TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

FACULTY OF CHEMICAL AND MATERIALS TECHNOLOGY

DEPARTMENT OF POLYMER MATERIALS

ELECTROSPINNING OF POLYMERS WITH CARBON ALLOTROPES

Master's thesis

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Tallinn 2015

Declaration

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

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other authors, important aspects from literature and data from elsewhere used in this thesis are cited or (in case of unpublished works) authorship is shown on the text.

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POLÜMEERMATERJALIDEINSTITUUT

POLÜMEERIDE TEHNOLOOGIA ÕPPETOOL

SÜSINIKU ALLOTROOPIDEGA POLÜMEERIDE LAHUSTE ELEKTROKETRUS

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Tallinn 2015

MASTER’S THESIS ASSIGNMENT

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Electrospining of polymers with carbon allotropes

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Aim and tasks of the master´s thesis:

The aim of this work is to study the effect of content and nature of added carbon allotropes, also to study the influence of polymeric matrix and solvents on solution viscosity and conductivity, fiber morphology and sizes, and on conductivity of electrospun mats.

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1. Introduction

1.1. The history of electrospinning

The term “Electrospinning” occurred from “electrostatic spinning” around 60 years ago. The Electrospinning is the most well-knownand promising industrial method of producing fibers and non-woven chemical fibrous material, and its advantage is instrumental simplicity, high energy efficiency and process flexibility, a variety of products and the ability to get fiber from virtually any soluble polymer.Theelectrospinning process refers to "dry" spinning by type of process.In the Electrospinning process occurs the deformation of the polymer solution, with the subsequent transportation of curable fibers after solvent evaporation and the formation of the fibre mats, this process is provided by an electrostatic field and in the same workspace. The polymer solution is passed through the needle and drop of initial solution stretches to form a continuous flow under the electrostatic field.The solvent evaporatesduring the movement of the jet to the opposite electrode and whereby to the collector falls already cured fiber material. These fibers have a random distribution and diameters from a few nanometers to tens of micrometers [1].

The electrohydrodynamic spraying liquids was the prototype for Electrospinning process, in this process low conductive liquid flow from the nozzle, which is under constant high voltage, and then goes the process of spraying the liquid by the repulsive forces of electric charges into very small droplets, which can then be precisely collected on the counter electrode.

The first patents for production of fibers from the jet of solution injected into the space with a high electric field issued in 1902 in the United States by Morton and Cooley. Morton claimed method of spraying liquids, and Cooley described apparatus for electrical dispersion of liquid to produce a fiber from a solution, consisting of high voltage source device for liquid discharge in an electric field and a special control surface. Also Cooley presented four types of indirectly charged spinning heads- a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating distributor. He also suggested to use recovery of solvents and to use dielectric liquid instead of a gas as the medium.

In the 1930-1940s there are a large number of patents which extends the idea of producing fibers in an electrostatic field, they offers a wide variety of settings which produce nonwoven webs.In 1936-1942 K.L.Norton developed a method for the electrospinning which he applied forthe rubber melts and a number of synthetic resins, however, there weren’t any serious practical application for these patents because of poor quality and questionable competitive ability of the final fiber products.

Anton Formhols in 1937 - 1944 patented different types of installations for electrospinning. A number of patents Formhols describe the installation for obtaining artificial mat that can be easily processed into yarn or thread without additional steps to obtain fibers. The cellulose acetate was used as solvent. He investigated that distance between has influence on morphology, if the distance was short the fibers stuck to collector and to each other, because of incomplete solvent evaporation [2].

Practical realization of the electrospinning process has been achieved in 1938 in the Soviet Union. In the Research Institute of Physical Chemistry named after L.Y. Karpov (Karpov), in the laboratory headed by N.A. Fuchs, N.D. Rosenblum and I.V. Petryanov-Sokolov when they were trying to get monodisperse aerosol particles by electrohydrodynamic spraying method of nitrocellulose solution in acetone and suddenly the formation of fibers began, wherein the liquid flowing out of the nozzle, instead of the expected Rayleigh jet breakup into droplets and they have time to harden for forming a continuous fiber having a diameter of several micrometers or less.The fibers are deposited on a grounded electrode and formed a continuous microfibre sufficiently strong layer of fibrous material. The authors of this failed experiment found out that this fibrous layer is a high smoke filter. After that they changed the purpose of research, optimized mode for fiber production, structure and mechanical properties of the fiber layer, and also they have been developed equipment for the industrial method of producing fibrous materials. In 1955 Drozin discovered the dispersion of a series of liquids into spray aerosols under high voltage. He used a glass tube with fine capillary and found out that under special conditions from solutions can be obtained dispersed aerosol with the droplets which has uniform size. He also captured different stages of dispersion.

The works of Baumgarten have rediscovered theelectrospinning process abroad not only aslaboratory technology, but also as commercial in nanotechnology. From the middle of 80's there were a huge number of publications in the world about electrospinning, as one of the effective methods of obtaining materials in nanotechnology. The studies and researches were carried out in this direction by different universities, venture capital firms, corporations in the US, South Korea, Russia, Germany, Israel, China, Czech Republic, Switzerland, Poland, Turkey, etc. The using of such materials considered promising in microelectronics, pharmaceuticals, biotechnology, fuel cells, etc. Studies have shown that the devices and products (sensors, 3D matrices for cell culture, medical bandages, skin substitutes, nanoelektroprovodyaschie fiber clothes) on the basis of nanofibers produced by Electrospinning have high consumer properties [3].

1.2.Description of Electrospinning process

Spinning is a technology in which endless filaments of shorter fibers or twisted fibers are put together to produce membranes or yarns that serve as key elements to assemble multivarious structural designs for diverse functions.More than fifty different polymers can be successfully electrospun into ultra thin fibers with different diameters. The main difference of electrospinning process from its prototype is that the polymer solutions are used as the working fluid. This difference due the rheological properties is resulting in their ability to cure by solvent evaporation in a sufficientlystrong fibers,inthe formation of a fibrous layer controlled in a wide range of microstructures and the macroscopic properties and in their resistance to deformation stresses and cavitation [1, 4].

On a first approach, electrospinning shown up as very simple and easily controllable technique able to produce polymeric nanofibers. The electrospinning process, in its simplest form based on a capillary tubewith a pipette of small diameter to hold the polymer solution, a high voltage source in the kV range, metallic collecting screen or counter-electrode. Electric current are usually in the order of milliamperes. Typical apparatus for polymer Electrospinning consists of an injection pump with hypodermic syringe to pump solution through the needle/nozzle, a grounded collector that can be either stationary of rotating, and a high DC voltage supply.The drum collector has alignment speed. This is a speed at which linear speed of the rotating cylinder surface matches evaporated jet deposition. If the surface speed of the collector is slower than the alignment speed, then the randomly deposited fibers can be obtained. The perfect alignment is difficult to achieve because the polymer jets have chaos motion and can’t be controllable. Experiments should be also carried out in a box in order to precisely control environmental conditions such as temperature and relative humidity [3].

Although electrospinning is a very simple process, requiring just simple laboratory equipment to yield fibers down to the nanoscale, the science behind it is not simple at all. Electrospinning process involves the understanding of electrostatics, fluid rheology and polymer solution properties such as rate of solvent evaporation, surface tension and solution conductivity. These fundamental properties are constantly interacting and influencing each other during the electrospinning process [5].

The process uses the electrostatic and mechanical force for spinning fibers from the tip of a fine orifice or spinneret. Spinning polymer solution follows with predetermined volumetric flow rate through the capillary/nozzle, which is maintained at positive or negative charge by a DC power supply. Under the influence of electrical forces the polymer solution forms a free jet, the axis of which coincides with the general direction of the electric field. This is first relatively easy adjustment step of electrospinning process, the stability and the results of which depends on all the other stages and of course on the final properties of the fibrous product [6].

The second stage consists of a number of processes which proceed simultaneously.Due to the fluctuations of lines in the electric field, jet unfolds across the direction of the field and braked at the same time increasing the power of resistance of the medium, forming f a cloud of expanding conus because of repulsive electric charges. At the same time sharply started at the first stage the solvent evaporation process and the curing of jet. When the electrostatic repelling force overcomes the surface tension force of the polymer solution, the liquid spills out of the spinneret and forms an extremely fine continuous filament. It has the misleading appearance of forming multiple filaments from one spinneret nozzle, but current theory is that the filaments do not split. These filaments are collected onto a collector with an electrode beneath of the opposite charge to that of the spinneret where they accumulate and bond together to form nanofiber fabric. The distance between the spinneret nozzle and the collector generally varies from 5 –25 cm. The process can be carried out at room temperature unless heat is required to keep the polymer in liquid state. The final fiber properties depend on polymer type and operating conditions. Fiber fineness can be generally regulated from ten to a thousand nanometers in diameter. For removing solvent vapors emitted into the environment during curing jet and ensure safe working conditions all the equipment installation should be located in continuously ventilated and electrically isolated cell. A schematic diagram of electrospinning is as shown on the figure 1.

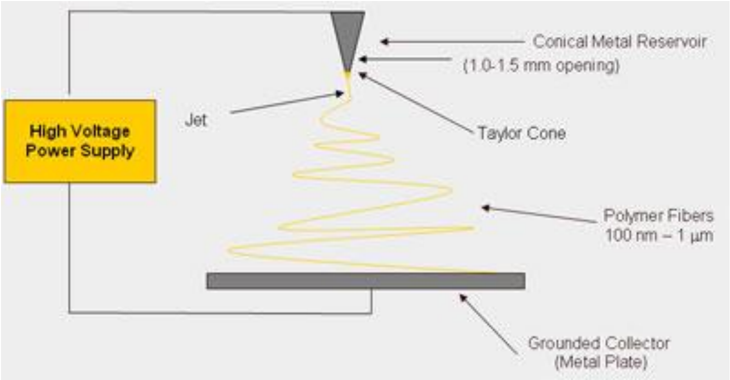


Figure 1. Scheme of electrospinning installation.

Manipulation of the components of the electrospinning apparatus and process conditions as well as the polymers and solvents employed in this technique allow the nanofiber product to be tailored to specific applications. In addition, various additives can be mixed into the polymer solution prior to electrospinning and incorporated into the resulting polymeric product, leading to novel nanofiber materials with a diverse array of properties [7].

As long as polymer can be electrospun into fibers, the main targets will be in: the diameters of fibers should be consistent and controllable, the fiber surface should be without defects or defect-controllable and the single continuous nanofibers should be collectable. The parameters affecting electrospinning and the fibers may be broadly classified into solution parameters, process parameters, and ambient parameters [8, 9, 10].

- **Solution parameters** include concentration, viscosity, elasticity, conductivity, molecular weight, surface tension and dielectric effect of solvent.
- **Process parameters** include applied electric field (voltage), tip to collector distance, collector types, diameter of needle and feeding or flow rate.

Each of these parameters significantly affects the fibers morphology obtained as a result of Electrospinning, see table 1.

Table 1. Electrospinning parameters and their effects on fiber morphology.

Parameters	Effect on fiber morphology
Viscosity	Low-beads generation, high-increase in fiber diameter, disappearance of beads.
Polymer concentration	Increase in fiber diameter with increase of concentration.
Molecular weight of polymer	Reduction in the number of beads and droplets with increase of molecular weight.
Conductivity	Decrease in fiber diameter with increase in conductivity.
Surface tension	No conclusive link with fiber morphology, high surface tension results in instability of jets.
Applied voltage	Decrease in fiber diameter with increase in voltage.
Distance between tip and collector	Generation of beads with too small and too large distance, minimum distance required for uniform fibers.
Feed rate	Decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate.
Humidity	High humidity results in circular pores on the fibers.
Temperature	Increase in temperature results in decrease in fiber diameter.

If considered the solution parameters, then the one of the most important characteristics of the fibers produced with the Electrospinning method is related to their diameter. Since the nanofibers are obtained from flying liquid jet of the polymer solution from which the solvent evaporates, the fiber diameters will initially be dependent on the size of these streams, as well as polymer content therein. In the distance between the capillary tip and the collector collecting primary jet solution can be divided into numerous smaller fiber diameters. Fiber dimensions and morphology depend strongly on molar mass, molar mass distribution, glass transition temperature, solubility, etc. The other problems in electrospinning process are defects like beads and pores. It was found out that polymer concentration can affect the formation of beds, high polymer concentration results in fewer beads. And the size of defects increase with concentration too, but it can be corrected with increase of surface tension, because surface tension is a function of solvent compositions. High solution conductivity causes a greater bending instability of the driven jet, resulting in decreasing of fiber diameter [11].

Obviously, on the first stage goes the deformation of the spinning solution, which increases the free surface of the latter.Therefore, the value of the surface tension of the solution is one of the most important properties that determine the cost of input to the process of electrical energy. The lower the surface tension of the solution, the more stable is liquid jet, and it’s easier to avoid overwhelming the process gas discharge from the nozzle. Another important property of the spinning solution is its dynamic viscosity. ***Viscosity*** of the solution is a significant parameter to exert its influence on the fiber diameter. The higher viscosity of solution is, the larger diameter of the fibers will be. However, when the solid polymer is dissolved in a solvent, the solution viscosity is directly proportional to polymer concentration. Thus, higher concentration of polymer is giving a result in fiber diameters. Empirically it was noted that the fiber diameter increased with increasing polymer concentration.Secondly, the viscosity dampens the capillary waves, which destructive liquid stream and enhances its stability. And finally, ability to withstand the deformation stresses and cavitation is related to its rheological properties through molecular weight and polymer structure of the spinning solution viscosity.

The increase the conductivity of solutions and thereby decreases the bead formation in electrospun nanofibers. At the same time reducing the concentration is below the threshold value results in a change in fiber morphology - the appearance of defects on the fiber in the form of beads. The main factors affecting the formation of beads during electrospinning, are the solution viscosity, surface tension and density of the resulting charge transferred to electrospinning jet. All of these properties are usually determined by the solvent used.

Higher surface tension leads to more spherical structures, in contrast to the viscosity and density of the resulting charge, which contribute to a higher value obtaining fibers with fewer defects. The conductivity of the solution represents the charge density of the jet and thus the amount of deformation, thus increasing the electrical conductivity can reduce the thickness of the fiber. Surface tension also affects the distribution of fiber diameters. The fiber thickness can be reduced by adding a surfactant to the solution.

In the electrospinning process a crucial element is the ***applied voltage*** to the solution. The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter and also rapid evaporation of solvent from the fibers results. This may result in a smaller and less stable Taylor Cone. At a higher voltage, there is a greater tendency for beads formation. Also the shape of the beads changes from spindle-like to spherical-like with increasing voltage.

Minimum ***distance*** to collector is required to give the fibers sufficient time to dry before reaching the collector, otherwise with distances that are either too close or too far, beads have been observed and excess solvent may cause the fibers to merge which may provide additional strength to the resultant fiber mat. Also the electric field strength will increase at the same time when the distance between the tip and the collector is reduced and this will increase the acceleration of the jet to the collector. ***The effect of tip and the collector distance*** on fiber morphology is not as significant as other parameters - flatter fibers can be produced at closer distances but with increase in distance rounder fibers can be produced. The minimal value of working distance is needed to ensure complete solvent evaporation, and maximum value for the electric field is effective in forming the Taylor cone and consequently the formation of nanofibers.

Apart from solution and processing parameters, there are also ambient parameters that include humidity, temperature etc. With increase in temperature, there is a yield of fibers with decreased fiber diameter, because of decrease in the viscosity of the polymer solutions at increased temperatures. There is an inverse relationship between viscosity and temperature. By increasing humidity there is an appearance of small circular pores on the surface of the fibers. Furtherincreasing the humidity leads to the pores coalescing.

1.3.Nanofibers and their applications

Because of the structure materials from the nanofibers have unique properties, which can be used in many different and unexpected areas. Nanofibers produced from electrospinning have a naturally formed porous structure with excellent pore interconnectivity and the pores are in range between tens of nanometers. The open pore structure and high permeability with the high surface area makes them ideal porous membranes. These materials can provide superior structural properties, which cannot be achieved by monolithic material alone [4,5].

New properties of nanofibers allow toimprove the characteristics of known materials - mechanical strength, reactivity, electrical conductivity, optical quality and membrane permeability. In this regard, there is a huge potential for application of nanofibres in areas such as energy storage and conversion, filtering liquids and air, food processing, packaging, medicine, personal hygiene and environmental protection.The porous structure and ability to adopt functional molecules and nanomaterials, nanofiber webs, has been used in various areas as batteries, conductive paints, bio medical, medical prostheses, fuel cells, protective clothes.

Nanofibers offers unlimited opportunities for creating materials with new properties as they allow you to change or functionalized nanofibrous membrane by a number of physical and chemical processes during production or after it. The functionalization can significantly improve the surface properties, for example, functionalization can be made by using materials with high super-hydrophobic (water-repellent) or super hydrophilic (water-absorbent) properties. Uniformity shells nanofibers, their thinness and high permeability make them indispensable material in many industries.

Properties of nanofibers are largely dependent on the source material. Today in industrial environments nanofibers can be made of dozens of kinds of polymers, including biocompatible (withstand exposure of biological environment) and environmentally friendly (biodegradable) polymers [3].

