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Coaxial electrospinning of carbon black based polymer solutions

Bachelor Thesis

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Süsinikallotroopidega polümeeri lahuste koaksiaalne elektroketrus

Bakalaureusetöö

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Table of content

1.INTRODUCTION	6
1.1 The Simple electrospinning	8
1.2 Coaxial electrospinning	11
1.3 Nanofibers	15
1.4 Carbon black.....	17
1.4.1 Composite nanofibers with carbon fillers.....	18
2. OBJECTIVES	21
3. EXPERIMENTAL WORK	23
1.1 Materials	23
1.2 Solution preparation.....	23
3.3 Instrumentation.....	24
3.3.1 Simple electrospinning	24
3.3.2 Coaxial electrospinning	25
1.3.3 Measurements.....	27
4. RESULTS AND DISCUSSION	28
4.1. Coaxial electrospinning of fully immiscible solutions of components	28
4.2. Coaxial electrospinning of fully miscible component solutions	34
4.3. Coaxial electrospinning of partially miscible component solutions.....	39
4.4 Main characteristics of coaxially spun fibers	57
CONCLUSIONS	61
REFERENCES	63
SUMMARY	66
KOKKUVÕTE	67

1.INTRODUCTION

The term “electrospinning” derive from term “electrostatic spinning”. Scientists evolved initial electrospinning technique in the early 1930s. [8]

There are different techniques of electrospinning, like simple and coaxial electrospinning, emulsion electrospinning and melt electrospinning.

There is also some other methods, with what we can make such kind of fibers, like drawing, template synthesesis, phase separation and self- assembly. However those methods takes a lot of time and with all those systems we can not produce continous fibers of single- strand form. Basically electrospinning process is a simple and fast process to make nano- size fibers. [14]

Coaxial electrospinning is about producing core-sheath fibers for tissue engineering. There have successfully produced core-sheath structured fibers PCL and gelatin using the coaxial electrospinning effect. With coaxial electrospinning process we can possess fibers, which have more attractive merits including controllable mechanical strength, better thermal and electrical conductivitiy. Based on the above mentioned the core- sheath schaffold exhibit better mechanical properties compared to gelatin schaffold. [14]

Emulsions can be used to create core shell or composite fibers without modification of the spinneret. However, these fibers are usually more difficult to produce as compared to coaxial spinning due to the greater number of variables which must be accounted for in creating the emulsion. During the electrospinning process the emulsion droplets within the fluid are stretched and gradually confined leading to their coalescence. If the volume fraction of inner fluid is sufficiently high, a continuous inner core can be formed.

Electrospinning of polymer melts eliminates the need for volatile solvents in solution electrospinning. Semi crystalline polymer fibers such as PE, PET and PP, which would otherwise be impossible or very difficult to create using solution spinning, can be created. The

setup is very similar to that employed in conventional electrospinning and includes the use of a syringe or spinneret, a high voltage supply and the collector. The polymer melt is usually produced by heating from either resistance heating, circulating fluids, air heating or lasers. In case of emulsion and melt electrospinning the prepared fibers are in large size, exceeding several microns. A versatile method for production nano- size fibers is simple and coaxial electrospinning. [1]

Electrospinning is a very wide-ranging technology for the production of nanofibers of natural and synthetic materials. This includes polymers like biopolymers, electrically conducting polymers, liquid crystalline polymers, textile fiber polymers and many others. With the electrospinning process we can produce fibers from polymers, ceramics, metals, semiconductors and their composites. [1]

Basically electrospinning is a process in which a charged polymer jet is collected on a grounded collector, a rapidly rotating collector results in aligned nanofibers while stationary collectors result in randomly oriented fiber mats. The polymer jet is formed when an applied electrostatic charge overcomes the surface tension of the solution. There is a minimum concentration for a given polymer, termed the critical entanglement concentration, below which a stable jet cannot be achieved and no nanofibers will form - although nanoparticles may be achieved. A stable jet has two domains, a streaming segment and a whipping segment. The whipping jet is usually invisible to the naked eye. Observing the length, thickness, the nanofibers being formed. [1]

By electrospinning, it is possible to generate fibers with diameters ranging from the sub-micrometer size down to the nanometer range by applying a high voltage to produce an electrically charged jet of polymer solution, which solidifies during its travel to the collector. With electrospinning process we can produce continuous fibers, then we are combining the small fiber size advantage with the advantage of high aspect ratio. Electrospinning has been used to produce porous metal oxide fibers with diameters with the single-digit nanometer to sub-micron range by using electrospun fibers of polymer-inorganic composite as the precursor. [1]

The versatile properties of polymer nanofibers give us opportunity to improve important applications such as nanoreinforcements, tissue engineering, wound dressing, drug delivery

systems, solar sails, light sails, sensors, specialty filters, and protective clothing. For example there is great interest in using electrospun conducting nanofibers in sensing applications such as humidity sensing and glucose sensing. Until today these types of sensors have been prepared only in film form and in the form of microtubule type sensors, which have less specific surface area than fiber type sensors. [1]

1.1 The Simple electrospinning

Simple electrospinning system consists of syringe, collector, syringe pump and high voltage power supply as shown in Figure 1. Electrospinning is continuous process, in which we create a horizontal electrical field, which is generated between collector and the needle.

In common electrospinning setup collector plate is used, which is made out of conductive material, like aluminium foil. Collector plate is also grounded, therefore there is a stable potential difference between the source and the collector. However there are experiments, where it is used non-conductive material as a collector. Fibers, which are collected with non-conductive collector, have usually lower packing density compared those fibers, which are collected with conductive collector. [8]

There is also difference between using static collector and moving collector. Rotating collector gives fibers chance to dry. This is really useful effect, because a rotating collector will give the solvent much more time to evaporate. [8]

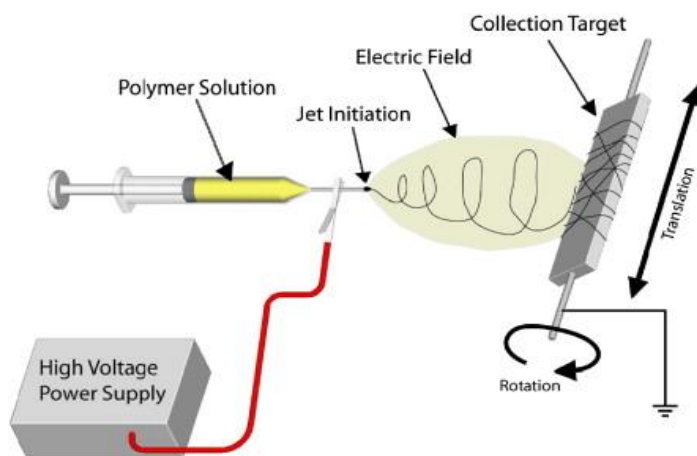


Figure 1 Basic electrospinning set up. Picture is taken from [6]

The electrospinning process is simple. One electrode is inserted into the polymer solution and the other is attached to the collector, which is grounded. When we applied the high voltage, the charge repulsion on the surface of the fluid causes a force directly opposite to the surface tension of the fluid itself. After we increased the electric field, the hemispherical surface of the fluid at the tip of the pipette elongates to become a conical shape named “Taylor cone”. A charged jet of fluid is ejected from the tip of the Taylor cone, after the repulsive electrostatic force overcomes the surface tension at a critical value of the electric field. Solvent evaporation takes place from the charged polymer fibers on the way to the collector, leaving behind non-woven matt fibers, which is collected on the conducting substrate.[1]

The advantages of electrospinning are the ability to control the fiber diameter from nanometer to micrometer dimensions, the various fiber compositions and the spatial alignment of multiple fibers. With electrospinning we can produce non-woven fiber mats with pores which penetrate the entire mat. However there are also a few limitations, like natural polymers, such as gelatin and collagen. They have very good biocompatibility for cell adhesion, but their mechanical strength is not sufficient to support the scaffold. However synthetic polymers, like PCL have very good mechanical properties, but the therapeutic effectiveness is no as good as natural polymers. [2]

Despite of the fact that most fibers, which are produced through electrospinning, are usually circular and solid filaments, there could be occasions when tubes, ribbons, coils and beaded structures may be presented. It depends of many factors, which can affect fibers production.

Molecular weight is very important solution parameter, which affects the morphology of electrospun fiber. Too low molecular weight solution tends to form beads rather than fibers and too high molecular weight solution gives fibers with larger average diameters. Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. [10]

The viscosity of solution has an important influence to electrospinning and fiber morphology. If the viscosity of solution is too low, then electrospinning can occur and polymer particles may formed instead of fibers. At lower viscosity is higher chance that beaded fibers are

obtained instead of smooth fibers. Therefore, factors which have an influence to the viscosity of the solution will also influence the electrospinning process and the resultant fibers. [9]

It is also important to know that in electrospinning the applied electrical voltage has a great influence to the jet stability and the fiber morphology. Solution conductivity is mainly determined by the polymer type, solvent used, and the availability of ionisable salts. When the conductivity of the solution is increased, more charges can be carried by the electrospinning jet. With the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, this results in insufficient elongation of a jet by electrical force to produce uniform fiber, and beads may also be observed. [10] [11]

In addition electrospinning process is also affected by the distance between the capillary tip and the collector. The distance influences the fiber deposition time, the evaporation rate and instability interval. There is also difference in which type collector is used for electrospinning. There are several types collectors like conductive paper, conductive cloth, wire mesh, pin, parallel or grided bar, rotating rod, rotating wheel and liquid non solvent such as methanol coagulation bath. Generally aluminium foil is used as a collector. [10][11]

There is also found that the flow rate of polymer solution affects the jet velocity and the material transfer rate with enhanced pore and fiber sizes and beaded structures.

The electrospinning process is influenced by the electrospinning environment. The air velocity, relative humidity, vacuum condition, etc are all affecting the fiber structure and morphology. It is known that the relative humidity higher than 60% causes incomplete drying in acrylic electrospun fibers. [11]

With increase in temperature, there is a part of fibers with decreased fiber diameter, because of decrease in the viscosity of the polymer solutions at increased temperatures. Furthermore there is an inverse relationship between viscosity and temperature. In addition by increasing humidity there is an appearance of small circular pores on the surface of the fibers. Further increasing the humidity leads to the pores coalescing. [10][11]

1.2 Coaxial electrospinning

Coaxial electrospinning is a recently discovered technique, it was first demonstrated by Loscertales in 2002. It is one of the most relevant techniques to fabricate polymer nanofibers with unique core-sheath or hollow structures such as micro/nanocapsules, hollow spheres, hollow fibers and coaxial fibers. [9]

The development of coaxial electrospinning of encapsulation can be useful in different industries, like in textile industry, nanosensors, material science, catalysis and also in food items, pharmaceuticals, controlled drug delivery, bioengineering, materials science, nanosensors. [9]

In the coaxial electrospinning two different dissolved materials flow through capillary and are drawn to generate the coaxial structures. Then at the micro-nano level one material is surrounded by the other at the micro-nano level. This method has potential applications for a wide range of uses such as

- a) Isolating an unstable component and minimizing its chances of decomposition under a high reactive environment;
- b) Improves material's mechanical properties. [5][9]

The technology of coaxial electrospinning is similar to simple electrospinning. The basic modification relies on the spinneret, which consists of a couple of capillary tubes where a smaller tube is inserted inside the bigger capillary to make a coaxial configuration. The schematic representation of the coaxial electrospinning setup is shown in Figure 2.

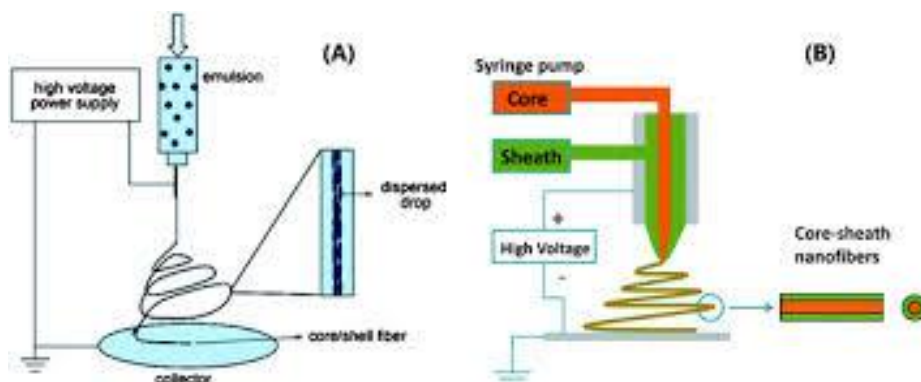


Figure 2 Coaxial electrospinning setup. Picture is taken from [7]

Coaxial electrospinning system consists of two syringes, two syringe pumps and the coaxial nozzle. In the coaxial nozzle there are needle for sheath and the disk for core solution. Both needle and disk can be with different parameters.

Both capillary tubes are connected to a reservoir independently supplied for a syringe-pump or air pressure system. This impulses both solutions to the coaxial spinneret, which presents two inputs. Inside this coaxial spinneret both fluids flow and in the tip of the device it is produced the injection of one solution into another. The shell fluid drags the inner one at the Taylor cone of the electrospinning jet.[9]

If the fluids are immiscible, it is possible to see core shell structure. In the case of miscible solution a fiber with distinct phases is obtained. For good results in electrospinning, the solvent in either of the solutions should not deposit the polymer from the other solution, when the solutions will get together at the tip of the capillary. For example the interfacial tension between the shell and the core should be low for generation of the stabilized Taylor cone.[9]

The liquid compound elongates and stretches due to the charge-charge repulsion to form a conical shape, which is called Taylor cone and when the charge accumulation reaches a certain threshold value due to the increased applied potential, a fine jet extends from the cone. It is known that when the compound cone is stable, the core is uniformly incorporated into the shell for core-shell fiber formation. On the way to the collector, the jet undergoes bending instability and follows a back and forth whipping trajectory, during which the two solvents evaporate, and the core-sheath nanofibers are formed.[9]

Moreover if the sheath and the core solutions are in contact and go through the same bending instability and whipping motion, the degree of dissimilarity between them, in terms of composition, also physical and rheological properties, has an important role in the formation of the composite fiber. The coaxial electrospinning process is affected by many factors. Most of them are the same with simple electrospinning, like concentration, flow rate and distance. [9]

To obtain fibers with smaller diameter we should use highly conductive solutions, which have high surface charge density. This causes an increase in the elongational force on the jet due to self-repulsion of the excess charges under a given electrical field.[13]

The type of solvent used in the core solution affects on the resulting morphology of the core-shell structure. High vapor pressure solvents, which evaporates quickly, creates a thin layer at the interface core-shell when it is used in the core. This causes lower interior solvent diffusion.[13]

An increase in the core concentration means to increase both the core and fiber diameters and decrease the thickness of the sheath, because of the same mass of the sheath distributed over a bigger core.[13]

The concentrations of both phases should exceed a critical value to maintain a uniform morphology. This is also affecting fibers dimensions. The increase in both core and sheath flow rates can enlarge their corresponding phases and total dimensions. Both flow rates should be matched, because of the core-sheath encapsulation structure. At very small core – sheath flow rate ratios, we cannot get continuous smooth core phase. By increasing its flow rate, the core phase will become consecutive and thicker. [13]

In coaxial electrospinning, the viscosity of the shell solution is required like viscous stress imparted by it on the core is adequate to overcome the interfacial tension between the two solutions and allows the formation of compound Taylor cone and a jet from the latter. Correspondingly, viscosity of the sheath solution is critical and the shell solution system should be electrospinnable by itself to lend to core-sheath structure formation. The demand for the spinnability of the core are not so important, because the jet break-up of the core fluid tends to be prevented by the sheath due to strain hardening of the interface between the sheath and lesser surface forces acting on the core solution surrounded by the sheath. The core fluid has to have certain minimum viscosity if it is to be entrained continuously without break up. [13][9]

In electrospinning can be also defects such as beads and pores. It has been found that the polymer concentration also influences the formation of beads. Higher polymer concentration results fewer beads. With higher concentration of polymer beads do not always completely disappear. Instead, the bead diameters, if any, at higher concentration are even larger. Although the shape of the beads changes from spherical to spindle like when the polymer concentration varies from low to high levels. However the increase of the electrical potential

causes also rougher nanofibers. It has been realized that, when some filler material is added to into a polymer solution, we can get fibers without beads. [9]

In the case of very low applied voltage the pumped solution will drop down, because of the electrostatic force is not sufficient to draw the whole liquid out. As result only sheath can be handled into jets. If the voltage increases successful drawing and efficient elongation process can be achieved. [5]

