity. From the graph it can also be seen that there is a abrupt rise from 0.1 up to 1.0% of MWCNTs in solutions without [Bmim]Cl. Starting from 1.0% of MWCNTs the rise is not so rapid anymore, only 0.78µS/cm from 1.0% up to 3.0% MWCNTs concentration. This means that at 1.0% of MWCNTs the SAN in DMSO solution without [Bmim]Cl is saturated and further dispersion of MWCNTs is not effective. A rapid rise in the electrical conductivity of the solution with [Bmim]Cl from 0.1 up to 1.0% of MWCNTs could be seen, but after 1.0% of MWCNTs the dependence becames linear until 3.0% of MWCNTs. This can be explained with the effect of [Bmim]Cl. [Bmim]Cl works as a sufficient dispersant for MWCNTs and helps to diminish the number and size of MWCNTs bundles in the solution. Moreover, it helps the formation of conductive networks between single and bundles of MWCNTs, therefore improving solution’s electrical conductivity.

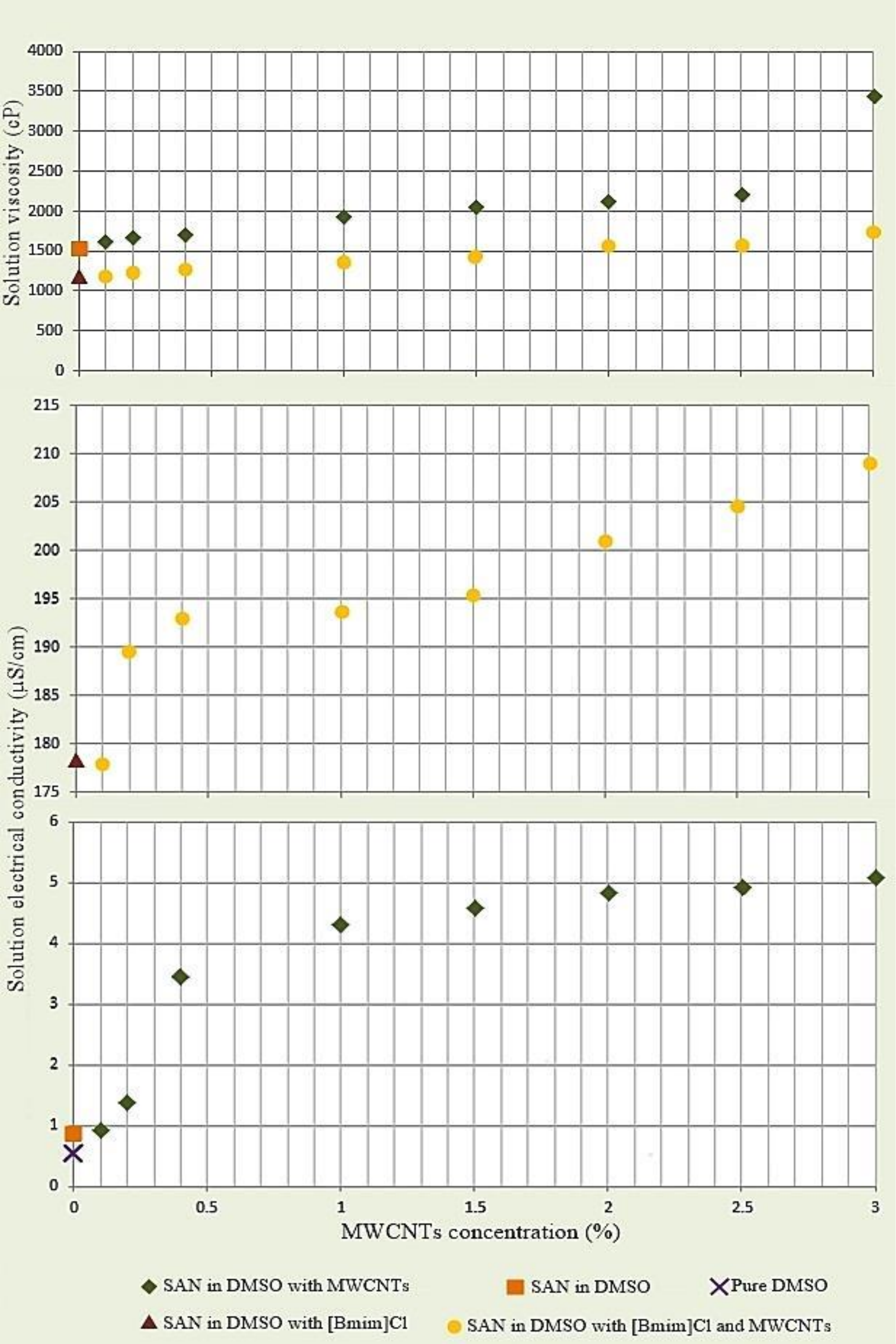


Figure 13: Solution viscosity and electrical conductivity dependence on MWCNTs content in SAN solutions with and without [Bmim]Cl.

7.4 Impact of MWCNTs and [Bmim]Cl on SAN membrane’s electrical conductivity, mechanical properties and obtained fibers morphology

To investigate the impact of MWCNTs on the SAN membrane’s electrical conductivity, mechanical properties and the morphology of the obtained nanofibers, membranes consisting of 20.0% SAN in DMSO with 0.1-3.0% MWCNTs were electrospun. In order to study the effect of [Bmim]Cl on the afromentioned materials, membranes consisting of 20.0% SAN in DMSO with 20.0% [Bmim]Cl and 0.1-3.0% MWCNTs were prepared, and their electrical conductivity, mechanical properties and the obtained fibers’ average diameter was measrued. All the results are presented on Figure 14.