With the help of the nanofibers can be changed the properties of known materials and create completely new materials. Range of applications is very wide nanofibers. Currently, their most frequently used is in the clean-air technology, because they are effective in removing submicron particles, including bacteria and viruses. Unlike electrically charged filters, high efficiency air cleaning using nanofibres does not deteriorate over time, and energy consumption during the filtering is much lower than that of the most common filters. Nanofilter membranes are capableto retain molecules in size from 0.5 to 10 nm. Fibrous materials used for filter media provide advantages of high filtration efficiency and low air resistance [6, 12].

In medicine nanofibers can be used as tissue engineering scaffolds. The principle is very simple: first the nanofibrous scaffold is placed together with tissue cells in culture liquid, then goes tissue growing and after that goes tissue implantation in vivo integration. The main idea of tissue engineering is to repair, replace, maintain, or enhance the functions of organ. The basic requirements for scaffolds are: high degree of porosity, with an appropriate size of pores distribution, large surface area, biodegradability of material of which will be scaffold made of; scaffold should be non-toxic and biocompatible.The blood vessels, bones, muscles and skins scaffold were made in recent years. Researchers from Northwestern University (USA) have created a nanomaterial that helps the body to grow new blood vessels. Researchershave developed a liquid which when administered to patients forms the matrix of loosely tangled nanofibers. Each fiber is covered with microscopic projections, which mimic the vascular endothelial growth factor: this protein causes chemical reactions leading to the growth of new blood vessels. Nanofibers have the same effect [13].

Nanofibers can be used in medicine also as wound healing. Would healing is a process in which required a set of biochemical action complex for repairing the damage. A wound dressing material should provide a physical barrier to a wound and be permeable to moisture and oxygen for protection of wound, exude extra body fluids from the wound area, decontaminate the exogenous microorganism, improving the appearance and sometimes accelerates he healing process. The nanofiber membranes and mats are the very good wound dressing samples, because they have big amount of advantages, for example: highly porous mat structure and well interconnected pores are important for exuding fluid from the wound, the small pores and very high specific surface area can assist in fluid drainage, and by production method we can add drugs into the nanofibers for any possible medical treatment and antibacterial purposes.

The nanofibers have proved themselves as good drug delivery release control. In this process nanofibers have large number of advantages like the simplicity of drug loading which carried out by Electrospinning process and applied voltage in this process has influence on drug activity. The high specific surface area and short diffusion passage length give the nanofiber drug system higher overall release rate that for the bulk material. Most developed for drug delivery nanoparticles are spheres, but researchers are exploring for a long time cylindrical particles. Already there is the first experimental evidence that cylindrical nanoparticles are able to survive in the bloodstream as much as necessary to achieve the goal, and then penetrate the cell membrane in order to deliver drugs to where they are most needed.

1.4.Conductive nanofibers and their applications

However, as it is known, polymers usually act as electrical insulators with conductivities around $10^{-12}÷10^{-13}$ S/cm (picoSiemens range). During last decades a great effort to incorporate conduction to polymers has been done, because conductive polymer composites in comparison with pure metallic conductors have the advantages of light weight, ease of shaping, low price, and wide range of electrical conductivities $10^{-12}÷10^{-3}$ S/cm as well as corrosion resistance [14, 15].

Properties of the fibers can be easily modified with differentadditives.As fillers can be used carbon black (CB), multi-walled carbon nanotubes (MW CNTs), conductive carbon nanotubes (cond CNTs), metal particles and conducting polymers. Typical electrical conductivity value for CB is 10^{2}S/cm, for carbonizedPAN fibers are 10^{4}S/cm and for metal particles or cooper are 10^{6}S/cm.Their typical function is serving as reinforcement component in electrospun polymeric fibres, but they are also used in order to modify electrical properties of fibres. Also the tensile strength can be improved when CB or CNT is added[16- 19].

The most common additives to polymeric materials are carbon nanotubes and carbon black.Carbon black (***CB)*** consists of elemental carbon and it has very comprehensive properties like a high surface-area-to-volume ratio, high strength to weight ratio, good chemical resistance and thermal and electrical conductivity. They were used as materials in automotive, aerospace and space industries [20-22].

Carbon black - highly dispersed carbonaceous material, which are formed by incomplete combustion or thermal decomposition of hydrocarbons (natural or industrial gases, liquid products of petroleum or coal origin).According to a method of producing carbon black can be divided into 4 types:thermal, channel, furnace or lamp. The dispersibility of particles and properties of the carbon black depend on the method of production.

Carbon naotubes (***CNTs***) are widely used as filler in electrospun fibers. Their typical function is serving as reinforcement component in electrospun polymeric fibers, but they are also used in order to modify electrical and mechanical properties of fibers. The nanotubes are known for their outstanding mechanical, electrical and thermal properties suitable for a wide range of applications in polymers.High electrical and thermal conductivity were also determined experimentally, with their values approaching or above metals. This combination of properties and product form that is compatible with current technology of polymer processing, provides a new structural materials.The use of carbon nanotubes to make polymers antistatic and conductive properties is by far the commercial practice and is distributed in industries such as electronics and automotive industries.One of the most promising aspects of carbon nanotubes - their flexibility, which does not affect the outstanding properties of this material, including strength. Many scientists hope that nanotubes will give us a bendable circuits, which can be applied in embedded electronics in clothing and translucent dashboard / panel [23-26].

Arc method refers to high temperature methods of production of CNTs.If vaporize graphite rod (anode) in an electric arc, then on the opposite electrode (cathode) hard carbon build-up (deposition) are formed, which containing multiwall nanotubes with a diameter of 15-20 nm and a length of 1 micron.But installation for electric arc synthesismetal-consuming, energy-consuming, but is universal for various types of carbon nanomaterials.Thus appeared the first works on the production of nanotubes by low-temperature method - the method of catalytic pyrolysis of hydrocarbons (CVD). Oversimplified mechanism of CNT growth is as follows. Carbohydrate produced by the thermal decomposition of a hydrocarbon,dissolved in metal nanoparticles. Upon reaching a high concentration of carbon particles on one of the faces of the particle catalyst occurs energetically favorable "allocation" of excess carbon in the form of distorted polufullerenovoy cap.Thus nanotube is born. Decomposed carbon continues to flow to the catalyst particle, and to reset its concentration in excess of the melt must constantly get rid of it. Rising hemisphere (polufulleren) from the melt surface drags dissolved excess carbon atoms which is molten form C-C bond, which is a cylindrical shell-nanotube.

Metal particles can be used as fillers too, but metals have a tendency to oxidize. Conductive composites have more advantages as low density, ease of shaping, corrosion resistance and etc. There are factors such as contact behavior between the fillers, pressure dependence and the thickness of film, which can influence the conductivity of composites.

1.4.1. Percolation theory

Percolation theory is the most common approach for the description of transportation in disordered systems. With its help, the probability of clusters formation of relating to each other particles can be consideredand by this theory values percolation thresholds and the properties of composites (electrical, mechanical, thermal, etc.) can be predicted.Percolation theory describes patterns of structure formation in the composites for each of the structural state, and represents the relative distribution of the matrix and filler [19, 27].

In percolation theory the medium is represented as a set of randomly distributed nodes, in which liquid can flow.The density of nodes determines the probability of creation of continuous strings of contacting nodes, this allows fluid to flow through the sample material. By analogy theory also applies to the description of current flow in the polymer matrix containing conductive particles.Consequently, the volume fraction of the conductive filler determines the probability of contact between the particles and the formation of conductive paths in the material.According to percolation theory the conductivity at a constant current depends on the volume fraction of electrically conductive filler [17].

In a mixture between a dielectric and a conductive component, the conductivity and the dielectric constant of this mixture show a critical behavior if the fraction of the conductive component reaches the percolation threshold. The behavior of the conductivity near this percolation threshold will show a smooth change over from the conductivity of the dielectric component to the conductivity of the conductive component. The percolation threshold depends on the nature of the filler distribution in the matrix, the particles shape of the filler and the type of matrix.For elongated particles percolation threshold is lower than for spherical particles.The length of the electrically conductive portions increases because of geometry of the larger particles and henceincreases the likelihood of creating a reliable contact that leads to the formation of an infinite cluster with the useof a small amount of fillers.A higher surface to volume ratio for these particles increases the probability of contact between particles at a lower concentration and thus to reduce the percolation threshold (creating a continuous conductive path in a polymer matrix). Furthermore, fibrous fillers such as carbon fibers, improve the mechanical properties of the composite. The attainment of the percolation limit is also depends on the solution viscosity. The higher the viscosity of solution and matrix, the higher is percolation limit.

The critical value in the production of conductive polymer composites is the filler content. This content should be as lower as possible and should allow to composite fulfill its electrical requirements [28].

1.4.2. The applications of PAN-based functional carbon nanofibers

At present, portable electronic devices such as mobile phones, computers, digital cameras and other gadgets are becoming increasingly multifunctional and have tendency to decrease in size,thickness, weight, bend and twist the possibility to meet the demands of the modern market. However, the development of technologies related to power sources and energy storage is still at a low level. Therefore, the production of energy sources with low specific weight, thus providing a large supply of energy and power, has the flexibility is relevant and promising task [29, 30].

Conventional energy sources for these applications are a capacitor and battery. However, none of them is not without drawbacks.For example, the capacitor shows a high charging and discharging speed (i.e. has a high specific capacity), but not capable to reserve a large amount of energy.Battery, in turn, has a high capacity, but a small rate of charge and it is not possible to develop significant power. In addition, the battery shows a limited number of charge-discharge cycles.

The problems of these devices can be solved by fairly new type of devices–rechargeable lithium-ion batteries (LIBs), supercapacitors and fuel cells. These devices combine the characteristics of capacitive battery power characteristics of capacitors, and thus demonstrate the long life cycle, the performances depend on the properties of their electrode material [31, 32].

Excellent materials are carbon network of carbon nanotubes and nano-layers of graphene as an electrode material for the manufacture of flexible supercapacitors and batteries. Carbon materials are more used in this area not because of their advantages like good chemical stability, electrical conductivity, but also because of high specific surface area and better charge transport properties.

Lithium-ion batteries (LIBs)

LIBs are used as power source for a wide range of devices such as cell phones, laptops and etc. Electrospun PAN based nanofibers showed themselves as good anode material for LIBs. Modern batteries include electrodes made of carbon whose specific capacity is about 370 mAh / g. There are works that make use of the carbon nanotubes. In this case the specific capacity is increased to about 1,000 mAh / g.

In addition, with a slight difference in the cost of production of lithium-polymer battery is superior to conventional batteries in comfort and environmental friendliness [33].

For improvement the second component can be added. Many carbon composite nanofibers were lately used, because carbon composite nanofibers can combine long cycle life because of carbon and high storage capacity from second component. For example, silicon nanopaticles, metal salts and the conductive polymer, like polypyrrole (PPy) were used for stabilization and carbonization. Also as second component tin (Sn) was considered as good anode material for LIBs, but Sn-based materials have poor cycling performance. The resultant carbon/Sn nanofiber anode exhibited large capacity and really good cycling performance in LIBs.

In addition carbon composite nanofibers can be employed as cathode material for LIBs. In this case as additional component the Li_2MnSiO_4 was chosen, but it has low conductivity and poor structural stability, on the other hand composite nanofibers have high discharge capacity and stable cycling performance. The resulting composite nanofiber cathode showed good electrochemical performance in terms of capacity, rate capability and life cycle.

Supercapasitors

Supercapacitor is an electrochemical power source, wherein the charge accumulation occurs at the electrode-electrolyte interface.At the present time to increase the capacity of supercapacitors are widely used all sorts of carbon structures - nanotubes, graphene, etc.

Supercapacitor based on the capacitance of the double electric layer at the electrode / electrolyte interface. As an electrode materials generally are used carbon materials such as activated carbon, carbon nanotubes and graphite. The increase in specific capacity of this type of supercapacitor is increased with the increase in the specific surface area of the material by increasing its porosity. However, the decrease in pore size leads to the problem of filling the electrolyte.

Solid-state supercapacitor based on CNTs was created, it combines high capacity and duration energy storage batteries with fast charging and high power capacitors.New electricity storage device is capable of operating in extreme conditions and it is a reliable and versatile power source that can be used everywhere: from microdevices to large power plants.

And, despite the fact that on the market there are already supercapacitors based on carbon nanotubes, these devices are not without drawbacks.Firstly, there is a fusion between a nanotube due to repeated recharge, leading to uncontrolled changes in the performance of the device during operation. And secondly, the thermal budget of the process of synthesis of CNTs can not use them in the integrated technology.

Dye-sensitized solar cells

Dye-sensitized solar cells (DSCs) are a low cost alternative to Si solar cells. Basic DSC consists of a photoanode and counter electrode separated by electrolyte. These cells are a third generation photovoltaic (solar) cell that converts any visible light into electrical energy.

DSC is a disruptive technology that can be used to produce electricity in a wide range of light conditions, indoors and outdoors, enabling the user to convert both artificial and natural light into energy to power a broad range of electronic devices.

Solar panels of this type are promising, as are made of cheap materials and does not require sophisticated equipment in the production. The cells have a simple structure composed of two electrodes and the iodine-containing electrolyte. It was suggested to change one electrode on new one, which was produced from CNTs. This new cathodereplaces expensive and brittle materials based on platinum, which are often used in earlier versions of the batteries. The new type also has less contact resistance with the electrolyte, allowing electrons to flow more freely. New cathode resistance which determines how well the electrons follow from the electrode into the electrolyte, it was 20 times less than in platinum-based cathodes. Also platinum cathods have high cost and they are susceptible to corrosion, carbon materials are abundant and possess high resistance against corrosion. Carbon nanofibers from electrospun PAN was chosen as a low-cost alternative and because of their properties, such as large surface area, low charge-transfer resistance and fast reaction rates.

Sensors

The carbon nanotubesare a promising basis for the creation of miniaturized sensors that determine the content of trace gases in the atmosphere, because they have high sensitivity of the electronic characteristics to the presence of molecules adsorbed on the surface and because of record specific surface area, which contributing to a sorption. There are many attempts to create a sensor based on a single nanotube. The principle of operation of such sensors is based on the change in the current-voltage characteristics of nanotubes due to sorption of gas molecules certain kind on its surface. Carbon materials were used because of their chemical inertness in most electrolyte solutions and relatively wide potential window. Carbon nanofibers from electrospun PAN have been employed in the area of sensors because of their remarkable characteristics as 1D nano-scale structure, electrochemical property, functionalization ability, mechanical flexibility and biocompatibility.

2. Overview of the subject

2.1.Definition of the project aim

The purpose of this project was to create conductive nanofibers by using method of electrospinning for application them in electronics, filtering materials or even for the production of conductive yarns.Such yarns can be used further in smart textiles.

As example, the smart fabric can consist of piezoelectric material and also conductive and non-conductive fibers. The smart material is created by weaving the fibers together, and mechanical and optical properties of material depend on the ratio of the fibers in the fabric [34].

The complexity of the preparation conductive fibers is in a good dispersion of carbon allotropes. The better the dispersion of additive in solution, so the higher is the conductivity. Carbon additive must interact with each other for obtaining the good conductivity and this can be achieved by improving dispersion of carbon allotropes in the solution or/and by increasing its content.

2.2.The main tasks of the project

To study the fiber morphology and conductivity in dependence on:

1. Nature of added CB and CNT;
2. Content of additives;
3. Method of preparation;
4. Used various polymeric matrixes;
5. Used different solvents.

3. Experimental part

3.1. Materials

In this work polymers polyacrylonitrile (PAN), with MW=150000, purchased from Polysciences, Inc., Polyvinylidene fluoride (PVDF), with MW=530000, Polystyrene (PS) with MW=192000, purchased from Sigma- Aldrich, Inc. and Cellulose diacetate (DAC) with MW=100000 were used as the polymer matrixes. As solvents dimethyl sulfoxide (DMSO), purchased from Sigma-Aldrich, Dimethylformamide (DMF), 1,2-dichloroethane (DCE), Methanol and acetone purchased from Merck were used. As additives, 15% fullerene containingCB (ISC ILIP, Russia), not purified MultiWallcarbon nanotubes (MWCNT; Nanocyl NC700 series)and conductive carbon nanotubes composites (cond.CNT; Cheap Nanotubes, USA) were used in this project. Multi-walled nanotubesconsist of multiple rolled layers (concentric tubes) of graphene, this type of additives known as nanotubes with high electrical and thermal conductivities. The MW CNTs has unique mechanical and physical properties combined with high aspect ratio and low density. Conductive carbon nanotubescan form conductive networks easily, nanotubes have special type of grain electrode conductive additives inside and because of this fact cond. CNTs can be easily dispersed in medium and the entangled nanotubes can be well separated, so the conductivity increases in times.[cheapnanotubes.com] All materials were used without additional purification. As well, for better dispersion of carbons, Ionic Liquid (IL), butyl-methyl imidazolium chloride, synthesized in our laboratory, was used [35].

