TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

A MECHANICALLY ROBUST AND CONDUCTIVE FIBER MATERIAL BASED ON CHITIN

KITIINIL PÕHINEV JUHTIV JA MEHAANILISELT VASTUPIDAV KIULINE

MASTER THESIS

Student:	Salma Hafez Efati
Student code:	KVEM177310
Supervisor:	Dr. Elvira Tarasova, Senior lecturer, Department of Materials and Environmental Technology.
Co-supervisor	Dr. James Mendez, Assistant Professor, Chemistry, Department of Division of science, Indiana university- purdue university columbus.

Tallinn, 2019

AUTHOR’S DECLARATION

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

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

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Author: ....

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Supervisor: ………………………

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Thesis is in accordance with terms and requirements

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Co-supervisor: ………………………

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Accepted for defense

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Chairman of theses defense commission: ....

/name and signature/

Department of Materials and Environmental Technology

THESIS TASK

Student: Salma Hafez Efati KVEM177310

Study program: KVEM 12/15 Technology of Wood, Plastic and Textiles.

main speciality: Plastic technology.

Supervisor(s): Dr. Elvira Tarasova, Senior lecturer, +372 620 2906

Consultants: Dr. James Mendez, Assistant Professor, +812 348 7332

Thesis topic:

(in English) *A mechanically robust and conductive fiber material based on Chitin*

(in Estonian) Kitiinil Põhinev Juhtiv ja mehaaniliselt vastupidav kiuline materjal.

Thesis main objectives:

1. To extract of chitin from Estonian mushrooms.
2. To find optimal conditions for electrospinning of PEO both with chitin and PEDOT and evaluate the effect of chitin and PEDOT content on solution properties and fibrous morphology of the composites.
3. To find suitable conditions for electrospinnability of PEDOT + PEO + chitin composite and study the effect of PEDOT/PEO/chitin ratio on morphology, conductivity and mechanical properties of PEDOT + PEO + chitin fibrous material.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature review	26.02.2019
2.	General structure of the thesis	15.03.2019
3.	Description and discussion of results	11.05.2019
4.	Complete work	26.05.2019

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

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PREFACE

This project was done following James Mendez’s investigations on bioproperties of chitin and supervised by Dr. Elvira Tarasova by a generous share of knowledge and time.

The main aim of this work was the production of conductive fiber material based on chitin and investigating the effect of chitin on the solution properties as well as morphology and mechanical properties of the membranes.

I would like to thank my supervisor Dr. Elvira Tarasova, for her guidance, help, patience, and all the shared knowledge regarding the topic of my thesis.

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Keywords: Chitin, electrospinning, fiber diameter, conductive membrane, tensile properties.

List of abbreviations and symbols

^{13}C NMR – (^{13}C) nuclear magnetic resonance

DI – Distilled Water

EDOT – 3,4- ethylenedioxythiophene

ES – Electrospinning

FTIR – Fourier Transform Infrared Spectroscopy.

HCl – Hydrochloric Acid

J – Joule

Kv – Kilovolt

ml – Milliliter

µS/Cm – Micro Siemens/Centimeter

MPa – Mega Pascal

NaOCl – Sodium hypochlorite

NaOH – Sodium Hydroxide

NMR – Nuclear Magnetic Resonance

PAN – Polyacrylonitrile

PCL– Polycaprolactone

PEDOT – Poly (3,4- ethylenedioxythiophene)

PEO – Poly Ethylene oxide

PSS – Poly (styrene sulfonate)

pS/cm – Pico Siemens/centimeter

PVA – Polyvinyl alcohol

RPM – Round per minute

SEM – Scanning electron microscope

W/v – Weight to volume

W% – Weight percent

1 INTRODUCTION

Polysaccharides are one of the vital materials in nature due to their unique structures and characteristics which make them different from other ordinary polymers. Among the various kinds of polysaccharides, cellulose and chitin are the most abundant biomass resources. Chitin and its deacetylated derivative, chitosan, have become very interesting since both are biodegradable and biocompatible; moreover, they represent the high potential of antibacterial activities; hence, a big area of medical application has been explored for these two natural biopolymers (Honarkar and Barikani, 2009).

Polymeric fibers with a diameter in the range of nanometer up to some microns have attracted scientists attention due to their particular characteristics. The small diameter of fibers can make them suitable for a variety of applications including as reinforcement in nanocomposites (Huang *et al.*, 2003), nanotubes *(*Hu *et al*., 1999), tissue engineering (Deitzel *et al.*, 2002).

Electrospinning is a suitable method for small-diameter fiber production. This is due to its fast and easy process, low cost, and the possibility of continuous fiber production (Ramakrishna, 2005).

The traditional problem with most conductive polymers is that they are rigid and not mechanically stable. In this project, the goal was to solve the aforementioned problem by coating *PEDOT* on chitin fibers to get the mechanical stability of chitin and maintain the electrical conductivity of *PEDOT* (Esrafilzadeh *et al*., 2016).

Three main objectives have been followed in this project:

First, the new route of chitin extraction from Estonian mushrooms.

Second, electrospinning chitin with the help of electrospinable polymer and evaluation the chitin existence in electrospinnability, viscosity, morphology, and mechanical properties of the polymer and chitin.

Third, the addition of conductive polymer to the last solution and evaluate its effect on the electrospinnability, viscosity, morphology, and mechanical properties of the fiber materials.

2 LITERATURE REVIEW

2.1 Electrospinning

Recently, Nanotechnology has become one of the most interesting topics among scientists. Nanometre size in the various field brings a wide range of new properties to the materials in respect of the higher range of surface to volume ratio. Nanofibers and nanofibrous are the obvious examples of applied nanotechnology in the scientific literature as well as industry. They have become interesting due to the superior properties like a high surface-to-volume ratio and a usually high potential for mechanical testing like elastic modulus and strength (Savest *et al.*, 2018). Electrospinning (*ES*) process is the best and efficient way to produce fibers with diameters in the nanometer to micrometer scale, from different materials (Ryu *et al.*, 2013).

Electrospinning is a term applied to describe the method for fiber formation in small diameters by using electrostatic forces, it is related closely to the more common technology, electrospraying, in which the electrostatic forces are used to form droplet (Rutledge and Fridrikh, 2007). The spinning term comes from textile technology applied spinning wheels to convert natural fibers like cotton to yarns (Rutledge and Fridrikh, 2007). Right now, electrospinning has become the most straightforward, convenient, and fastest for making nanofibers from polymers comparing to the other techniques (Ramakrishna, 2005).

In the lab scale, usually, single-needle electrospinning is used, which is started by the polymer solution. *Fig. 1* represents the schematic of the simple electrospinning. In the electrospinning process, the polymer solution is pumped at a controlled feeding rate through a thin nozzle (*Fig. 1*) and by applying a high-voltage electric field, the fibers are produced on the collector. To fiber production, the surface electrical forces come from induced electrical charges in the polymer solution should overcome the surface tension and produce an electrically charged jet (Reneker, 1999). The high voltage of usually 10 - 50 *KV* is applied to the nozzle. The nozzle in electrospinning acts as an electrode and high voltage applied between the nozzle (electrode) and counter electrode (collector) (Byzova *et al.*, 2014), having dried or solidified the produced jet, the electrically charged fibers will be collected mechanically (Reneker, 1999).

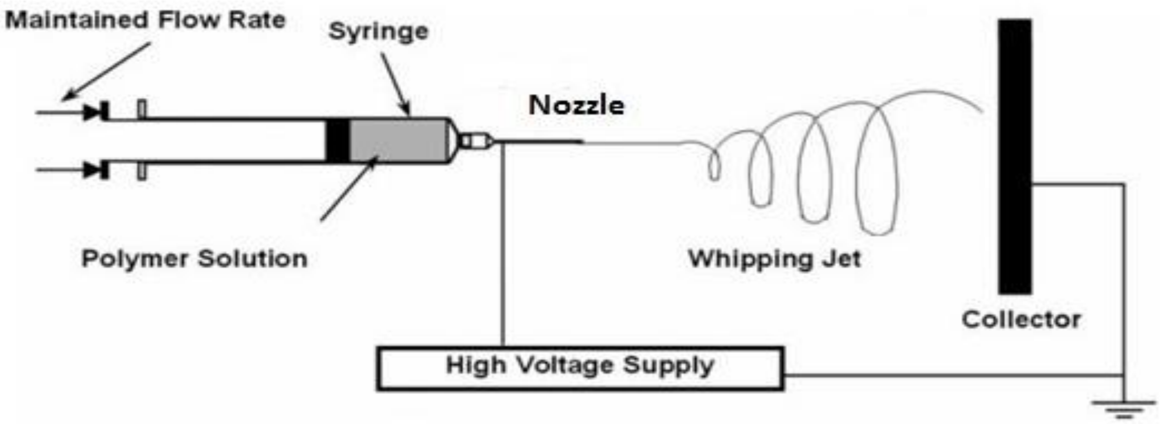

Figure 1. Schematic of the electrospinning process (Moghe and Gupta, 2008).