Difference in conductivity between core-shell solutions can also influence core-shell fiber formation. For example if the core solution is pulled at a higher rate by the applied electric force and caused discontinuity in the core sheath structure, however high shell conductivity, would not hinder the process of core-sheath fiber formation but rather result in higher shear pressure on the core material.[9]

It is also known that the longer collection distances, the longer whipping process the jets can experience and thus the fibers can get sufficiently elongated.[5]

The most important points in coaxial electrospinning:

- a) shell solution has to be spinnable by itself;
- b) core viscosity must be lower than shell's;
- c) low interfacial surface tension between core-shell solutions;
- d) vapor pressure must be low in core solution;
- e) core solution conductivity must be lower than shell's. [9]

Fibers which are produced with coaxial electrospinning process possess more attractive merits including controllable mechanical strength, and better thermal and electrical conductivities than single structure fibers. [5]

Usually core- sheath fibers are little bit larger than those which are obtained from conventional electrospinning. There have obtained core- sheath fibers from coaxial electrospinning with a diameter around 200 nm. Different materials can be integrated into core or sheath phases with desired functions and nano fibers with two unique nanostructures have been developed possessing amazing properties. [5]

Coaxial electrospinning process has a very wide range of use, such as isolating an unstable component and minimizing its chances of decomposition under a highly reactive

environment, reinforcing a material to improve its mechanical properties or serving as scaffold for engineering tissues in which a less biocompatible polymer is covered with a more biocompatible material.[5][9]

However, there are also some challenges, like the dimension and order of the obtained nanofibers. The improved performance in their applications and the expanded applications of the core–sheath and hollow nanofibers. So far, the fine dimension of the core–sheath nanofibers is about 60 nm, which is much larger than fibers which are created with conventional electrospinning.[5]

1.3 Nanofibers

Nanofibers are defined as solid linear materials and their aspect ratios is greater than 1000:1. In textile industry, this definition is often extended to include fibers as large as 1000 nm diameter. Materials, which contains nanofibers, must have at least one dimension equal to or less than 100 nanometers. Nanofibers can be produced by interfacial polymerization, electrospinning or electrostatic spinning. Nanofibers based on carbon, can be produced by catalytic synthesis. [14]

Nanofibers have unique thermal and mechanical properties compared to normal fibers. It is known that electrospun fibers have lower crystallinity, glass transition temperature and melting temperature than semicrystalline fibers. Nanofibers have several amazing characteristics like very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance compared with any other material. Mechanical properties of electrospun nanofibers are influenced by their nanostructured surface with small pores. [14]

Most nanofibers are obtained in non-woven form, which can be used for relatively small number of applications. However there are also techniques, which have been attempted to align electrospun nanofibers.

It is also known that fiber formed materials have a great practical and fundamental importance. There have been recognized that different fiber sizes have a great influence in bio-reactivity, in electronic properties and in mechanical properties. For example only a viscoelastic material, which can undergo string deformations and be at the same time cohesive enough to support stresses, developed during pulling can be made into nanofibers through drawing. [14]

It is also interesting to know that when the nanofiber diameter increases, then the strength of the nanofiber increases exponentially.

One of the most easier method to make continuous carbon nanofibers is to use for electrospinning polyacrylonitrile (PAN) followed by stabilization and carbonization. Copolymers, which consists PAN, are more readily soluble in spinning solvents, allowing better macromolecular chain orientation in precursor fibers and making carbonized and stabilized fibers more structurally homogeneous. Unlike most polymers, electrospinning of PAN is driven by electrical force instead of mechanical force. One of the benefits of PAN is that carbon nanofiber mat from electrospun PAN is easy to handle, because of the interconnected nanofiber network structure. This results the elimination of polymer binders and conductive fillers in electrodes. Electrospun PAN nanofibers are also known for being good anode material for Li-ion batteries. [15]

Nowadays scientists are concentrating on nanofiber applications, because of their remarkable properties. There have been lot of extensive investigations in particular areas, such as catalysis, filtration, nanocomposites, tissue scaffolds, drug delivery systems, wound dressing, protective textiles and storage cells for hydrogen fuel cells.[1]

For example in wound healing nanofibers assemble at the injury site and stay put, drawing the body's own growth factors to the injury sites. Protective materials include sound absorption materials, protective clothing against chemical and biological warfare agents and also sensor applications for detecting chemical agents. [1]

Energy applications for nanofibers, include rechargeable Li- ion batteries, photovoltaic cells, membrane fuel cells and dye-sensitized solar cells. Previously mentioned elements are urgently demanded to fulfil the increasing energy needs of modern society. Other applications are micropower to operate personal electronic devices. [3][15]

Li- ion batteries are used in versatile power sources for wide range of electrical devices such as cell phones and laptop computers and hybrid electric vehicles. [15]

Most of the human tissues and organs are deposited in nanofibrous structures. Tissue engineering involves the use of living cells, manipulated through their extracellular environment or genetically to develop biological substitutes for implantation into the body. A Basic idea of tissue engineering is to repair, replace, maintain the function of a particular tissue or organ. In addition PLLA nanofibers are used for nervous tissue repair. Furthermore human bodies cannot heal deep dermal injuries, therefore electrospun nanofiber is good for wound dressing material, because of its properties such as the highly porous mat structure and well interconnected pores. [16]

Nanofibers can be also used as filter. In most of engineering fields filtration is really necessary. Fibrous materials used for filter media provide advantages of high filtration efficiency and low air resistance. Because of the high surface area to volume ratio and resulting high surface cohesion, particles of the order of $< 0,5 \mu\text{m}$ can be trapped in the electrospun nanofibrous structured filter without any problems. [9]

Furthermore nanofibers show strong promises as ideal protective clothing. Due to their great surface area, nanofiber fabrics are capable of the neutralization of chemical agents and without impedance of the air and water vapor permeability to the clothing. All in all electrospun nanofibers present both minimal impedance to moisture vapor diffusion and extremely efficiency in trapping aerosol particles. [9]

Nanofibers can be seen even in cosmetics industry. Commonly electrospun nanofibers are used as skin mask, which can be applied gently and painlessly as well as directly to the three dimensional topography of the skin to provide healing or care treatment to the skin. [9]

1.4 Carbon black

Carbon black consists mainly of elemental carbon and it is in the form of spherical particles, which have been fused together to form aggregates that are typical around 30-100 nm in size.

People have used carbon black as a pigment in black ink. It is also used in copymachines and printers. Futhermore carbon black has been also added to rubber to enhance the tear strength. It is also known that plastics, which are filled with carbon black, have better electrical conductivity and high specific surface, nessessary for filtering application. [17]

For the production of carbon black is usually used the thermaloxidative process. In production of carbon black, natural gas is combusted in air and then mixed with coal tar or crude oils. After there are filters, which seperate the carbon black from the tail gas. Large particle are sent to the pelletizer, where they are mixed with water. For a size distribution wet particles have to be dried and screened. To remove iron or rust contamination particles will pass through magnets and then particles are going for storage in silos. [17][20]

Carbonaceous fillers have been used to improve polymers physical properties such as electrical conductivity, electromagnetic interference shielding and thermal resistance. CB and carbon nanotubes have been used as fillers, because of their ability to impart high electrical conductivity to a polymer matrix at low filler content. Futhermore there are some other advantages of CB like low cost, small particle size and aggregation behavior. Although there have been found that the mechanical properties of nanocomposite fiber webs are influenced by the fiber morphology and fiber-web structural features. The incorporation of particulate fillers such as carbon black, increases the mechanical properties and electrical conductivity. [21] [17] [20]

1.4.1 Composite nanofibers with carbon fillers

Electrospinning method can also be used to create materilas with nanoparticulate fillers. Composite nanofibers are maerials, which combine one or more seperate components and which are designed to exhibit overall the best components of each component. The addition of fibrous fillers to polymer matrices yields benefits number of areas such as strength, stiffness, thermal and electrical conductivities which are generally enchanced by the high aspect ratio of the fibers. However the intrest of electrically conductive polymer matrix composites is caused by their unique multifunctional properties like ability to combine flexibility to conductivity and lightweighth. [12][1] [17]

There is important effect to the filler structure on the electrospinning process. For example carbon black particle size, loading and structure was found to have significant effect on the morphology and mechanical properties of electrospun butyl rubber nonwoven mats. Fiber diameter decreased with:

- a) increasing carbon black content;
- b) decreasing particle size;
- c) increasing carbon black structure.[12]

There are some properties of particle-filled polymer composites, which are influenced by primary characteristics of the filler such as the particle size, polymer- to filler interaction and uniformity of particle dispersion. When the CB particles are separated into discrete primary aggregates, the good dispersion is achieved. It is also known that at the higher levels of CB, the fiber surface are more irregular than at lower levels, however there is also appearance of the agglomeration of CB particles on the fiber surface. At higher CB content it is possible to see increase in fiber diameter and greater variability in the fiber size distribution. Scientist have discovered that the CB presence in the fiber web increases the web strength up to 3.65 vol % (nominal), the electrical conductivity and thermal stability increases up to 5.54 vol % (nominal) . [17]

Therefore carbon nanofiber composites are promising materials in many areas such as electrical devices, electrode materials for batteries, supercapacitors and as sensors. From these applications it can be seen that electrical conductivity is the first priority what needs to be considered. [17]

In the case of coaxial electrospinning method, the nanofiber composites morphology will depend on both thermodynamic and kinetic factors. In the electrospinning process, the rapid solvent evaporation rates result in kinetic factors have a much larger influence to the structure formation. For example higher fiber to fiber bond density can be seen, when the CB is increased. This is most likely caused by the slow rate of solvent evaporation during the fiber formation between the spinneret and the collection surface due the presence of more CB particles at the higher concentrations and their tendency to absorb as a result of that it is slowing down the evaporation of solvents .[17]

In addition to solubility parameters, viscosity and molecular weight will be important factors in structure development. Solution viscosity well known to have influence to fiber geometry, however the bulk viscosity of materials will become a dominant factor as the solvent evaporates. In most electrospinning experiments constant viscosity solutions have been used, however nanoscale fillers will typically change the viscosity of the starting materials, thus a constant viscosity solution will have a lower concentration of primary fiber material. [12]

The addition of carbon black filler was also found to decrease the number of beads. With increasing carbon black content density of the electrospun mats decreased. It is also known that changes in the fiber structure and mat morphology have an important influence on the final properties of material. [12]

All in all the CB fillers gives to composite nanofibers their unique strength and thermal stability. With higher content of CB the electrical conductivity of the composite fiber web can be increased 3 orders of magnitude. This way nanofiber composites are very promising potential materials in various applications. [17]

2. OBJECTIVES

Previously, in our lab it was shown that addition of CB to PAN matrix allows getting fibrous mat with conductivity up to microSiemens range [1]. Another useful application of such membranes could be filtering materials. For both these applications produced membranes should be mechanically strong enough to withstand applied force and contain large amount of CB.

However, as it was found out in the work, when the ratio was $CB/PAN \geq 1/2$, the prepared PAN+CB membranes were mechanically rather fragile. Therefore, in current work the attempt to enforce the PAN+CB membranes was done by preparation of core-sheath fibres, where sheath is PAN+CB, and core is any other material serving just as enforcing element. Such core-sheath fibers are possible to produce by so-named “coaxial electrospinning”.

Therefore, the aim of the study was to produce CB-containing composite fibers by coaxial electrospinning, which can be used as conductive materials in electronics or filtering materials in purifying devices.

To achieve this goal the following experimental tasks should be studied:

- a) The possibility of producing core-sheath structure of CB- base composites by coaxial spinning of two fully miscible systems;
- b) The possibility of coaxial electrospinnability of CB- base composites by coaxial spinning of two partyally miscible systems;
- c) The electrospinnability of CB- base composites by coaxial spinning of two fully immiscible systems.

For this purposes different polymer-solvent systems will be used and effect of solution properties, such as viscosity and conductivity, and electrospinning parameters (pumping rate, distance, voltage) on morphology of obtained membranes will be studied.

Finally the following testing of electrospun membrane will be done:

- a) Testing the conductivity properties of coaxial membranes;
- b) Testing their tensile properties;
- c) Testing their specific surfaces for filtering application.

3. EXPERIMENTAL WORK

1.1 Materials

The polyacrylonitrile (PAN) with empirical formula $(C_3H_3N)_n$, the polystyrene (PS) formula $(C_8H_8)_n$, polyvinyl alcohol (PVA) $(C_2H_4O)_n$, Polylactic acid (PLA) $(C_3H_4O_2)_n$ and carbon black (CB) were used. The solvents used were N,N-dimethylformamide $(CH_3)_2NC(O)H$, dimethyl sulfoxide (DMSO) $(CH_3)_2NC(O)H$, 1,2-dichloroethne (DCE) $C_2H_4Cl_2$ and water.

1.2 Solution preparation

All polymer solutions (without CB) were prepared by simple method. Firstly polymer was dissolved in solvent. Then this solution was mechanically stirred with magnetic stirrers at 50-60°C until transparent and visually homogeneous polymer solution was formed. When the solution was ready then it was cooled to ambient temperature for electrospinning, viscosity and conductivity measurements.

Concentration of polymer in solution was calculated by the formula:

$$C = \frac{\text{mass of polymer}}{\text{mass of (polymer + solvent)}} \cdot 100\%$$

Preparation of solution polymer + CB in solvent differs a little bit from previously mentioned solution preparation method. Firstly CB was dispersed into solvent. The carbon black content in solution was CB/PAN= 1/1 or CB/PAN= ½. Then dispersion was put under the ultrasound treatment for 3.5 hours. After sonication of CB solution, polymer was added into it. Then

whole solution was mechanically stirred with magnetic stirrers at 60 °C until visually homogeneous polymer solution was formed. Then the solution was cooled to ambient temperature for electrospinning, viscosity and conductivity measurements. In given work solutions were prepared at different polymer concentrations such as 8-10% for PAN, and 14-30% for PS.

3.3 Instrumentation

3.3.1 Simple electrospinning

In present work simple electrospinning were done at room temperature with atmosphere conditions. For such electrospinning simple electrospinning device was used, which consists of a high voltage power supply (Gamma High Voltage Reaserch Ormond Beach, FL with 0-30 kv power ranger), electric drum, syringe pump (New area pump system, Inc), syringe, like it was discussed in paragraph 1.1.1 and shown in Figure 3.

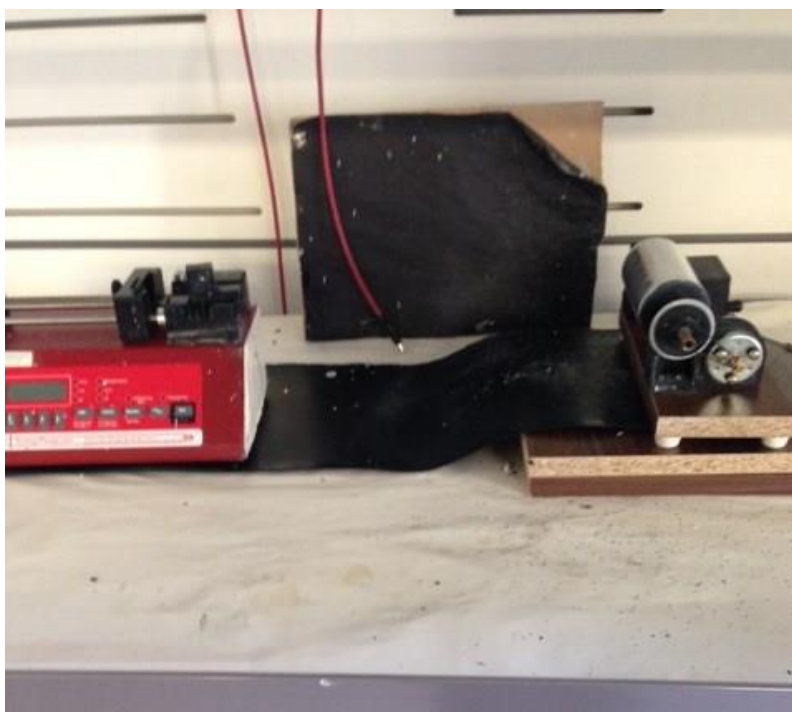


Figure 3 Simple electrospinning setup

As a collector it was used electrically rotating drum, which is better for creating a mat of fibers, because of spinning drum fibers can aligned and dry. In present work a pumping rate in the range of 0.2-1.5 ml/h was used.

3.3.2 Coaxial electrospinning

Coaxial electrospinning was done with typical coaxial electrospinning setup, consisting of a high voltage power supply, which is the same with simple electrospinning, two syringe pumps (New Era Pump Systems, Inc) and spinneret (LONG LI TECH) as it was discussed in paragraph 1.2.1 and shown in Figure 4.