3.2. Preparation of solutions

All solutions of polymer + CB (*m:n)*, where*m:n*=CB:PAN=1:20; 3:20; 1:4; 1:2; 1:1; 3:2 in certain solvent (DMSO, DMF, 4:1 DMF/AC, 4:1 DCE/Me) were prepared with using of ultrasound treatment. As polymers PAN, PVDF, PSand DACwere used. At first suspension of CB in certain solvent was prepared and sonicated during 3-6 hours and after that the polymerin the form of powder or granules was added to suspensionof CB in solvent. Further, whole solution was mechanical mixed during 24 hours. Sometimes additional US of solution were needed. The data about concentrations of studied systems are presented in table 2.

Table 2. Concentration of polymer solutions with CB.

Polymer	Solvent	Concentration, wt%
PAN	DMSO, DMF, DMF/Ac	8.5-10
DAC	DCE/Me	7
PVDF	DMF	18.4
PS	DMF	25

In some cases the ionic liquid BMIMCl was added to the solutions with PAN+CB to achieve better dispersion of CB in solution and higher conductivity of material. The content of IL in the solutions was 5% to the weight of whole solution. Thesolutions were stirred mechanically for 24 hours.

The solutions with cond. CNT and MW CNT were prepared by two different ways. At first both CNT were dispersed(suspended) by mechanical mixing in certain solvents for 3 hours, and after that the polymer was added to solution of CNT and the whole solution was mechanically stirred for 24 hours. The amount of CNT in solution was varied, the ratio of cond.CNT to mass of PAN in solution was cond. CNT:PAN=1:200; 1:100; 1:50; 3:100; 7:100; 3:20. For DAC, PVDF, PS solutions the ratio of cond. CNT was cond. CNT:Polymer=1:200; 1:100.The content of MW CNT was MW CNT:Polymer=1:200; 1:100.

Second way was with using US. CNTs were sonicated in the same solvents for 3 hours (instead of mechanical mixing) and after addition of polymer, whole solution was mechanically stirred for 24 hours. The polymer concentrations were kept the sameas in the previous experiments.

3.3.Methods

• Electrospinning

In present research electrospinning was conducted at room temperature with atmosphere conditions. A polymer solution was loaded into the syringe and this liquid was extruded from the needle tip at a constant rate by a syringe pump. The pumping rate, r, was varied from 0.5 up to 2.5 ml/h. The applied voltage (V) was 15 up to 20 kV and distance to collector (D) was 15 up to 20 cm. However, some polymers may emit unpleasant or even harmful smells, so the processes were conducted within chambers having a ventilation system.

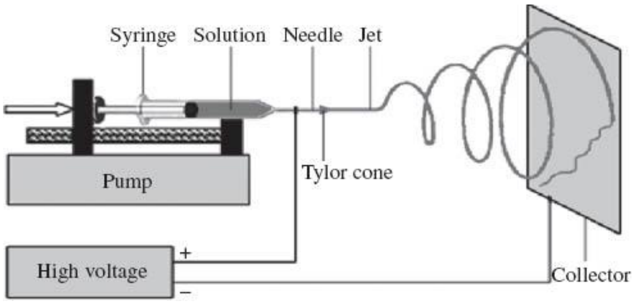


Figure 2. Schematic diagram of horizontal set up of electrospinning apparatus.

Typical set up of electrospinning apparatus was used, which consists of a high voltage power supply (Glassman High Voltage with 0–40 kV power range), a syringe pump (New Era Pump Systems), a syringe with needle (diameter 0.6-0.8 mm) and a drum collector, to which the foil was attached , where the sample was collected as a fiber web. Electrospinning experiments were carried out under the parameters mention above.

Figure 3. Electrospinning device which was used in our project.

- **Viscometer**

In this project we used viscometer Brookfield DV-II. Viscometer measures fluid viscosity at given shear rates. Viscosity is a measure of a fluid’s resistance to flow.

Spindle number is selected depending on the solution. We used spindle number 21 and 27, because it was suitable for measuring the viscosity of our solutions.

Rotation speed for solutions was measured in the range of 0.5-100 RPM. Measurements were performed at room temperature.

- **Conductivity**

For measuring conductivity we used Conductivity Meter Mettler Toledo SevenCompact. First we have calibrated our device and then measured the conductivity of our samples.

Conductivity of mats was measured by High Resistance Meter Model HR2. The membrane was fixing between two electrodes and then the voltage was applied, but in this method it is also necessary to take into account the dimensions of the sample (lengh, height and width), because there is a dependence of the conductivity of the membrane on the sample thickness. This means that for comparison all the parameters should be taken into consideration.

- **Ultrasonic treatment**

Dispergation of CB into polymer solution was conducted by means of ultrasonic treatment during 3-6 hours. In given work BANDELIN SONOPULS HD 2070 with horn configuration for volumes from 2 ml up to 50 ml ultrasonic device was used.

4. Resultsand Discussions

The data obtained for the whole period of research are described in this work. Information on viscosity, conductivity solutions, fiber's morphology and membrane conductance united in tables and graphics for better comparison of the results.

The factors affecting the viscosity and conductivity of the solution as well as the morphology of the fibers and conductivity of membrane solid phase were studied. Very important to keep track of how the solution was prepared, as well as which additives and its content have been added, what solvents and what polymeric matrixes were used. All these parameters greatly influence the morphology of the fibers. CB and CNTs can formed aggregates that’s why it is so necessary to explore how the solution was prepared.

Preparation processes, which especially include strong shearing of the polymer/filler mixture, can affect the conductivity properties of the polymer composite. Actually, during preparation of conductive polymer composites two conflicting aspects should be balanced: (a) the added conductive fillers should be uniformly dispersed throughout the polymer matrix; for this purpose the polymer/filler mixture should undergo severe and long-time stirring, which are supposed to improve the conductivity of the composite; (b) on the other hand, however, such severe stirring can lead to some damage or breakage of the CB aggregate, which can hinder formation of conductive paths in the polymer matrices and consequently reduce the conductivity. As it has been observed by several authors during mixing the composite, the mixing time, temperature and order of adding of the materials will strongly affect the conductivity of the composite [36-38]. Therefore, the process of composite preparation should be carefully studied and a well-balanced combination of the homogeneous dispersion of the conductive filler and a noticeable conductivity improvement should be achieved [14].

4.1.Effect of preparation

In this work we have studied three different preparation procedures for PAN with CB. This data was published in journal Fullerenes, Nanotubes and Carbon Nanostructures(2014) 23, 695–700. In these methods the combination of sonication and mechanical stirring is used. Ultrasonication offers a great potential in the processing of liquids and slurries, improving the mixing—it generates alternating low pressure and high-pressure waves in liquids, leading to the formation and violent collapse of small vacuum bubbles [39]. These effects are used for the de-agglomeration and fragmentation of micrometer and nanometer-size materials, which can be both agglomerates of polymeric molecules and CB aggregates.

In Method 1, the CB in its original powder form was mixed in different proportions with PAN powder. After mixing the powders, they were dissolved in DMSO. Concentration of the solution was always considered as the concentration of pure PAN in DMSO, and was kept the same 8.5wt% to fulfill the requirements for continuous Electrospinningprocess with formation of beads-free fibers. The prepared solution (or rather suspension) of PAN+CB in DMSO wassonicated afterwards during different time periodsto fragment the large aggregates of CB into smaller ones.

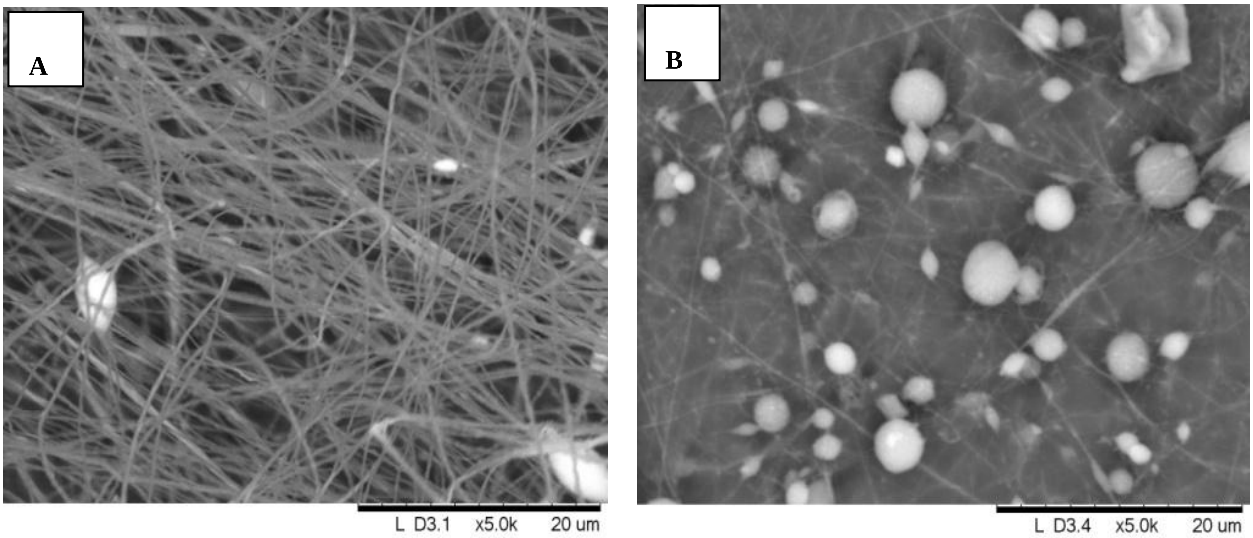


Figure 4. SEM images of electrospun Sample 1 fiber mats prepared at different sonication times: (a) 2 hours, (b) 6.5 hours.

Figure 4 represents examples of the morphology of electrospunSample 1 fiber mats prepared at different sonicationtimes: a) 2 hours, b) 6.5 hours. As can be seen from the SEM images, the time of sonication significantly affects the finalmorphology of the studied materials. It was observed that at short sonication time (2 h) the fibers with average fiber diameter of 560 nm (see Table 3) could be produced. However, big CB aggregates can be detected in fiber web. While the fibers themselves prepared at short sonication time turn out to be uniform and defect free (exclude CB aggregates), those prepared at longer sonication time show bead-on-string morphology with a fibrous structure characterized by the presence of numerous droplets of various sizes. Moreover, fiber diameter decreases twice and become 220 nm on average (beads are excluded from calculation). At the same time, longtime sonication helps to comminute CB aggregates. It shouldbe noticed here that PAN+CB solution prepared withoutsonication (t=0 in Table 3) contained a lot of big CB aggregates.Such aggregates permanently blocked the syringe needlepreventing to collect any fibers onto collector. Therefore,data related to fiber morphology and conductivity are absentin Table 3.

Table 3. Effect of sonication time on solution and material properties of Sample 1.

Sonication time, hrs	Conductivity of solution, μS/cm	Viscosity, cP	Average fiber diameter, nm	Conductivity of electrospun mat, 10^{-3} μS/cm
0	43.3	6300	--	--
2	92.1	5600	560	0.01
6.5	120.6	1000	220	0.1

Such pronounced drop in fiber sizes can be related to the decrease in viscosity under sonication: the longer the sonication, the lower is the viscosity of solution. Such effect is widely known in literature for all polymer solutions [40]. Lower solution viscosity, in turn, leads to the formation of thinner fibers, as stated elsewhere in literature [42, 43].For the thinning of the fibers the increased conductivity of the solution may also be responsible. As it is seen from Table 3, conductivity of the solution increases with increasing sonication time. By these facts it can be suggested that fiber diameters are reduced due to both increased conductivity and decreased solution viscosity after sonication.

As it was found out, sonication affects not only solution conductivity, but also conductivity of solid fiber mats. The increase in conductivity of both solution and fibers can be explained as follows. During mixing, fillers tend to interact more with the polymer molecules and a net reduction of filler-filler bonds are expected. If the mixing time is prolonged, better filler dispersion may be expected. When the CB aggregates are comminuted into discrete primary ones, the optimal dispersion can be obtained. During the sonication, the fragmentation of aggregates into smaller ones occurs, affecting the conductivities of the systems, because the better the dispersion of the conductive filler, the higher is the conductivity [43].

In spite of higher conductivity of fiber mats obtained at higher sonication times, their mechanical properties are very poor, and obtained mats are extremely fragile, because small thicknesses of fibers as well as bead areas act as stress concentration points and affect the mechanical properties of the mat [44]. In contrast, short sonication time does not provide a good dispersion of CB and, as a result, low conductivity of the mere Pico Siemens range can be achieved (see Table 3).

To improve mechanical properties of fiber mats and prepare nanofibers with homogeneous fiber morphology it needs to optimize the conditions for CB dispersion in polymer matrix which plays a significant role in achieving effective properties in nanofibers. All these facts point to the necessity to develop other methods to obtain conductive fibers.

In Methods 2 and 3, used in this work, at first, a stable CB suspension was obtained by a suspension of CB in DMSO being held for 6 h under ultrasonication to fragment big CB aggregates. CB was homogeneously dispersed and stabilized showing a black ink-like appearance without visible precipitation for several days. Then, PAN was added into a stable suspension of CB/DMSO at room temperature and mechanically stirred with magnetic bars during 24 h (Method 2). In Method 3, mechanical stirring of PAN+CB was done only during 1 h, and immediately after that the PAN+CB mixture was sonicated again during 3 h.

As it is known, the conductivity of polymer composites loaded with conducting filler depends largely on the content of fillers. To increase the conductivity of PAN+CB systems the content of CB in the composite was doubled and tripled, so mixtures with CB:PAN=1:1 and 3:2 were prepared by three methods and compared. High content of CB also can be useful to increase specific surface for such applications where it is required.

Solution and fiber properties of Sample 3 prepared bythree different methods are listed in Figure 5 and Table 4, asexamples. Surprisingly, despite of the high solution viscosity caused by the high CB content, these solutions were still possible to electrospin.

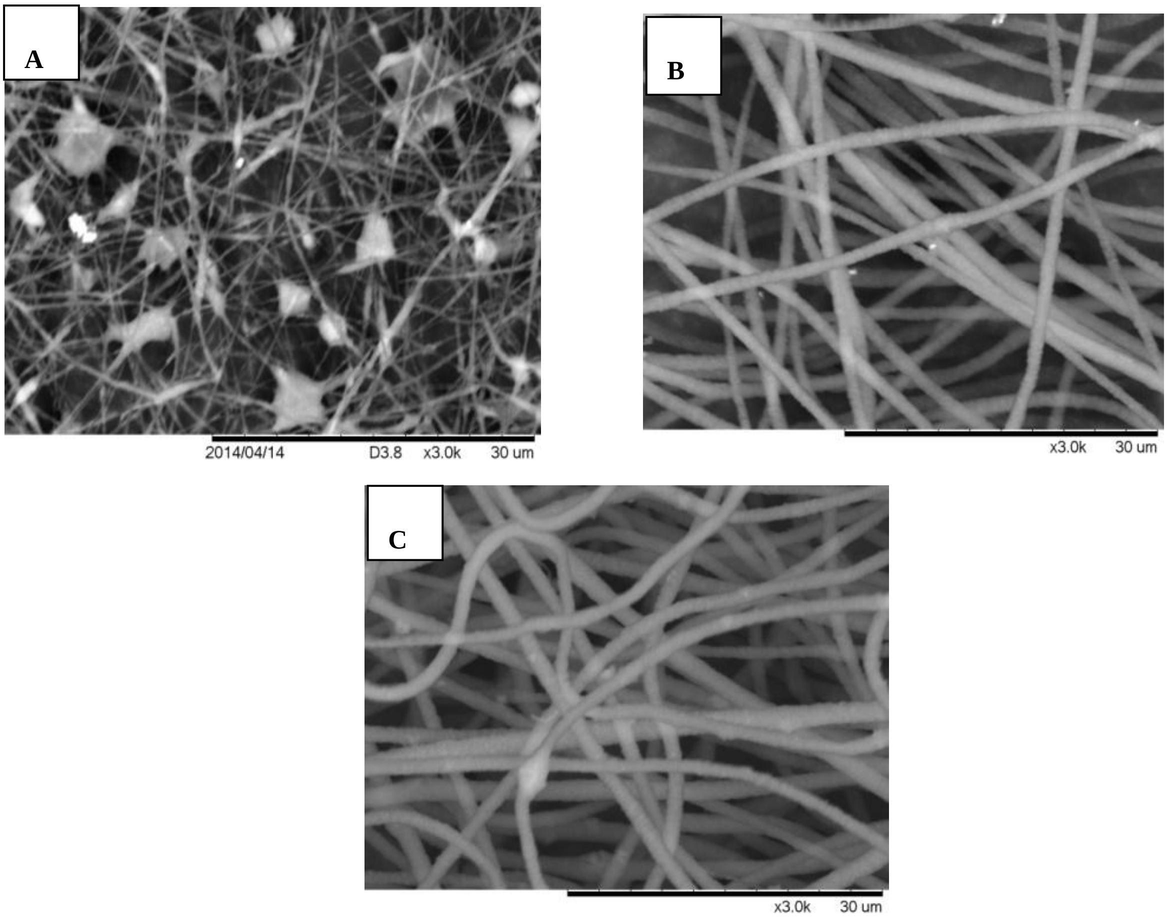


Figure 5. SEM images of electrospun mats of Sample 3 prepared by different methods: (a) Method 1; (b) Method 2; (c) Method 3.