7.4.1 Membrane electrical conductivity

It can be seen from the membrane’s electrical conductivity diagram, that a pure SAN membrane is not conductive, as polymers are generally isolators. In fact all of the SAN membranes with 0.1-3.0% MWCNTs are not conductive. According to the percolation theory, when the content of CNTs is low, the CNTs distribute randomly in the matrix and do not form a conductive network. However, as [Bmim]Cl works as a dispersant for MWCNTs in SAN solutions, then it helps to create the network between single MWCNTs and agglomerates of MWCNTs in electrospun membranes, and as a result makes the membrane conductive. [52] Raising the MWCNTs content also increases the membrane’s electrical conductivity in [Bmim]Cl containing membranes from 0.244μS/cm at 0% of MWCNTs up to 5.954μS/cm. This can be explained with the conductive nature of CNTs and [Bmim]Cl.

7.4.2 Membrane mechanical properties

Firstly, it can be seen from the tensile stress diagram, that the tensile stress of pure SAN membrane is 2MPa and the addition of [Bmim]Cl increases the membrane tensile stress up to 4.8MPa. Such increase is caused by the increased electrical conductivity of the electrospinning solution due to addition of [Bmim]Cl, which in turn increases the stretching force. Therefore during electrospinning the polymer molecules place more regularly, which increases the crystallinity in the obtained fibers, which in turn improves the membrane’s mechanical properties.

From the figure, it can also be seen, that the tensile stress of membranes containing [Bmim]Cl grows with increasing amounts of MWCNTs until it peaks at 1.0% of MWCNTs concentration and then decreases distinctively. This phenomena is caused by the usage of

[Bmim]Cl as a dispersant of MWCNTs during electrospinning, which helps to create more uniform dipersion of single MWCNTs and by that improve the strength of membrane. However, the decrease of the membrane's tensile stress, with amounts higher than 1.0% of MWCNTs is caused by the repletion of MWCNTs in the solution, resulting in micro-crack diffusion in membrane and deterioration of the membrane's mechanical properties. [53] Moreover, the decrease in the tensile stress of the membrane can also be explained with the increase in the solution's viscosity, while adding MWCNTs. Since, higher viscosity means that electrospinning jet presents greater resistance to the charges trying to stretch the jet, resulting in more irregular polymer molecules placements in the obtained fiber and consequently membranes with lower tensile stress. It can be concluded that dispersion of MWCNTs is only efficient until 1.0% of MWCNTs in the solution.

It can be seen from the tensile stresses diagram of [Bmim]Cl free membranes that for all MWCNTs concentrations from 0.1 to 3.0%, the membranes tensile stress was lower in comparison to the pure SAN membrane. Moreover, there is no dependence between the MWCNTs content in the membrane and the tensile stress of the membrane, which may be caused by the insufficient dispersion of MWCNTs into SAN in DMSO solution. Due to that, the obtained fibers contain bundles of MWCNTs, which create areas of defects that cause membrane fractures during applied stress, leading to decrease in the membrane's mechanical properties. [54]

7.4.3 Morphology of obtained membranes

During this research, it was found that the solution preparation method has a certain effect on the obtained fiber's average diameter. From the Figure 14 it can be seen that the addition of 20.0% [Bmim]Cl into pure 20.0% SAN in DMSO solution decreases the average fiber diameter from 862nm to 720nm. Although the aforementioned solutions were prepared using ultrasonication, the average diameters of fibers demonstrated on Figure 12 were electrospun from mechanically mixed solutions instead. At [Bmim]Cl concentrations of 0% and 20.0%, the average fiber diameters are 1326nm and 504nm, accordingly. The reason why the average diameter is smaller for solutions prepared by the ultrasonication method, is that ultrasonication destroys the longest polymer macromolecules, which in turn decreases the solution's viscosity and the resistance to stretching forces, resulting in SAN in DMSO obtained fibers diameters to decrease from 1326nm to 862nm at 0% concentration of [Bmim]Cl. [55] Moreover, sonication also degrades the imidazolium-based ILs into hydrogen peroxide and acetic acid, which are relatively innocuous compounds, and this in turn lowers the solution’s electrical conductivity i.e. there are fewer charges in the solution jet during electrospinning. The result is weaker stretching, which leads to fibers with a larger diameter at the 20.0% concentration of [Bmim]Cl. [56]

While studying the impact of MWCNTs on the morphology of the obtained fibers, it was found that by increasing the content of MWCNTs in SAN in DMSO solution with [Bmim]Cl, the obtained fiber’s diameter decreases from 720nm at 0% of MWCNTs to 291nm at 1.0% of MWCNTs. This effect can be explained with the addition of MWCNTs, which diminishes the resistance of the polymeric system, and in turn advances the electrical conductivity and charge density of the jet during electrospinning. These impacts promote elongation of the fibers during formation, resulting in fiber diameter decrease. [57] However, over 1.0% of MWCNTs content, the obtained fibers’ diameter starts to increase again, which is caused by the increased viscosity of the solution. A higher viscosity means a greater resistance to charges that try to stretch the electrospinning jet, and due to that the obtained fiber’s diameter increases.

Lastly, it was found that the average diameter of fibers obtained from SAN in DMSO and MWCNTs electrospinning solutions, is higher compared to fiber diameters obtained from the pure SAN in DMSO solution. This can be explained with the viscosity increase, of adding MWCNTs into the solution, resulting in increased fiber diameters. However, there is no dependence between the MWCNTs content and the obtained fiber’s diameter. These results can be caused by poor dispersion of MWCNTs into the SAN in DMSO solution, and due to that, the obtained fibers contain MWCNTs agglomerates, which leads to fluctuation in the fiber’s diameters. From the SEM images it can also be seen, that in both cases fibers obtained from solutions with and without [Bmim]Cl contain beads at MWCNTs concentrations higher than 1.0%. This effect is probably due to an unstable solution jet during electrospinning, which in turn is caused by the poor dispersion of CNTs. [58] The higher the CNTs concentration, the greater the amount and size of CNTs bundles and the greater the jet instability.