Figure 4 Coaxial electrospinning setup

The spinneret consists of a couple of capillary tubes where smaller one is inserted inside the outer capillary to make coaxial configuration. In present work different needles with variable parameters such as length (shorter and long) and diameter (0.6 and 0.8 mm) were used. The needle length is important, because the longer needle is equal with the spinneret, but the shorter one does not as it is shown in Figure 5. With the shorter needle the Taylor cone is

formed on the tip of the spinneret, but with the longer needle it is formed on the tip of the needle.

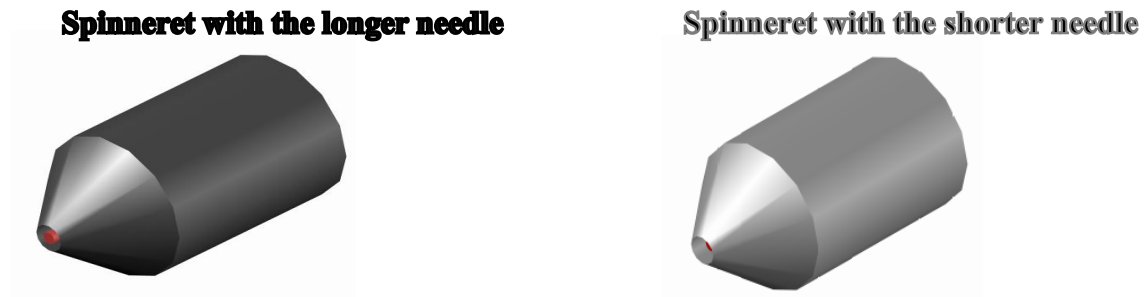


Figure 5 Different lengths of needles in the spinnerets

For coaxial electrospinning electrically rotating drum was also used. Pumping rate, concentration of solution C , voltage V , and distance to collector D , were varied as it is listed in Table 1.

Table 1 Parameters of simple and coaxial electrospinning

Pumping rate	0.2- 1.5 ml/h
Voltage	15-20 kv
Distance to collector	15- 20 cm

1.3.3 Measurements

Viscosity measurements were done at temperature 22°C with rotating Brookfield viscosimeter DV-II+ Viscosimeter, which is shown in Figure 6.

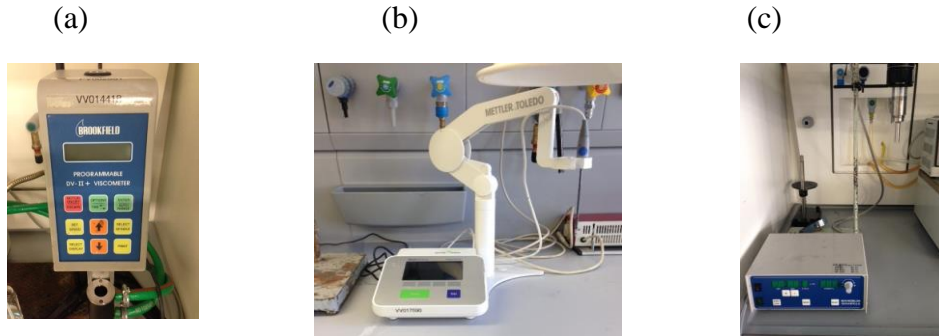


Figure 6 (a) The viscosimeter (b) The device for conductivity measurements and (c) The ultrasonic device

Conductivity measurements were also done at temperature 21- 22°C with Benchtop conductivity meter SevenCompact™ S230, which is shown in Figure 6.

Sonication was done by the ultrasonic device Bandelin electronic device of horn type, which can be seen also in Figure 6.

Tabletop scanning electron microscope TM-1000 Hitachi and polarized light microscope Zeiss Axioskop 2 were used to observe the morphology of fiber mats.

4. RESULTS AND DISCUSSION

4.1. Coaxial electrospinning of fully immiscible solutions of components

Coaxial systems, as it is obvious, consist of two different systems, which will be named further components. The coaxial component solutions are: core solution which is used in inner layer and sheath solution used in an outer layer. In the coaxial electrospinning both solutions (core and sheath) are combined together to produce coaxial fibrous materials.

In present work the first attempt to produce coaxial fibers was done with fully immiscible component solutions. In some scientific articles [9] it was written that if the fluids are immiscible, it is possible to produce core-shell fibrous structure. For this purpose the solution of PAN in DMF with CB (PAN/CB= 1/1) was used as outer layer (sheath) and Poly(vinyl alcohol), PVA, in water/alcohol solvent without CB was used as inner layer (core). Such coaxial systems are fully immiscible because water and DMF are not miscible. Moreover, the sheath solvent DMF is not a solvent for core polymer PVA and the core solvent water is not a solvent for the sheath polymer PAN. The electrospinning parameters and solution characteristics of obtained coaxial systems are presented in Table 2.

Table 2. Solution and electrospinning parameters for coaxial spinning of fully immiscible components

Samp. code	Components		Concent-s %		Pumping rates ml/h		Needle type	Voltage kV	Distance cm	Fiber diameter nm
	<i>sheath</i>	<i>core</i>	<i>sheath</i>	<i>core</i>	<i>sheath</i>	<i>core</i>				
C1	PAN+CB (1:1) in DMF	PVA in water/alcohol	10	NA	0.9	0.5	0.8 mm long	15	15	400
C2	PAN+CB (2:1) in DMF	PVA in water/alcohol	10	NA	0.8	0.4	0.6 mm short	17	15	270

Each coaxial system has its own code name in Table 2, where letter *C* means coaxial as example C1 and C2. If the same sample was studied at different electrospinning conditions, it will have additional marks, like C5-1 and C5-2. Coaxial system is a combination of two individual components, information about which is presented in Table 3.

Core and sheath solutions were tested and electrospun separately by simple electrospinning setup to get solution properties and morphology of individual components. Analogically to Table 2, each individual system (component) has its own code name, where letter *S* means simple (electrospinning). For example, coaxial sample C1, presented in Table 2 and which is under consideration now, is a combination of S8 (PVA in water/alcohol) and S3 (PAN+CB (1:1) with C=8.5%) presented in Table 3. The schematic representation of coaxial samples C 1 and C2 are shown in Figure 7.

Table 3. Characteristics and electrospinning conditions of individual systems used as components for coaxial electrospinning

Samp. Code	Component solution	Concent. %	Viscosity cP	Solution Conductivity	Fiber diameter nm	Pumping rate ml/h	Voltage kV	Distance cm
S1	PAN in DMF	9	840	39	230	1.5	15	15
S2	PLA in DCE/Me	10	650	1.3	800	1	20	20
S3	PAN+CB (1:1) in DMF	8.5	8300	9.3	240	0.9	20	15
S4	PAN+CB (2:1) in DMF	10	1160	51.8	250	0.5	15	15
S5-1	PAN in DMSO	16	25 000	24	550	0.5	15	15
S5-2		9	2795	21	220		20	15
S6-1	PS in DMF	14	51	0.10	Beads	0.5	15	15
S6-2		16	82	0.4	Beads/200			
S6-3		20	138	0.15	Beads/950			
S6-4		25	1820	0.4	2200			
S6-5		30	5180	0.15	2100			
S7-1	PAN+CB (1:1) in DMSO	8	5200	14.2	400	0.5	15	15
S7-2		9	6200	7.3	700			
S8	PVA in water/alcohol	Conc. 1	1150	710	380	0.5	15	15

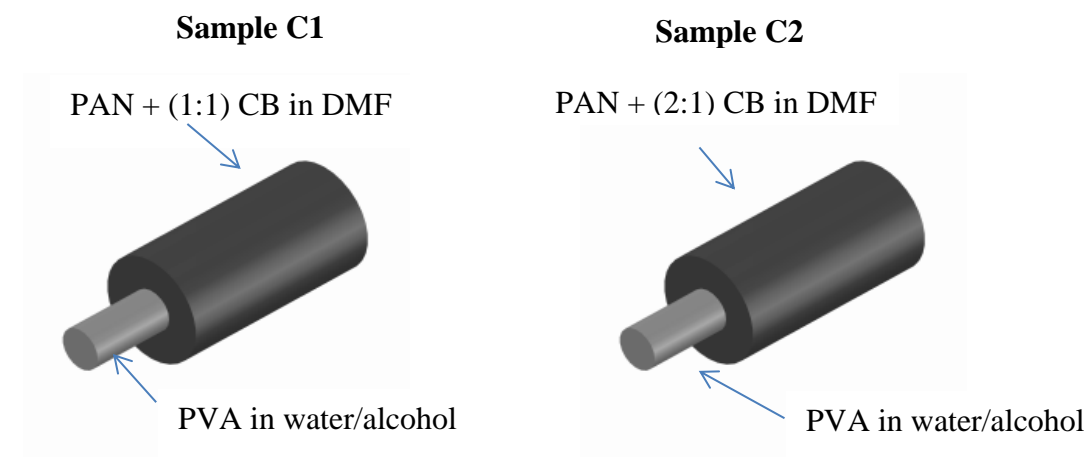


Figure 7 Coaxial fiber of sample C 1, inner part is PVA in water/alcohol and outer is PAN + (1:1) CB in DMF; Coaxial fiber of sample C 2, inner part is PVA in water/alcohol and outer is PAN + (2:1) CB in DMF

For the first attempt to produce coaxial fibers from solution of PVA in water/alcohol with PAN + CB (1:1) in DMF (coaxial sample C1, see Table 2), the longer needle (OD 0.8 mm) was used, due to the viscosity of solution of PAN + (1:1) CB in DMF was rather high (8300 cP). According to the theory, solutions with higher viscosity barely flow through the smallest nozzles and solutions with lower viscosity drip from the largest nozzles. Initially in the coaxial electrospinning equal pumping rates (0.5 ml/h) were used for both, inner and outer layers. However, instead of proper Tylor cone, there was possible to see two separate solution phases as it is shown in Figure 8. There was also no continous material tranfer, probably due to incompatibility of two layers and high viscosity of sheath solution (PAN + (1:1) CB in DMF).



Figure 8 Two pahases in Tylor cone (on the Figure the black part presents the carbon black and the white part is the PVA in water / alcohol)

To solve this problem various pumping rates were tryed for core and sheath solutions. The most appropriate results were obtained when the pumping rate for core solution was preserved as 0.5 ml/h and for sheath it was increased to 0.9 ml/h.

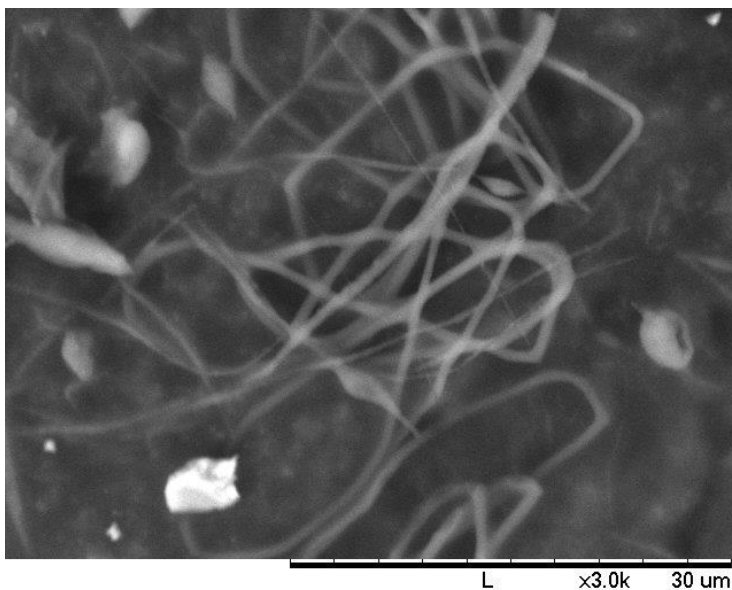


Figure 9 Fibers of coaxial electrospinning of C1

From Figure 9 it is possible to observe the morphology of electrospun fiber mat of sample C1. As it is possible to see from the figure the morphology of fibers are rather rough and containing many beads. The diameter of fibers is small, approximately 400 nm. After several attempts to produce coaxial fibers of sample C1, it became obvious that there was not possible to do proper electrospinning process. As all the attempts to produce coaxial fibers from PAN+CB (1:1) were not successful, probably due to high viscosity of such system, it was decided to decrease twice the content of CB in solution. Therefore, the solution of PAN+CB (2:1) in DMF was prepared and used as a sheath component in coaxial fibers, producing sample C2. As it is listed in Table 3 the solution of PAN+CB (2:1) in DMF is less viscous (viscosity is 1160 cP) than the solution of PAN+CB (1:1) in DMF (8300 cP) due the lower content of CB in the solution. Apart from the viscosity of PAN+CB (2:1) solution is rather low now, it is still higher than viscosity of PVA solution, and the rule that core viscosity must be lower than shell's is not violated.

Initially the coaxial electrospinning of sample C2 (it is not presented in Table 2), were done under conditions such as equal pumping rates for core and sheath 0.5 ml/h, distance 15 cm, voltages 15 kv, longer needle (OD 0.8 mm). Despite of the decreased content of CB in solution, it was still possible to see two separate phases in Tylor cone. To avoid such separation, the configuration of spinneret was changed and the longer needle was exchanged with the shorter needle (OD 0.6 mm). With shorter needle and various pumping rates for both phases the sheath solution covered the core more easily and only one phase was observed in Tylor cone. During the coaxial electrospinning process the applied voltages were also increase from 15 kv to 17 kv, in order to improve the material transfer.

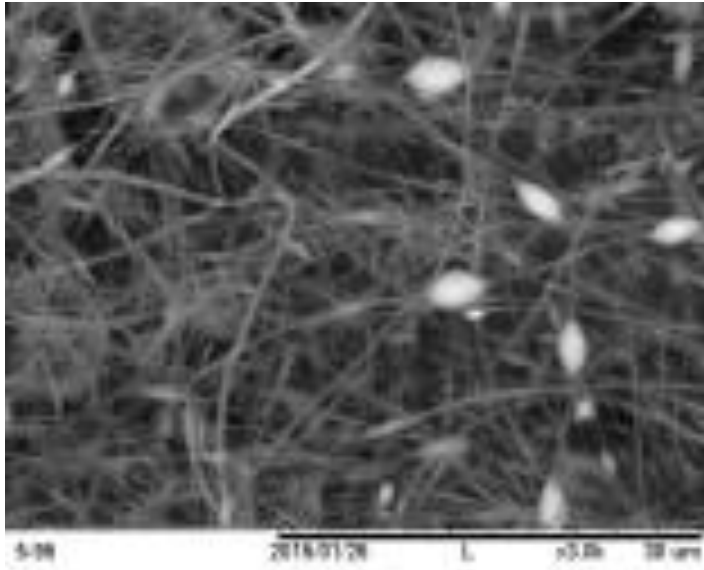


Figure 10 Fibers of coaxial electrospinning of C2

Figure 10 shows the morphology of electrospun fiber mat of coaxial sample C2. As seen, fibers are thinner (270 nm) compared with sample C1, and are containing also some beads. By their sizes and morphology, it can be suggested that two layers electrospun separately, without producing core-sheath structure.

Taken into account that electrospinning process of fully immiscible systems was not stable and continuous and obtained fibers had a lot number of cracking and cavities in fiber morphology, it can be suggested that solvent in either of the solutions deposits the polymer from the other solution, when the solutions get together at the tip of the capillary and separation into two phases as well as precipitation of polymers from their solutions take place resulting in unstable and irregular electrospinning process. Therefore, in next chapters the fully or partially miscible fluids are considered.

4.2. Coaxial electrospinning of fully miscible component solutions

The second attempt to produce coaxial fibers was done with fully miscible component solutions. For this purpose the solution of PAN in DMF was used as inner layer (core) and PAN+ CB in DMF in amount PAN/CB= 1/1 was used as outer layer (sheath). Such coaxial system are fully miscible because the same solvent is used both for inner and outer layer, and it is a solvent for polymers used both in inner and outer layers. The electrospinning parameters and solution characteristics of obtained coaxial systems are presented in Table 4. Coaxial sample C3, which is under consideration now, is a combination of S1 (PAN in DMF with C=9%) and S3 (PAN+CB (1:1) with C=8.5%) presented in Table 3.