Figure 5 shows SEM micrographs as example of the electrospun Sample 3 fiber mat prepared by three different methods. Polymer concentration and electrospinning parameters in all solutions were kept constant. As can be seen from Figure 5(a), Method 1, as expected, gives thin fibers with beaded morphology and free, not incorporated into fibers CB particles aggregates. Moreover, the prepared fiber mat was extremely fragile and it was not even possible to make any manipulations with it, including the conductivity measurements. Even if the conductivity of such sample were high enough, the poor mechanical performance would be an obstacle for its application elsewhere.

In contrast to Method 1, Methods 2 and 3 give fibers with a perfect morphology (see Figure 5): they are uniform in diameters, defects-free, and no big CB aggregates can be observed. However, the fiber surface is not smooth. The roughness of fiber surface can be explained by the presence of CB particles or small fragments of CB aggregates since an amount of CB in the composite was very high. The fiber diameters of samples prepared by Methods 2 and 3 are thrice as high as that for Method 1. The difference in solution viscosity is the reason for the difference in the fiber diameter obtained by Method 1 and Methods 2/3 (see Table 4) taking into account that the conductivities of the all solutions were nearly at the same level. If all processing conditions (concentration of polymer, CB content, etc.) are kept the same, only sonication can be responsible for the drop in viscosity.

Due to rather large thickness of fibers (around 1200–1300 nm) prepared by Methods 2 and 3 and beads-free morphology, the fiber mats have a good toughness and could be easily operated with. For such samples the conductivity measurements were conducted, the results are listed inTable 4. It is seen that conductivity of the samples has reached the high conductivity in Micro Siemens range.

Table 4. Influence of preparation procedure on properties of electrospun Sample 3 fiber mat.

Method number	Preparation process	Solution viscosity, cP	Average fiber diameter, nm	Conductivity of mat, μS/cm
1	PAN+CB in DMSO is sonicated 6 h	80500	410	Fragile
2	1. CB in DMSO is sonicated 6 h 2. PAN is added and PAN+CB is mechanically mixed 24 h	90000	1300	0.3
3	1. CB in DMSO is sonicated 6 h 2. PAN is added and PAN+CB is mechanically mixed 1 h 3. PAN+CB is again sonicated 3 h	87000	1200	0.5

The same behavior was observed for Sample 2. However, conductivity of Sample 2 fiber mat prepared by Methods 2 and 3 was around 0.01 mS/cm, which can be explained by lower CB content in composite.

Though Method 3 differs a little from Method 2, it gives the identical results. But it should be noticed here that if sonication time applied to the whole mixture PAN+CB in Method 3 exceeds three hours, fiber morphology and properties deteriorate again and resemble those of the Method 1. Comparing all methods it has been concluded that the preparation of a stable CB/solvent suspension under sonication is a very important initial step in producing homogeneous defects-free conductive fibers. Such methods in addition allow producing strong enough fiber mats with high CB contents where all CB particles are bound to the polymer constituents and no free particles are present.

Comparing all three samples we can suggest that an increase in conductivity (approximately by four orders of magnitude) is a result of both increased CB content and better dispersion of CB in the polymer matrix. As the amount of the conductive filler material increases and reaches some critical value, the composite undergoes an insulator-to-conductor transition [44]. Below this critical value, the fillers localize in the matrix as isolated substances with the large voids between them and it creates an obstacle in producing electron conductive network through the matrix. If critical content is exceeded, conductive networks in the matrix will suddenly form and increasing filler content will lead to large increase in conductivity. That is why, the conductivity of Sample 1 and Sample 3 differs by six orders of magnitude. However, the conductivity will never appear (even at high filler content) if a conducting path between fillers is not established. It has been reported that small particle size leads to the formation of more conducting paths per unit volume [45]. The smaller particles merge together forming small aggregates, but their greater number reduce the distance between aggregates, helping the movement of electrons by hopping or tunneling and leading to increased conductivity. Sonication of CB in the solvent helps to fragment big CB particles into smaller ones and this probably causes the formation of good electron paths inside the polymer matrix; as a result higher conductivity values can be achieved.

4.2.Effect of Content and structure of added carbon allotropes

In current research the CB, MW CNT and cond. CNT were used as additives.Each of these additives affect the conductivity of the membrane and the morphology of the obtained fibers differently.

a) *CB-based composites*

At first the effect of the added CB and its content on the morphology andsolution properties as well as conductivity of obtained fibers based on PAN polymer will be discussed. The content of CB:PAN was varied from 1:20 up to 3:2. The solvent used was DMSO.

The morphology of fibers was analyzed by the Scanning electron microscopy (SEM).Snapshots of various areas of electrospun mats at different magnifications were recorded.Figure6 shows the SEM image of PAN nanofibers websat different content of CB. The diameter of the nanofibers was measured by ImageJ software using SEM images.

At first the solutions with small content (from 1:20 up to 1:4) of CB were prepared. The morphology of fibers is presented on figure 6. As can be observed there are no beads and inhomogeneities, fibers are cylindrical, uniform and not aligned. Despite the good morphology of fibers, the conductivity of solid membrane is very low in picoSiemens range. Toimprove the concductivity of fiber membranes itwasdecidedtosignificantly increasethecontentofCB up to CB:PAN=1:2 and higher.

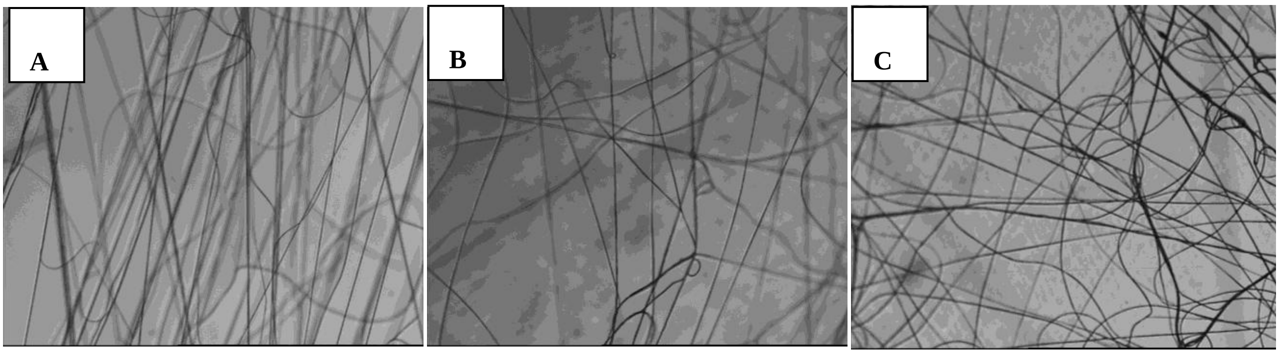


Figure 6. LED pictures of PAN fibers with CB, magnification 10X. Thecontent of CB:PAN: (a) 1:20; (b) 2:20; (c) 1:4.

The morphology of fibers obtained from solution PAN+CB (1:2)is not perfect. There are big amout of beads and solvent drops, the fibers are not uniform and homogeneous. The fiber diameter was 570±150 nm.As was mentioned above the content of fillers affects the morphology of fibers and their characteristics. All data about solutions properties and obtained fibers are presented in Table 5.

Table 5. Obtained data for PAN+CB (m:n) in DMSO.

CB:PAN	Viscosity, cP	Solution conductivity, µS/cm	Conductivity of membrane, µS/cm	Fiber sizes, nm
1:2	6235	50	0.01	570
1:1	7215	53	0.1	2000
3:2	82900	60	0.5	1300

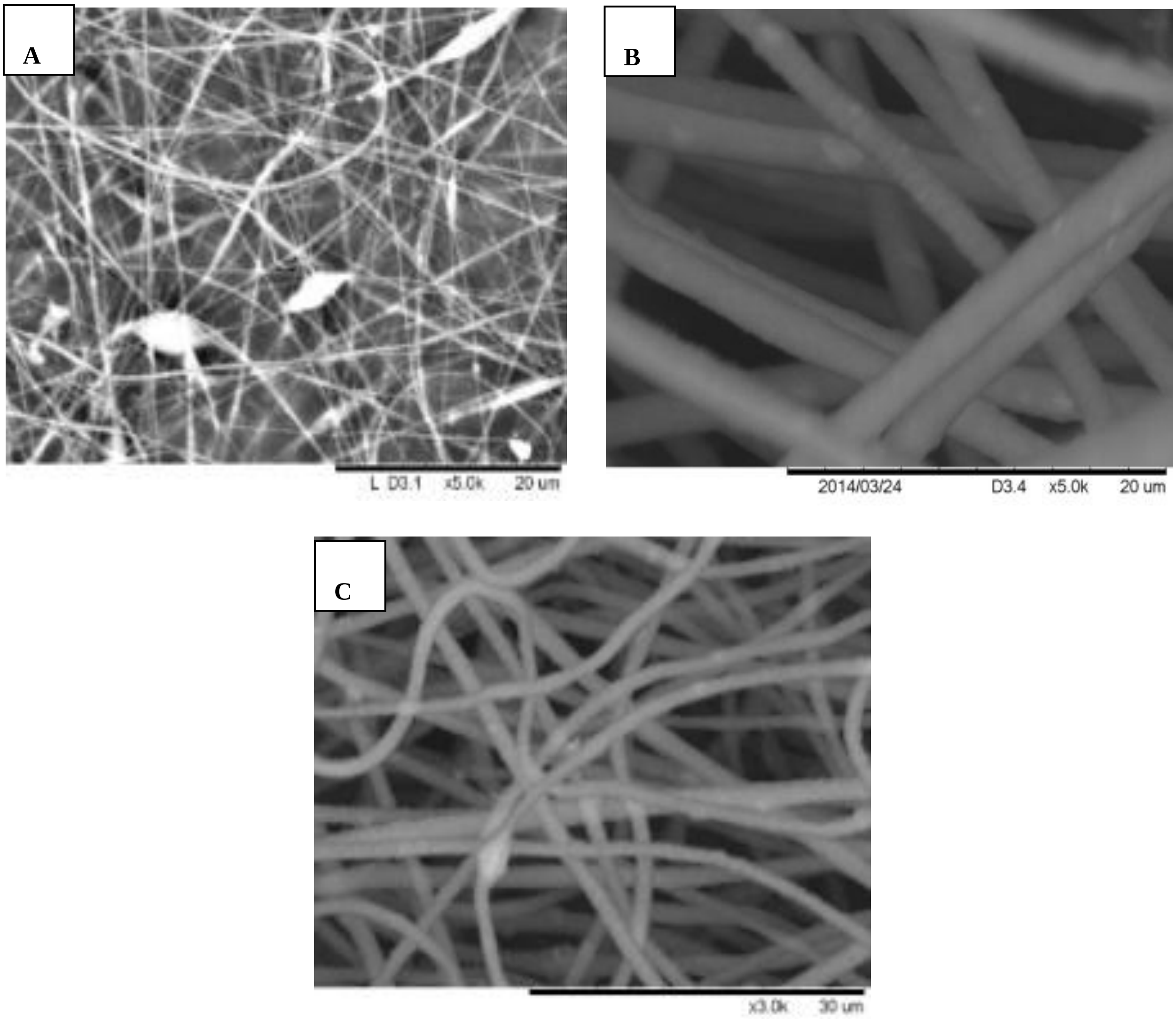


Figure 7. SEM pictures of polymers in solutions, magnification 3000X. The ratio CB:PAN: (a)1:2; (b) 1:1; (c) 3:2.

Interestingly, as can be seen from figure7, the structure of the fibers obtained from solution PAN+CB (1:1)is homogeneous. There are no nodules and beads. The fibers are uniform in diameter. The fibers have a large diameter 2.0±0.3µm that can be explained by the fact that solution had higher viscosity comparing with PAN+CB (1:2).In comparison, the fibers from solutionPAN+CB (1:2) have the lowest value of diameter, it can be due low content of additives, low viscosity of solution and low solution conductivity. The valuesof solutions viscosity arepresented in table 5.

The fibers electrospun from solution PAN+CB (3:2)in DMSO as can be seen from the pictures also had homogeneous structure, no knots and beads, and fibers have rather narrow diameter distribution.But average diameter is lower than for PAN+CB (1:1), and is 1.3±0.3µm. This may be explained by several factors, because solution parameters and process parameters can influence the morphology of fibers. Despite this solution had the higher value of viscosity, due to higher content CB in solution, solution conductivityis the highest from all studied samples as can be seen from the table 5, leading todecrease in the diameter of fibers during process.

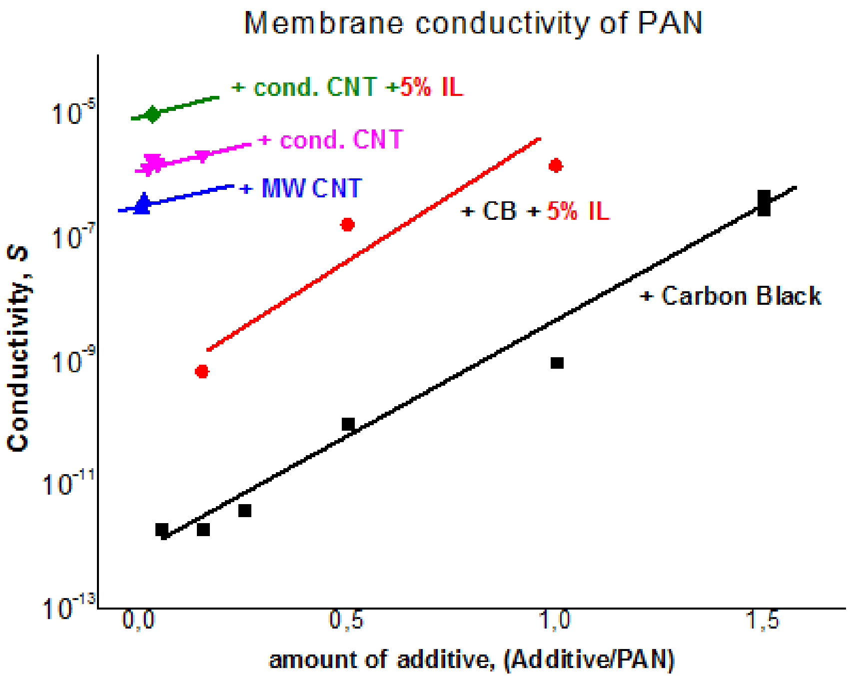


Figure 8. Membrane solid phase conductivity.

The most important findings of the work is the dependence of membrane conductivity on content of added CB.

It can be seen from figure 8that the conductivity of the membrane increases with a gradual increase in the amount of additives. Membrane conductivity was started in the range of picoSiemens and then with the increasing of concentration of carbon black transferred to the microSiemens range – membranes show the semi conductance.

To increase the conductivity of membranesto even more extent,the ionic liquid BMIMCL was addedto some solutions. The ionic liquid known as good electrolytes, also this liquid can conduct electricity very well. The ionic liquid is a generated solvent, with big amount of advantages like excellent dissolution ability, high thermal stability, and ease of recycling.Also ionic liquid is a green solvent and this makes it friendly for environment.

After the addition of even a small amount of IL to the spinning solution, the conductivity of solution increases in times, because ionic liquids are largely made of ions and short-lived ion pairs.Due to high conductivity of the electrospinning solutionthe fibers became more aligned, oriented in one direction with electric field and ordered in electrospinning process, as can be seen from Figure 9.

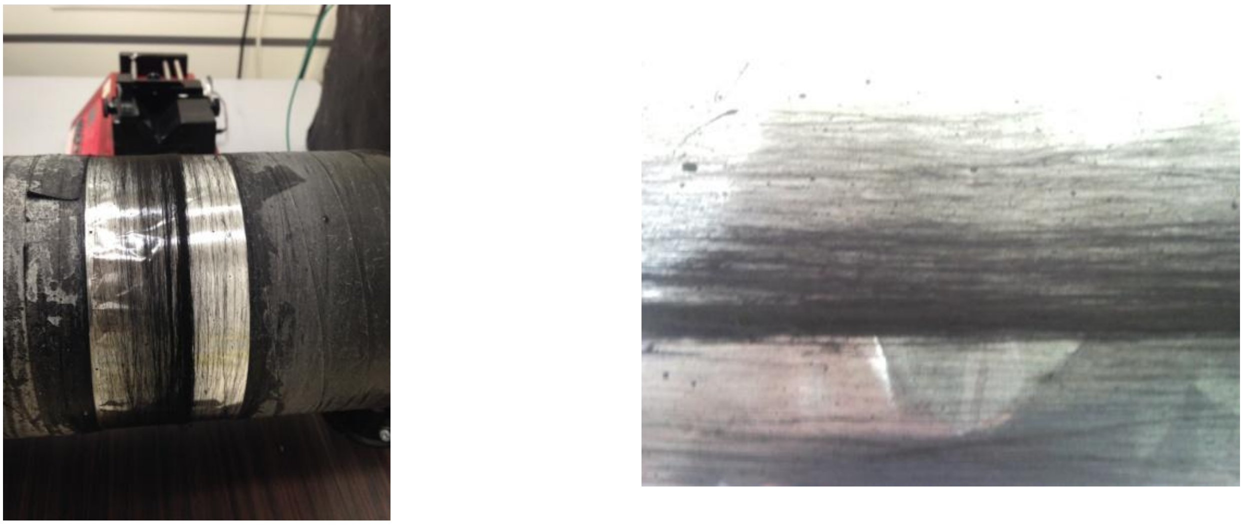


Figure 9. The appearance of PAN fibers after addition of IL.