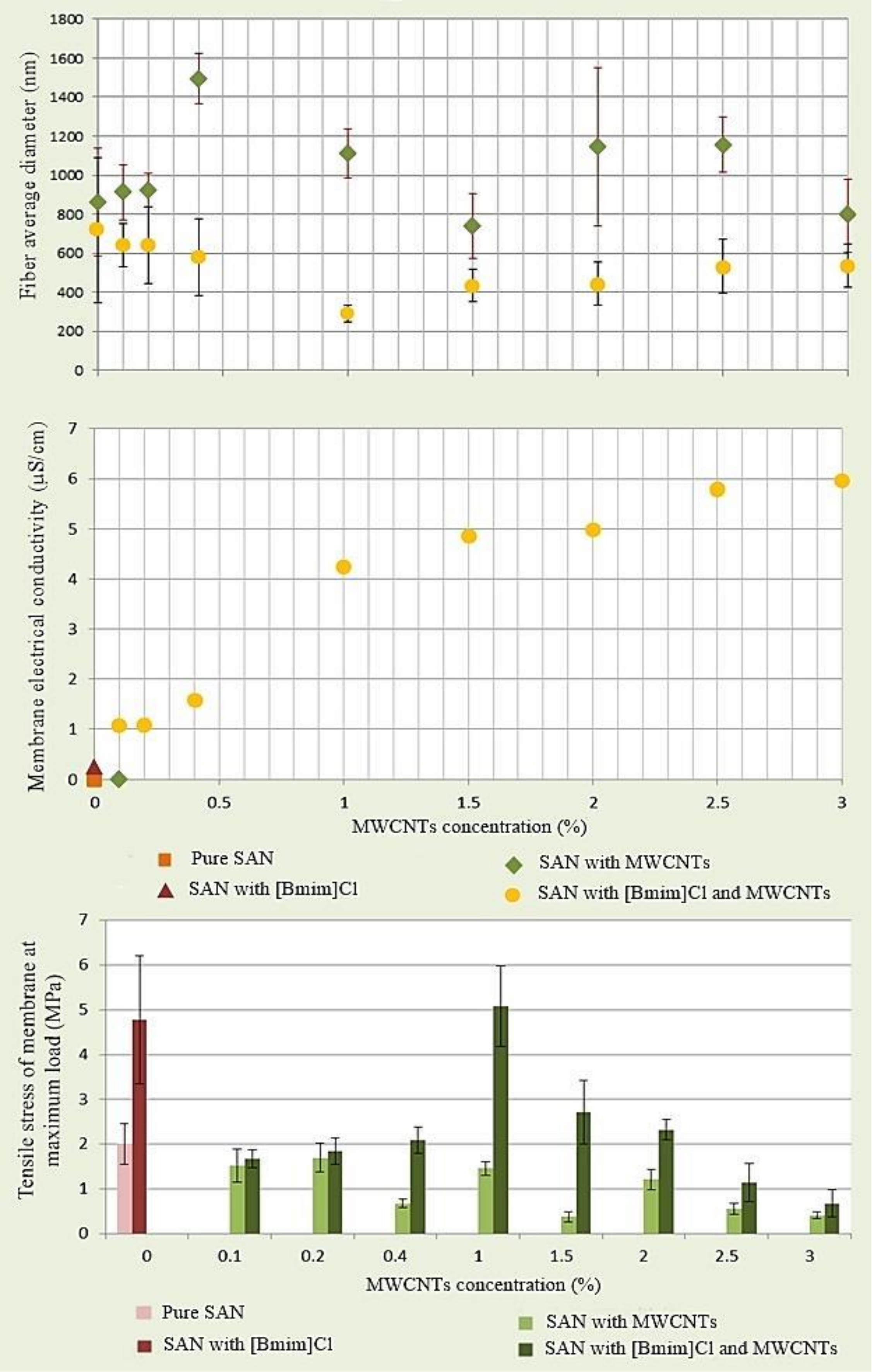
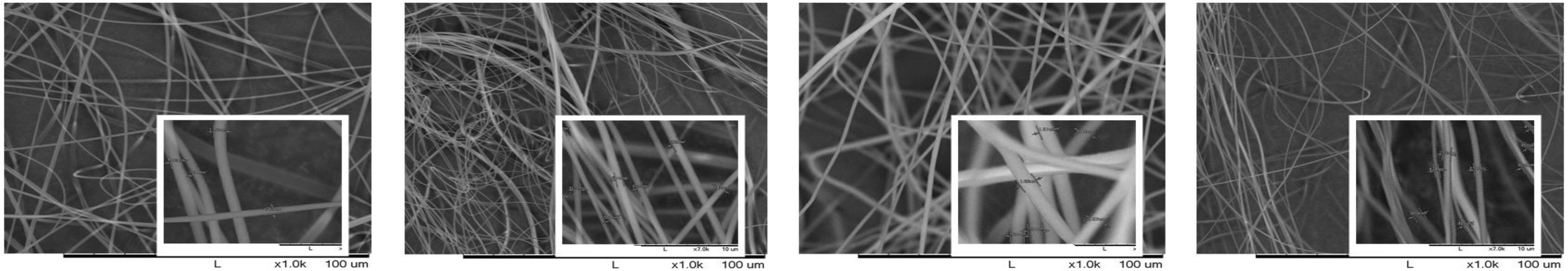


Figure 14: SAN membrane fibers average diameter, electrical conductivity and mechanical properties dependence on MWCNTs content, with and without [Bmim]Cl.