Table 4. Solution and electrospinning parameters for coaxial spinning of fully miscible components

Sample code	Components		Concentration %		Pumping rates ml/h		Needle type	Voltage kV	Distance cm	Fiber diameter nm
	sheath	core	sheath	core	sheath	core				
C3	PAN+CB (1:1) in DMF	PAN in DMF	8.5	9	0.9	0.9	0.8 mm long	20	15	350
C4		PS in DMF		16	0.5	0.5				1070

The schematic representation of attempted coaxial fiber is shown in Figure 11.

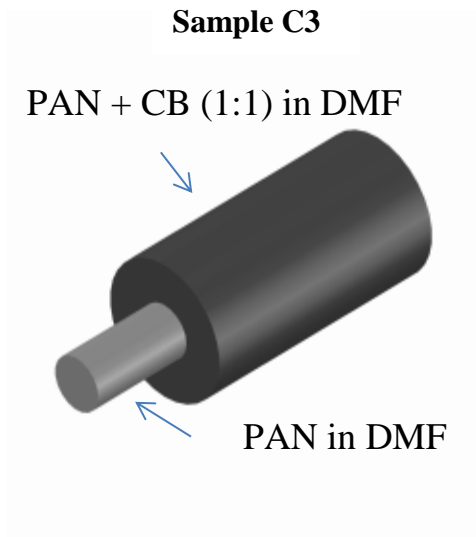


Figure 11 Coaxial fiber of (inner) PAN in DMF and (outer) PAN +CB in DMF (see C3 in Table 2)

According to theory the core viscosity must be lower than sheath's. In our case, due to presence of CB in solution, the viscosity of CB containing systems is much higher than pure polymer solutions, as seen from Table 2. The longer needle with outer diameter (OD) 0.8 mm was used for coaxial electrospinning, due to the high viscosity of sheath. The pumping rate was equal 0.9 ml/h for both layers - sheath and core. Solutions were electrospun and studied with scanning electron microscope.

Sample C3

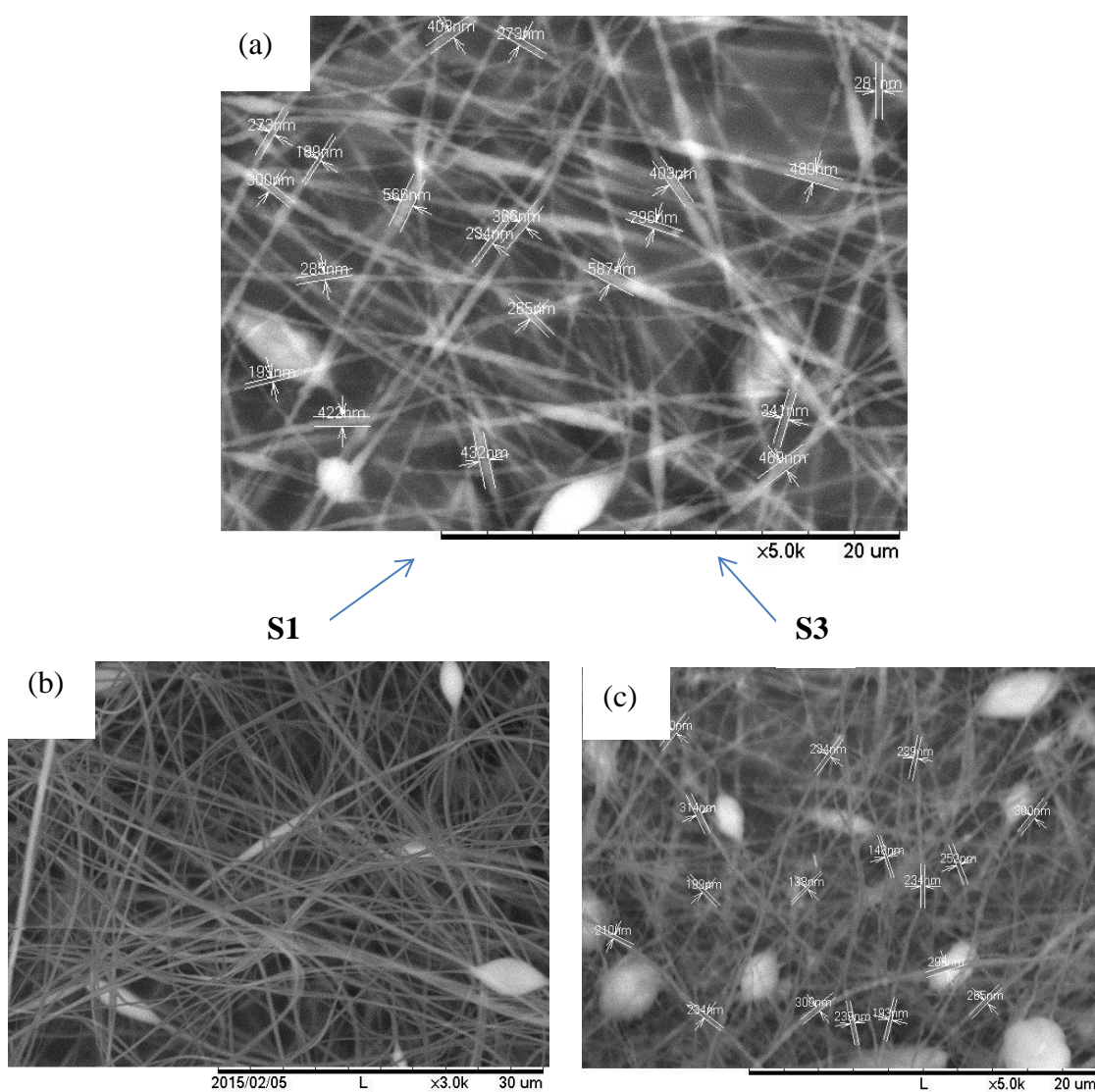


Figure 12 Fibers of coaxial electrospinning, where inner layer is PAN in DMF and outer is PAN+ (1:1) CB in DMF (sample C3), (b) PAN in DMF fibers of simple electrospinning (S1), (c) PAN+ (1:1) CB in DMF (S3)

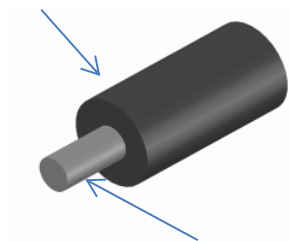
Figure 12 represents the morphology of coaxially spun sample C3 (see table 4). It is seen that fiber diameters are rather small, around 300 nm, fibers are inhomogeneous and contain beads. Taken into account small fiber sizes the simple electrospinning of individual components, PAN+ (1:1) CB in DMF (S3) and PAN in DMF (S1), was done and fiber morphology was analyzed. The SEM images for studied components are also presented in Figure 12 (b and c)

Comparing morphology of coaxial fibers C3 with morphology of individual components S1 and S3, it became obvious, that they are identical. S1 and S3 have the same morphology and fiber sizes (230 and 240 nm, respectively). In spite of coaxial sample C3 has a little bit larger fiber diameter (300-340 nm), it can be explained just by thicker needle diameter used in coaxial spinning comparing with simple spinning of components. Therefore, it can be suggested that two component systems were mixed up in coaxial spinneret and no coaxial (two phase) fibers can be seen. Fibers were looking similar to simple electrospun fibers.

In order to avoid mixing up of component solutions in coaxial spinneret, another polymer, namely polystyrene PS, was attempted to be processed. To preserve the full miscibility of systems, PS was dissolved in the same DMF solvent. The concentration of PS in solution was chosen 16%. The solution of PS in DMF (S6-2 in Table 3) was used as a core and PAN+CB (1:1) in DMF (sample S3) was used as a sheath to produce coaxial sample C4 as it is shown in Figure 13. All the electrospinning parameters and solution characteristics of components (core and sheath layer) for coaxially electrospun sample C4 are listed in Table 3 and Table 4.

Sample C4

PAN + CB (1:1) in DMF



PS in DMF

Figure 13 Coaxial fiber of PS in DMF and PAN + 1:1 CB in DMF (C4)

The coaxial electrospinning of sample C4 was done under the same conditions as sample C3 (voltages 20 kv, distance 15 cm, longer needle with OD 0.8 mm), although the pumping rate was decreased to 0.5 ml/h for both inner and outer layer, because 0.9 ml/h pumping rate was too fast for PS and the Taylor cone was not formed.

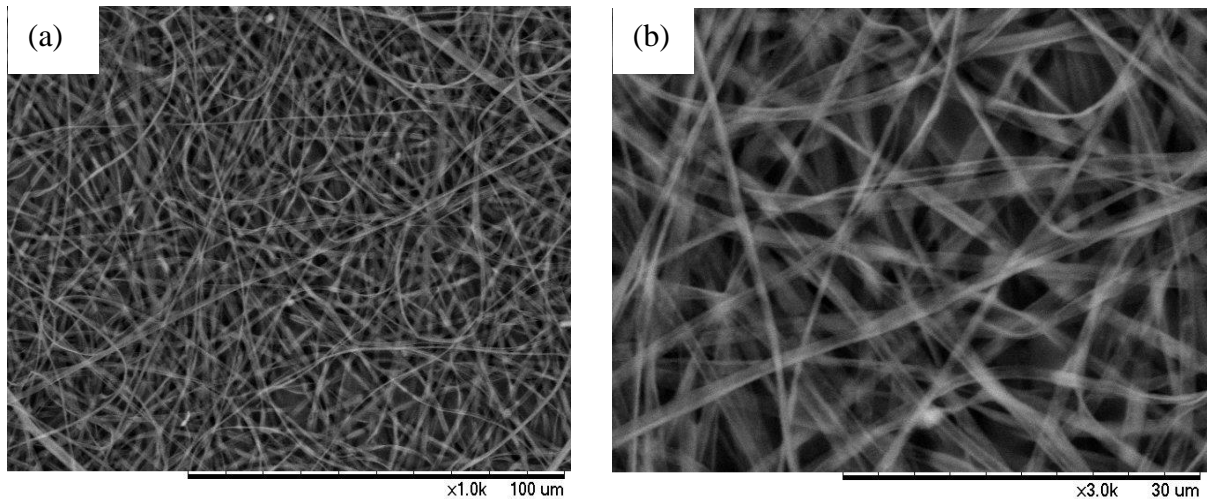


Figure 14 SEM images of coaxially spun fibers of sample C4 with PS core and PAN+ CB (1:1) sheath a) magnification 1000x b) magnification 3000x.

Figure 14 is presenting the morphology of the coaxial fibers, electrospun from C4 (PS in DMF core (S6-2) and PAN+ CB (1:1) in DMF sheath). As can be seen from the Figure 13 fibers do not contain any beads. However, the obtained fibers of C4 are not cylindrical, but ribbon-like. Probably, the reason for formation of ribbons is the use of the same solvent (DMF) in both layers [22]. The fiber mat characterized by nanofibers with no beads-on-string morphology with a ribbon-like fiber structure, due to use of the same solvent. The fiber diameter is much larger than it was for C3. The average fiber diameter of C3 was 350 nm, however the diameter of C4 was 1070 nm. Higher values of fiber C4 diameters can be explained by larger diameters of PS fibers.

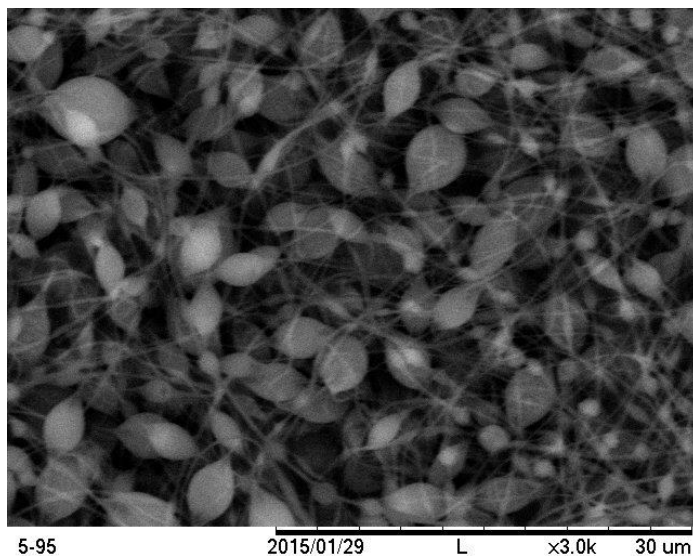


Figure 15 Fibers of simple electrospun PS in DMF (S6-2)

Figure 15 shows the SEM image for simply spun PS in DMF with concentration 16 % (S6-2). It is clearly seen that mostly morphology of PS in DMF at used concentration represents the beaded structure with only tailoring of fibers. Such beaded morphology can be explained by low viscosity of 16% solution. Perhaps, such concentration of PS is not enough to produce sufficient amount of polymer entanglements and fiber morphology cannot be obtained. However, due to ribbon-like structure of such coaxial system, it was pointless to prepare PS in DMF with higher concentration to avoid beads in fiber morphology of PS core. It is more expected to get again ribbon-like fibers. Therefore to get cylindrical fibers the solvent should be changed.

4.3. Coaxial electrospinning of partially miscible component solutions

Taking into account that for fully miscible systems as well as for fully immiscible systems it was not possible to get any adequate results, I attempted to use and study the systems which are partially miscible. In this case core and sheath solvents are miscible with each other. However, one of these solvents is not a good solvent for core or sheath polymer. For example, sheath consists of Sheath Polymer +Sheath Solvent; core comprises from Core Polymer +Core Solvent. Partial miscibility can mean that Solvent 1 and Solvent 2 are miscible, but:

- a) Sheath Solvent is not solvent for Core Polymer and Core Solvent is not solvent for Sheath Polymer (only solvents are miscible with each other);
- b) Sheath Solvent is not a solvent for Core Polymer (but core solvent is a good solvent for sheath polymer, i.e. core solvent can dissolve both sheath and core polymers);
- c) Core Solvent is not a solvent for Sheath Polymer (but sheath solvent is as good solvent for core polymer, i.e. sheath solvent can dissolve both sheath and core polymers).

Let's consider firstly the first variant of miscibility (variant a). To achieve this goal, two different component solutions were chosen:

Sample C5:

- Core – PLA in binary solvent 4:1 Dichloroethane: Methanol (sample S2);
- Sheath – PAN+CB (1:1) in DMF (sample S3).

The obtained sample is marked as C5 in Table 5. The systems are partially miscible, due to the DCE and Methanol is miscible with DMF. However PLA does not dissolve in DMF as well as PAN in DCE. Schematically the expected fiber structure is shown in Figure 16. For comparative analysis coaxially spun pure components (without CB) was also prepared and analysed. It's schematic representation is also included into Figure 16.

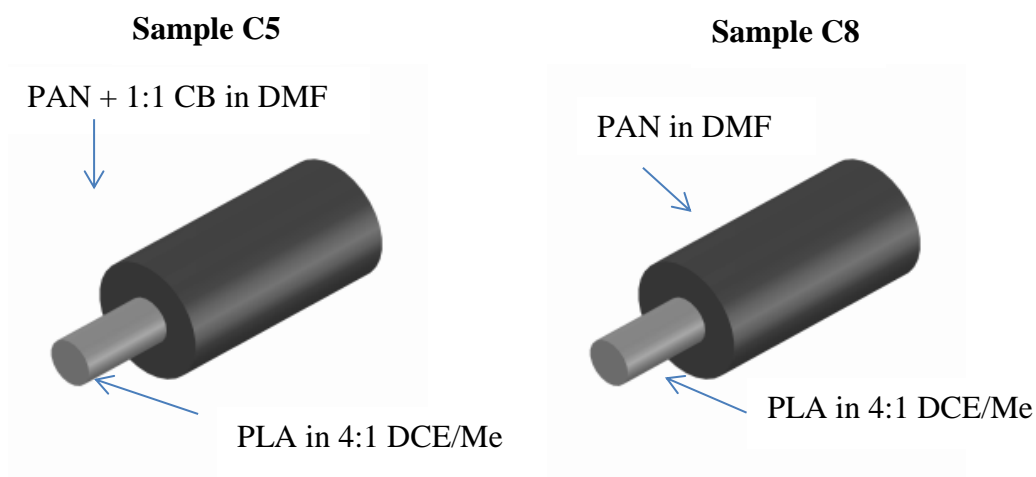


Figure 16 Coaxial fiber of sample C5 where inner part is PLA in 4:1 DCE/Me (S2) and outer is PAN + (1:1) CB in DMF (S3); Coaxial fiber of sample C8 where inner part is PLA in 4:1 DCE/Me (S2) and outer is PAN in DMF (S1)

All the necessary information about partially miscible systems which were coaxially electrospun is presented in Tables 5 and 6. Table 5 shows the data for systems where CB-based solution was used as a sheath and Table 6 gives information about similar systems without CB.