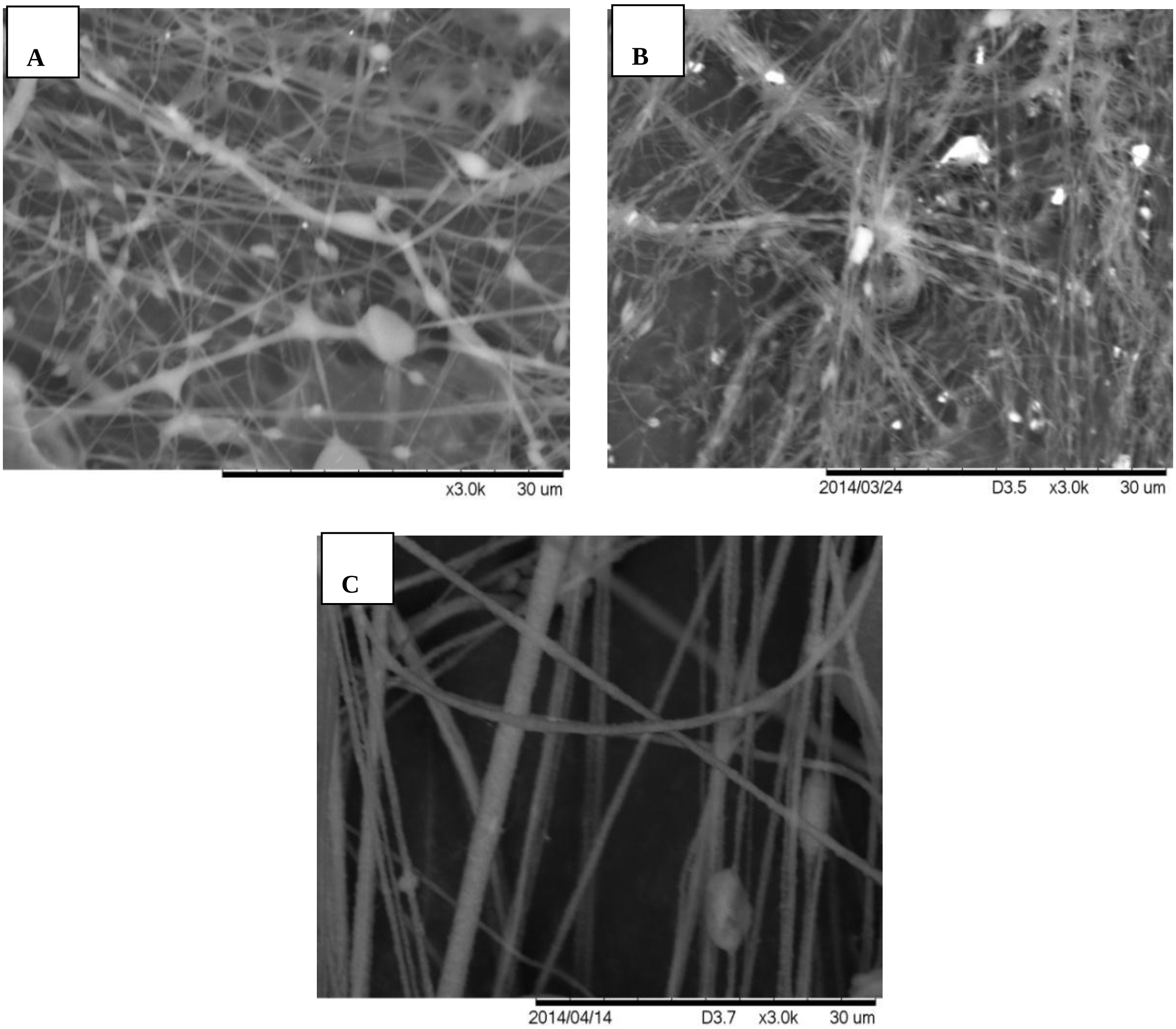


Figure 10. SEM pictures of PAN+CB fibers with IL, magnification 3000X. The content of CB:PAN (a) 3:20; (b) 1:2; (c) 1:1.

The morphology of fibers with IL presented on figure 10. FromSEMpicturesitcanbeseen that there are drops of ionic liquid, the structure of fibers became inhomogeneous and nonuniform. Thefiberdiameterdecreased in two times:forcomparison the diameter of fiber obtained from solution PAN+CB(1:1) was 2000 nm before the addition of IL, and after it became 960 nm. Thesamesituationwithsolution PAN+CB(1:2): before addition the size of fibers was 580 nm, after it became 260 nm. The diameter reduction can be explained by the increaseof solution conductivity by three orders of magnitude and a decrease of viscosity of whole solution, because after addition of small amount of IL the viscosity of solutions decreased.

As it can be seen from table 6, the fiber diameter after addition of IL increase with increasing CB content.

Table 6. The obtained data for PAN+ CB solutions withIL.

Solution	Solution conductivity, mS/cm	Fiber diameter, nm	Membrane conductivity, nS/cm
PAN+CB (3:20)+IL	2.5	260	0.7
PAN+CB (1:2)+IL	3.15	360	165
PAN+CB (1:1)+IL	3.8	958	1500

After addition of IL the membrane conductivity increased too. Beforethe addition the membrane conductivity of PAN+CB(1:1) was 0.5 μS/cm, and after it became 1.5 μS/cm. Then it can be concluded that addition of even small amount IL improves the conductivity in three times. The comparison of membrane conductivity presented on figure 8.

b) CNT- based composites

For comparative purposes the influence of CNT on fiber properties was studied. In this research two types of CNT were used:

1. UnmodifiedMW CNT
2. Modifiedconductive MW CNT composites (with addition of special type of grain electrode), named further as cond. CNT

Taken into account that preparation plays important role in resulting final morphology, both types of composites were prepared by two different methods. In mechanical mixing at first CNT were dissolved in certain solvents for 3 hours, and after addition of polymer the whole solution was mechanically stirred for 24 hours. In second method US was used: CNT were sonicated in the same solvents for 3 hours and after addition of polymer, whole solution was mechanically stirred for 24 hours.

The morphology of fibers obtained from PAN solutions with cond. CNT and MW CNT is presented on figure11,12,13, 14. Here can be checked how the morphology of fibers changed depending on type of additives and preparation procedure.

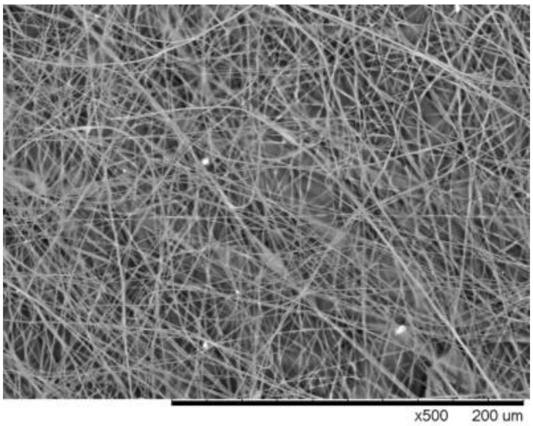
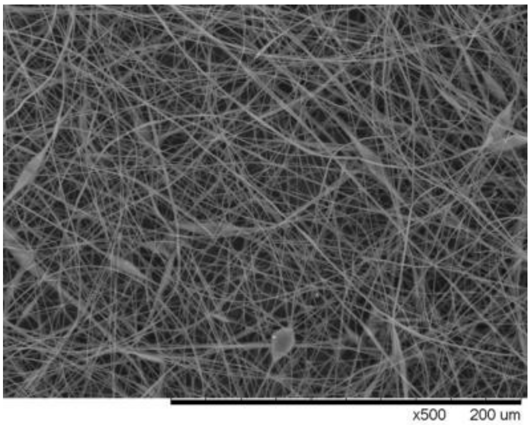
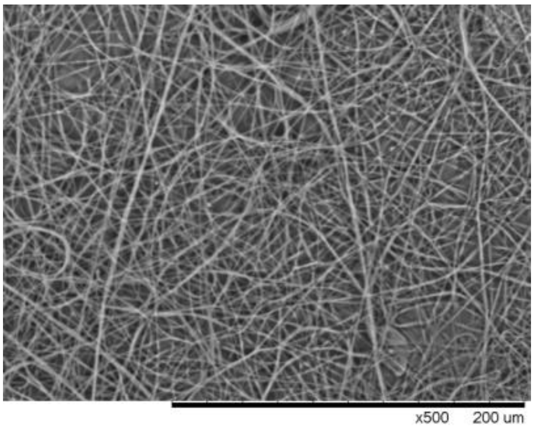
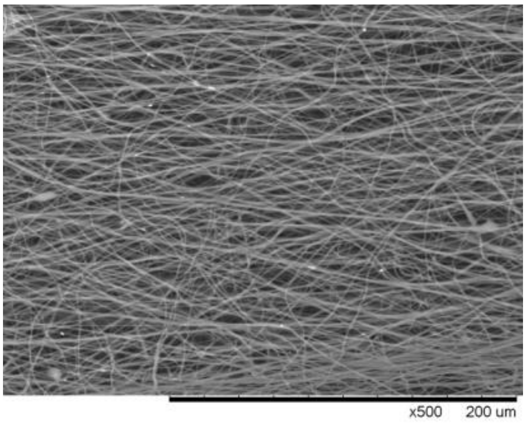
Method Type ofCNT	Mechanical mixing	US
PAN+cond. CNT (1:100)		
PAN+MW CNT (1:100)		

Figure 11. SEM pictures of fibers from solutions prepares by different methods, magnification 500X.

As can be seen from the Figure 11fibers with cond. CNT prepared bymechanical mixing are homogeneous in sizes, uniform, thick and there are no inhomogeneities and fibers are beads free. However, fibers obtained from solution prepared by US are heterogeneous, there are inhomogeneities and beads. Moreover the diameter of such fibers is lower than that of fibers obtained by mechanical mixing. Fibers prepared by US had average diameter 655 nm, while the average size of fibers prepared by mechanical mixing was 900 nm. This can be explained by difference in conductivity. The value of solution conductivity prepared by mechanical mixing was 25 μS/cm, for solution prepared by US it was 32 μS/cm. Possibly,for suchtype of nanotubes it’s not good to use sonication treatment, because they are composed of specific materials providing good solubility of Cond. CNT in liquid medium without additional treatment. Sonication seems to deteriorate the special composite structure of cond. CNT, dropingtheconductivityandviscosityofsolution. This leads to smaller fiber diameters and worse morphology of obtained fibers.

Fibers obtained from polymer solution with MW CNT prepared by mechanical mixing have inhomogeneous structure with many irregularities, beads and solvent drops. For MW CNT prepared with using US, it can be concluded that the morphology of fibers has changed after sonication. The fibers are thin and cylindrical. Number of beads and knots are reduced, the structure becomes more uniform and aligned. In this case sonication helps to provide better CNT dispersion and incorporateion them into nanocomposites, and as a result, better fibe morphology can be obtained.

Therefore, it can be concluded that for cond.CNT it’s better to use mechanical method of preparation, whereas for solutions with MW CNT it’s better to use ultrasonic energy.This fact is confirmed by values of membrane conductivity. The conductivity of electrospun mat obtained from solution with cond. CNT prepared by mechanical mixing was higher than for US and it was 9.5 µS/cm, the value for membrane with cond. CNT prepared by US was 3 µS/cm. In case of membrane with MW CNT prepared by US the conductivity was higher than for prepared by mechanical mixing. For US the conductivity was 3.7µS/cm and for mechanical it was 0.4µS/cm.

The effect of content of cond. CNT on morphology ispresented on figure 12. Fibers with small amount of additives (1:200 up to 3:100) have good morphology. There are no beads or solvent drops, the fibers are cylindrical, homogeneous and uniform in size. With increasing the amount of additives the deterioration of morphology of the fibers can be observed. The fibers became heterogeneous with presence of beads and irregularities. Because of high content of additives the viscosity of solutions also significantly increases,as can be easily seen from table7. Surprisingly, that increase in cond CNT content does not affect much the solution conductivity. Therefore, increase in fiber sizes can be attributed to the increase in solution viscosity. However, content of added CNT affect the membrane conductivity: the higher the content of CNT, the higher is the conductivity of membrane. But it should be noticed, that this effect is not significant, and only slight increase in conductivity can be observed.

Table 7. Data for PAN solution with cond. CNT.

cond. CNT:PAN	Viscosity of solution. cP	Solution conductivity, μS/cm	Fiber sizes, nm	Membrane conductivity, μS/cm
1:200	15125	18	615	17.31
1:100	17750	27	655	9.55
1:50	16350	23	950	13.7
3:100	22950	24	520	18.1
1:25	26450	33	1200	15.8
3:20	32650	24	873	22.1

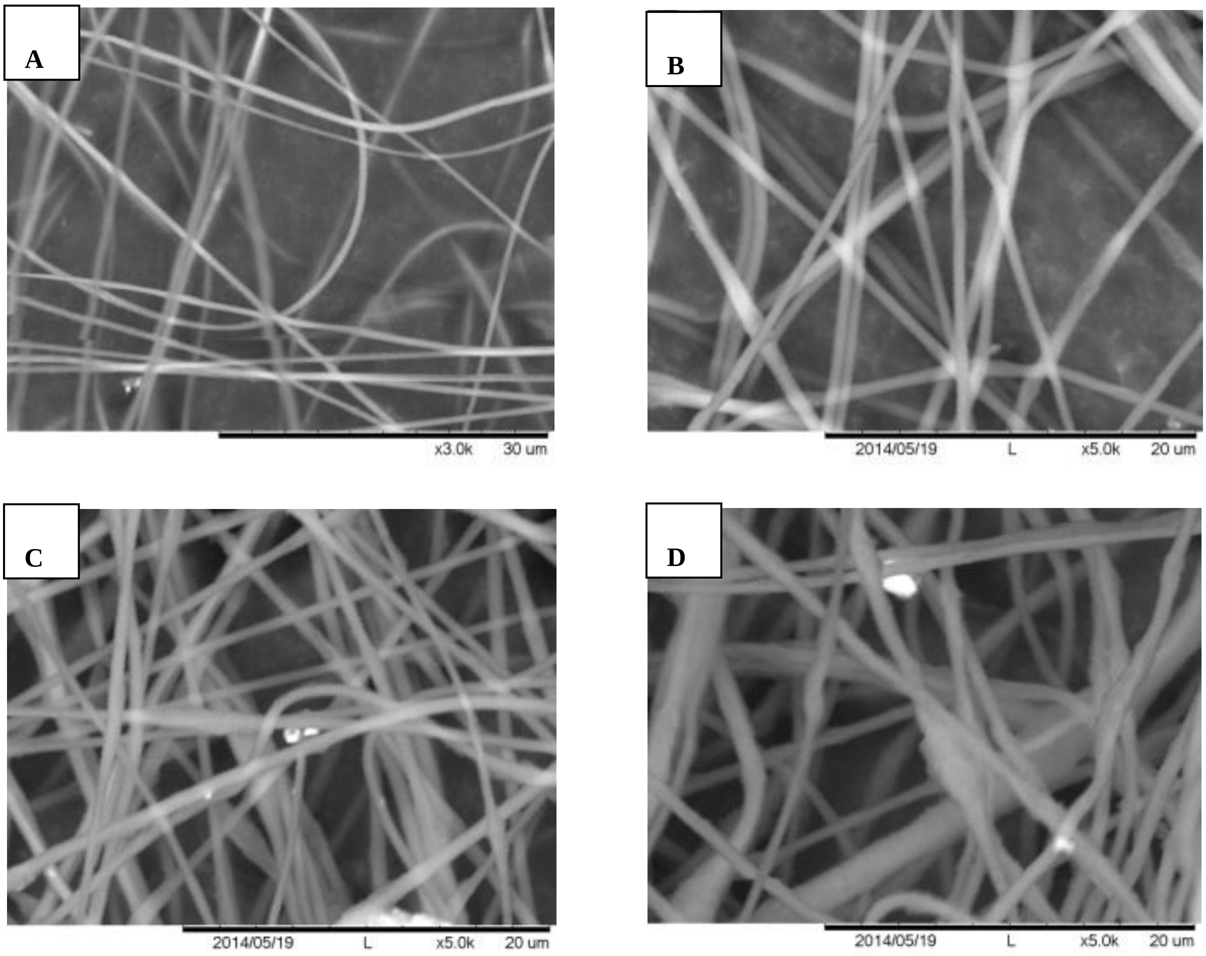


Figure 12. SEM pictures of PAN with cond. CNT, magnification 5000X. The content of cond. CNT:PAN: (a) 1:200; (b) 3:100, (c) 7:100; (d) 3:20.

It can be concluded that increasing amount of CNTslightly improves the conductivity of obtained membrane. But big amount of additives exert a bad influence on morphology of obtained fibers and viscosity of solution, because of formation of big agglomerates due higher content of additives. It should be noticed that for cond. CNT- composites the obtained solid membrane conductivity was always in microSiemens range, irrespective of CNT content.