2.2 Effective factors in the electrospinning process and fiber properties

Fiber diameter and morphology are the most critical area in electrospinning technology. Final fiber diameter is determined by the stretching properties and speed of fiber jet before solidification (Moghe and Gupta, 2008). Various factors affect fiber diameter in electrospinning including solution properties (concentration, viscosity, and conductivity) and process parameters (applied voltage, polymer feed rate, capillary size, type of collector and the distance between the tip of the needle and the collector) (Li and Xia, 2004; Zander, 2013).

2.2.1 Solution properties

The concentration of polymer solution is a crucial factor determined how the process is going on. At very low concentration the possibility of electrospraying is increased while in slightly higher polymer concentration we will have a mixture of beads and fibers and in very high polymer concentration, spinning is not possible due to the fast drying the solution on the needle tip (Bhardwaj and Kundu, 2010).

Viscosity is another compelling factor for fiber diameter, which should be in an optimal value, with low viscosity, the fiber cannot be produced continuously, and very viscose solution jets cannot eject easily from the polymer solution (Bhardwaj and Kundu, 2010).

Since the basis of pulling the solution to the collector in electrospinning is induced an electrical charge, the conductivity of the solution is an essential factor in more uniformed nanofiber production (Zhenyu LI, 2016).

2.2.2 Process parameters

The way the electrospinning is set up is fundamental in obtaining smooth and uniformed fibers.

- High voltage, is vital to produce stable Taylor cone (Reneker, D. H *et al.*, 2007). In very high voltage, the amount of charge in the electrical field increases and causes a faster speed of the jet, also, more volume of the solution comes out of the needle; hence the Taylor cone is less stable. As a result, the elongation and evaporation of solvent happen faster, and finally the resulted fiber diameter decreases (Ramakrishna, 2005); however, in the weaker electrical field, the acceleration of jet is reduced, and there is more time for solvent evaporation as well as jet stretching. As a result, the fiber would be thinner (Ramakrishna, 2005).
- Polymer feed rate is another critical factor which is essential in the jet velocity as well as solvent evaporation in the fiber production process. For more acceptable fiber properties, it is suggested to decrease the feed rate as much as possible (Bhardwaj and Kundu, 2010).
- The inner diameter of the needle should be considered to eliminate needle blocking during electrospinning. The smaller the needle diameter, the more voltage is needed, and finally, thinner fibers will be produced (Andrady, 2008).
- The collector plays a determinant role in electrospinning; the non-conductive collectors cause lower density fibers due to the repulsion of accumulated charges on the collector (Ramakrishna, 2005). The high porous surface of the collector provides the situation for faster solvent evaporation so fibers can be dried quickly and residue on the collector. Usually, in electrospinning, which the evaporation speed is low, the rotating collector is used to producing aligned fibers (Ramakrishna, 2005).
- The distance between the needle and collector is a factor that affects flying time and electric field influence in electrospinning. On the other hand, by decreasing this distance, the strength of the electric field increases which results in the increasing of the speed of jet to the collector; hence, there is not enough time for solvent evaporation, and the fibers should be re-dried before usage. While increasing the distance between the tip of the needle and collector, causes longer flying time, so the fibers have more time for stretching, and this is followed by thicker produced fibers since in higher distance the strength of the electrical field is less and fiber stretching decreases (Ramakrishna, 2005).

2.3 Chitin and chitosan

Chitin, poly (b-(1-4)-N-acetyl-D-glucosamine) is the second most abundant polymer in the environment and is the main polysaccharide in Arthropods (such as crabs and insects) and cell walls of fungus and yeast. *Fig. 2* represents the structure of chitin and its derivative. Chitin produced in some lower plants and animal kingdom serves as reinforcement and strength (Rinaudo, 2006). Moreover, Chitin has been known as one part of the spinelessness (Brunner *et al.*, 2009).

Chitin is a white, hard and inelastic polysaccharide which although there is nitrogen in its structure (*Fig. 2*) is hydrophobic and highly insoluble in common solvents and has a low chemical activity (Majeti N.V., 2000).

Chitosan poly-D-glucosamine is the deacetylated derivative of Chitin. Compared to chitin; chitosan has better solubility due to the NH_2 group in its structure (Honarkar and Barikani, 2009). Chitosan can be solved in dilute acids such as acetic acid, formic acid, etc. (Majeti N.V., 2000).

Both of these two polymers are non-toxic, antibacterial, biodegradable and biocompatible biopolymers; hence, they have been interesting materials for researchers for the biomedical applications (Noh *et al.*, 2006), in addition, considering the high amount of nitrogen in chitin and chitosan compare to cellulose, they are more interesting commercially since they act as an excellent chelating agent (Muzzarelli, 2002).

Nanofibers containing chitin or chitosan yield potential applications in areas such as filtrations, recovery of metal ions, drug release, dental, tissue engineering, wound healing, protective clothing, cosmetics, biosensors, medical implants and energy storage (Anderson *et al.*, 1998; Gironi *et al.*, 2011).

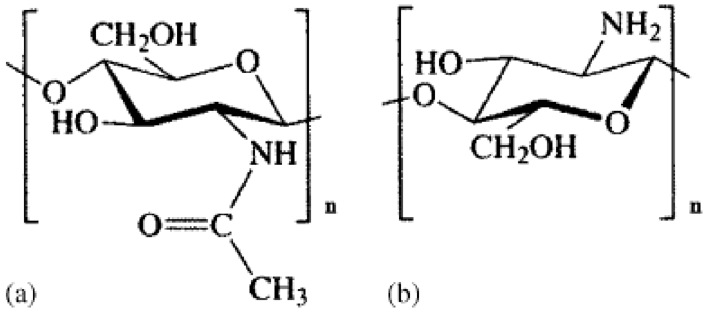

Figure 2. Chemical structure (a) chitin poly(N-acetyl-b-Dglucosamine) and (b) chitosan (poly(D-glucosamine) repeat units (Rinaudo, 2006).

2.3.1 Extraction of chitin

Chitin can be found in marine spineless, insects, and yeast and Crustacean shells (Mendez *et al.*, 2015). However, these resources are limited regarding the seasonal supply. However, one benefit of the extraction of chitin from fungi mycelia, is that it can be cultivated throughout the year, and its process is fast (Álvarez *et al.*, 2014).

Chitin is bound to a variety of proteins, minerals, and organic pigments dependent on the specific species but independent of the source of chitin, the extraction method is the same. Alkaline treatments are the most common method for chitin isolation (Álvarez *et al.*, 2014). In these methods, a base is mostly used to remove unwanted protein from the chitin source material, and acid usage is for demineralization step (Mendez *et al.*, 2015).

Álvarez and her colleagues used Alkaline treatment with sodium hydroxide solution (*NaOH*) at a ratio of 1: 30 (w/v). In their experience, molar concentrations, temperature, and reaction time were varied for each solution; the final product was decolorized by potassium permanganate and oxalic acid. Chitin was obtained in the amount of 78-413 mg in different assays (Álvarez *et al.*, 2014).

Mendez et al. extracted chitin from Red Swamp Crawfish shells (Procambarus clarkii) thorough the Alkaline process. They used various concentrations of Sodium hydroxide and hydrochloric acid in different reaction time (various protocols), as a bleaching agent, 4% solution of sodium hypochlorite was used (Mendez *et al.*, 2015).

Raw crab shells (Portunus pelagicus) are another chitin resource used by Wijesena and his colleagues for nanofiber and nanoparticle preparation based on chitin. Alkaline treatment is the method is used to extract chitin in their experience (Wijesena *et al.*, 2015).

Recent research have shown that the Alkaline treatment, using base and acid, which was mostly used for crab and shrimp, can be used for extract quality chitin from various resources including honeybees (Draczynski, 2008), mushrooms (Ifuku *et al.*, 2011) and crawfish (Mendez *et al.*, 2015) as well. Extracted chitin is normally kept in a wet suspension. By drying, due to the formation of hydrogen bonding among chitin molecules, obtaining chitin nanofiber would be more difficult; hence, the sample should be kept wet for nanofiber production (Abe, Iwamoto and Yano, 2007).

Mushrooms are one of the proper resources for chitin due to their abundance and no limitation in their production (climate, season, etc.). It is known that the properties of chitin extracted from various resources are different noticeably; however, the general and comprehensive comparison is still under studies (Mendez *et al.*, 2015). In the present work, Estonian mushrooms have been used as the source for chitin extraction. The method of extraction is explained in *section 4.2*.

2.3.2 Degree of acetylation

In spite of the chemical difference between chitin and chitosan, they are usually considered as a family of polysaccharide varying only in acetyl content (M.L. Duarte, 2002). Also, it is said that the N-deacetylation never is completed in the chitin/chitosan solution (Majeti N.V., 2000); hence, a parameter named degree of acetylation (*DA*) should be defined. *DA* shows how the deacetylation process went on, which has a strong effect on the solubility of the chitin/chitosan solution (M.L. Duarte, 2002). In other words, in the higher number of N-acetyl-glucosamine units in the biopolymer, chitin term is used (higher *DA*). While, when there are more N-glucosamine units, the term chitosan is used (less *DA*) (Khor and Lim, 2003).