Table 5. Characteristics and electrospinning parameters of CB-based coaxially spun partially miscible systems

Samp. code	Components		Concentrations %		Pumping rates ml/h		Needle type	Voltage kV	Distance cm	Fiber diameter nm	
	<i>sheath</i>	<i>core</i>	<i>sheath</i>	<i>core</i>	<i>sheath</i>	<i>core</i>					
C5	PAN+ (1:1) CB in DMF	PLA in 4/1 DCE/Me	8.5	10	0.5	0.5	0.8 mm long	20	15	700	
C6	PAN+ (1:1)CB in DMSO	PVA in water/alc.	9	?	0.8	0.3	0.6 mm short	18	15	1100	
C7-1	PAN+ (1:1) CB in DMSO	PS in DMF	9	16	0.5	0.5	0.8 mm long	20	20	2500	
C7-2							20	15	2800		
C7-3							20	15	1550		
C7-4				20	15	940					
C7-5				25	16	470					
C7-6				8	30	0.5	0.5	0.8 mm long	15	15	900
C7-7							0.2				840
C7-8							0.8				1200
C7-9				25	16	15	850				

The results of viscosity and conductivity measurements as well as fiber sizes for components are shown as usual in Table 3.

Figure 17 (a) presents the morphology of the simply electrospun fibers of PAN + (1:1) CB in DMF (S9). As can be seen from the Figure 17 (a) fibers have a very small diameter, equals to 240 nm (see Table 3). The morphology of the fibers S9 was not homogeneous, but contains beads. The fiber surfaces are not smooth. Such beaded morphology can be explained both by the presence of CB aggregates and not enough polymer concentration for eliminating the beads.

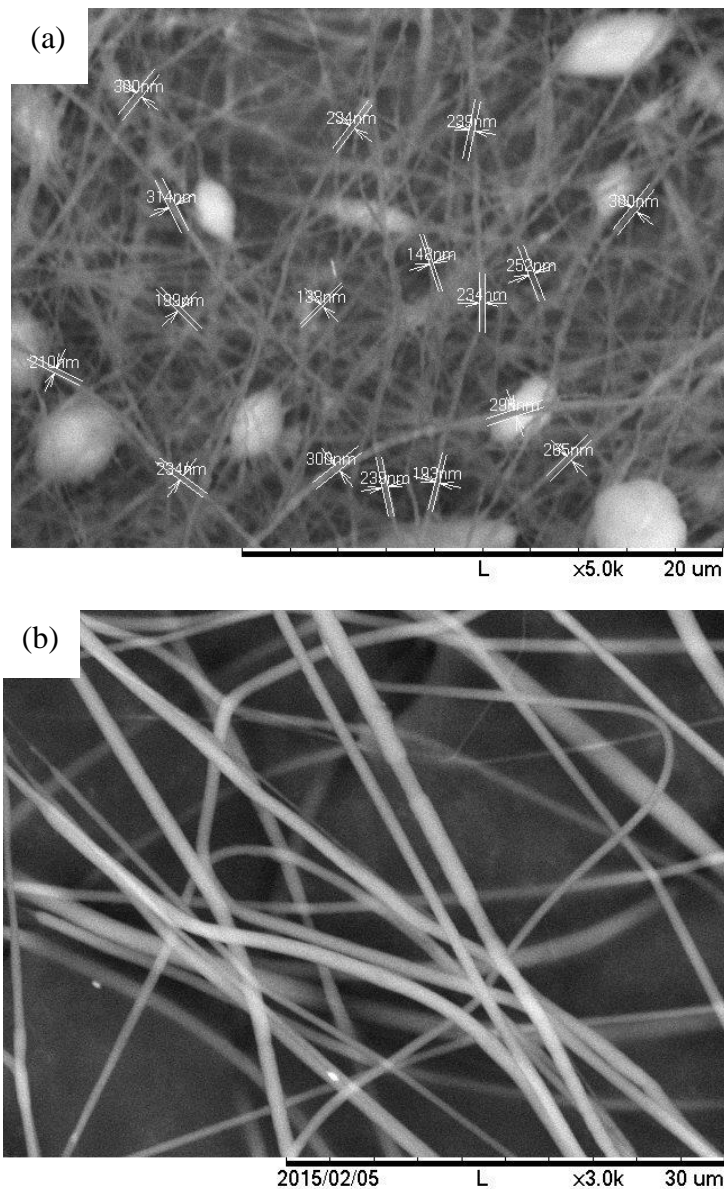


Figure 17 (a) SEM images of simply spun fibers of sample S3, PAN + (1:1) CB in DMF (b) Fibers of simple electrospun PLA in DCE/Me (S2).

Figure 17 (b) shows the SEM image for simply spun PLA in DCE/Me with concentration 10% (S2). As it can be seen from the Figure 17 (b), the morphology of PLA in DCE/Me at used concentration shows not beaded structure with smooth surfaces of fibers.

The coaxial electrospinning of C5 was done under the same conditions as it was for C4 (voltages 20 kv, distance 15 cm, longer needle with OD 0.8 mm). For core and sheath solutions the same pumping rate 0.5 ml/h was used. Solutions were electrospun and obtained fibers were studied by scanning electron microscopy. The coaxial electrospinning with pure components

without CB was done for comparison. In Table 6 such system is presented as C8. Note that C8 is comprised from samples S1 (pure PAN in DMF without CB) and S2.

Table 6. Solution and electrospinning parameters for coaxial spinning of partial miscible components without carbon black.

Samp. code	Components		Concentrations %		Pumping rates ml/h		Needle type	Voltage kV	Distance cm	Fiber diameter nm
	sheath	core	sheath	core	sheath	core				
C8	PAN in DMF	PLA in 4/1 DCE/Me	9	10	0.5	0.5	0.8 mm long	20	15	480
C9	PAN in DMSO	PVA in water/alc.	9	-	0.5	0.5	0.6 mm short	20	15	450
C10-1		PS in DMF	9	16	0.5	0.5	0.8 mm long	20	15	280/2300
C10-2								20	15	3100
C10-3							0.8 mm long	20	15	370/7800
C10-4							0.8 mm long	15	15	250
C10-5							20	15	340/1800	
C10-6							0.8 mm long	15-18	15	3300
C10-7							16	25	0.5	0.5

Figure 18 (a) shows the morphology of electrospun fiber mats produced from C5. As seen fibers of the mat are cylindrical but there are some spherical beads.

From the Figure 18 (b) it can be seen that fibers without CB (sample C8) have smaller diameter (480 nm) than fibers of sample C5 (700 nm), due to big difference in viscosities of solutions with and without CB. The figure also shows that the fiber morphology of C8 is less beaded and fibers have smoother surfaces than C5, which can be explained by absence of CB

in their structure. But in general, both systems C5 and C8 demonstrates the similar fibrous structure.

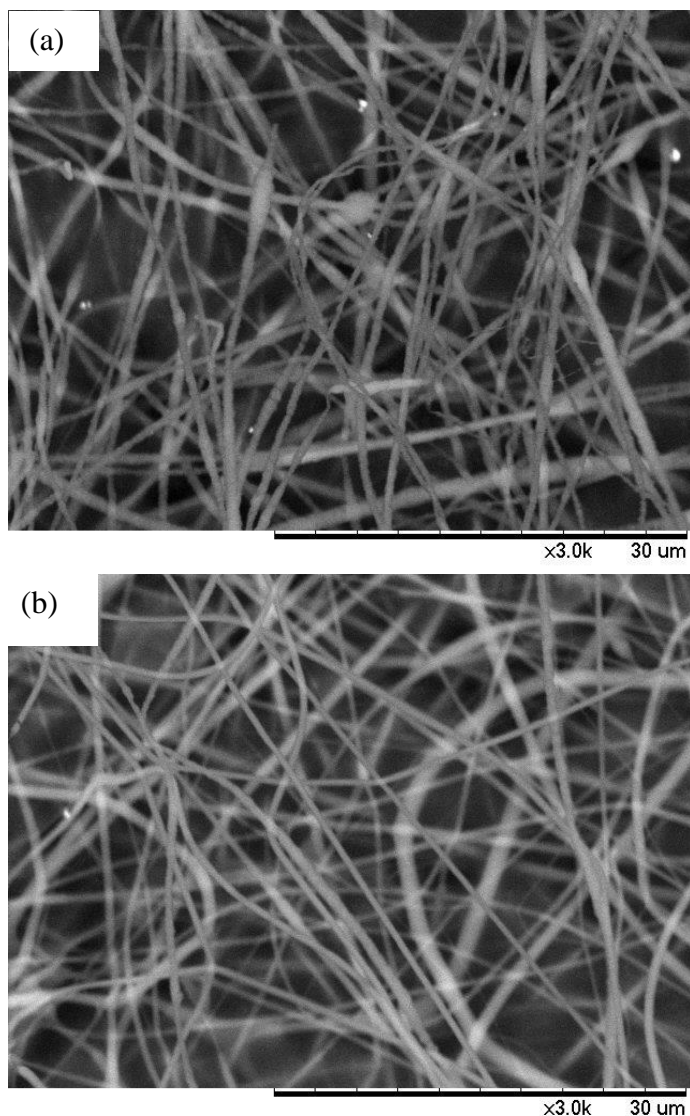


Figure 18 SEM image coaxially spun fibers of samples (a) C5 outer part is PAN + (1:1) CB in DMF and inner is PLA in 4:1 DCE/ Me, (b) C8 outer part is PAN in DMF and inner is PLA in 4:1 DCE/ Me

However, during the coaxial electrospinning a lot of processing problems occurred such as fast evaporation of DCE resulted in improper Tylor cone, and permanent blockage of the needles. Therefore, it was hard to obtain any contiuiuos electrospinning process, with such solvent as DCE/Me.

One of the solutions of this problem was to find a solvent with lower volatility, which will not evaporate so fast but will be miscible with another solvent. The appropriate candidate solvent pair is DMSO+water. DMF is not suitable for this purpose because it is not miscible with water. Taken it into account, the following system was studied, coded as C6 in Table 5:

Sample C6:

- Sheath is PAN+ (1:1) CB in DMSO (sample S 7);
- Core is PVA in water (sample S 8).

The systems can be still considered as partially miscible due the DMSO is miscible with water, although it is not solvent for PVA and at the same time water is not solvent for PAN. The expected fiber structure is conceptually shown in Figure 19. The similar fibers, without CB, were also tried to be obtained.

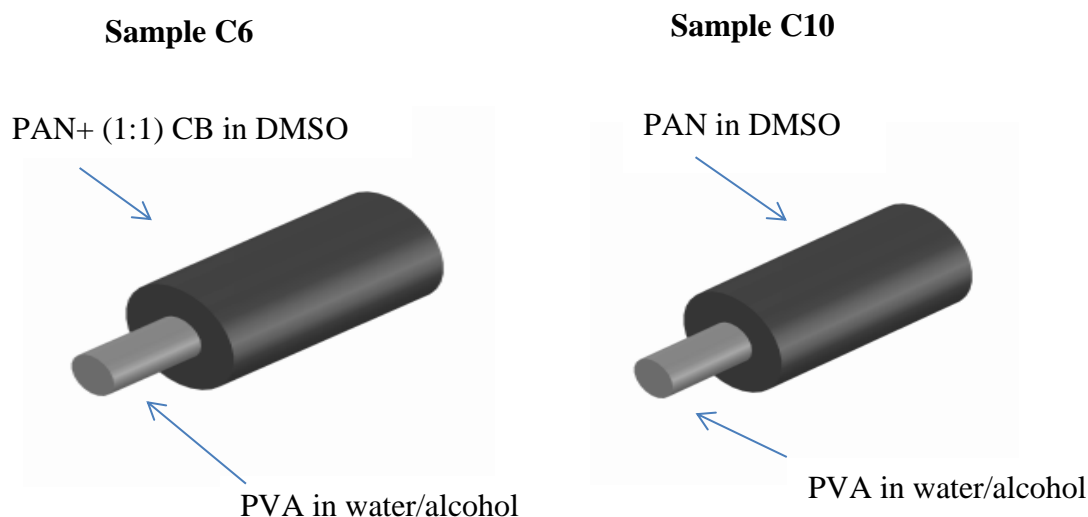


Figure 19 Coaxial fiber of sample C6, where inner part is PVA in water/alcohol (S8) and outer is PAN + (1:1) CB in DMSO (S 7-2); coaxial fiber of sample C9, where inner part is PVA in water/alcohol (S 8) and outer is PAN in DMSO (S 5-2)

All the parameters, which were used during the coaxial electrospinning, of sample C6 can be found in Table 5. The useful information about coaxial systems without CB is demonstrated in Table 6.

The information about viscosity, conductivity measurements and fiber sizes are presented in Table 3. The short needle, with OD 0.6 mm, was used for electrospinning. With a purpose to

avoid same problems during electrospinning, which were observed before for sample C1, different pumping rates for inner (0.3 ml/h) and outer part (0.8 ml/h) were used. The lower pumping rate for inner part was chosen by the fact of better and faster electrospinnability of PVA, than PAN+CB.

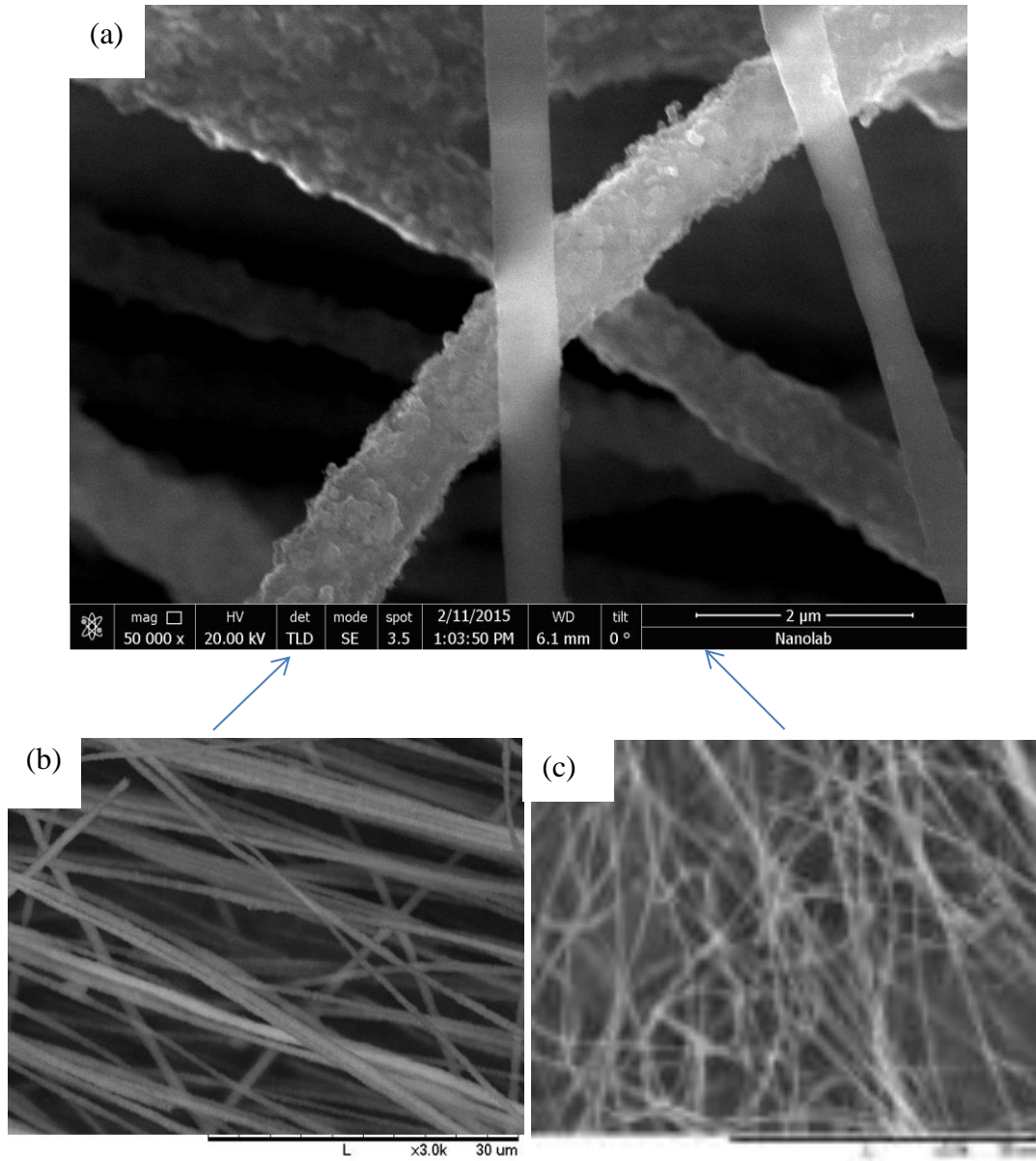


Figure 20 Fibers of coaxial electrospinning, where inner layer is PVA in water/alcohol and outer is PAN+ (1:1) CB in DMSO (sample C6), SEM images of simply electrospun fibers of sample (b) (S7-2) PAN + (1:1) CB in DMSO and (c) S8, PVA in water/alcohol .