Figure 13. Membranes with different content of cond. CNT

From figure 13 it can be seen that color of the membrane changes with increasing the content of additives. The membrane obtained from solution PAN+cond. CNT (3:20) has more dark fibers than membrane obtained from solution PAN+ cond. CNT (3:100).

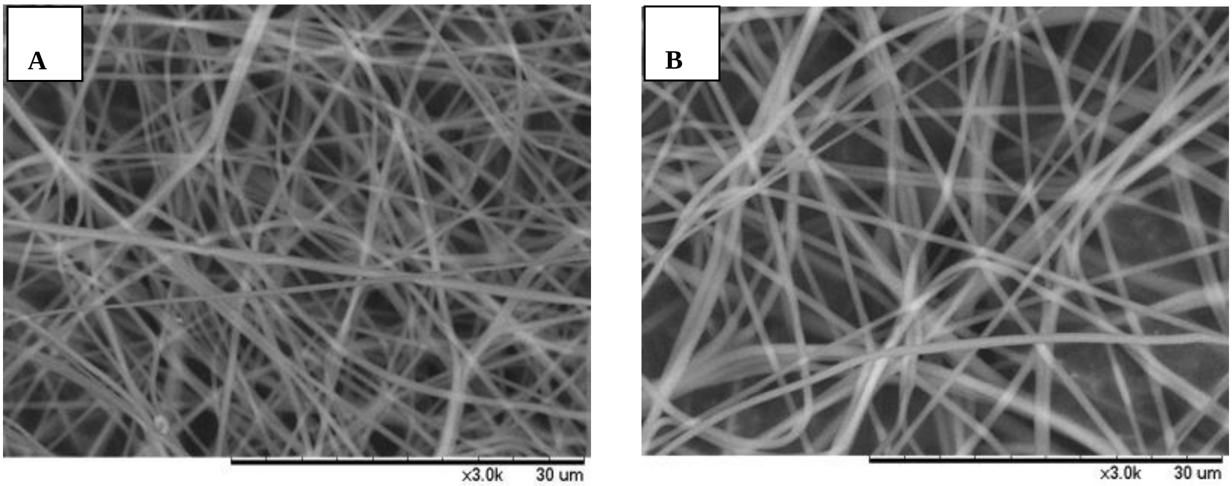


Figure 14. SEM pictures of PAN with MW CNT, magnification 3000X. The content of MW CNT:PAN: (a) 1:200; (b) 1:100.

Now let’s consider the morphology of fibers obtained from solutions withMWCNT. Composite with unmodified MW CNT was prepared and studied. For comparative purpose only two different contents of unmodified MWCNT were chosen – MWCNT:PAN=1:200 and 1:100 and compare with the cond. CNT:PAN=1:200and 1:100.

As can be seen from figure 14 the fibers from solution PAN+MW CNT (1:200) are beads-free, cylindrical, homogeneous and uniform. The diameter of fibers is 500±100 nm and it's lower than for fibers obtained from solution PAN+MW CNT (1:100). This can be explained by the fact that solution PAN+MW CNT (1:100) has higher value of viscosity because of the higher content of additives in solution. The values of solution viscosity and conductivity are presented in table 8.

Table 8. The data for solutions with MW CNT.

MW CNT:PAN	Viscosity of solution, cP	Solution conductivity, μS/cm	Fiber sizes, nm	Membrane conductivity, μS/cm
1:200	15600	20	500	3.8
1:100	17550	23	690	4.3

The MW CNT content affects the final conductivity of membranes in similar manner: as can be seen from figure 8 the membrane conductivity increase with the increasing of additive content. Comparing results for cond. CNT (Table 7) and MW CNT (Table 8) it is clearly seen, that cond. CNT gives higher conductivity values. Moreover, in general CNT gives higher conductivity in comparison with CB.

Finally, the membrane conductivity of samples with both cond.CNT and MWCNT ranges in micro Siemens range. However, using cond. CNT allows one to get the highest conductivity of the membrane because of special grain electrode conductive additives inside. These nanotubes can better dispersed in the environment, as well as better distributed in the solution to provide a higher conductivity of mats compared to conventional carbon nanotubes.

If compare the type of all additives then it can be concluded that even small amount of cond.CNT givesthe highest value of membrane conductivity, than with using of CB or MW CNT.Large content of CB complicates the working process, because solution viscosity became very high. MW CNT are known as difficult to be disperse, for this type of additives needs long time of ultrasonication. And as presented on figure 8, the membranes with CB and MW CNT is lower than for cond. CNT.

As a trial,ionic liquid were added to cond. CNT:100=3:100, the ratio of polymer solution to IL was 20/1 and after that the solutions were electrospun. In this case, the addition of ionic liquid improves the conductivity of membrane too.The addition of only small amountgreatly increased the conductivity of membrane in solid state, the conductivity of membrane increased by 3 orders of magnitude. For example in case of CB membrane after addition of IL the value of membrane conductivity increased in 3 orders of magnitude. ThesamecanbesaidaboutCNTmembranes.

It can be concluded that it's better to use cond.CNT because simple method of preparation and the addition of a small amount (0.5-7 wt%) greatly changes the conductivity of the fibers.The membrane conductivity obtained from solutions with cond. nanotubes isalways in microSiemens range.It can be explained by the fact that cond. CNT have grain electrode conductive additives and they are well dispersed in liquid medium. The morphology of fiber membranes are good, there are no beads and no inhomogeneties. Also the conductivity of solution increased.

4.3.Effect of Polymeric Matrix

In order to explore how a polymer matrix affects the conductivity of membrane and morphology of fibers, solutions with various polymeric matrixes asPAN, PVDF, PS and DACwere prepared. The PVDF was chosen because of its interesting piezo electrical properties. The piezoelectric activity of PVDF is determined by the coefficients of proportionality between the mechanical causes and the electrical effects. The DAC polymer was chosen as natural polymer. The cellulose diacetate is biodegradable and hydrophilic. And PS and PAN were chosen as the most widely used conventional polymers on production lines.In this experiment the CB:Polymer=1:1, CNT:Polymer=1:100 and identical conditions for all the samples preparation were used.

a) Pure polymer systems

Figure 15demonstrates the SEM images of fiber morphology obtained from pure polymer solutions without addition of CB or CNT.

As can be seen from figure 15 pure PAN fibers as well as DAC and PS, are homogeneous, cylindrical, uniform in size, there are no beads and inhomogeneities.

The fibers electrospun from PVDF solution had poor fiber morphology; the fibers aren't uniform, the structure is curly and heterogeneous, this can be explained by the fact that the combination of solvent (DMF) and non-solvent (acetone) was used in spinning. Acetone isn't a solvent for PVDF, it makes the structure of polymer in solution compact. And also it's really hard to dissolve PVDF in solutions, and with the presence of acetone in the solution makes it difficult, but acetone is an important component for good spinning of this polymer.

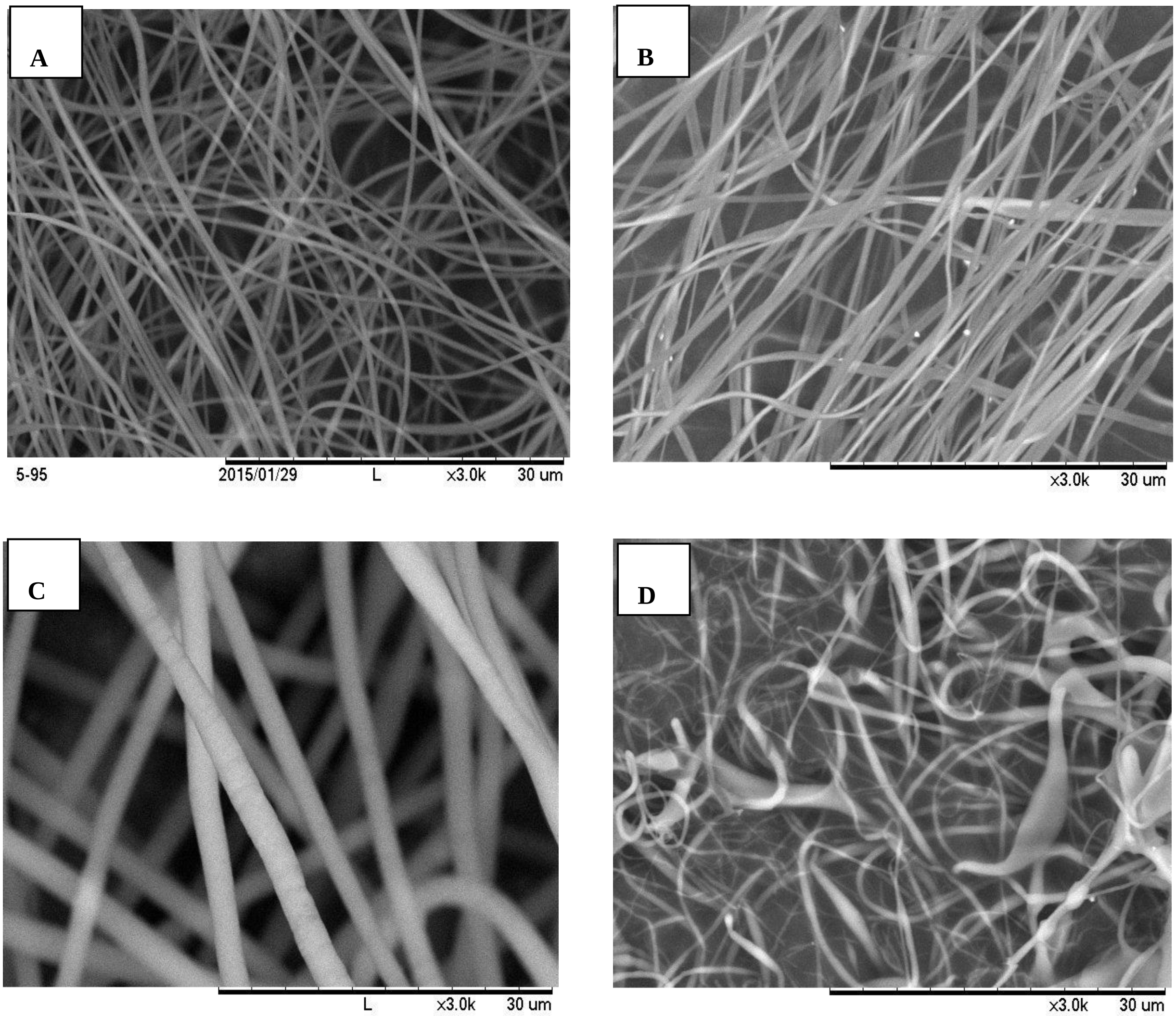


Figure 15. SEM pictures of polymers in solutions, magnification 3000X: (a) PAN in DMSO; (b) DAC in (4/1)DCE/Methanol; (c) PS in DMF; (d) PVDF in (3/2)DMF/Ac.

b) CB-based composites

Also the polymer composites with CB were studied. The ratio CB:Polymer was fixed and it was 1:1.

As can be seen from figure 16the morphology of fibers changed after addition of carbon black.Unfortunately, we could not prepare solution with PVDF, therefore the results are not presented here. We tried to prepare this solution twice, at first CB was sonicated for 3 hours and then polymer was added, but it was not dissolved. The solution looked like wet sand.

The structure and solution properties of PAN composites were explained in previous chapter. The analyzed results for PAN solutions are presented in the table 9.

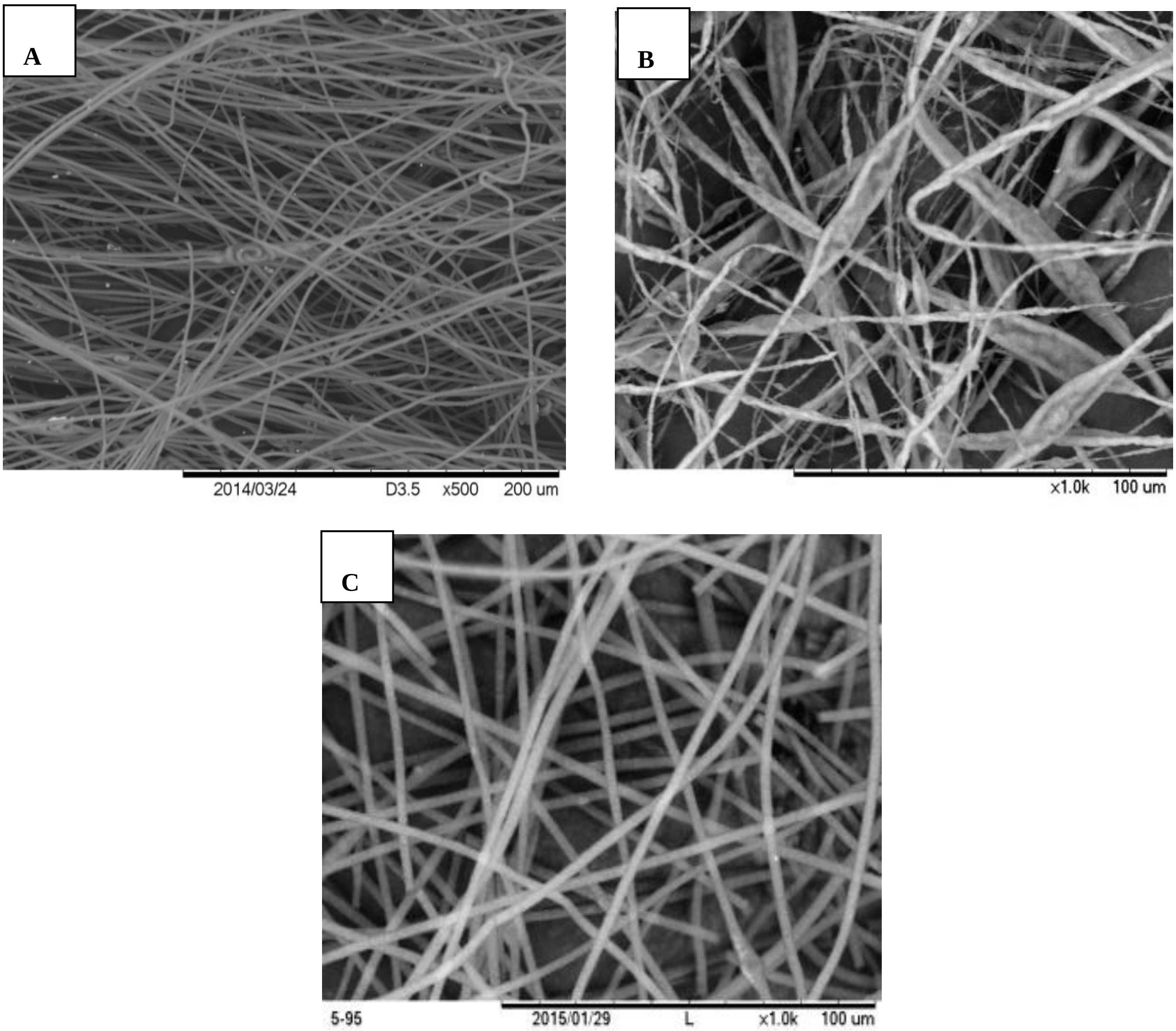


Figure 16. SEM pictures of polymers with CB in solutions, magnification x1000. The content of CB is kept constant for all samples and is CB:Polymer=1:1. (a) PAN+CB in DMSO; (b) DAC+CB in (4/1)DCE/Methanol; (c) PS+CB in DMF.

Table 9. Results of measurements for PAN solution.

PAN solution	Viscosity, cP, (5 RPM)	Conductivity of solution, µS/cm	Average diameter, nm
Pure	6990	23.6	390
+CB	7215	53	2100
+cond. CNT	17600	25.5	735

The **PAN**fiber diameter increased after addition of CB and cond. CNT, because the viscosity of solution increased too.

Fibers with CB produced from solution **DAC**+CB (1:1) have another morphology comparing with PAN fibers and with pure DAC solution. The fibers are heterogeneous, unordered, with different diameters and there are a lot of inhomogeneities and beads. Probably, because of rigid polymer structure of DAC, CB particles can't normally be dispersed in a polymermatrix. Also the bad dispersion can occur because of the another used solvent. The table 10 shows the obtained data for DAC solutions.

Table 10. Results of measurements for DAC solution.

DAC solution	Viscosity, cP, (10 RPM)	Conductivity of solution, μS/cm	Average diameter, nm
Pure	420	2.3	1250
+CB	2010	4.1	895
+cond. CNT	520	7	650

Polymers viscosities, electrospinning concentrations and other solution properties can not be directly compared with each other due to different chemical structures, molar masses and solvents used. All these parameters influence the overlap concentrations (which is related to concentration of electrospinning of fibers) and solution properties like viscosity, conductivity etc. However the final properties of solid membranes can be compared.

DAChas another molar mass and chemical structure than PAN and as consequence another overlap concentration. As well, another solvent was used that results in lower values of viscosity, comparing with PAN. However, it does not influence the fiber diameter. As it can be seen, the sizes of DAC fibers are comparable with PAN. How it influence the conductivity of membrane will be discussed later.