DA can be determined by different methods, including *FTIR* spectra, ^{13}C *CP/MAS NMR* spectra, while studies show the *FTIR* spectra is the best way of *DA* determination (M.L. Duarte, 2002). Domard et al. defined the *DA* as the ratio of the intensity of the carbonyl peak to the hydroxyl peak in chitin *FTIR* spectra (Domard et al., 1983) which will be used in this study.

$$\mathrm{DA\%} = \frac{\mathrm{A\,(1650)}}{\mathrm{A(3450)}} \times \frac{100}{1.33} \tag{1.1}$$

2.4 Chitin/chitosan nanofiber

A chitin nanofiber usually has diameter in 2-5 *nm* consists of 18-25 chitin molecules (Vincent and Wegst, 2004). In general, two routes are used in chitin nanofiber engineering, “top-down” and “bottom-up.”

In “top-down” approach the natural material as one complex break down to the individual building blocks; however “bottom-top” approach is based on self-assembly of the single molecules to the desired products (Zhang and Rolandi, 2017). Because of the less solubility of chitin in the molecular level, the first approach (top-down) is mostly used to produced chitin nanofibers. Wijesene and colleagues produced chitin nanofibers by applying top-down methods and chemical treatment, and after ultrasonication of the nanofibers, the produced fibers have a diameter less than 20 *nm* which was mixed with chitosan nanofibers (Wijesena *et al.*, 2015).

In the second approach, “bottom-up” the chitin should be dissolved in a solvent, and due to the chitin characteristics, there are limited numbers of enough suitable solvents. Electrospinning method usually used for spinning the solution of depolymerized chitin. A few solvents like hexafluoroacetone, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) have been usually used for that. The diameter of the prepared nanofibers by this method is less than 100 nm. α-chitin from shells of special shrimps with *PVA* was used to produce nanocomposite fiber mats (Jayakumar *et al*., 2010). On the other hand, chitosan is soluble in most of the acids. Ohkave and co-workers studied the effect of various solvents and chitosan concentration on the morphology of the electrospun fiber mat of chitosan solutions. It is reported that under the experimental conditions, chitosan fibers with a mean diameter of 330 *nm* were produced (Ohkawa *et al.*, 2004). In different articles, the combination of chitosan and other polymers like *PVA, PEO, PLA*, etc. have been studied since the mechanical, antibacterial, biocompatibility and other properties of the chitosan nanofibers were significantly enhanced by the addition of these polymers (Jayakumar *et al*., 2010).

Although chitin nanofibers produced by electrospinning method have broad fiber diameter distribution, the average diameter for most of them is reported less than 100 nm (Min *et al.*, 2004). These fibers have a lot of applications, particularly in medical sections because of their biodegradability and high surface to length properties. (Honarkar and Barikani, 2009). Min and colleagues applied electrospun chitin nanofibers for the wound dressing application (Min *et al.*, 2004).

2.5 Application of chitin and chitosan

It is known that Chitin is biodegradable regarding the existence of chitinase enzyme, non-toxic, and inert. Moreover, it is one of the part in microfibrillar arrangements in living organisms in a protein matrix with a diameter 2-5 *nm* (depends on the origin of the chitin) and regarding these microfibrils, chitin and its deacetylated derivative, chitosan, have become a suitable candidate for fiber spinning. Various methods have been used for spinning chitin/ chitosan sample (Majeti N.V., 2000); however, recently, electrospinning has become more common to nanofiber preparation with unique characteristics from various materials include chitin (Min et al., 2004).

Another factor has made chitin, and chitosan more attractive for scientists is their capability to be processed into different forms such as micro/nanoparticles, membranes, gels, sponges, scaffolds, as well as nanofibers which can be used in various applications (Anitha et al., 2014).

The problem of working with chitin extracted from various national resources, is its poor solubility, hence, usually the combination of chitin and chitosan with better solubility is used which provides scientists with a vast range of applications (Majeti N.V., 2000). Following paragraphs, summarized some of the most common applications of chitin and chitosan.

- Fibers from chitin and chitosan can be used as absorbable sutures (able to withstand bile, urine, etc. despite the other stitches) (Nakajima, 1984).

- Chitosan is a suitable material in photography due to its resistance to abrasion and optical properties and compares to silver complexes, which are easily penetrated, is preferable (Muzzarelli, 1997).
- Tissue engineering is an approach in medical care, which is replacing the damaged tissue or organ (bone, skin, etc.), by an artificial one. Regarding this medical care, various biomaterials and synthetic polymers have been tested, and chitin and chitosan represent a promising potential in the biomedical field (Rinaudo, 2006). In terms of bone tissue engineering, although chitin and chitosan are biodegradable and biocompatible (Majeti N.V., 2000), they are not strong and stable enough for bone replacement and is believed that they should be used as a blend with other stronger polymers to have improvement in their mechanical properties (Li *et al.*, 2005).
- Chitin and chitosan can be used in food to improve the quality and properties of that food, Austin and his colleagues, showed that adding a small amount of chitinous materials to the cows' diet can improve the quality of their milk in terms of digestion (P. R. Austin, 1981). Adding some percentage of chitin to the chickens' diet, improved their food compared to those who are fed just by whey (Zikakis, 2012).
- Chitin and chitosan have been very active in the biomedical application, including drug delivery. The vast amount of research has been done on the chitin-based polymers to be used as drug delivery agent; Park et al. prepared an inorganic-organic membrane sensitive to PH which is reported, has excellent potential for drug delivery application (Park *et al.*, 2001). Li et al. used another method to make membrane using chitosan interacted with glucose dialdehyde, the rate of drug-delivering is related to the length of alkyl change, the longer chain, the more hydrophobic membrane which affects the speed of the delivery (Li et al., 2002).

2.6 Conductive polymer

Discovering conductive polymers is one the very important advances in the polymeric science since these polymers are capable of substituting the traditional metallic conductors and semiconductors and when it goes to the electrical, mechanical and optical properties of the polymers, conductive polymers would be promising materials for more studies and applications (Kumar and Sharma, 1998). Some of the examples of conductive polymers examples are polyacetylene, polyaniline, polypyrrole, and polythiophene (*Table 1*). The origin of the conductivity of such polymers are related to their chemical structure, the electrons in P_z orbital have high mobility compared to the valence electron in sigma bond of the SP^2 hybridization in the conductive polymers which provide them the situation to conduct electricity. The conductivity numbers of the most common conductive polymers have been shown in *table 1* (Kumar and Sharma, 1998).

Table 1. Conductivity of various materials.

Conductive polymer	**Conductivity (S/Cm)**
Polyacetylene	~10^4
Polyaniline	~10^2
PEDOT	~10^3
Carbon black	~10^{-1}–10^2
Silver	~10^7
Gold	~10^7

Poly(3,4-ethylenedioxythiophene) (*PEDOT*) is one of the most promising conductive polymers due to its high electrical properties *(Table 1)*, excellent stability, and biodegradability (Kirchmeyer and Reuter, 2005). This conductive polymer can be produced by electrochemical (Mohamed Ali *et al.*, 2008) or chemical (Luo *et al.*, 2008) polymerization of 3,4-ethylenedioxythiophene (*EDOT*) monomer. *Fig. 3* represents the chemical structure of PEDOT (Groenendaal *et al.*, 2000).

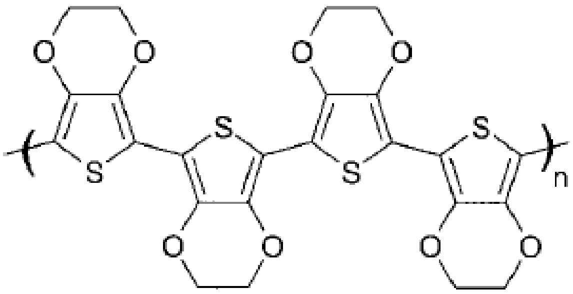

Figure 3. Chemical structure of PEDOT (Groenendaal *et al.,* 2000).

Extensive applications of *PEDOT* in the different areas have been known, including photovoltaic devices, organic thin-film transistor, and antistatic coating (Denneulin *et al.*, 2008; Petraki *et al.*, 2010). Recently *PEDOT* has found its place in bioengineering and medical fields such as delivery systems (Chikar *et al.*, 2012), conductive coating (Green, 2013), tissue engineering (Abidian, M. R., 2012) and biosensors (Nikolou and Malliaras, 2008) which have been noticeable for scientists.

In the process of *PEDOT* polymerization, some dopants can be added to provide the final polymer with some specific properties. Poly (styrene sulfonate) (*PSS*) is one of those which is reported as *PEDOT: PSS* polymer is in collaboration with biomedical molecules like peptide and growth factors (Green, Lovell, and Poole-Warren, 2010). Sui and coworkers produced *PEDOT: PSS*: chitosan coating using electrochemical reactions to use them on a platinum electrode, and the results showed this electrode could be applied for electrochemical biosensing (Sui *et al.*, 2017). It is reported that *PEDOT: PSS* is a preferred conductive polymer for scientists because of high conductivity, low cost, dispersibility in water, and excellent processability. (Yoo et al. 2015).