Figure 20 (a) shows the morphology of the coaxially electrospun sample C6 (see Table 5). It is seen that fiber diameters are rather large, around 1100 nm, fibers are looking homogeneous and

with rough surface. The roughness of fiber surface is caused by large amount CB. Although there are a few number of smooth fibers, they are probably a fibers of pure PVA in water/alcohol. From figure 20 (a) can be also seen that sample C6 do not contain beads. The simple electrospinning of individual components were also done and these fiber diameters are smaller than coaxially electrospun fibers diameters. As it can be seen from Table 3 and Figure 20 (b and c), the medium diameter of PVA in water/alcohol (S8) is 380 nm and for PAN+ (1:1) CB in DMSO (S7-2) it is 700 nm.

The comparison of morphology of coaxial fibers C6 with morphology of individual components S 8 and S 7-2 shows clearly that they are different. It can be observed from Table 3 that coaxial sample C6 has much more bigger diameter (1100 nm), hence it can be suggested that coaxial fibers covered with CB are formed, but some uniaxial PVA fibers are also present.

For comparison with sample C6 the coaxial electrospinning were also done with pure systems, not containing CB. This sample was presented as C9 in Table 6, where one can also find all the parameters, which were used during the coaxial electrospinning of sample C9.

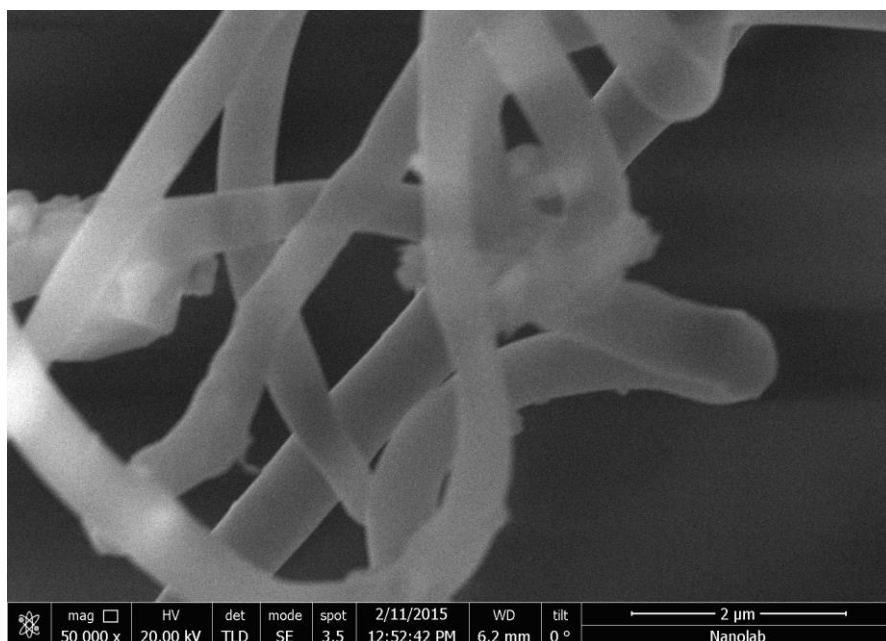


Figure 21 Fibers of coaxial electrospinning, where inner layer is PVA in water/alcohol and outer is PAN in DMSO (sample C9).

Figure 21 shows the morphology of the coaxially electrospun fibers of sample C9. As it is possible to see from the figure the morphology of fibers is rather smooth compared with sample C6. The fiber

diameter is also smaller, around 450 nm, this is approximately two times smaller than the diameter of sample C6.

Now let's consider the second variant of miscibility (variant b). For this purpose, two different component solutions were chosen:

Sample 7:

- Core – PS in DMF (sample S6);
- Sheath – PAN + (1:1) CB in DMSO (sample S7).

The systems are partially miscible, due to DMSO is miscible with DMF, and at the same time DMF is also solvent for PAN, however DMSO is not a solvent for PS. Schematically the expected fiber structure is shown in Figure 22.

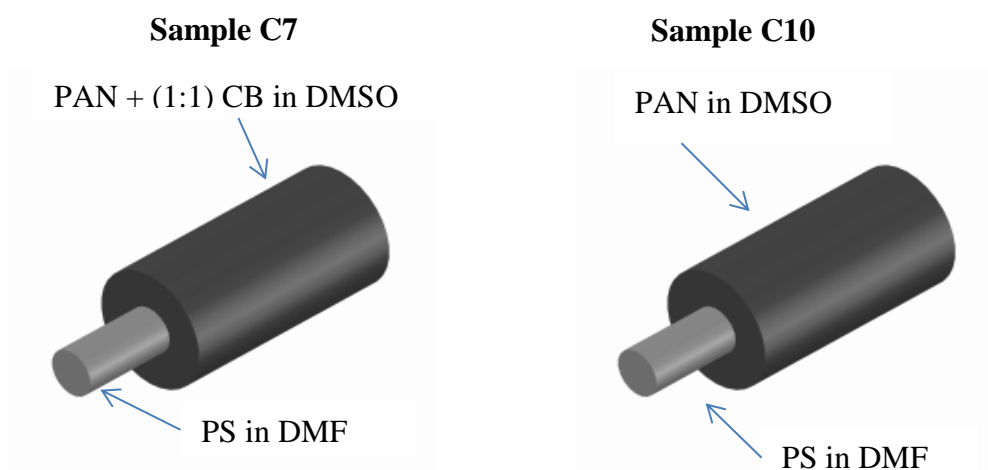


Figure 22 Coaxial fiber of the partially miscible system, where the inner part is PS in DMF and outer is PAN + (1:1) CB in DMSO ; Coaxial fiber of pure system, where the inner part is PS in DMF and outer is PAN in DMSO

On the base of this coaxial system the different processing conditions and their effect on fiber morphology were applied and studied.

a) The effect of various concentrations of electrospinning solutions in coaxial electrospinning

The concentration of polymer solution, which is going to be electrospun, has an effect to both the viscosity and surface tension of liquid, which ultimately decides the electrospinnability of the solution into nanofiber with increased diameters as the polymer concentration increases. Therefore at the concentrations of a certain limit the viscosity of the solution becomes expendingly high and the flow of the polymer solution through the capillary is disturbed. There should be optium solution concentration for the elctrospinning process. [23]

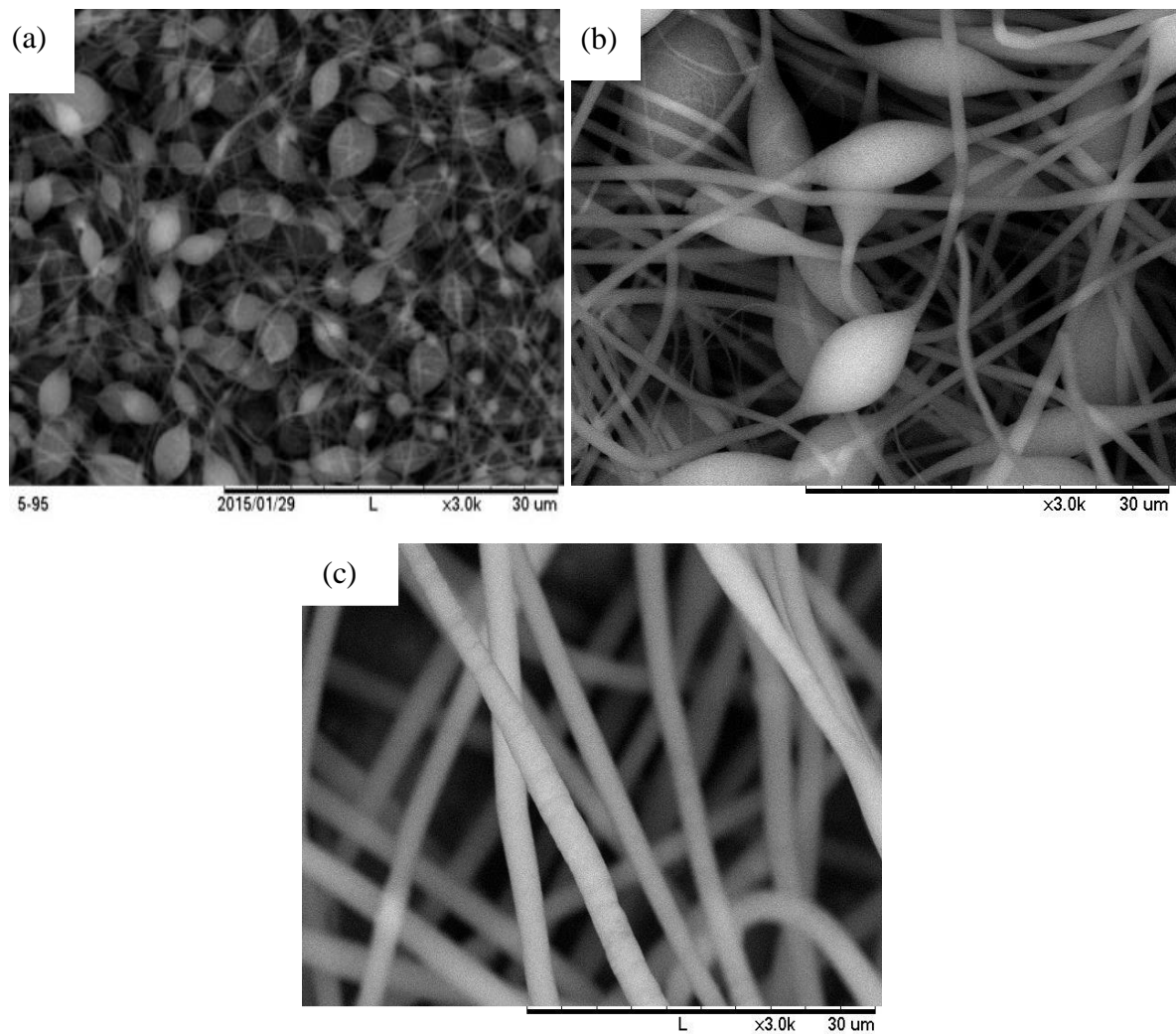


Figure 23 SEM images of simply electrospun fibers of samples (a) S6-4 b) S6-2 c) S6- 3.

To check the effect of core concentration on morphology of fibers, PS in DMF of various concentrations was studied. Figure 23 shows that with simple electrospinning of lower core solution concentration mixture of fibers and beads are observed. At lower concentration of solution (16 wt% of PS in DMF) bigger and spherical beads are more often to see. The fiber morphology is rough and clearly not homogeneous. With increasing concentration transition from electrospinning with beaded structure to electrospinning with fibrous structure is observed. At higher concentration of solution (25 wt% of PS in DMF) the morphology of fibers is fully fibrous. Spherical beads are disappearing due to the higher viscosity, leading to formation of uniform and smooth but thick fibers.

To study the effect of core concentration on final morphology the coaxial electrospinning of PAN + (1:1) CB in DMSO (sheath) samples with different concentrations of PS in DMF, serving as a core, were done. As it was mentioned in Experimentl section the solutions of PS in DMF were prepared at different polymer concentrations such as 14- 30% (see Table 3). The information about samples of coaxial fibers is presented in Table 5, where one can also find all the parameters, which were used during the coaxial electrospinning. In table 6 the necessary information about pure systems is presented and the results for simply spun coaxial components can be found in Table 3.

It is known that the viscosity of solution is largely dependent on the polymer concentration. The larger the concentration of PS, more viscous the solution is. As a result, the fiber morphology is changed greatly with viscosity. In our work, the dependence of viscosity on polymer concentration was also detected and can be seen in Table 5.

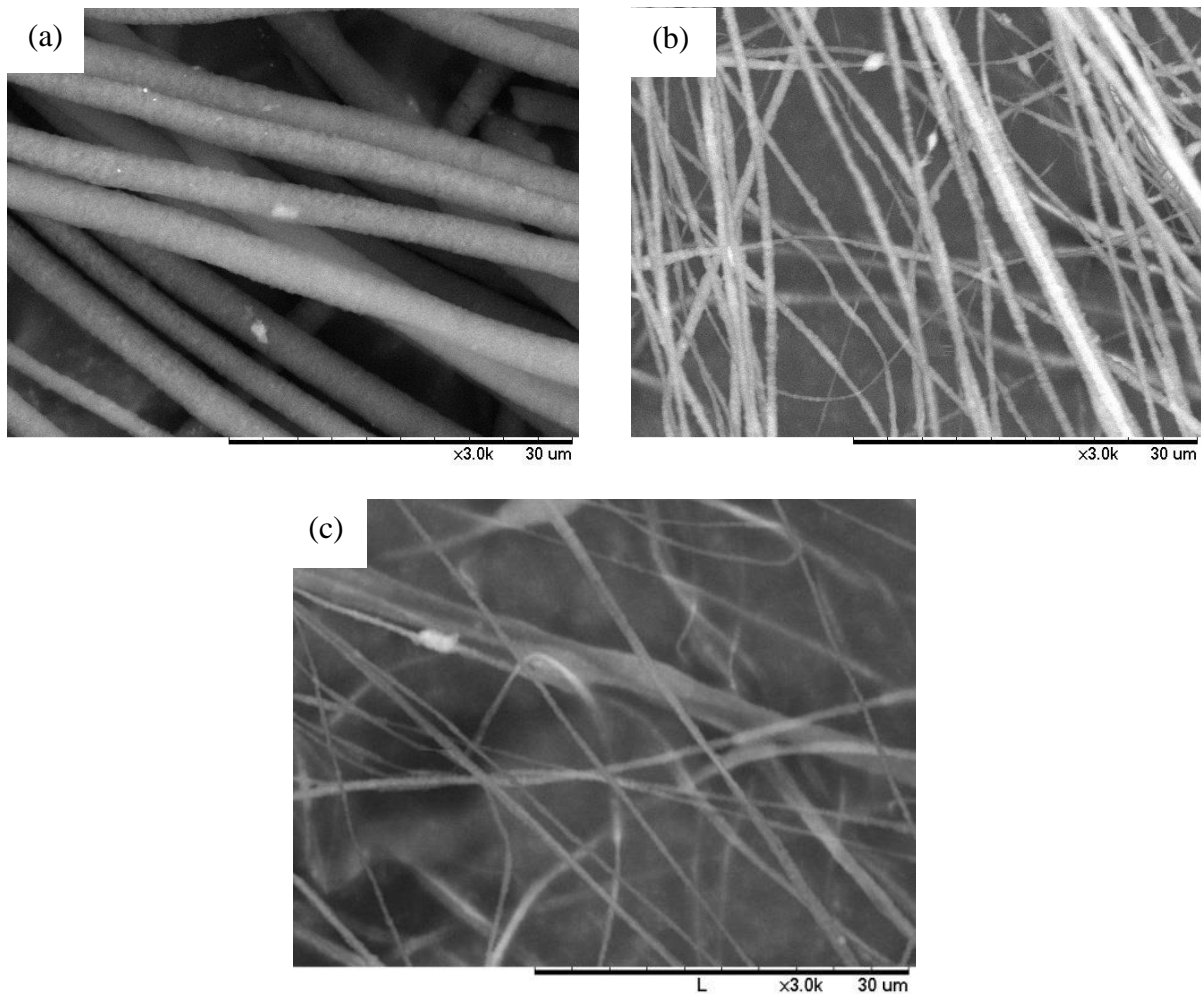


Figure 24 SEM images of coaxially electrospun fibers of samples (a) C7-2, concentration of core solution is 16% b) C7-4, $c_{\text{core}} = 20\%$ c) C7-5, $c_{\text{core}} = 25\%$.

From Figure 24 it is possible to observe the changes in morphology of coaxial electrospun fibers at different core solution concentrations. As seen, fibers, which were coaxially electrospun at higher core concentration, are much thinner than fibers electrospun at lower concentration of core. The most probable reason for such behavior is the following: 16% solution of PS in DMF has very low viscosity (82 cp) in comparison to viscosity of PAN+CB (6200 cp). At such low concentration no fibers of PS are formed as shown in Figure 24 (a), and beads/droplets do not affect electrospinnability of PAN+CB solution. Therefore, the morphology of coaxially spun PAN + CB with 16% PS core imitates the morphology of simple spinning of PAN+CB. Increase in core concentration leads to an increase in a viscosity of core solution (see Table 3) and as a result, morphology of coaxially spun samples

at highest core concentration (C7-5) contains two types of fibers with low diameters (~ 500 nm) and a large ones ($\sim 3 \mu\text{m}$) as seen in Figure 24 (c). It means that additionally to coaxial spinning, the process of simple spinning of individual components is observed.