Moreover the larger the amount of added carbons, the greater the viscosity, because the rigid structure of CB and CNT add some additional impact to viscosity.The high viscosity of the solution contributes to the increase in diameter of the fibers. And the expanding content of additives contributes to high solution conductivity. High conductivity of solution in turn reduces the diameter of the fibers.In our case the size reductionof DAC fibers can be explained by the summation of all these facts.

Analogically to PAN matrix, fibers obtained from **PS** solution of chosen concentration 25% had very good morphology, fibers are aligned, homogeneous and uniform in diameter.

Table 11. Results of measurements for PS solution.

PS solution	Viscosity, cP, (5 RPM)	Conductivity of solution, µS/cm	Average diameter, nm
Pure	525	0.2	2300
+CB	3300	29	2650
+cond. CNT	545	0.4	3300

In table 11 presented obtained data for PS solutions. As it can be seen the fibers diameter increases with addition of additives. Also the concentration of polymer affected the fiber diameter. Fibers obtained from PS solutions with different carbons have the highest value of fiber diameter from all studied samples, that is just internal property of PS solutions, taking into account another chemical structure, molar mass and overlap concentration.

Hence, PAN and PS matrixes can be used as matrix for CB-based composites, giving a perfect fibrous morphology, in comparison to DAC and PVDF. However, perfect fibrous morphology does not guarantee the highest membrane conductivity. Indeed, the membrane conductivity of PAN+CB sample was 0.3µS/cm and for PS+CB sample the value was much lower, it was 0.004 µS/cm.

c) CNT-based composites

Now the behavior of different polymer solutions with CNT will be discussed.

From Figure17 one can see the morphology of fibers obtained from solutions with PAN, PVDF, PS and DAC and as additive in this case cond. CNT was used. All solutions were prepared at the same conditions.

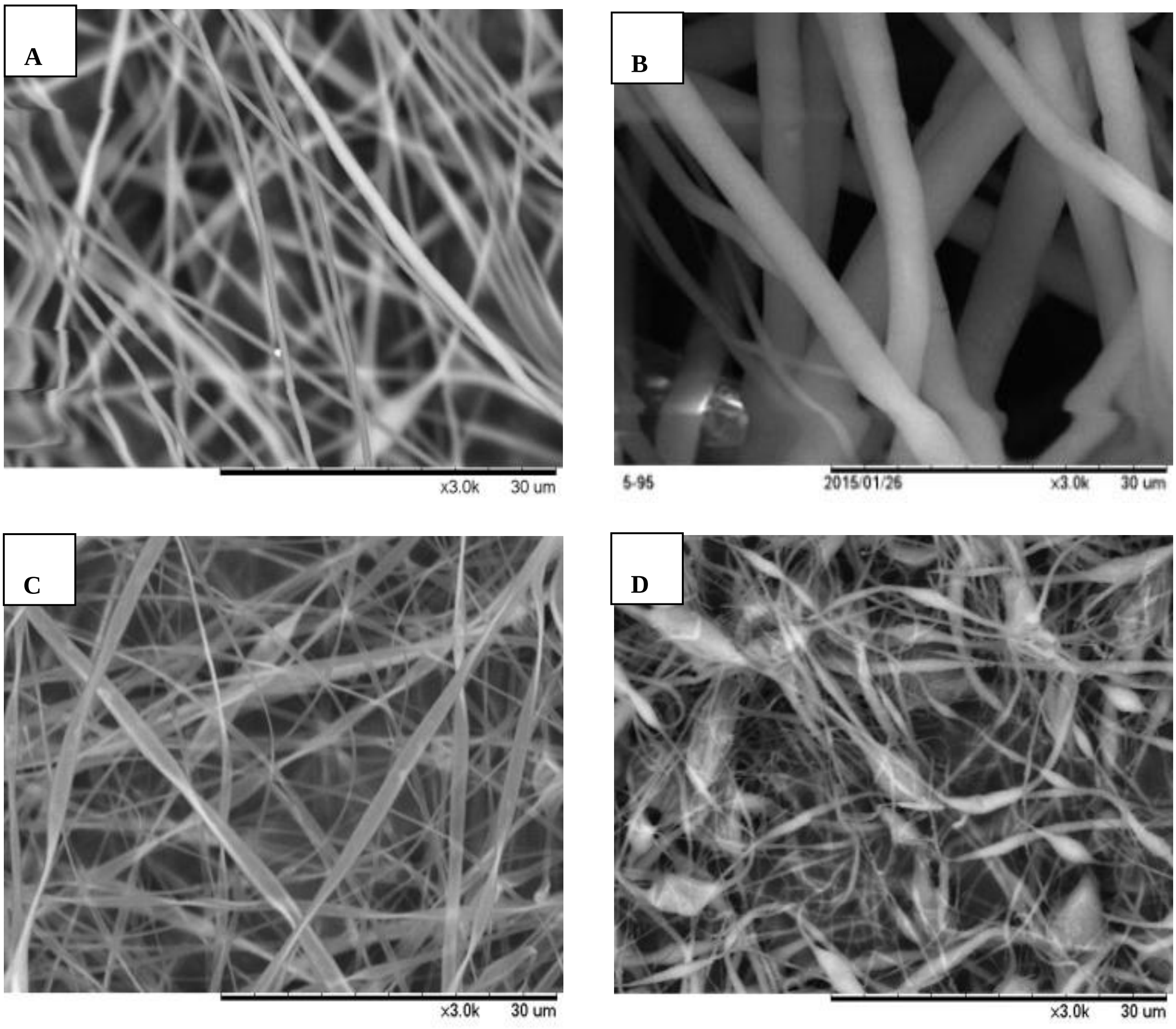


Figure 17. SEM pictures of polymers with cond.CNT in solutions, magnification x3000. The content of cond. CNT is kept constant for all samples and is cond. CNT:Polymer=1:100. (a) PAN+ cond. CNT in DMSO; (b) PS+cond. CNT in DMF; (c) DAC+cond. CNT in (4/1) DCE/Methanol; (d) PVDF+cond. CNT in (3/2)DMF/Acetone.

PAN-based fibers with CNT was thoroughly discussed in previous chapters. If consideredthe structure of fibers with **PAN** +cond. CNT (1:100) prepared by mechanical mixing, then the fibers are homogeneous in sizes, aligned, uniform, thick and there are no inhomogeneities and conductive CNT well dispersed in the medium.

Electrospun mat produced from solution with **PVDF** has different morphology, because of bad dispersion of additives in solution. In case of this solution for better dispersion of polymer and CNT in polymeric matrix it is needed to apply sonication. The structure of fibers is heterogeneous and curly.Fibers are wet and stacked together. Generally, morphology of PVDF+CNT samples is not fibrous but film-like with tailoring of fibers. The fibers obtained from pure PVDF solution and PVDF+cond. CNT (1:100) solution have the same morphology, so here we can’t estimate the dispersion of additives in this polymeric matrix. But the conductivity of membrane obtained from PVDF+ cond. CNT (1:100) solution is high, even despite the poor morphology of fibers.The sizes of fibers diameter are presented also in table 12.

Table 12. Results of measurements for PVDF solution.

PVDF solution	Viscosity, cP, (5 RPM)	Conductivity of solution, µS/cm	Average diameter, nm
Pure	3290	1.8	515
+CB	Was not able to produce		
+cond. CNT	3250	3	442

Fibers obtained from solution with **DAC** has an elongated ribbon-like form, however they are heterogeneous in size, due to presence of some amount of beads.

The fibers obtained from **PS** solutions had very good morphology, the fibers are beads-free, cylindrical, homogeneous, uniform in size and have the highest value of diameter.

The aim was to study the effect of polymeric matrix on conductivity of solid membrane phase. For this goal the dense membranes were obtained bymethod of electrospinning from polymer solution. The mats from all polymeric matrixes were manufactured at the same electrospinning conditions: voltage was 15kV, distance was 15 cm and pumping rate was various. The conductivity of mats was also measured and presented in Table 13.

Table 13. Membrane solid phase conductivity.

Polymer	Membrane solid phase conductivity, µS/cm	
	+CB	+cond. CNT
PAN	0.3	19.6
DAC	0.013	0.015
PS	0.004	0.004
PVDF	-	8

The obtained data on conductivity of membranes with cond. CNT will be discussed below.

The membrane conductivity of samples with DAC as polymeric matrix ranges in nano Siemens. As well as the DCE/Me can be not suitable solvent for such types of additives. Comparing it with solution PAN+CB (1:1) it is seen that the conductivity is lower in 20 times. Then it can be concluded that PAN and DMSO can provide better dispersion of CB and CNT in solution.

If consider solutions with PVDF as matrix the mat has conductivity in micro Siemens range. The PVDF exhibits piezoelectric and pyroelectric properties, that’s why even because of bad morphology, it can provide high value of membrane conductivity.

In comparison with other membranes the PS membrane conductivity has the lowest value. The reason for that can be the largest fiber diameters of PS fibers in comparison with all other polymers. The most probable, that such huge amount of pure PS material in fiber shields the contact between carbon particles. By percolation theory it means that the decrease in electric conductivity of whole composite samples could be observed. In this case it would be wise to decrease the PS concentration to achieve smaller fiber diameters, but however as it was shown in our laboratory at lower concentration of PS in DMF the beaded PS morphology is obtained.

Electrospun mats with PAN have better morphology and higher conductivity, so it be can conclude that PAN is the most optimal polymeric matrix for use.

4.4.Effect of the solvent

Different solvents may have different effects on morphology and properties of obtained fibers. So in this study we investigated the effect of different solvents on the conductivity of electrospun membranes with CB and cond. CNT. For this purpose, PAN was chosenas polymeric matrix.Solvents was chosen to be the same with those used in spinning of different polymer matrixes (PS, PVDF): DMSO, DMF and mixture of DMF and acetone. Solvent DCE can’t be used because it is not a solvent for PAN.Concentration of PAN in all solvents was kept the same and equal to 10 wt%.

a) Pure PAN in different solvents

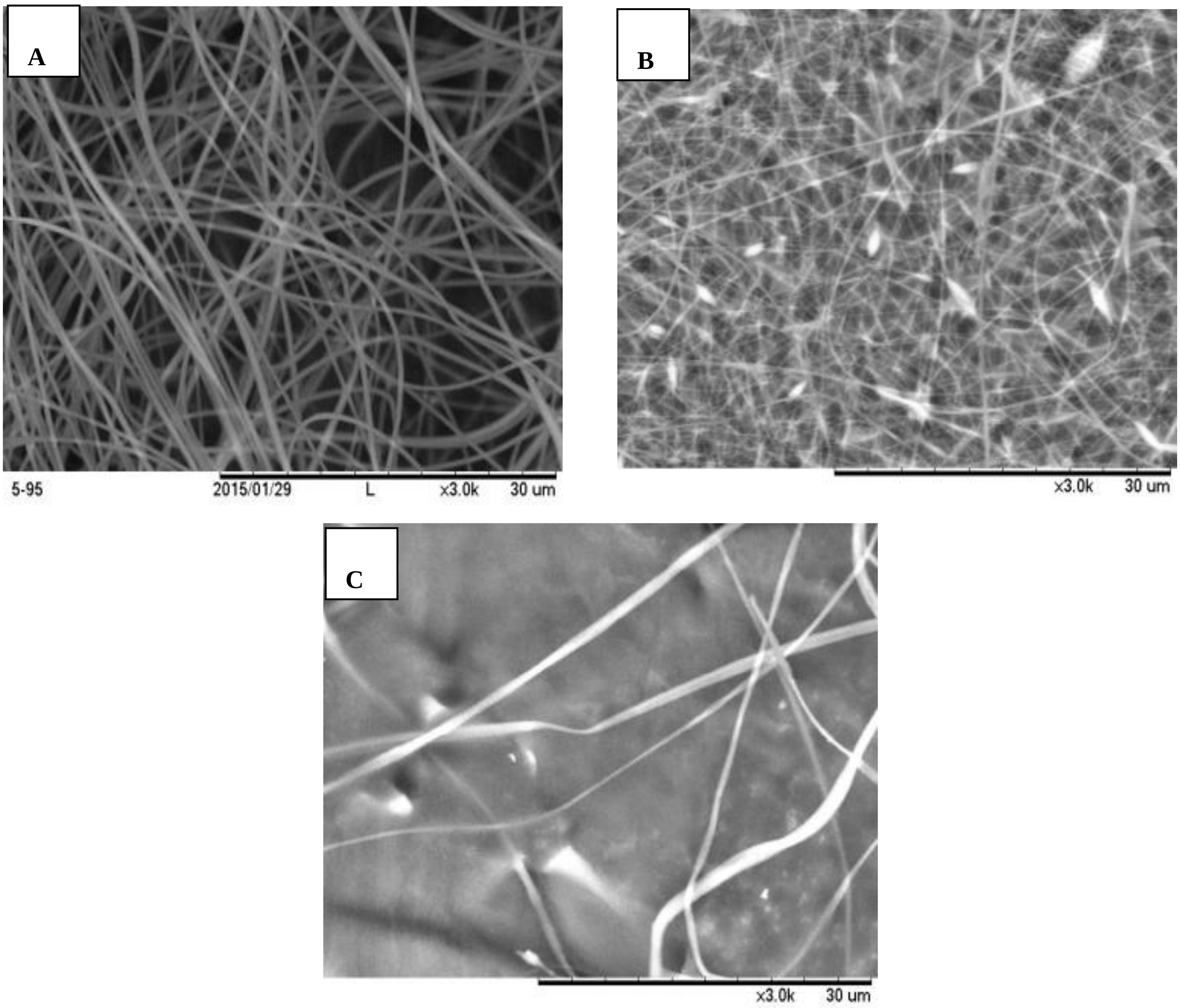


Figure 18. SEM pictures of PAN in solutions, magnification 3000X. (a) PAN in DMSO; (b) PAN in DMF; (c) PAN in (3/2)DMF/Acetone.

The fibers morphology of all studied samples presented on figures18, 19,20.As was mentioned above PAN fibers where as solvent DMSO was used, are homogeneous, uniform in size, there are no beads and inhomogeneities. And in case of additives the fibers have good fiber morphology and uniform structure.

For pure PAN solution in DMF it can be seen that the fibers contains beads at used concentration, fibers are heterogeneous and unordered.

For pure solution PAN in DMF/Ac it can be seen that the fiber morphology are poor, there are a lot of solvent drops, inhomogeneities and fibers are heterogeneous. It can be explained by the fact that acetone is not a solvent for PAN and the structure of solution and properties of solution changed after addition of acetone. The prepared solution of PAN in DMF/Ac had jelly structure and the process of Electrospinning is practically impossible, because irregularities do not pass and stuck in the needle.

b) CB-based PANsolutions

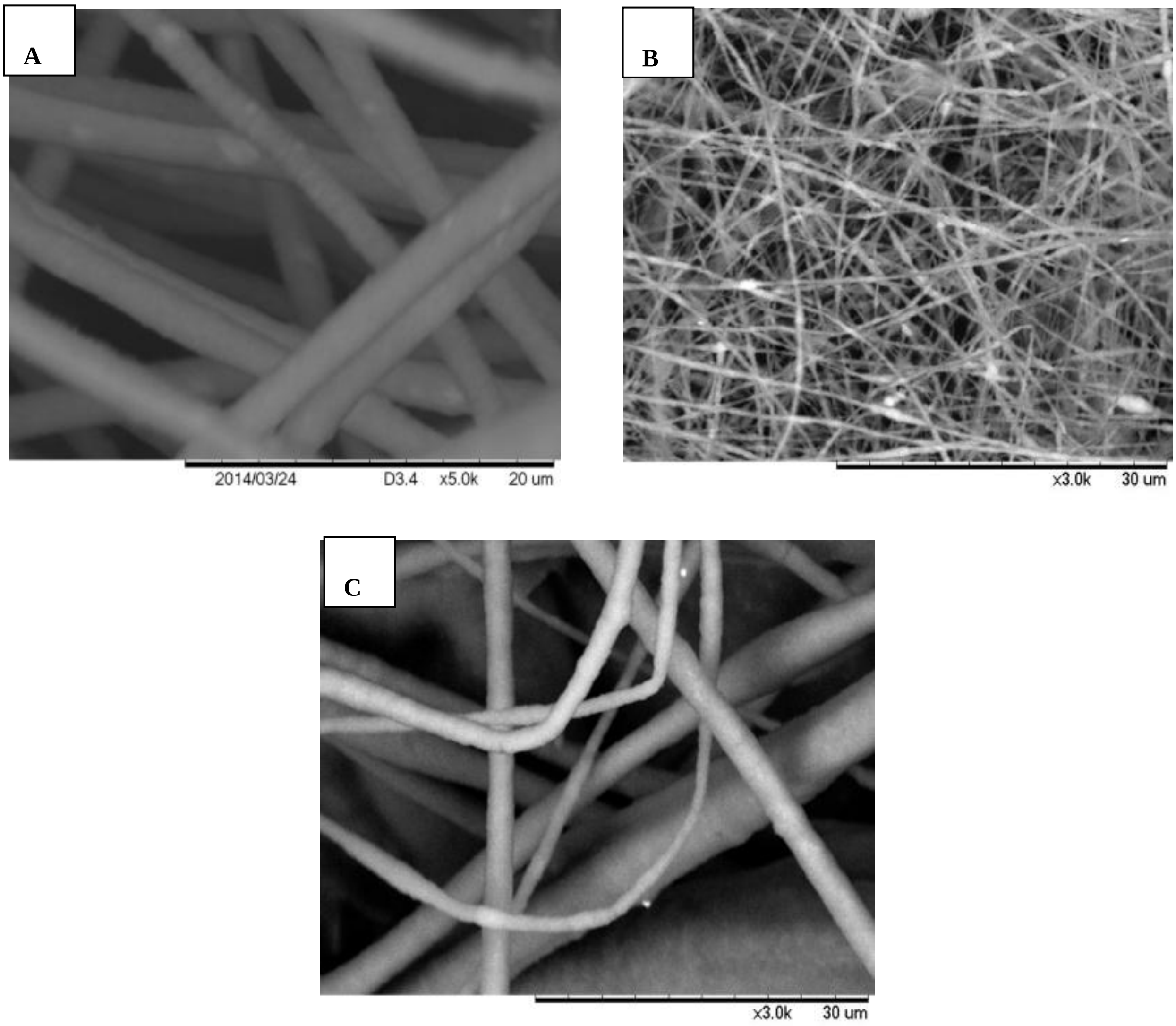


Figure 19. SEM pictures of PAN with CB in solutions, magnification x3000. The content of CB is kept constant for all samples and is CB/PAN=1:1 (a) PAN+CB in DMSO; (b) PAN+CB in DMF; (c) PAN+CB in (3/2)DMF/Acetone.