One of the practical methods to produce *PEDOT* is a polymerization method named BAYTRON P (*Fig. 4*) synthesis. In this method, *EDOT* (monomer) in an aqueous *PSS* solution in the existence of an oxidizer ($Fe_2(SO_4)_3$) is polymerized to a dark blue solution of *PEDOT: PSS* at room temperature (Groenendaal *et al.*, 2000). The various oxidant can be used in the process of *EDOT* polymerization, like iron trichloride ($FeCl_3$) and ammonium persulfate ($(NH_4)_2S_2O_8$) or *APS* (Luo *et al.*, 2008). In this project, for better understanding and move convenient reading process, I will use *PEDOT* instead of *PEDOT: PSS*.

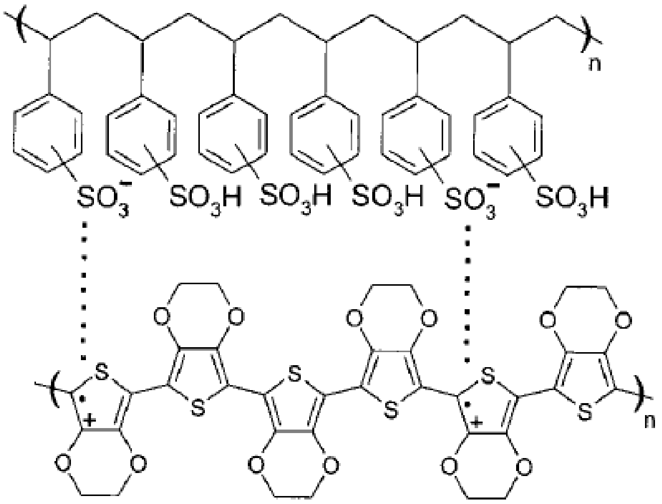

Figure 4. PEDOT blend produced by BAYTRON P method (Groenendaal *et al.*, 2000).

2.7 Electrospun polymer

Most of the conductive polymers are insoluble in the typical solvent, which results in too low solution viscosity. Hence, they cannot be stretched enough in the electrical field of the electrospinning process, and the nanofiber production will be difficult (Xu et al., 2010). A wide range of polymers is suitable to be applied in electrospinning. Synthetic polymer, natural polymers or a blend of both can be used to produce electrospun nanofibers. More than fifty different polymers have been electrospun, and the fiber diameter in the range of three *nm* to nearly one *µm* have been created (Huang *et al.*, 2003). Some of the polymers used in electrospinning are *PAN, PCL, PVA, PEO*, etc. (Levitt *et al.*, 2018).

PVA is a poly hydroxyl polymer and has been studied intensively due to its suitable characteristics, for numerous fields include high hydrophilicity, processability, biocompatibility, and good chemical resistance (Shao *et al.*, 2003). These properties make this polymer, suitable choice in many different applications (Yang, Qin, and Wang, 2008). *PVA* electrospun membranes dissolve in water; hence, crosslinking and stabilizing is very important for its application. Hydroxyl groups in the structure of PVA make it capable of being cross-linked with different compounds (Yang, Qin, and Wang, 2008). Liu and his colleagues electrospun *PEDOT: PSS* conductive polymer with *PVA* (Liu *et al.*, 2011). In another experiment, *PVA* was used to make the polymeric mixture of *PEDOT* and Plasma-modified chitosan, electrospinnable (Kiristi, Uygun, and Ulusoy, 2013). In another experiment, *EDOT* as a monomer of *PEDOT* was mixed with *PVA,* and the polymer blend was electrospun in the existence of chlorine as the oxidizer agent (Xu *et al.*, 2010).

PEO is another biocompatible polymer which has been used for various medical applications (Yoshii *et al.*, 1999). *PEO* can be electrospun Solo (Yang Y *et al*., 2005), as well as blended with other polymers (Jin *et al.*, 2002). Fretnot and his colleagues used *PEO* as a carrier polymer to spin various cellulose derivatives (Yang *et al.*, 2010). An example of blending *PEO* and chitosan was done in Dobrovolskaya' work, which a composite of chitosan and *PEO* is prepared by using the wet spinning method (Dobrovolskaya *et al.*, 2016).

PEDOT: PSS is one of the other cross-linking agents for *PEO* solution. Huang's work represents the successful cross-linking between polymers (Huang *et al.*, 2013). In this work, *PEO* was added to *PEDOT: PSS* as a colloidal dispersion in water to improve its conductivity (Wang *et al.*, 2005). To nanofiber production, special system, developed by their laboratory, was used (Huang *et al.*, 2013). The cross-linked network between *PEO* and *PSS* obtained in the strong acidic environment and high temperature, which results in improving the water resistance of the membrane. In another work, *PEDOT* blended with *PEO* and *PVA* was electrospun, and fibers with 200-300 *nm* obtained. The tests represented increasing the amount of *PEDOT* resulted in the production of fiber mat with a diameter of less than 200 *nm* (Khanum *et al.,* 2014).

According to my knowledge and regarding the literature review the combination of PEDOT: PSS and PEO in the presence of chitin/chitosan to produce electrospun membrane, has not been done and this work investigates that new combination of polymers in various aspects.

3 AIM OF THE STUDY

The main scope is to develop mechanically stable and electrically conductive fiber material based on chitin by electrospinning.
Estonian mushrooms have been used as the source of chitin; the Alkaline treatment was used as the extraction process.
PEO was chosen as the carrier and electrospinable polymer for helping chitin solution to be electrospun. The effect of chitin on the electrospinnability, viscosity, conductivity, morphology, and mechanical properties of the produced composite has been studied.

PEDOT has been used as a conductive additive to produce the electrically conductive fiber material of *PEDOT + PEO* + chitin, and the effect of its content on electrospinnability, viscosity, conductivity, morphology and mechanical properties of the final membrane was evaluated.

Objectives

- To extract of chitin from Estonian mushrooms.
- To find optimal conditions for electrospinning of *PEO* both with chitin and *PEDOT* and evaluate the effect of chitin and *PEDOT* content on solution properties and fibrous morphology of the composites.
- To find suitable conditions for electrospinnability of *PEDOT* + *PEO* + chitin composite and study the effect of PEDOT/PEO/chitin ratio on morphology, conductivity and mechanical properties of *PEDOT + PEO* + chitin fibrous material.

4 EXPERIMENTAL PART

4.1 Materials

- The Estonian mushroom, Tinder Bracket (Fomes Fomentarius).
- Acetic acid (*AcAc*), Molarity (C_M): 60.05 g/mol. *Merck.*
- Dimethylformamide (*DMF*), purity >99.8%. *Sigma-Aldrich.*
- Ammonium persulfate (*APS*), *Fisher Chemical*.
- Poly (ethylene oxide) (*PEO*), average molecular weight: 200,000, *Sigma-Aldrich.*
- 3, 4 Ethylenedioxythiophene (*EDOT*), 99% solution, *Across Organic.*
- Poly (sodium-p-styrene sulfonate) (*PSS*), average molecular weight: 70,000 and 500,000. *Sigma-Aldrich*.
- Poly (vinyl alcohol) (*PVA*), average molecular weight: 166,000. *Aldrich Chemistry*.
- Sodium hydroxide *(NaOH)*, *Stanchem.*

4.2 Chitin extraction from mushrooms

Regarding the aim of the project in using chitin for electrospinning, the solubility of the chitin/chitosan solution is significant. Mendez and his colleagues figured out that regardless of the source of material, the *NaOH* steps in the Alkaline extraction method, is the determining stage in producing deacetylated chitin, the lower *DA* will be obtained by the higher concentration of sodium hydroxide (Mendez *et al.*, 2015); hence, for the extraction process, a solution of 10 M *NaOH* is selected.

1. The mushroom (Tinder Bracket) was collected from the forest around Tallinn. It was washed with water to remove extra and unwanted materials and dried for 24 hours at 70°C. Finally, the particles are ground for size reduction and sealed in a container for use in the experience.
2. 10 M, *NaOH* solution in distilled water (*DI*) was prepared and mixed with 10 g sample at reflux for around 5 hours.

3. The centrifuging method was used for separating the base from the sample (approximately 10 times) until solutions become natural.
4. Wet samples were mixed with 100 ml, *HCl* 2M for removing any inorganic and unwanted materials at room temperature.
5. Again samples were centrifuged with *DI* till natural PH.
6. In the end, 2% (mass ratio) *NaOCl* was added to the sample as the bleaching agent for only 5 minutes.
7. Final samples should be kept in a solution of *DI* for the next experiment.

4.2.1 Degree of Acetylation determination

A thin film of the sample was tested by infrared spectroscopy, *FTIR,* to obtain the sample *DA* according to the *formula 1.1*. Considering the intensity of the carbonyl group (represents chitin), 1634 and that of the hydroxyl group (related to chitosan), 3404, the *DA* of our sample is determined as 42.53 % (Czechowska-Biskup, 2012).

4.3 Synthesis of PEDOT

Regarding the literature review (Sui *et al.*, 2017) and the properties of the conductive polymer is needed in my experiment, the following procedure for *EDOT* polymerization was chosen: 4% (*w/v*) *PSS* (Sodium salt) of 70,000 MW was dissolved in 2 M *AcAc*. The same percentage of *APS* was added to the stirred solution. Having added 2% (*w/v*) *EDOT* monomer, the solution was left for 24 hours to be mixed at room temperature. The Final product was dark blue, aqueous *PEDOT* dispersion (Wagner, Harman and Ivaska, 2013). *FTIR* was used to clarify the creation of *PEDOT* during the synthesis (*Fig. 5*).