The coaxial electrospinning of CB-free components, PS in DMF and PAN in DMSO were done for comparison. It showed a similar dependence between the concentration of core and fiber diameters, as it can be seen from Figure 25.

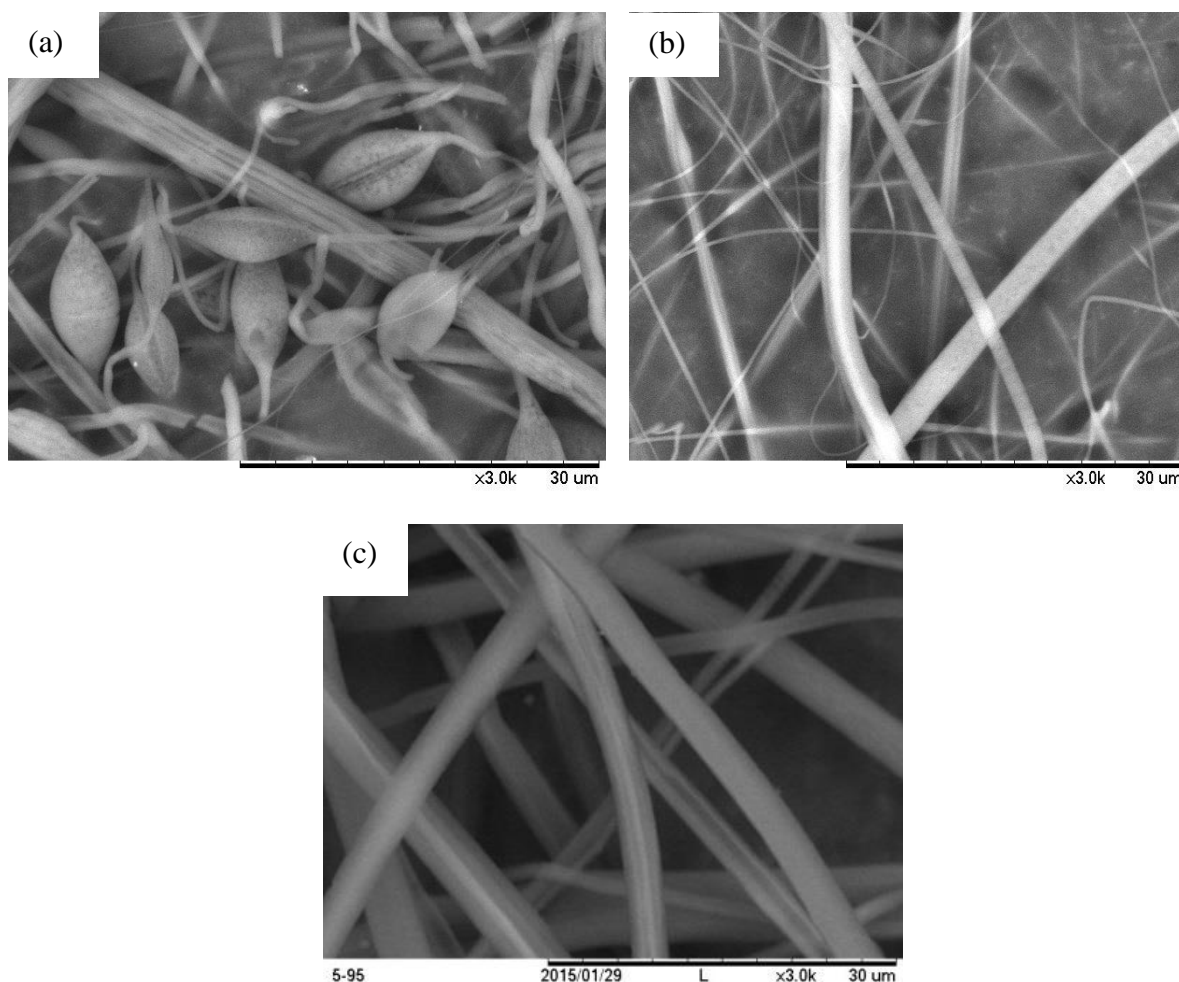


Figure 25 SEM images of coaxially electrospun fibers of samples without CB (a) C10-2 b) C10-5 c) C10-6.

Furthermore, in present work the coaxial electrospinning at different sheath concentrations were also done while core concentration was kept constant ($c = 25\%$ PS in DMF). The samples, which are describing this effect, are presented as C7-5 and C7-9, having sheath concentration 9% and 8%, respectively. All the information about the characteristics of both spinning processes are shown in Table 5.

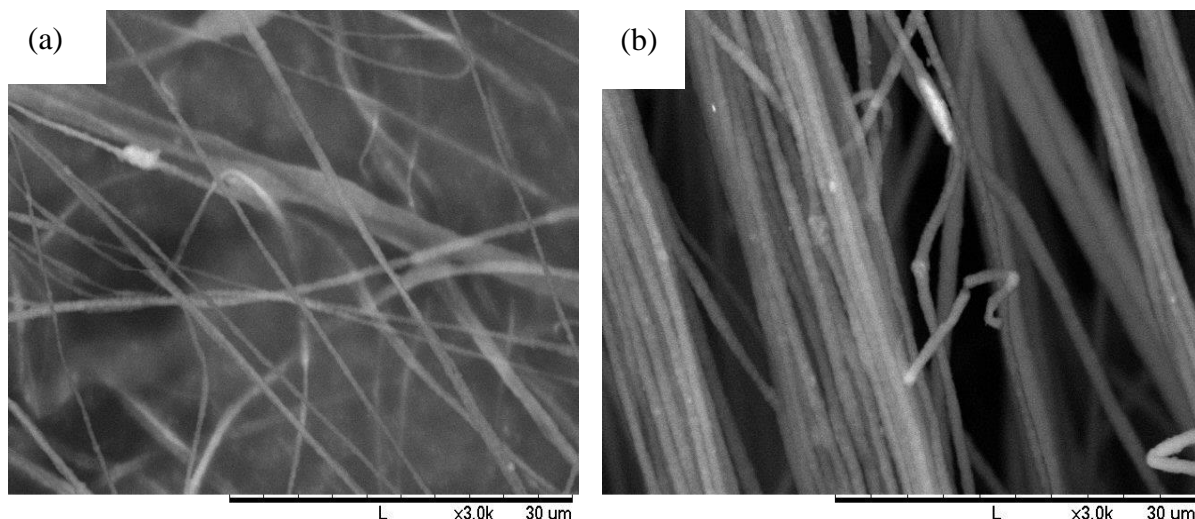


Figure 26 Effect of different sheath concentration with CB on fiber morphology a) C7-5 and b) C7-9

Figure 26 shows the effect of sheath concentration on fiber morphology. As it can be seen from Figure 26 (a) there are two types of fibers, one type has a rather small diameter (350 nm) and the other type has a rather large fiber diameter (670 nm). However, from Figure 26 (b) it is possible to see that the morphology of fibers of sample C7-9 are more homogenous and with a much smoother surface compared with sample C7-5. All fibers have approximately identical fiber diameters.

For comparison in present work the same effect was also studied with pure systems. During the coaxial electrospinning at different sheath concentrations the core concentration was kept constant ($c = 25\%$ PS in DMF). The samples, which are describing this effect, are presented as C10-6 and C10-7, having sheath concentration 9% and 16%, respectively. The PAN concentration was increased to 16% for sample C10-7, to increase viscosity of solution and make it similar to viscosity of PAN +CB. All the information about the characteristics of both spinning processes are shown in Table 6.

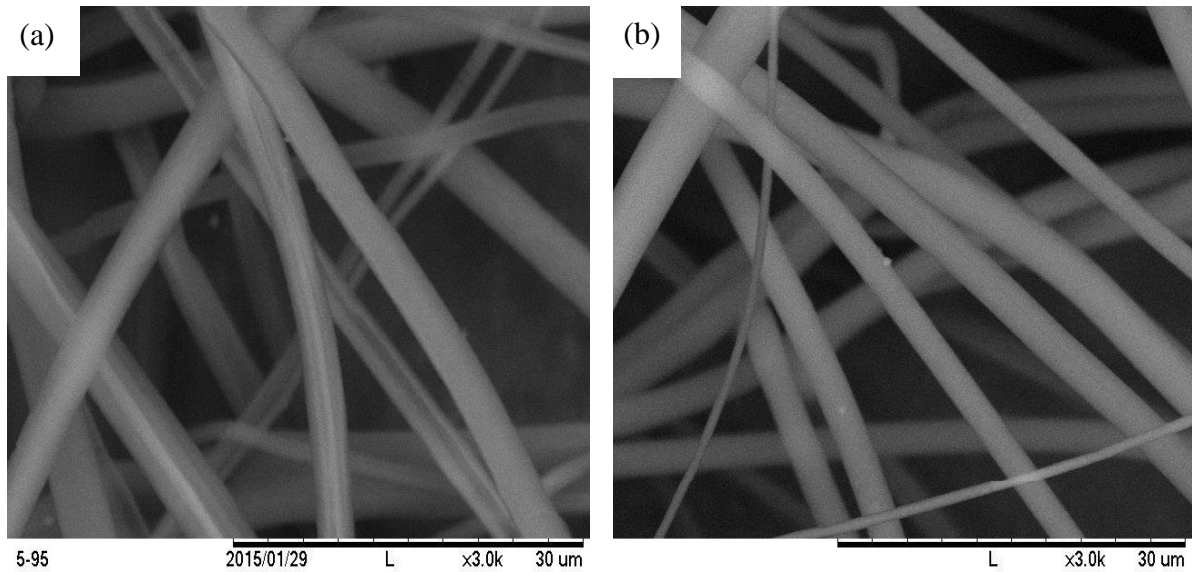


Figure 27 Effect of different sheath concentration to fiber morphology in pure systems (without CB) a) C10-6 and b) C10-7.

From the Figure 27 it is possible to observe that there is only one type of fibers in both samples. The morphology of fibers is smooth and homogenous in both cases. Although the Figure 27(a) reveals that with lower sheath concentration ($c = 9\%$) the diameter of fibers is larger (3300 nm) compared with higher concentration of sheath ($c = 16\%$), where the average fiber is approximately 2200 nm.

According to theory, the solution concentration is one of many parameters, which influences morphology of coaxially electrospun fibers. At lower polymeric concentrations the charged jet fragments into discrete droplets before reaching the collector, due to the effect of applied voltages and surface tension of the polymeric tension. Therefore with low solution concentrations mixture of fibers and beads can be observed. At an increased polymeric concentration, the viscosity also increases the chain entanglement between polymeric chains improves and nanofibers are formed. With increased solution concentrations the shape of the beads changes from spherical to spindle-like and uniform fibers are formed because of the higher viscosity resistance.

b) The effect of various distances to collector on fiber morphology

The effect of different distances to collector was also studied with the coaxial sample C7. The distance to collector can also influence the morphology of fibers. Therefore in present work effect of distance was also investigated. The C7 was spun at various distances, such as 15 cm (C7-1) and 20 cm (C7-2). (see Table 5)

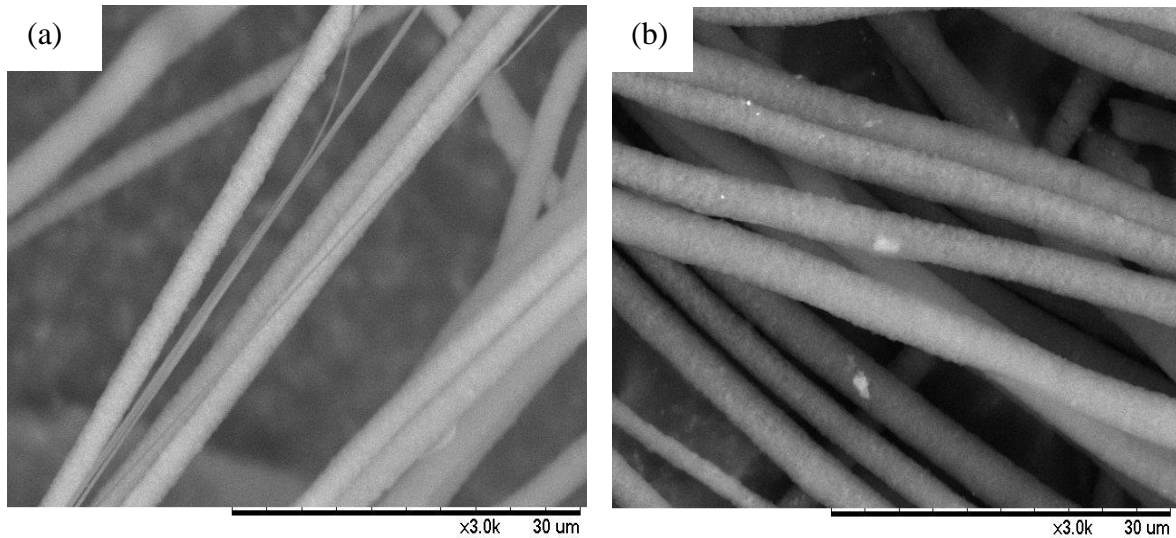


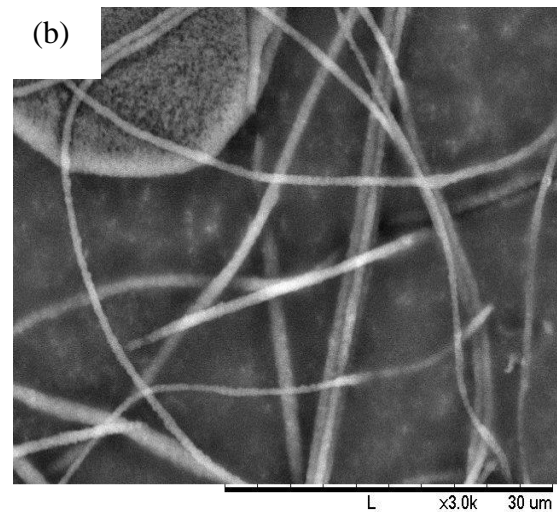
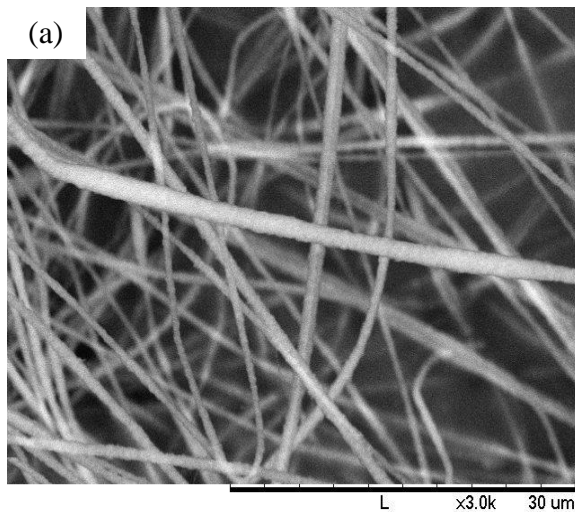
Figure 28 Coaxially electrospun fibers at different distances a) C7-1 b) C7-2

Figure 28 shows how different distances between the capillary tip and the collector, influences the fiber formation. As seen, the fiber diameter is slightly decreasing with longer distance (see Table 5), due to different fiber deposition time and various evaporation rates. From the information of theory it appears also that the distance between the spinner and collector is important, due it gives the fibers sufficient time to dry before reaching the collector. In cases where the distance is either too far or too close beaded morphology of fibers can be observed. [8]

c) The effect of various core flow rates on fiber morphology

The effect of different pumping rates was also studied with the same coaxial sample C7. The used pumping rates for core were 0.2 ml/h (C7-6), 0.5 ml/h (C7-7) and 0.8 ml/h (C7-8), while the flow rate for sheath was kept konstant 0.5 ml/h.