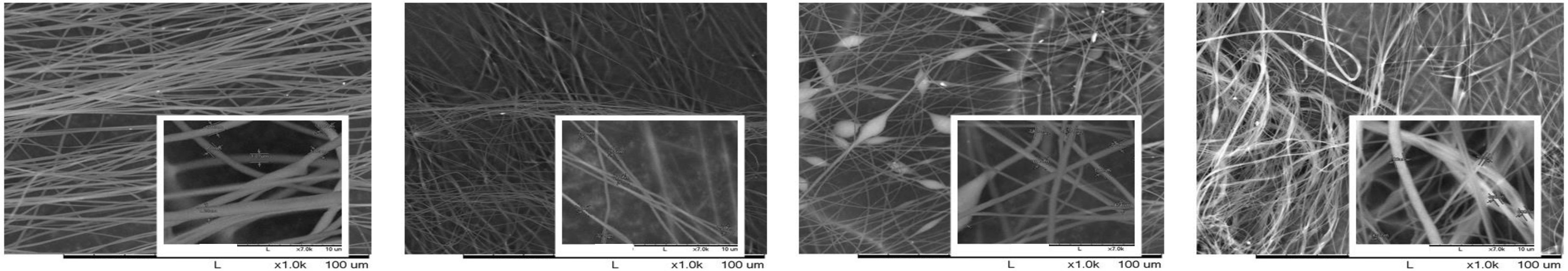


[A] SAN + 0.1.0% MWCNTs

[B] SAN + 20.0% [Bmim]Cl + 0.1% MWCNTs

[C] SAN + 0.4% MWCNTs

[D] SAN + 20.0% [Bmim]Cl + 0.4% MWCNTs

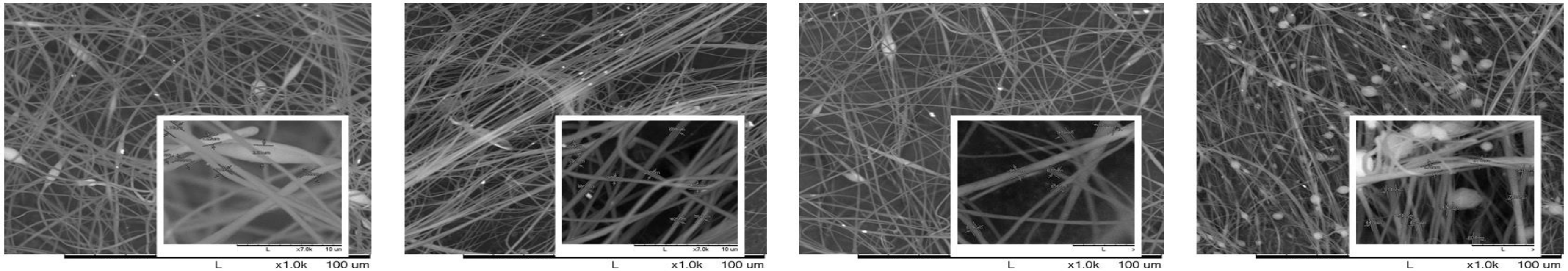


[E] SAN + 1.0% MWCNTs

[F] SAN + 20.0% [Bmim]Cl + 1.0% MWCNTs

[G] SAN + 1.5% MWCNTs

[H] SAN + 20.0% [Bmim]Cl + 1.5% MWCNTs



[I] SAN + 2.5% MWCNTs

[J] SAN + 20.0% [Bmim]Cl + 2,5% MWCNTs

[K] SAN + 3.0% MWCNTs

[L] SAN + 20.0% [Bmim]Cl + 3.0% MWCNTs

Figure 15: SEM micrograph of SAN two types of fibers, with and without [Bmim]Cl, with different MWCNTs concentrations (0.1-3.0%).

Conclusions

The aim of this research was to study how the electrospinning process, the morphology, electrical conductivity and mechanical properties of the obtained membranes are affected by the addition of MWCNTs and IL [Bmim]Cl into SAN in DMSO electrospinning solution.

Firstly, was found that the most optimal SAN in DMSO solution concentration is 20.0% and the best electrospinning parameters are 20kV and 20cm. Secondly, the impact of [Bmim]Cl on SAN in DMSO solution was elaborated. It could be inferred from the experiments that by increasing the [Bmim]Cl content in the solution, the electrical conductivity of the solution increases, while the solution viscosity and the average diameter of the obtained fibers decreases. Therefore the 20% [Bmim]Cl concentration was chosen as the most optimal for futher studies.

Thirdly, was studied the impact of MWCNTs with and without [Bmim]Cl on SAN in DMSO solutions and membranes. Experiments showed that by increasing the MWCNTs content in both solutions, with and without [Bmim]Cl, the viscosity and electrical conductivity of the solution increased. However, only membranes with [Bmim]Cl were conductive and with increasing MWCNTs content, the electrical conductivity of membranes increased. Membranes without [Bmim]Cl were not conductive. The tensile stress of membranes containing [Bmim]Cl increased with increasing MWCNTs content, until it reaches its peak 1.0% of MWCNTs, after that the tensile stress decreased. There was no dependence between MWCNTs content and tensile stress in membrane’s without [Bmim]Cl. The diameter of fibers made of [Bmim]Cl containing solutions decreased with increasing MWCNTs content until 1.0% of MWCNTs and increased distinctively after that, while fibers obtained from [Bmim]Cl free solutions did not show fiber diameter dependence on MWCNTs content. However, SEM investigations showed that in both cases, with and without [Bmim]Cl obtained fibers contained beads at MWCNTs concntration higher than 1%.

The goal of this research was achieved, as the impact of MWCNTs and [Bmim]Cl to the SAN in DMSO electospinning solution and obtained membranes was elucidated. In the future it will be possible to study the mechanical properties and morpholgy of membranes, after IL is washed out from the membrane, as IL is washable with water. Moreover, try to polymerize IL inside the obtained fiber, to improve fiber’s processability, flexibility and durability.

Abstract

The impact of carbon nanotubes and ionic liquid on the properties of electrospinning solutions and obtained membranes

The aim of the master thesis was to investigate how addition of MWCNTs and [Bmim]Cl into SAN in DMSO solution affects the properties of electrospinning solution and obtained membranes. Solutions with [Bmim]Cl concentration from 0% up to 20.0% w/w from SAN content were prepared, to study the impact of [Bmim]Cl. To investigate the impact of MWCNTs, two types of SAN in DMSO with MWCNTs solutions were prepared, with and without [Bmim]Cl. MWCNTs concentration in both types of solutions was 0% up to 3% w/w from SAN content. In both cases, studying the impact of [Bmim]Cl and MWCNTs with and without [Bmim]Cl, for all the solutions viscosity and electrical conductivity was measured, and all the obtained fibers were investigated by SEM analysis. Furthermore, electrical conductivity and tensile stress at maximum load was also measured for obtained membranes containing MWCNTs, with and without [Bmim]Cl.