To disperse *PEDOT* evenly through liquid media, such polymer as *PSS* was used as usual. Content of PSS in polymerisation was the same as *EDOT.* In the text, the abbreviation of *PEDOT* will be used instead of *PEDOT + PSS,* but it should be noticed that *PSS* is present in all solutions with *PEDOT.*

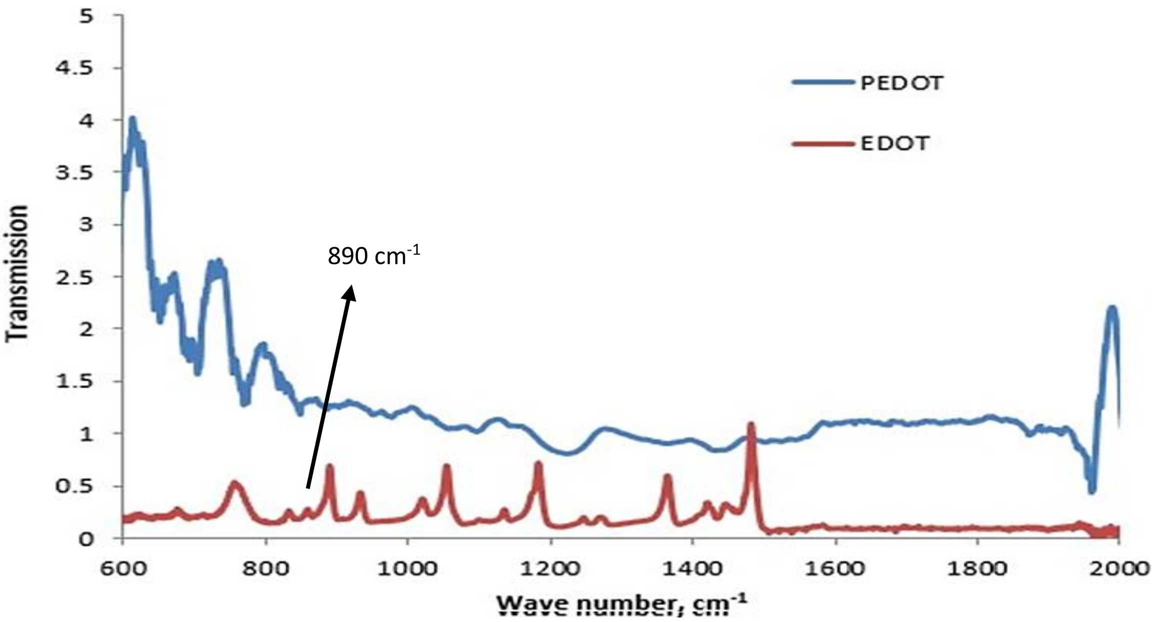

Figure 5. FTIR spectrum of EDOT and PEDOT (testing by the author).

The strong bond can be seen in 890 cm^{-1} in the *EDOT* spectrum is related to the C-H bonding mode; this peak should disappear in the spectra of PEDOT (Selvaganesh, S. V, 2007). Absence of the peak in 890 cm^{-1} in the *PEDOT* spectra (*Fig. 5*) reveals that the synthesis of *PEDOT* was done successfully in the present work. Another indirect confirmation of polymerization is changing the color of the mixture from Yellow to dark blue, which was happened after 24 hours synthesizing.

4.4 Solution preparation

Three different carrier polymers have been tested initially. The solutions of various concentration of *PSS* in different solvents were prepared and *electrospun* (*Table 2*). *PVA* and *PEO* in the concentration of 10 w% in 2 M *AcAc* were mixed with different amounts of chitin and electrospun (*Table 3*)

The solutions of *PEDOT*/*PEO* in the ratio of 2/10, 5/10 and 10/10 were mixed mechanically in 2 M *AcAc* for around 24 hours at room temperature to achieve a homogeneous solution for electrospinning (*Table 4*). The next step was the addition of chitin in the amount of 0.1 w%, 0.3 w%, 0.5 w%, 1 w% and 2 w% to the weight of the solution.

4.5 Electrospinning

Electrospinning was used for nanofiber production. A standard set up of electrospinning apparatus was used, including a high voltage power supply (Glassman High Voltage with 0–40 *kV* power range), a pump (New Era Pump Systems), a syringe with needle diameter of 0,6 mm and a drum collector covered with particular textile, where the nanofibers were collected as a fiber web. The present research was done at, room temperature with atmospheric conditions. The prepared solution was loaded into the syringe, and this liquid was extruded from the needle tip at a constant rate by using a syringe pump. The parameters for electrospinning were: the pumping rate of 0.3 *ml*. h^{-1}, the distance of 11 *cm* and applied voltage of 13 *kV*. *Fig. 6* represents the electrospinning set up in the Laboratory of polymers and textile technology.

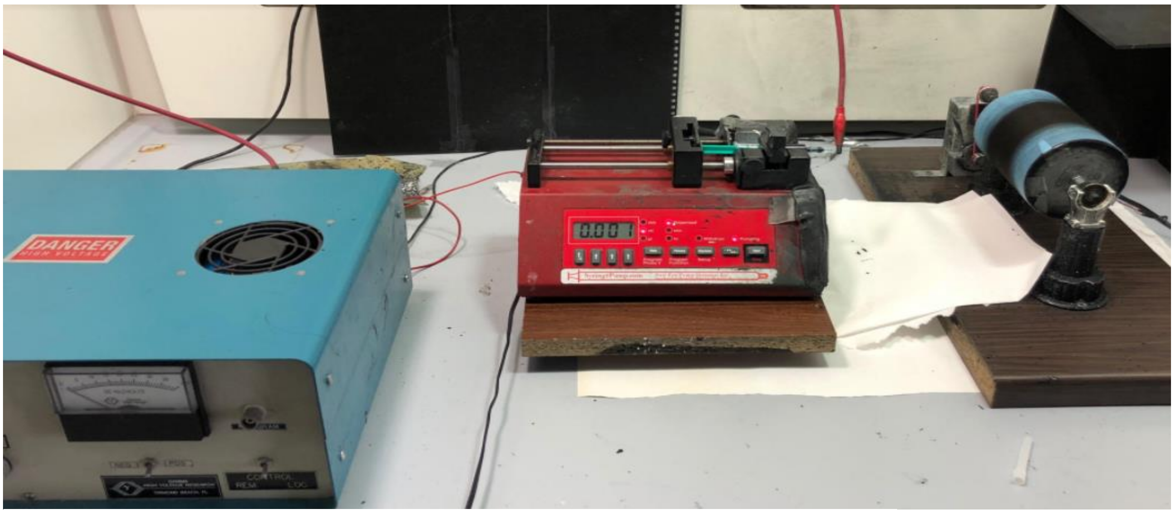

Figure 6. Electrospinning set up (taken by the author).

4.6 Characterization

Before electrospinning, some properties of the solutions were measured, including Viscosity and conductivity.

4.6.1 FTIR study

The transmittance *FTIR* spectra of Chitin/chitosan mixture and pure *PEDOT* polymerized in our research have been tested by Interspac 200-X *FTIR* spectrometer, with 16 scans averaged at the resolution of 1 cm^{-1}.

4.6.2 Solution viscosity

The viscosity of the solutions was measured by a BROOKFIELD, DV-II+ Viscometer at the standard temperature 23˚C.

4.6.3 Solution electric conductivity

The conductivity of prepared solutions was measured by Seven Compact conductivity measuring device (Mettler Toledo Inc.) at room temperature. The final value was submitted after five measurements.

4.6.4 Fiber mat electric conductivity

The conductivity of fiber mats was measured by using the high resistance and low conductance meter HR 2 (Alpha Lab Inc; USA). The thickness of the mat was measured using a device purchased from Sony Magnescale Inc.

For calculation, 1 cm^2 of the mat is separated, and regarding the thickness and measured conductance (S) and using the following formula, the conductivity of the membrane was recorded in nS/cm.

$$\sigma = S \times \frac{L}{W.\ T} \qquad (1.2)$$

Where σ − conductivity,

S − Conductance (*nS*) read from the apparatus,

T − Thickness of the mat (cm),

L − Length of the specimen (cm),

W − Width of the specimen (cm).

4.6.5 Morphology study

The morphology of the electrospun fibers has been analyzed with a scanning electron microscope (*SEM*) Gemini Zeiss Ultra 55 (Carl Zeiss, Germany). The statistical analysis was carried out for 150-200 fiber diameters measured at different surface locations in 5-7 images.

4.6.6 Mechanical testing

Mechanical properties of the membranes have been measured at room temperature by an Instron 5866 (Instron Corporation, UK) tensile tester. The sample was cut into the rectangular shape, and the average thickness of each sample was measured from three different part of it, the load cell of maximum capacity 2.5 N was used for tensile testing of the specimen. The speed of the load was 10 mm/min, the collected data was analysed, and the tensile stress and strain at maximum load were measured.