The dependence of flow rate on fibers morphology of simply electrospun sample is discribed in many articles [23]. According to previous the flow rate of the polymer solution through the capillary influences the nanofiber porosity, diameter and geometry of the electrospun nanofibers. As the flow is raised to higher values, the available polymer volume is high, which increases the diameter of fibers. If the flow rate is too high, the nanofibers are unable to dry before reaching the collector and therefore there is higher change to observe beaded morphology of fibers. When the flow rate is too low beads are also possible to see and the diameter of electrospun fibers is smaller. Flattened and ribbon – like fiber morphology can also be observed as a result of incomplete drying of nanofibers, because of the high flow rate. Beads, which are produced with too high flow rate are bigger than these, which are produced at lower values of pumping rate, due to the larger droplet at the end of the capillary. Our studies showed also such kind of trend.



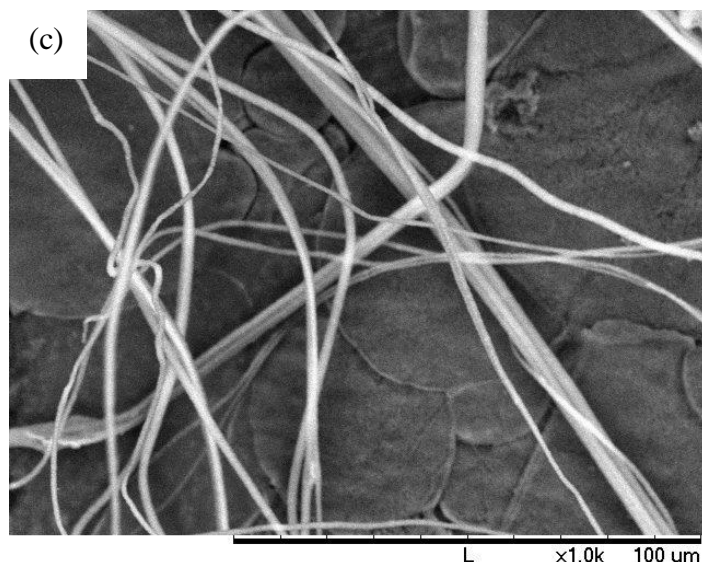


Figure 29 SEM images of coaxially electrospun fiber samples with carbon black sample 7 at various pumping rates a) 0.2 ml/h (C7-6) b) 0.5 ml/h (C7-7) and c) 0,8 ml/h (C7-8).

Figure 29 shows the fiber morphology, which is influenced by various pumping rates. As it can be observed from the figure, diameters of fibers were increased with higher pumping rate. It is also possible to see that there are no beads.

The third variant of component miscibility (variant C) was not part of our interest, therefore in present work C variant is not considered.

4.4 Main characteristics of coaxially spun fibers

As the main purpose of the work was the preparation of conductive but mechanically strong membrane, the most successful coaxially electrospun membrane, namely C7-9 was checked by tensile testing and conductivity measurements. The same sample was also checked to reveal their specific surface values.

a) Conductivity of membranes

The coaxial sample C7-9 was checked to its conductive properties. These are coaxial membranes of (outer) PAN+ (1:1) CB in DMSO and (inner) PS in DMF. For this purpose, the thick membrane was obtained by coaxial electrospinning. Sample C7-9 was further compared with PAN +CB, which was obtained by simple spinning, S7-1 The conductivity of PAN +

(1:1) CB (sample S7-1) was 0.442 $\mu\text{S}/\text{cm}$ and at the same time the coaxial membrane of PAN+ (1:1) CB with PS core (sample C7-9) showed approximately the same value 0.453 $\mu\text{S}/\text{cm}$. It can be concluded that addition of PS core does not change the conductivity of membrane, and consequently coaxial spinning does not deteriorate the conductivity properties of membranes and can be used for preparation of conductive fibers. However, the advisability of using of coaxial spinning will be obvious if core-sheath structure will enforce the mechanical properties of membranes. Therefore, the testing of mechanical properties is necessary for this issue.

b) Tensile testing

The purpose of tensile test is to understand, how different materials will react to forces being applied in tension. During the test, it is possible to find the strength value of the material and how much it will elongate. [25]

From tensile testing it is possible to get a lot of information about substance. The material is continuously pulled until it breaks and the complete tensile profile will be obtained. The strain-stress curve shows, how the material reacted to applied forces. The failure point is normally named as ultimate strength or UTS on the chart. From the chart it is usually possible to see that the relationship between the applied force and the elongation the specimen exhibits is linear. This linear part of the line obeys the relationship, which is called as Hooke's law, where the ratio of stress to strain is a constant or $\delta/\varepsilon = E$. E is the slope of the line in this region, where stress δ is proportional to strain ε and is named as Young's modulus. [25]

The Young's modulus is a measure of a material stiffness, although it only applies in the linear region of curve. The ultimate tensile strength is the maximum load the specimen sustains during the test. [25]

In current study one coaxial membrane, namely C7-9, was tested by Tensile Test Instrument. For comparative analysis, the membrane obtained by simple electrospinning from PAN + (1:1) CB in DMSO (S 7-1) was also checked by tensile test.

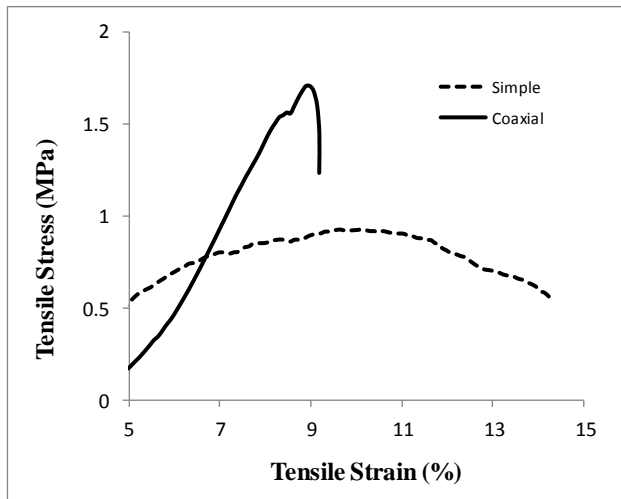


Chart 1 Selective stress-strain tensile curves

Chart 1 shows selective stress-strain tensile curves obtained for listed above membranes. As can be seen from Chart 1, besides simply spun membrane show a little bit longer extension at break, the ultimate strength and Young's modulus are higher for coaxial fibers than for simply spun fibers. It means that coaxial membranes are really stronger and more rigid than simple membranes.

c) Specific surface

Specific surface is a measure of a solid material. Previous compares the surface area of the object to its mass. For design of chemical processes, which involve surface reactions specific surface is important aspect. Although specific surface is difficult to measure directly, however it can be calculated from knowledge of surface structure. Generally the rougher the surface, the higher will be the specific surface. [26]

Fibers have usually high specific surface areas. Nanofibers are typically two to three orders of magnitude smaller than fibers, which are conventionally produced. Therefore, fibers have two to three orders of magnitude higher specific surface area. [27]

In present work the specific surface and the porosity of fibers was measured in Skeleton OÜ.

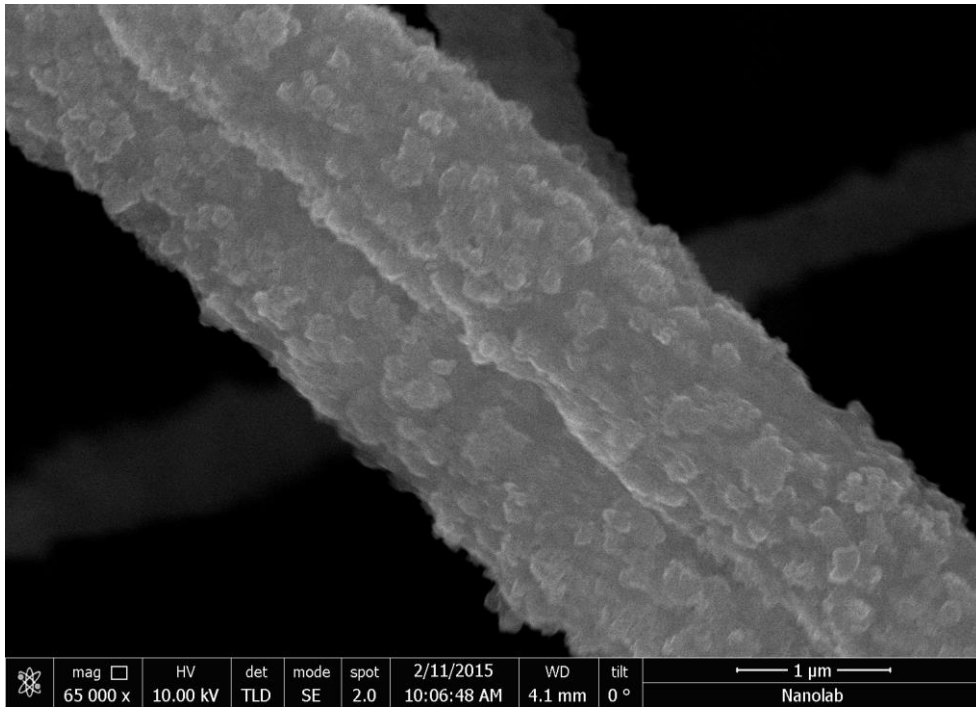


Figure 30 SEM figure of coaxial fibers of sample C7-9, where the inner part is PS in DMF (S6-4) and the outer is PAN + (1:1) CB in DMSO (S7-2).

Figure 30 shows the fiber morphology of sample C7-9, the diameter of fibers is approximately 850 nm (see Table 5). As it is possible to see from the Figure, the surface of fibers is really rough, due to presence of huge amount of CB particles. Therefore, it was expected that such samples could show the high values of specific surface.

However, from Table 7 it is possible to see that specific surfaces of samples is quite moderate compared with specific surface of pure carbon powder ($S_a = 1000 \text{ m}^2/\text{g}$). This result is probably caused by the polymer, which blocked the major part of CB surface. However, interesting fact is that specific surface of coaxial PAN+CB is in 1.5 times higher than PAN+CB electrospun by simple spinning setup and total porosity of coaxial samples is also higher.

Table 7 Characteristics of surface area

	Coaxial PAN +CB	Simple PAN+ CB
Specific surface (Sa)	53.2 m ² /g	36.0 m ² /g
Total porosity (Vt)	0.121 cm ³ /g	0.116 cm ³ /g
Microporsity (Vm)	0.001 cm ³ /g	0.005 cm ³ /g

It showed, that even high CB content, equal to polymer content in solution is not enough to reach appropriate specific surface. However, in any case, coaxial spinning helps to improve specific surface in comparison to simple spinning.

CONCLUSIONS

In this study, CB containing composite fibers was produced by coaxial electrospinning. For this purpose different polymer-solution systems such as fully immiscible, fully miscible and partially miscible were studied. Furthermore the effect of electrospinning process like solution conductivity, viscosity, specific surface and tensile properties were also analyzed. The conclusions about this research are made beneath:

- CB containing composite fibers of fully immiscible polymer-solution system were not so successful as it was expected. The electrospinning process was not stable and continuous and obtained fibers had a lot number of cracking and cavities in fiber morphology.
- The morphology of CB containing composite fibers of fully miscible polymer-solution system was identical to morphology of individual components. Two component systems were just mixed up and no coaxial fibers were seen.
- The morphology of CB containing composite fibers of partially miscible polymer-solution system was homogenous, cylindrical and had sizes bigger than that of individual component. In some cases even additive affect of sizes of individual

components to the size of coaxial fiber can be observed. In this research the best results were achieved with this type of miscibility.

- Coaxial fiber membrane of PAN+CB with PS core has an identical to simple spun PAN+CB values of electric conductivity. consequently coaxial spinning does not deteriorate the conductivity of membranes.
- Tensile test showed that coaxial membranes are actually stronger and more rigid than uniaxial or simply spun membranes.
- Specific surface of coaxial fibers was quite moderate, comparing with pure CB particles. However, the surface of coaxial PAN+CB was in 1.5 times higher than simply electrospun one.

Taken into account identical conductivity, but better tensile properties and higher specific surface of coaxial PAN+CB membranes in comparison to simple membranes, the coaxial electrospinning seems to be more favourable method for preparation of strong enough membranes of polymers with high content of CB.

However, this research focuses mostly to general fiber structure so the core-sheath structure of obtained membranes is not certain. For the previous purpose additional and complicated SEM and TEM tests should be done.

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SUMMARY

The main purpose of preparation of CB- based membranes is to produce conductive fibrous materials. In our lab it was shown that addition of 100 % CB into PAN matrix allows to get fibrous mat with conductivity up to 300 nS [1]. Another application of such membrane could be filtering materials, due to presence of huge amount of CB particles. For both these applications is important that the produced membrane should be mechanically strong enough to withstand applied force.

As it was checked before the prepared PAN + (1:2) CB membranes were rather fragile. Therefore, in current work the attempt to enforce the PAN + CB membranes was done by preparation of core- sheath fibres, where sheath is PAN + CB, and core is any other material serving just as enforcing element. Such core- sheath fibers are possible to produce by so named “coaxial electrospinning”. Therefore, the aim of the study was to produce conductive composite fibers by coaxial electrospinning.

For the previous purpose different polymer-solution systems were studied. The coaxially electrospun fiber mats were produced from different solutions. Scanning Electron Microscopy and Polaryzed Light Microscopy were used to study the morphology of fibers and analyze the influence of electrospinning process on fiber morphology.

The results of this reaserch exhibit that the best solution to produce cylindrical and conductive coaxially electrospun composite fibers is to use partyally miscible coaxial component solutions. With such system the electrospinning process was mostly stable and obtained fibers had cylindrical and homogenous morphology. Fibers which were produced by using fully

miscible or fully immiscible systems had a lot number of cracking and cavities in their morphologies.

The results of main characteristics of coaxially spun fibers were quite moderate. The conductivity of PAN + (1:1) CB and the coaxial membrane of PAN+ (1:1) CB with PS core showed approximately the same value. Therefore it was possible to conclude that addition of PS core did not change the conductivity of membrane. The results of tensile test showed coaxial membranes are really stronger and more rigid than simple membranes, because the ultimate strength and Young's modulus were higher for coaxial fibers than for simply spun fibers. However, the surface of coaxial PAN+CB was in 1.5 times higher than simply electrospun one.

KOKKUVÕTE

Tööstuslikul tahmal baseeruva kiu membraani peamiseks tootmise eesmärgiks on saavutada elektrit juhtiv kiuline materjal. Varasemalt sooritatud katsete tulemuste põhjal oli teada, et 100 % tööstusliku tahma lisamine PAN maatriksisse võimaldab saavutada kiu mati, mille elektri juhtivus võib küündida kuni 300 nS. Tänu suurele tahma kogusele võib viimaseid kasutada ka filtreerimisel. Mõlema eelmainitud ülesande täitmiseks on oluline kiu mattide tugevus, et vastupidada rakendatud mehhaanilisele jõule.

Varasemate katsete tulemused näitasid, et PAN + (1:2) CB membraanid olid pigem haprad. Seetõttu valmistati PAN + CB membraanid koaksiaalsel elektroketruse meetodil, kus kiu väliskihiks oli PAN + CB ning tuumaks mingi teine materjal. Tuginedes eelnevale oli käesoleva bakalaureuse töö eesmärgiks toota koaksiaalsel elektroketrusel elektrit juhtivaid kiu membraane.

Eesmärgi saavutamiseks kasutati koaksiaalsel elektroketrusel erinevaid polümeeri lahuseid. Koaksiaalse elektroketruse protsessi mõju hindamiseks kiu morfoloogiale olid kasutusel valgusmikroskoop ja skaneeriv elektronmikroskoop.

Töö tulemuste põhjal võib öelda, et parima kihilise ja elektrit juhtiva kiu mati saab kasutades koaksiaalsel elektroketrusel osaliselt lahustuvaid lahuseid. Viimaste korral oli elektroketruse protsess stabiilseim ning saadud kiud olid silindrilised ja homogeense morfoloogiaga. Omavahel segunevate ja mite segunevate lahute korral ilmnis kiu mattides lõhenemist ning õõnsuseid.

Koaksiaalselt elektrokedratud kiudude omadused olid mõõdukad. Elektrijuhtivus elektrokedrusel saadud PAN + (1:1) CB membraanil oli praktiliselt võrdne koaksiaalsel elektroketrusel saadud PAN+ (1:1) CB koos PS tuumaga. Tuginedes viimasele oli võimalik järeldada, et PS – kiu lisamine tuumana, ei mõjuta membraani elektrilisi omadusi. Tõmbetugevuse testi tulemusel sai selgeks, et koaksiaalsel teel saadud kiu membraanid on tugevamad kui tavalisel elektroketrusel saadud kiu membraanid. Lisaks oli PAN + CB kiu membraani eripind 1,5 korda kõrgem kui tavalisel elektroketrusel saadud kiu membraanil.