Investigations showed that addition of [Bmim]Cl helps to obtain more uniform nanofibers during electrospinning, as the solution electrical conductivity increases, while solution viscosity and fiber's diameter decreases with increasing [Bmim]Cl content in the solution. Moreover, experiments also showed that [Bmim]Cl assists better dispersion of MWCNTs, which in turn improves the electrical conductivity and mechanical properties of electrospun membranes. However, addition of [Bmim]Cl into the solution is sufficient until 1.0% of MWCNTs concentration. Membranes containing only MWCNTs were not electrically conductive in all MWCNTs concentrations and there was no dependence between tensile stress and MWCNTs concentration, as well as between fiber's average diameter and MWCNTs concentration.

The impact of [Bmim]Cl and MWCNTs on the properties of electrospinning solutions and obtained membranes is significant. The properties are most improved, when both [Bmim]Cl and MWCNTs are used, however until 1.0% of MWCNTs concentration.

This thesis is written in english and is 55 pages long, including 7 chapters, 15 figures and 2 tables.

Resümee

Süsiniknanotorude ja ioonvedeliku mõju elektrokedratavate lahuste ja saadud membraanide omadustele

Töö eesmärgiks oli uurida, kuidas mõjutavad mitmeseinaliste süsiniknanotorude ja ioonvedeliku [Bmim]Cl lisamine SAN DMSO-s lahusesse elektrokedratavate lahuste ja saadavate membraanide omadusi. [Bmim]Cl mõju uurimiseks valmistati lahused erinevate [Bmim]Cl konsentratsioonidega, 0% kuni 20.0% SAN-i kogusest lahuses. Mitmeseinaliste süsiniknanotorude mõju uurimiseks valmistati kahte tüüpi lahused, mitmeseinalised süsiniknanotorud koos ja ilma [Bmim]Cl-ta. Mitmeseinaliste süsiniknanotorude kontsentratsioon mõlemat tüüpi lahustes jäi vahemikku 0% kuni 3.0% SAN-i kogusest lahuses. Kõigi lahuste puhul, uurides [Bmim]Cl ning mitmeseinaliste süsiniknanotorude mõju koos ja ilma [Bmim]Cl-ta, mõõdeti lahuse viskoossust ja elektrijuhtivust ning vaadeldi kõiki saadud nanokiude ka skanneeriva elektronmikroskoobi all. Lisaks mõõdeti mitmeseinalisi süsiniknanotorusid sisaldavate membraanide, koos ja ilma [Bmim]Cl-ta, elektrijuhtivust ning tõmbetugevust maksimaalse koormuse juures.

Katsete käigus selgus, et [Bmim]Cl aitab elektroketruse protsessil saada ühtlasemaid nanokiude, kuna lahuse elektrijuhtivus suureneb ja viskoossus ning keskmine kiu diameeter väheneb [Bmim]Cl kontsentratsiooni kasvuga lahuses. Lisaks aitab [Bmim]Cl mitmeseinalisi süsiniknanotorusid lahusesse paremini dispergeerida, mis omakorda parandab elektrokedratud membraanide elektrijuhtivust ning mehaanilisi omadusi, kuid [Bmim]Cl lisamine lahusesse on efektiivne kuni 1.0% mitmeseinaliste süsiniknanotorude kontsentratsioonini. Membraanid, mis sisaldasid ainult mitmeseinalisi süsiniknanotorusid ei olnud elektrit juhtivad kõigi mitmeseinaliste süsiniknanotorude kontsentratsioonide juures ning samuti ei esinenud mingit sõltuvust tõmbetugevuse ja mitmeseinaliste süsiniknanotorude kontsentratsiooni vahel, ega ka keskmise kiu diameetri ja mitmeseinaliste süsiniknanotorude vahel.

Uuringute käigus selgus, et [Bmim]Cl ja mitmeseinaliste süsiniknanotorudel on suur mõju elektrokedratavate lahuste ning saadud membraanide omadustele. Membraani omadused on kõige paremad [Bmim]Cl ja mitmeseinaliste süsiniknanotorude koosmõjul, kuid seda maksimaalselt 1.0% mitmeseinaliste süsiniknanotorude kontsentratsioonini.

Käesolev magistritöö on kirjutatud inglise keeles ning on 55 lehekülge pikk, koosnedes 7 peatükist, 15 joonisest ja 2 tabelist.

References

[1] Ramalingam M., Tiwari A. Intelligent Nanomaterials: Processes, Properties, and Applications.. New Jersey: Scrivener Publishing LLC, 2012, 864. [*Online*] Knovel. (23.04.2014)

[2] Ali U., Zhou Y., Wang X., Lin T. Electrospinning of Continuous Nanofiber Bundles and Twisted Nanofiber Yarns - *Nanofibers – Production, Properties and Functional Applications*.InTech Europe, 2011, 485. [WWW] http://cdn.intechopen.com/pdfs-wm/23296.pdf (23.02.2015)

[3] Nayak R., Padhye R., Kyratzis I. L., Truong Y. B., Lyndon A. Recent advances in nanofibre fabrication techniques - *Textile Research Journal*, 2011, 82(2), 129–147. [WWW] http://trj.sagepub.com/content/82/2/129.full.pdf+html (23.02.2015)

[4] Hegde R. R., Dahiya A., Kamath M. G. Nanofiber Nonvowens – *Materials Science and Engineering*, 2004. [WWW] http://www.engr.utk.edu/mse/Textiles/Nanofiber%20Nonwovens.htm (23.02.2015)

[5] Lu P., Ding B. Applications of Electrospun Fibers - *Recent Patents on Nanotechnology,* 2, 169-182. Bentham Science Publishers Ltd., 2008. [*Online*] ScienceDirect. (18.03.2014)