5 RESULTS AND DISCUSSION

5.1 Finding the suitable carrier polymer

5.1.1 Poly (styrene sulfonate)

To disperse *PEDOT* evenly in liquid media such polymer as *PSS* was used. Therefore, it was logic and wise to use this polymer as a carrier for electrospinning, hence, *PSS* with different molecular weights (70,000 and 500,000) was tested at various concentration and solvents; unfortunately, in all tested conditions *PSS* was not electrospinnable, hence could not be a good choice to be used as the carrier polymer. *Table 2* illustrates the tested solutions for *PSS*.

Table 2. Testing the PSS solution.

Solvent	Cons in solvent	Solution conductivity	Spinnability
AcAc	10	14	Not spinnable
Water	7	12.53	Not spinnable
Water	5	17.41	Not spinnable
AcAc	5	11.18	Not spinnable
Water/DMF	10	12.21	Not spinnable

5.1.2 Polyvinyl alcohol

PVA was the next electrospinable polymer which has the potential for being spun with *PEDOT* (Xu et al., 2010) and chitin (Zhou, Yang, and Nie, 2007) separately; therefore *PVA* has been tested as a carrier polymer for electrospinning of chitin. Various concentration of chitin in the solution of 10% *PVA* was tested. Spinning process and *SEM* images of all of them represent this polymer is not a suitable option for this study. *Fig. 7* reveals the *SEM* image of the electrospun fibers of 10% *PVA* with 0.1% chitin in the 2 M *AcAc*. Besides, PVA creates fibers with chitin; the membrane is not uniform, wet, and fibers are in-homogenous by size and shape.

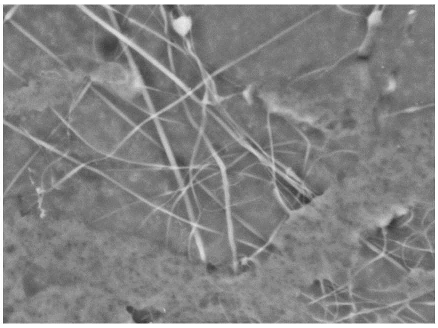

Figure 7. SEM images of PVA 10% with 0.1% chitin in 2 M AcAc.

5.1.3 Poly Ethylene oxide

Therefore another polymer, *PEO,* has been chosen because of its biocompatibility, degradability, and water solubility. The *SEM* images of electrospun 10% pure *PEO* in 2 M *AcAc* and its combination with 0.3 w% chitin is available in *fig. 8*. As can be seen from the figures, *PEO* with chitin can be electrospun, resulting in good fiber morphology. So, *PEO* is considered a perfect carrier polymer in this study due to its water-solubility, well compatibility with chitin and the potential for medical application (Chen *et al.*, 2016). Fiber distribution for fiber above mats is unimodal, which is a result of good mixing of the components and production of one type of fibers.
(*Fig. 8*).

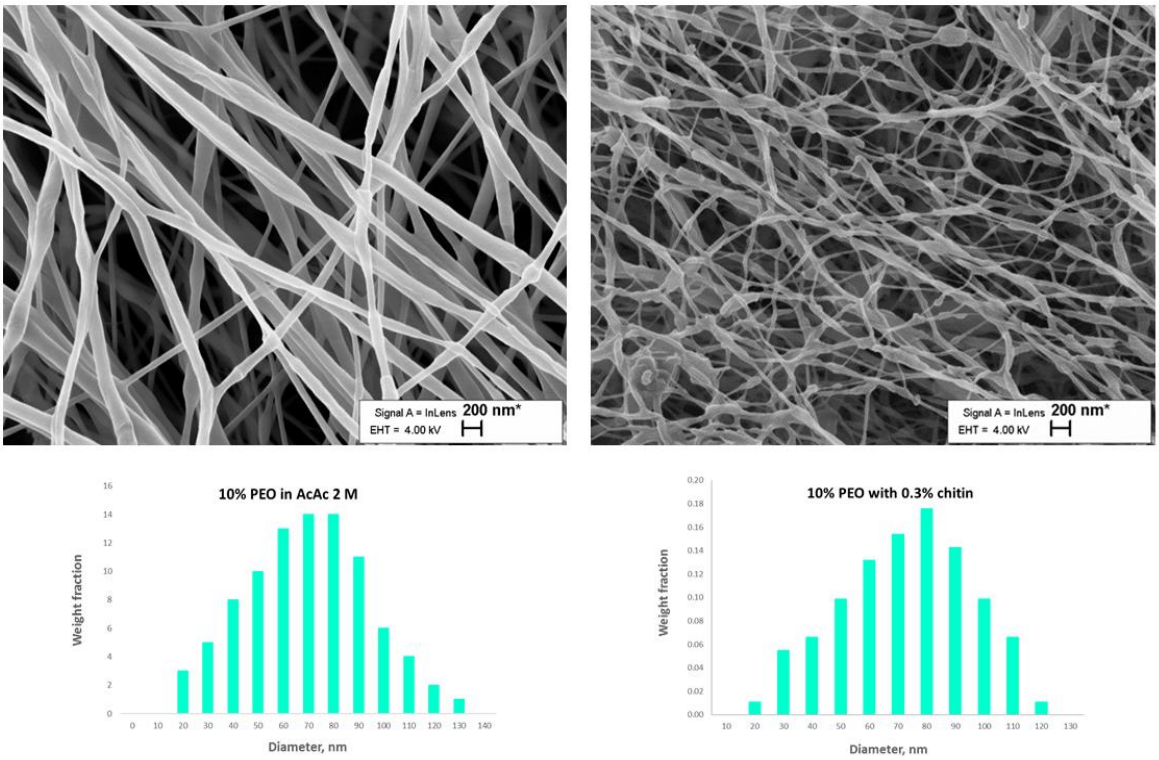

Figure 8. 50000x magnified SEM images of The solution of 10% of pure PEO and in the combination of 0.3% of chitin in 2 M AcAc with the related fiber diameter distribution.

5.2 Effect of chitin

Different amounts of chitin (from 0.1% up to 2%) were added to a *PEO* solution, and the solution properties, as well as morphology, were studied. *SEM* images of the electrospun membranes are available in *fig. 9*. As can be seen from *fig. 9* the *PEO* + chitin demonstrates good fiber morphology with fibers in the nanometer range. They are thin, homogenous, and their size distribution is unimodal. The example of fiber diameter distribution can be seen in *fig.10*. The similar size distribution has been observed for all other *PEO* + Chitin samples. It is clear, the *sample 7* (*Table 3*) containing 2% chitin, did not show acceptable electrospinnability, and no fibrous material was prepared for this sample.

Table 3. Summary of parameter changes by chitin addition to the solution of PEO.

Sample	**Carrier Polymer**	**Cons of PEO in AcAc**	**Chitin cons. In solution, %**	**Viscosity in cP; (40 RPM)**	**Solution Conductivity mS/cm**	**Fiber Diameter (nm)**
1	PEO	10	-	2342	0.76	70
2	PEO	10	0.1	2380	0.92	69
3	PEO	10	0.3	2500	1.21	66
4	PEO	10	0.5	2743	1.34	64
5	PEO	10	1	3100	1.50	60
6	PEO	10	1.5	3400	1.52	53
7	PEO	10	2	3600	1.51	Not spinnable

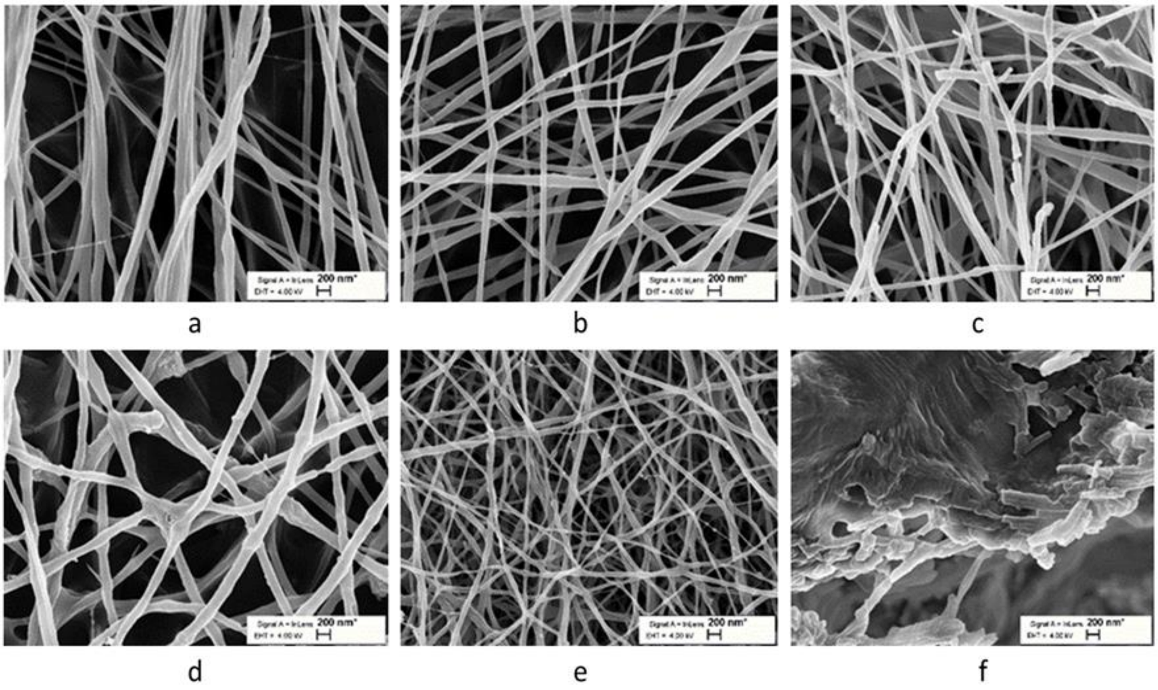

Figure 9. 50000x magnified SEM images of 10% PEO with (a) 0.1%, (b) 0.3%, (c) 0.5%, (d) 1%, (e) 1.5% and (f) 2% chitin in 2 M AcAc.