Now let’s consider the behavior of PAN solutions with addition of CB, on figure19the morphology of fibers electrospun from different solutions with CB are presented.The content of CB:PAN was 1:1 and kept constant for all used solvents.The fibers obtained from DMF solution had another morphology if comparewith fibers obtained from DMSO solution: fibers aren’t uniform, heterogeneous, small amount of solvent residues or other irregularities are observed. The average size of fibers was 460±120 nm for DMF solution and for DMSO solution it was 2100±130 nm. The differences in diameter can be explained by the fact that DMF and DMSO solutions have different viscosity, as can be seen fromtable 14.

ThefibersfromsolutionwithDMF/AChadpoor fiber morphology; the fibers aren’t uniform, wet, the structure isheterogeneous, this can be explained by the fact that we used acetone in preparation. After addition of acetone the solution became inhomogeneous, structure of solution becamejelly-like. And the fiber diameter was 2450±140 nm.Thisincrease in fiber size in comparison with the previous size of fibers can be explained by heterogeneous solution structure and the high viscosity of solution. As can be seen from Table 14 for DMF the viscosity was 4800 cP at rate 10 round/min, and for DMF/AC it was 10800 at the same speed. Therefore, only few fibers can be easily spun (that enough for SEM analysis), but it is hard to get thick membrane for conductivity measurements.

c) CNT-based PAN solutions

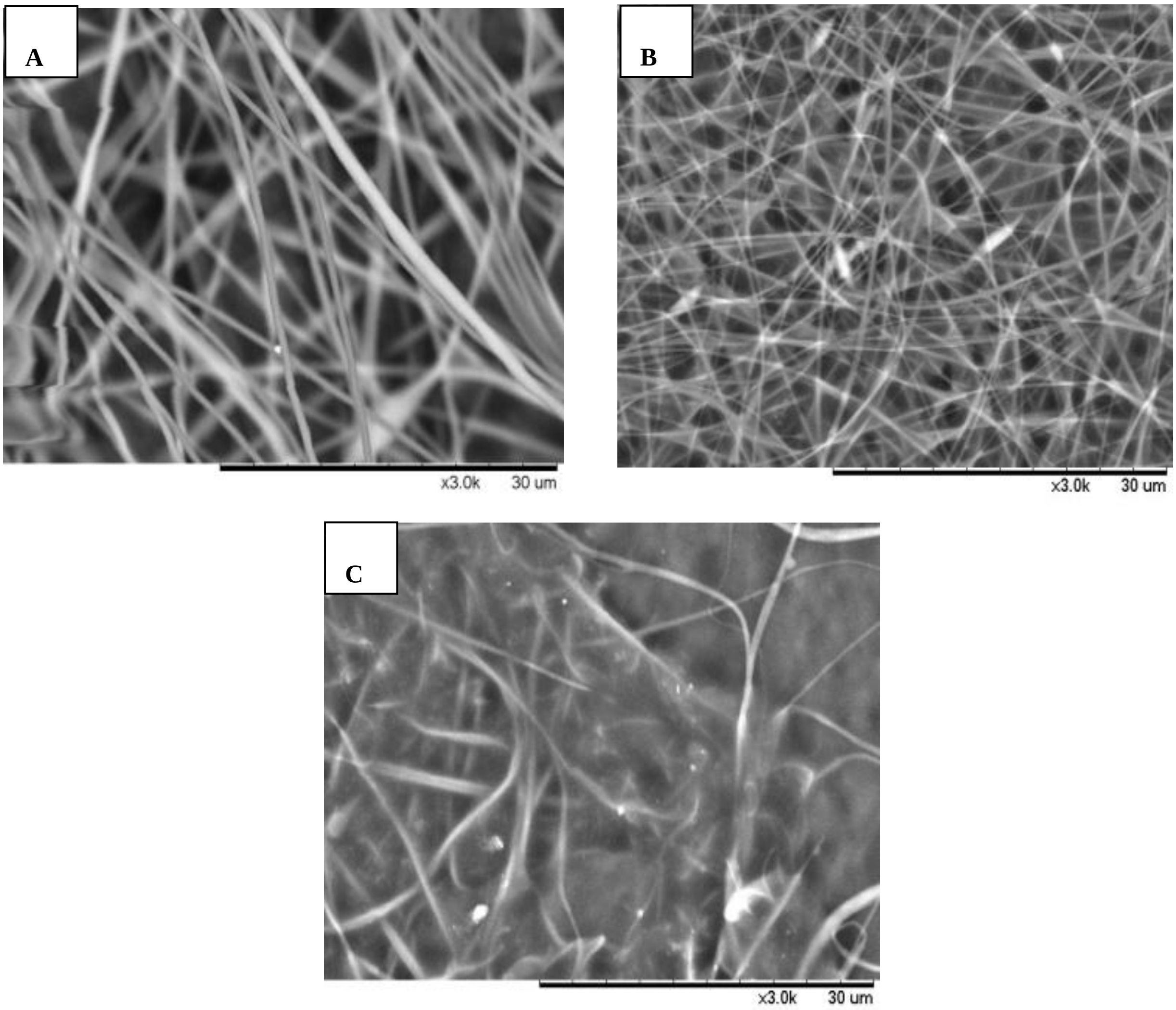


Figure 20. SEM pictures of PAN with cond. CNT in solutions, magnification x3000. The content of cond. CNT is kept constant for all samples and is cond. CNT:PAN=1:100. (a) PAN+ CNT in DMSO; (b) PAN+CNT in DMF; (c) PAN+ CNT in (3/2)DMF/Acetone.

Also the PAN solutions with cond. CNT in different solvents were studied. On figure 20 the image of morphology of fibers in different solvents are presented. The content of cond. CNT:PAN = 1:100 was kept as constant during preparations for all samples. The fibers obtained from DMSO solution had highest fiber size 735±135 nm. Information about fiber diameter, solution viscosity and conductivity, and also about the conductivity of dense membrane is presented in table 14.

Morphology of fibers obtained from solution with DMF isalso presented on figure 20. The fibers are heterogeneous, uniform in size, the fibers are aligned, but there is small amount of beads. The average size of fibers is 245±50 nm. This small diameterof DMF fibers can be explained by the sum of facts, like conductivity of DMF solution is higher than for DMSO solution, also DMF solution hadthe lower value of viscosity.

Interesting fact, that in case of using cond.CNT it was possible to prepare the solution in DMF/acetone and electrospin it.However, the fiber morphology of solution is poor. The fibers are heterogeneous, there are big amount of solvent drops, irregularities, beads and some of fibers are wet and mesh together. Morphology of PAN fibers in DMF/acetone is similar to that obtained for PVDF in DMF/acetone. Fibers are wet and stacked together. Generally, morphology of PAN+CNT samples is not fibrous but film-like with tailoring of fibers, similar to that obtained for PVDF based sample.The fiber diameter was 510±165 nm, because of heterogeneous structure of solution.

d) Conductivity results

All obtained data for solutions are presented in table 14. It wasn’t able to produce dense membranes from solutions where DMF/AC was used, because after addition of acetone structure solution greatly changes and becomes non-uniform, and during the Electrospinning process solution stuck in the needle.

If the conductivity of membranes is considered, then can be said that for CB it’s better to use as solvent DMF, becausethe conductivity is higher. Andfor this type of additives DMF is more suitable and CB can be easily dispersed there.

Table 14. The results obtained for PAN matrixes in different solvents.

Type of solvent	Viscosity, cP (10 RPM)	Conductivity of solution, µS/cm	Average size of fibers, nm	Membrane solid phase conductivity µS/cm
PAN+CB (1:1)				
DMSO	6834	53	2100±130	0.3
DMF	4800	51	460±120	4.13
DMF/Ac	10800	54	2450±140	Was not able to produce membrane
PAN+cond. CNT (1:100)				
DMSO	17600	25.5	735±135	19.6
DMF	1225	49.2	245±50	5.3
DMF/Ac	900	49.5	510±165	Was not able to produce membrane

For cond. CNT it’s better to use DMSO, because thisadditive needshydrophilic solvent. This type of additives can be easily dispersed in hydrophilic or water solutions without any additional treatment, and to get higher conductivity value of fibers small amount of additives is needed.

5. Conclusions

In this study, electrospun fiber mats were produced from different composites and analyzed. For a better analysis content of added cond. CNT and CB was the same, conditions of preparation and methods of preparation were the same, hence composites with different compositions were prepared and successfully electrospun. Scanning Electron Microscopy and Light Scattering Microscope were used to study the morphology of fibers under different electrospinning parameters, such as concentration of solution, voltage, distance to collector, conductivity of solution on morphology of fibers.

As a result of the work:

- ***The effect of content of added carbon allotropes and its nature was studied***

  With the increasing concentration of additives in solution conductivity of the membranesis increased.Withthe increase in the content of carbon allotropes,membrane conductivity increases from Pico Siemens to Micro Siemens range with, regardless the chemical structure of carbon additives. Addition of ionic liquid dramatically increases the conductivity composite membranes. Comparing the effect of structure of additives on the membrane conductivity it may be noted that the greatest effect has cond. CNT, and the lowest CB. CB needed to be taken in a very large amount, up to about 3: 2, to get the values that are identical to CNT.
- ***The effect of polymeric matrix on solution conductivity, viscosity and membrane conductivity was studied***

  From presented polymeric matrixes it can be concluded that PANfiber matdemonstrates the highest solution and membrane conductivity than other samples. Additives like CB and CNT can easily disperse in this polymeric matrix. PS and DAC show good morphology but low conducting values, PVDF does not show fibrous structure, but gives appropriate conductivity value.
- ***The effect of solvent on morphology and membrane conductivity***

  From the analysis of all the obtained data it can be concluded that DMSO is the best solvent for cond. CNT because the membrane conductivity is highest. This solvent is more suitable for this type of additives. For CB it’s better to use DMFsolvent, because PAN+CB membrane electrospun from this solvent showed highest conductivity values irrespective not perfect fibrous structure. The perfect fibrous morphology was detected only for DMSO-based polymer solutions.

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7. Acknowledgements

The Archimedes Foundation Implementing Agency of Structural Support is acknowledged for support under grant no. “Carbon Nanotube Reinforced Electrospun Nano-fibres and Yarns”, no. 3.2.1101.12-0018”.

Iwant to thank my supervisor Dr. Elvira Tarasova for her help,excellent guidance, support and patience.She kindly read my paper and offered invaluable detailedadvices on the theme and organization of this thesis.

Also I want to thank Dr. Natalja Savest for her help and advices.

I would like to express my deepest gratitudeto the entiredepartment of Polymer Materials.

And thanks to the Tallinn University of Technology for taking me in this master's program.

8. My publications

- Elvira Tarasova, Arina Byzova, Natalia Savest, Mihkel Viirsalu, Viktoria Gudkova, Triin Märtson, Andres Krumme. Influence of Preparation Process on Morphology and Conductivity of Carbon Black Based Electrospun Nanofibers. Fullerenes, Nanotubes and Carbon Nanostructures. 2014. 23: 695–700.
- Electrospinning of polymers with carbon allotropes. Book of abstract, p. 36. Baltic Polymer symposium 2014. Laulasmaa, Estonia, September 24-26, 2014.

9. Summary

Different parameters can significantly affect the fiber morphology and membrane conductivity. So the purpose of this project was to find out the best conditions to produce electrically conductive fibersby electrospinning. Fullerene-containing Carbon black (CB), Multi-wall CNT (MW CNT) and conductive CNT composites (comp. CNT) were used as electroactive additives.The effect of content and nature of added carbon allotropes, and also the effects of polymeric matrix and solvents on solution viscosity and conductivity, fiber morphology and sizes, and finally on the conductivity of electrospun mats was studied.

The results of the work indicate that conductivity of membranes increases with the increasing concentration of additives in solution.With the increase in the content of carbon allotropes,membrane conductivity increases from Pico Siemens to Micro Siemens range irrespective the chemical structure of carbon additives. The addition of ionic liquid increases the value of membrane conductivity in three orders of magnitude for CB-based samples, and in 1.5-2 times for CNT. Comparing the effect of structure of additives on the membrane conductivity the following trend can be revealed: CB<MWCNT<cond.CNT.

As shown by measurements the type of matrix and solvent has a strong influence on the dispersion of additive in polymer matrix, which in turn influences the morphology and conductivity of membranes. PAN, PS, PVDF, DAC were used as a polymeric matrix. It can be concluded that PAN fiber mat demonstrates the highest solution and membrane conductivity than other samples, and morphology of these fibers are very good. The conductivity increases in following direction: PS<DAC<PVDF<PAN

If consider the effect of solvent on morphology and membrane conductivity, then it can be said, that it is better to use DMSO for CNT, because the membrane conductivity is highest. For CB, DMF shows the best results.

(eestikeeles)

Erinevad parameetrid võivad oluliselt mõjutada kiu morfoloogiat ja membraani juhtivust. Selle projekti eesmärgiks oli leida parimad tingimused elektrijuhtivate kiudude tootmiseks rakendades elektroketrust. Elektriaktiivsete lisanditena kasutati fullereene sisalduvat tahma, mitmeseinalisi süsiniknanotorusid ning juhtivaid süsiniknanotorude komposiite. Uuriti lisatud süsinikallotroopide sisalduse ja loomuse ning samuti polümeeri maatriksi ja lahusti mõju lahuse viskoossusele ja juhtivusele, kiu morfoloogiale ja suurusele, ning lõpuks elektrokedratud mattide juhtivusele.

Töö tulemused näitavad, et membraanide juhtivus suureneb lisandi kontsentratsiooni suurenemisega lahuses. Süsinikallotroopide sisalduse suurenemisega, membraanide juhtivus kasvab picoS 'st mikroS' ni sõltumatu süsiniku lisandi keemilisest struktuurist. Ioonvedeliku lisamine suurendab membraani elektrijuhtivust kolm korda tahmaga proovide puhul ning 1,5-2 korda süsininanotorudega proovide puhul. Järgmist trendi võib näidata kui võrrelda lisandi struktuuri mõju membraani juhtivusele: tahm< mitmeseinalised süsiniknanotorud <juhtivad süsiniknanotorud.

Mõõtmised näitasid, et maatriks ja lahusti tugevasti mõjutavad lisandi dispersiooni polümeeri maatriksis, mis omakorda mõjutab membraanide morfoloogiat ja juhtivust. PAN, PS, PVDF, DAC polümeere kasutati polümeeri maatriksina. Võib järeldada, et PAN matt näitab kõige kõrgemat lahuse ja membraani juhtivust võrreldes teiste proovidega. Nende kiudude morfoloogia on ka väga hea. Juhtivus kasvab järgmiselt: PS<DAC<PVDF<PAN.

Kui võtta arvesse lahusti mõju morfoloogiale, siis on parem kasutada DMSO süsiniknanotorude puhul, sellepärast et membraani juhtivus on kõige kõrgem. Tahma puhul parimat tulemust näitab DMF.

10. Appendix

Appendix A

METADATA

Title of thesis (in Estonian): Süsiniku allotroopidega polümeeride lahuste elektroketrus

Title of thesis (in English): Electrospining of polymers with carbon allotropes

Author: Arina Byzova

Supervisor(s): Dr. Elvira Tarasova

Date of defence: 10.06.2015

Working language: English

Institution (in Estonian): TTÜ

Institution (in English): TTÜ

Faculty (in Estonian): Keemia-jaMaterjalitehnoloogiateaduskond

Faculty (in English): Faculty of Chemical and Materials Technology

Institute (in Estonian): Polümeermaterjalideinstituut

Institute (in English): Department of Polymer Materials

Chair (in Estonian): Polümeeridetehnoloogiaõppetool

Chair (in English): Chair of Polymer Technology

Keywords /if available/ (in Estonian):

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