[6] Frenot A., Chronakis S. I. Polymer nanofibers assembled by electrospinning - *Current Opinion in Colloid and Interface Science*, 8, 64-75. Elsevier Science Ltd., 2003. [*Online*] ScienceDirect. (09.03.2014)

[7] Cramariuc B., Cramariuc R., Scarlet R., Manea L. R., Lupu G. I, Cramariuc O. Fiber diameter in electrospinning process. - *Journal of Electrostatics*, 1-10. Elsevier B.V, 2013. [*Online*] ScienceDirect. (09.03.2014)

[8] Huanga Z-M., Zhang Y-Z., Kotakic M., Ramakrishna S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites - *Composites Science and Technology*, 63, 2223-2253. Elsevier Ltd., 2003. [*Online*] ScienceDirect. (09.03.2014)

[9] Andrady A. L. Science and technology of polymer nanofibers. New Jersey: John Wiley & Sons, Inc., 2008, 403. [*Online*] Knovel. (10.04.2014)

[10] Baji A., Mai Y-M.,Wong S-C., Abtahi M., Chen P. Electrospinning of polymer nanofibers. - *Composites Science and Technology,* 70, 703-718. Elsevier Ltd., 2010. [*Online*] ScienceDirect. (12.03.2014)

[11] Viikna A. Kiuteadus. Tallinn: Tallinna Ülikooli Kirjastus, 2005, 184.

[12] Reneker D.H., Yarin A.L., Zussman E., XU H. Electrospinning of Nanofibers from Polymer Solutions and Melts - *Advances in Applied Mechanics 41*, 2007, 43-195, 345-346. [Online] ScienceDirect. (10.04.2014)

[13] Manas C., Salil K. R. Plastics Technology Handbook, fourth edition. New York: Taylor & Francis Group, LLC, 2007, 896.

[14] Li Z., Wang C. One-Dimensional nanostructures - *SpringerBriefs in Materials 2*. Springer, 2013, 15-28. [WWW] http://link.springer.com/chapter/10.1007%2F978-3-642-36427-3_2#page-1 (20.03.2014)

[15] Ramakrishna S., Fujihara K., Teo W-E., Ma Z. An introduction to electrospinning and nanofibers. Singapore: World Scientific Publishing Co. Pte. Ltd, 2005, 358.

[16] Reneker D.H., Yarin A. L. Electrospinning jets and polymer nanofibers – *Polymer*, 49, 2387-2425. Elsevier Ltd., 2008. [*Online*] ScienceDirect (20.03.2014)

[17] Subbiah T., Bhat G. S, Tock R. W., Parameswaran S., Ramkumar S. S. Electrospinning of Nanofibers - *Journal of Applied Polymer Science*, 96, 557–569. Wiley Periodicals, Inc., 2005. [*Online*] ScienceDirect. (18.03.2014)

[18] Polar Protic? Polar Aprotic? Nonpolar? All About Solvents. [WWW] http://www.masterorganicchemistry.com/2012/04/27/polar-protic-polar-aprotic-nonpolar-all-about-solvents/ (20.04.2015)

[19] Wypych G. Definitions and Solvent Classification - *Handbook of Solvents*, 2, 73-117. ChemTec Publishing, 2014. [*Online*] Knovel. (22.04.2015)

[20] Brown T. L., LeMay H. E., Bursten B. E. Chemistry: The Central Science. 10th Edition. New Jersey: Pearson/ Prentice Hall, 2005, 1248.

[21] Intermolecular Forces. [WWW] http://www.science.uwaterloo.ca/~cchieh/cact/c123/intermol.html (15.05.2015)

[22] Ghandi K. A Review of Ionic Liquids, Their Limits and Applications - *Green and Sustainable Chemistry*, 2014, 4, 44-53. [WWW] http://www.scirp.org/journal/PaperInformation.aspx?paperID=43349#.VV35F0as1wh (24.03.2015)

[23] Freemantle M. An introduction to Ionic Liquids. Cambridge: The Royal Society of Chemistry, 2009, 266.

[24] Wypych G. Ionic liquids - *Handbook of solvents*, 1459-1484. ChemTec Publishing, 2001. [*Online*] Knovel. (14.02.2014)

[25] Kokorin A. Ionic Liquids: Theory, Properties, New Approaches. Croatia: InTch, 2011, 748.

[26] Wasserscheid P., Welton T. Ionic Liquids in Synthesis. Wiley-VCH Verlag GmbH & Co., 2002, 355. [WWW] http://files.rushim.ru/books/mechanizms/ionic-liquids-in-synthesis.pdf (12.05.2014)

[27] Monthioux M., Kuznetsov V.L. Who should be given the credit for the discovery of carbon nanotubes? - *Carbon*, 2006, 44 1621–1623. [*Online*] ScienceDirect (22.02.2014)

[28] Grobert N. Carbon nanotubes – becoming clean - *Materialstoday*, 2007, 10 (1-2), 28-35. [*Online*] ScienceDirect (10.01.2014)

[29] Single-wall Nanotubes (SWNT). [WWW] http://www.nanocyl.com/en/CNT-Expertise-Centre/Carbon-Nanotubes/Single-wall-Nanotubes-SWNT (22.09.2014)

[30] Terrones M. Science and Technlogy of the Twenty-First Century: Synthesis, Properties, and Applications of Carbon Nanotubes - *Annual Review of Materials Research*, 2003, 33, 419-501. [WWW] http://www.annualreviews.org/doi/abs/10.1146/annurev.matsci.33.012802.100255 (23.02.2014)

[31] Multi-wall Nanotubes (MWNT). [WWW] http://www.nanocyl.com/en/CNT-Expertise-Centre/Carbon-Nanotubes/Multi-wall-Nanotubes-MWNT (22.09.2014)

[32] Double-wall Nanotubes (DWNT). [WWW] http://www.nanocyl.com/en/CNT-Expertise-Centre/Carbon-Nanotubes/Double-wall-Nanotubes-DWNT (22.09.2014)