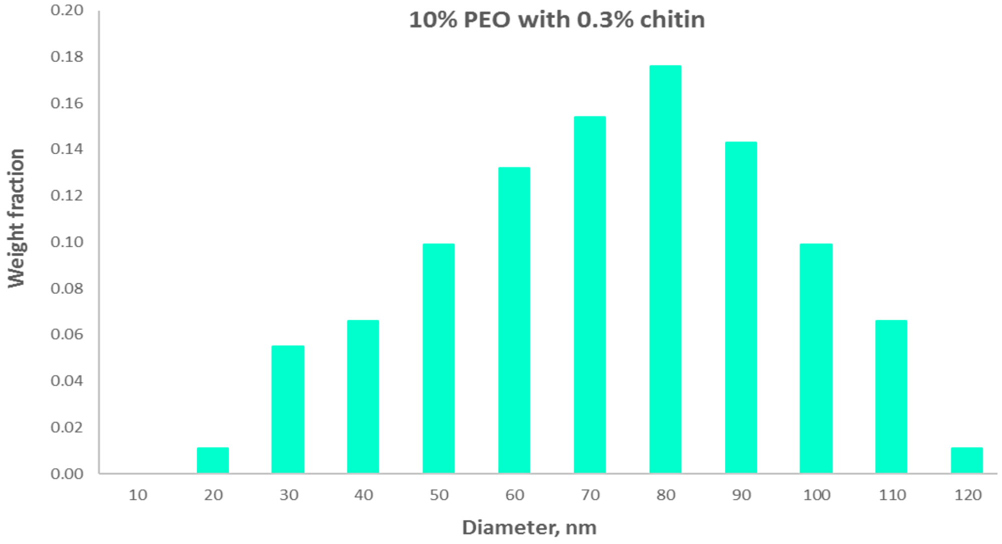

Figure 10. Fiber diameter distribution of 10% PEO solution with 0.3% chitin in 2 M AcAc.

As can be seen from *table 3*, increasing the amount of chitin reduces the average fiber diameter in the membrane. This effect can be explained by either viscosity or conductivity behavior of the solution. The changes of viscosity at 40 RPM and conductivity of solutions are shown in *fig. 11* and *fig. 12* respectively.

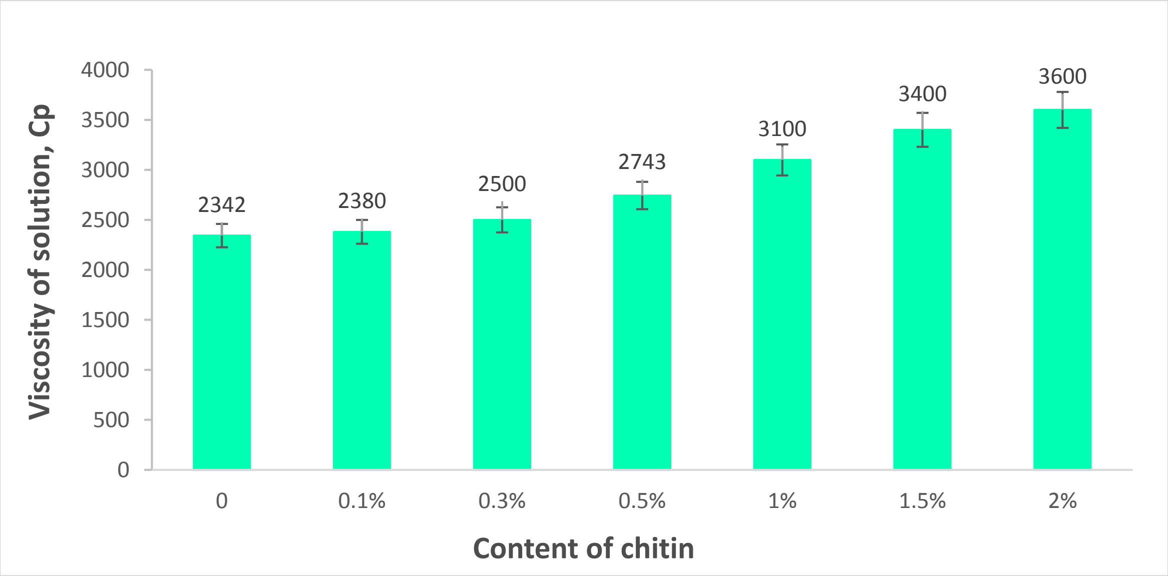

Figure 11. Viscosity change in 40 RPM of the solution of 10% PEO with different amount of chitin in 2 M AcAc.

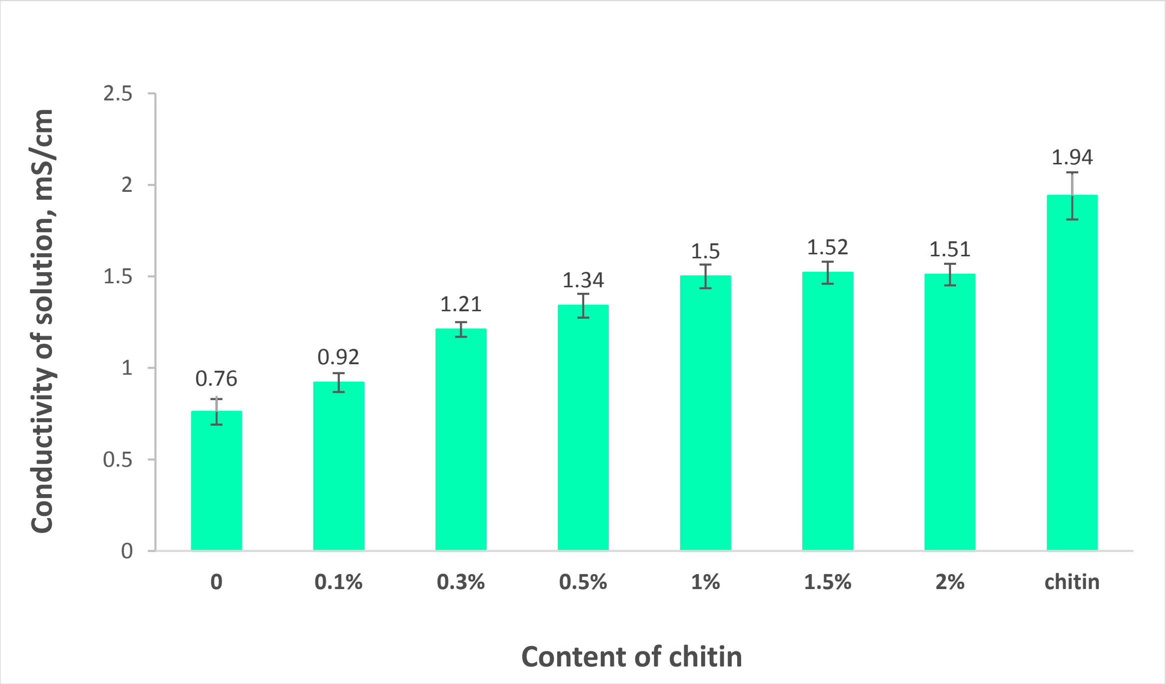

Figure 12. Conductivity change of the solution of 10% PEO with different amount of chitin in 2 M AcAc.

As is clear from the diagram in *fig. 11*, increasing the amount of chitin has shown raising effect on the viscosity. This result was predictable since by increasing the chitin percentage, the general amount of polymer in solution is increasing. Hence, the viscosity should grow up. On the other hand, *fig. 12* represents the rising effect of chitin addition on the conductivity of the solutions. Having considered the conductivity of chitin, which is 1.94 *mS/cm*, we can conclude that chitin improves twice the conductivity of *PEO* solution from 0.76 to nearly 1.52 *mS/cm*.

As is known from the literature, the fiber diameter is firmly dependent on the viscosity and conductivity of the solutions. It is known that the electrospinning of more viscous solution results in larger fiber diameter (Bhardwaj and Kundu, 2010); however, more electrically conductive solutions produce thinner electrospun fiber, (Zhenyu LI, 2016).