[33] Rosolen J. M., Montoro L. A., Matsubara E. Y., Marchesin M. S., Fontanetti do Nascimento L., Tronto S. Step-by-step Chemical Purification of Carbon Nanotubes Analyzed by High Resolution Electron Microscopy - *Science Highlights*, 2006, 44, 36-39. [WWW] http://lnls.cnpem.br/PDF/07-06.pdf (12.02.2014)

[34] Agboola A. E., Pike R. W., Hertwig T. A., Lou H. H. Conceptual design of carbon nanotube processes - *Clean Technologies and Environmental Policy*, 2006, 7, 289-311. [WWW] http://www.mpri.lsu.edu/Conceptual%20Design%20of%20Carbon%20Nanotube%20Processes%20-%20Clean%20Technology.pdf (12.10.2014)

[35] The Role of Chemistry in History. [WWW] http://itech.dickinson.edu/chemistry/?cat=74 (21.02.2014)

[36] Rao CNR, FRS, Govindaraj A. Nanotubes and Nanowires. Cambridge: The Royal Society of Chemistry, 2005, 531.

[37] Ken Donaldson K., Poland C., Duffin R., Bonner J. The Toxicology of Carbon Nanotubes. Cambridge: Cambridge University Press, 2012, 264.

[38] Low I. M. Ceramic-Matrix Composites: Microstructure, Properties and Applications. Cambridge: Woodhead Publishing, 2006, 632.

[39] Popov V. N. Carbon nanotubes: properties and application - *Materials Science and Engineering*, 2004, 43, 61–102. [*Online*] ScienceDirect (23.02.2014)

[40] Thermal conductivity. [WWW] http://www.cnanotech.com/pages/store/6-0_online_store.html (03.03.2015)

[41] Alagirusamy R., Das A. Technical Textile Yarns - Industrial and Medical Applications. Cambridge: Woodhead Publishing , 2010, 586. [*Online*] Knovel (05.03.2015)

[42] Geckeler K. E., Premkuma T. Carbon nanotubes: are they dispersed or dissolved in liquids? – *Nanoscale Research Letters*, 2011, 6, 136. [WWW] http://www.biomedcentral.com/content/pdf/1556-276x-6-136.pdf (12.10.2014)

[43] Dyke A. C., Tour M. J. Overcoming the Insolubility of Carbon Nanotubes Through High Degrees of Sidewall Functionalization – *Chemistry A European Journal*, 2004, 10, 812-817. [WWW] http://onlinelibrary.wiley.com/doi/10.1002/chem.200305534/epdf (20.10.2014)

[44] Gupta L. M., Sydlik S. A., Schnorr J. M., Woo D. J., Osswald S., Swager T. M., Raghavan D. The Effect of Mixing Methods on the Dispersion of Carbon Nanotubes During the Solvent-Free Processing of Multiwalled Carbon Nanotube/Epoxy Composites – *Journal of Polymer Science, Part B: Polymer Physics*, 2013, 51, 410-420. [WWW] http://onlinelibrary.wiley.com/doi/10.1002/polb.23225/epdf (20.10.2014)

[45] Taquahashi Y., Ogawa Y., Takagi A., Tsuji M., Morita K., Kanno J. An improved dispersion method of multi-wall carbon nanotube for inhalation toxicity studies of experimental animals - *The Journal of Toxicological Sciences*, 2013, 38, 619-618. [WWW] https://www.jstage.jst.go.jp/article/jts/38/4/38_619/_pdf (02.04.2014)

[46] Paradise M., Goswami T. Carbon nanotubes – Production and industrial applications. Materials and Design, 2007, 28, 1477–1489. [Online] ScienceDirect (23.02.2014)

[47] Sun Y-P., Fu K., Lin Y., Huang A. W. Functionalized Carbon Nanotubes: Properties and Applications. Accounts of Chemical Research, 2002, 35 (12), 1096-1104. [WWW] http://pubs.acs.org/doi/abs/10.1021/ar010160v (23.02.2014)

[48] Rogers R., Heather D., Huddleston J., Reichert W., Visser A., Broker G. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation – *Green Chemistry*, 2001, 3, 156–164. [WWW] http://pubs.rsc.org/en/content/articlepdf/2001/gc/b103275p?page=search (20.05.2014)

[49] Walker M. DMSO: Nature's Healer. New York: Avery Publishing Group Inc., 1992, 340.

[50] Yanfang G., Tengfang W., Dahong Y., Changjun P., Honglai L., Ying H. Densities and Viscosities of the Ionic Liquid [C_4mim][PF_6]+ N,N-dimethylformamide Binary Mixtures at 293.15K to 318.15K - *Chinese Journal of Chemical Engineering*, 2008, 16 (2), 256-262. [*Online*] ScienceDirect (20.02.2015)

[51] Seoul Y-T., Kim C-K. Baek. Electrospinning of Poly(vinylidene fluoride)/Dimethylformamide Solutions with Carbon Nanotubes - *Journal of Polymer Science*, 2003, 41, 1572-1577. [WWW] http://onlinelibrary.wiley.com/doi/10.1002/polb.10511/pdf (22.11.2014)

[52] Islam S., Ashaduzzaman Md., Masum S., Yeum J. H. Mechanical and Electrical Properties: Electrospun Alginate/Carbon Nanotube Composite Nanofiber. *Dhaka University Journal of Science*, 2012, 60, 125-128. [WWW] http://www.banglajol.info/index.php/DUJS/article/view/10350 (13.12.2014)

[53] Zha J-W., Sun F., Wang S-J., Wang D., Lin X., Chen G., Dang Z-M. Improved mechanical and electrical properties in electrospun polyimide/multiwalled carbon nanotubes nanofibrous composites – *Journal of Applied Physics*, 2014, 116, 134104. [WWW] http://scitation.aip.org/content/aip/journal/jap/116/13/10.1063/1.4897230 (15.03.2015)

[54] Yang B-X., Shi J-H., Pramoda KP., Goh S-H. Enhancement of stiffness, strength, ductility and toughness of poly(ethylene oxide) using phenoxy-grafted multiwalled carbon nanotubes – *Nanotechnology*, 2007, 18, 125606/1–7. [WWW] http://iopscience.iop.org/0957-4484/18/12/125606/pdf/0957-4484_18_12_125606.pdf (23.04.2015)

[55] Margulis M. A. Sonochemistry/Cavitation. Amsterdam: CRC Press, 1995, 543.

[56] Xuehui L., Jinggan Z., Qianhe L., Lefu W., Shik C. T. Ultrasonic chemical oxidative degradations of 1,3-dialkylimidazolium ionic liquids and their mechanistic elucidations - *The Royal Society of Chemistry*, 2005, 1875-1880. [WWW] http://pubs.rsc.org/en/content/articlepdf/2007/dt/b618384k (13.12.2014)

[57] Macossay J., Sheikh F. A., Cantu T., Eubanks T.M., Salinas M.E., Farhangi C.S., Ahmad H. Imaging, spectroscopic, mechanical and biocompatibility studies of electrospun Tecoflex®EG 80A nanofibres and composites thereof containing multiwalled carbon nanotubes – *Applied Surface Science*, 2014, 321, 205–213. [*Online*] ScienceDirect (18.04.2015)

[58] Xu J., Xie Y., Zhang H., Ye Z., Zhang W. Fabrication of PLGA/MWNTs composite electrospun fibrous scaffolds for improved myogenic differentiation of C_2C_{12} cells – *Colloids and Surfaces B: Biointerfaces*, 2014, 123, 907–915. [*Online*] ScienceDirect (23.04.2015)

[59] Wypych G. Handbook of polymers: SAN poly(styrene-co-acrylonitrile). ChemTec Publishing, 2012. [*Online*] Knovel. (24.02.2014)

[60] Material Safety Data Sheet. [WWW] http://www.sigmaaldrich.com/catalog/product/sial/41640?lang=en&region=EE (21.02.2014)

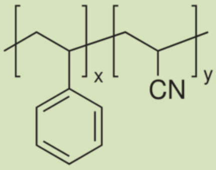
[61] Masten S. A. Review of Toxicological Literature: Ionic liquids. North Carolina: Integrated Laboratory Systems, Inc., 2004, 64. [WWW] http://ntp.niehs.nih.gov/ntp/htdocs/Chem_Background/ExSumPdf/Ionic_liquids_508.pdf (24.04.2014)

[62] NANOCYL^{TM} NC7000 series Product Datasheet. [WWW] http://www.nanocyl.com/en/Products-Solutions/Products/Nanocyl-NC-7000-Thin-Multiwall-Carbon-Nanotubes (17.04.2014)

Appendices

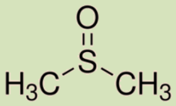
APPENDIX 1

Data of SAN [59]

Common name		Copolymer of styrene and acrylonitrile
Acronym		SAN
Monomers structure		
Mass average molecular weight	g/mol, amu	165 000; 185 000
Acrylonitrile content	%	25; 40
Density at 20°C	g/cm^3	1.07; 1.09; 0.97 (melt)
Glass transition temperature	°C	Calc. = 111; exp. = 103; 112
Decomposition temperature	°C	260
Color		Colorless
Young's modulus	MPa	3550
Good solvent		Acetone, acetophenone, chlorobenzene, cyclohexanone, diethyl ether, Methyl ethyl ketone (MEK), Tetrahydrofuran (THF)
Blends		Suitable – polycarbonate (PC); polymethyl methacrylate (PMMA); polystyrene (PS); polyphenyl ether (PPE); polycaprolactone (PCL), ethylene propylene diene monomer rubber (EPDM) Unsuitable – most thermoplastics
Outstanding properties		Outstanding transparency, excellent gloss, good chemical resistance, rigidity, high strength, dimensional stability and thermal shock resistance
Processing		Extrusion, thermoforming, injection and blow molding
Applications		Medical parts, safety glasses, filters, respirators, cover for tools and batteries
Manufacturers		BASF; DOW; Polimeri Europa

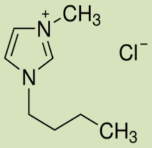
APPENDIX 2

Data of DMSO [60]

Common name		Dimethyl suloxide
Acronym		DMSO, Me_2SO
Structure		
Molar mass	g/mol	78.13
Melting point	°C	16-19
Boiling point	°C	189
Density at 20°C	g/cm^3	1.10
Dielectric constant		48.9
Miscible		Alchols, esters, ketones, lower ethers, chlorinated solvents, aromatics, water
Dissolves		Carbohydrates, inorganic salts, organic molecules, polymers, gases, charged or ionic materials
Incompatible materials		Acid chlorides, phosphorus halides, strong acids, strong oxidizing agents, strong reducing agents
Applications		Medicine field, agricultural, coatings, inks, electronic, polymers

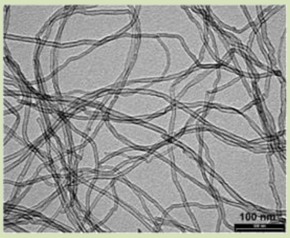
APPENDIX 3

Data of [Bmim]Cl [61]

Common name		1-butyl-3-methylimidazolium chloride
Acronym		[Bmim]Cl
Structure		
Molar mass	g/mol	174.67
Melting temperature	°C	55 (≥ 95% purity) -69
Soluble		Acetone, acetonitrile, ethyl acetate (hot), isopropyl alcohol, methylene chloride, water
Incompatible materials		Hexane, toluene and water (not entirely)
Density at 80°C	g/cm^3	1.0528
Viscosity at 80mPas		146.8
Conductivity at 25°C	µS/cm	30

APPENDIX 4

Data of MWCNTs [62]

Series of MWCNTs		NANOCYLTM NC7000 
Average diameter	nm	9.5
Average length	µm	1.5
Carbon purity	%	90
Metal oxide	%	10
Surface area	m^2/g	250-300
Production		CVD process