In this study, the addition of chitin to *PEO* results in increasing the viscosity of the solutions, but the fiber diameter is still reducing from 70 nm (*Sample 1*) to 53 *nm* (*Sample 6*). Considering the data, we can infer that, the conductivity is dominating factor affecting the morphology of the electrospun membrane. Addition of chitin causes an increase at viscosity by nearly 40% while conductivity impact is approximately twice bigger (100%). It can be concluded that the conductivity increase compensates the effect of rising viscosity on the morphology of the membrane and plays as a drastic factor in the reduction of fiber diameter.

As the conclusion, it can be said that the maximum content of chitin which can be added to PEO to be electrospun, is 1% - 1.5%.

5.3 Effect of PEDOT

To produce the conductive material, PEDOT as a conductive additive was used. The next step in this project was testing the effect of the addition of *PEDOT* to *PEO* solution in various ratios and studying the membrane morphology and properties of the produced solutions. Summary of the solution preparation for the electrospinning is shown in *fig. 13*.

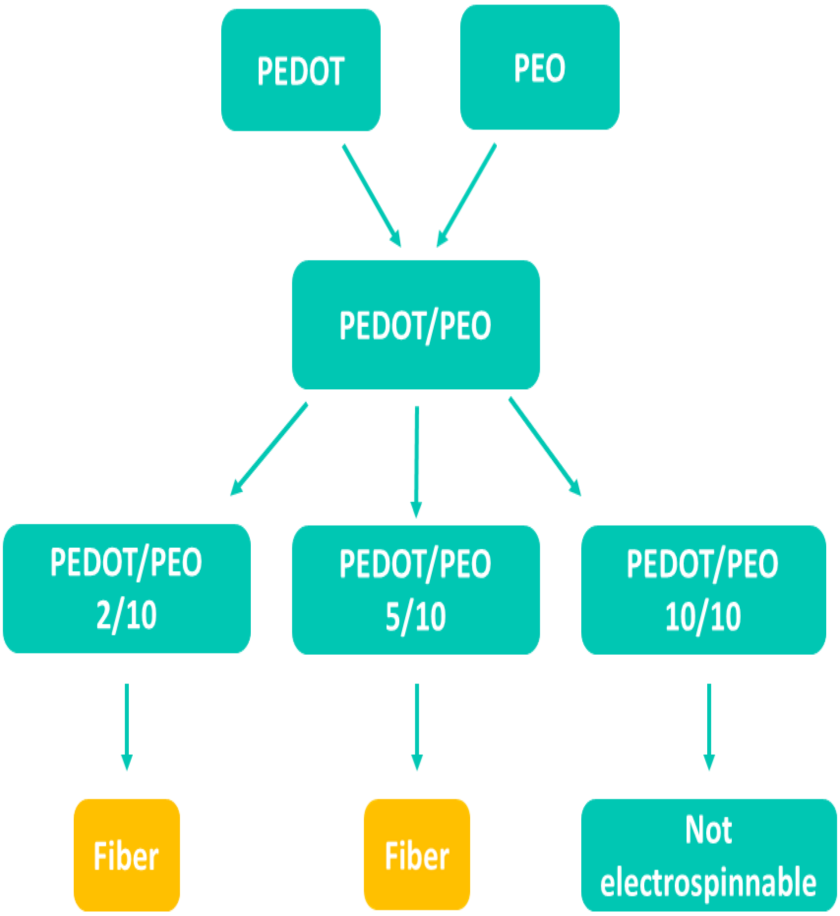

Figure 13. Summarized process of polymer preparation for electrospinning.

The tested ratios of *PEDOT* to *PEO* were 2/10, 5/10, and 10/10. To produce conductive fiber, the content of *PEDOT* in fibers should be as high as possible.

Unfortunately, 10/10 *PEDOT/PEO* sample was not possible to electrospin; however, 2/10 and 5/10 gave perfect fibrous morphology as can be seen from *fig. 14*.

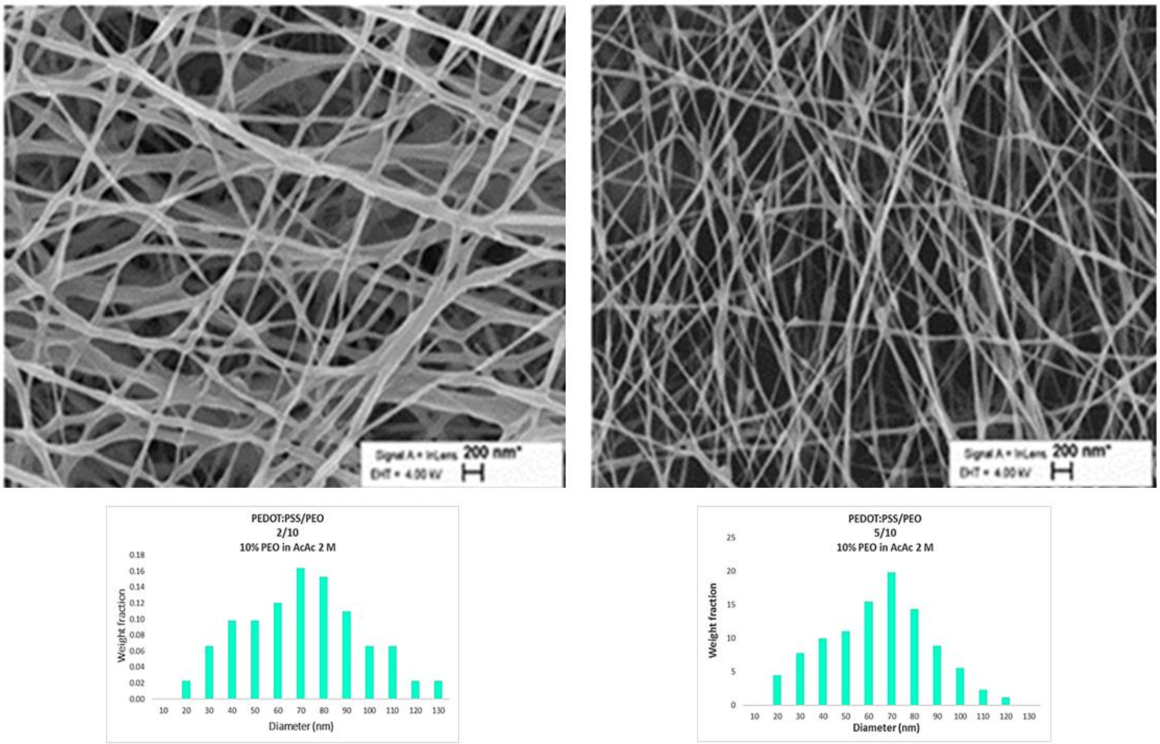

Figure 14. 50000x magnified SEM images of the solution of 10% PEO and the ratio of PEDOT/PEO 2/10 and 5/10 in 2 M AcAc with the related fiber diameter distribution.

SEM investigation (*Fig. 14)* reveals that observed size distribution is again unimodal but rather wide and the mean average of the fiber of *PEDOT/PEO* with the ratio of 2/10 and 5/10 was measured 71 and 61 *nm* respectively. It can be concluded that increasing the amount of *PEDOT* result in a slight decrease in the fiber diameter of the membrane.

Table 4. Summary of preparing solutions with PEDOT/PSS and PEO.

Sample	**Carrier Polymer**	**Cons of PEO in AcAc**	**PEDOT / PEO**	**Viscosity in cP; (40 RPM)**	**Conductivity mS/cm**	**Fiber Diameter (nm)**	**Conductivity of membrane, µS/cm**
8	PEO	10	2/10	1553	4.43	71	0.33
9	PEO	10	5/10	1568	6.22	61	0.60
10	PEO	10	10/10	Not electrospinnable			

The morphology of the membranes was studied, considering the two effective factors: viscosity and conductivity of the solutions. The data reveal that considering the experimental error (±5%), viscosity data remains the same for both solutions while conductivity is significantly increased. The results are logic since the concentration of the conductive polymer is rising. Regarding the data, It can be concluded that the reducing trend in the fiber diameter can be the result of increasing the conductivity of the solution (Zhenyu LI, 2016).

Membrane conductivity is an important factor which is presented in *table 4*. Logically, the higher the amount of conductive polymer, the higher the conductivity of the membrane. As is clear from the data, in *sample 9,* the concentration of *PEDOT increased* twice in comparison with *sample 8*, which results in a double amount of membrane conductivity. On the other hand, comparing the membrane conductivity of pure *PEO* which was measured around 1000 *pS/cm* (0.001 *µS/cm*), it can be confirmed that the addition of *PEDOT* results in the conductivity increase of *PEDOT/PEO* material.

5.4 Development of the composite PEDOT/PEO/chitin fiber

Since *PEO* + chitin and *PEDOT + PEO* were tested for their electrospinnability, next step was to prepare triple-component composites containing chitin, *PEDOT* and *PEO*. Following the objectives of this study which is producing an electrospun membrane with the maximum amount of conductive polymer and chitin in the solution, the solution of *PEDOT/PEO* in the ratio of 5/10 was chosen for further tests since it contains the highest possible amount of conductive polymer. The amount of chitin added to *PEDOT/PEO* solution has been varied from 0.1% to 1.5%. Unfortunately, 1.5% chitin-based solution was not electrospinnable. The summarized information about solution preparation can be seen in *fig. 15*.

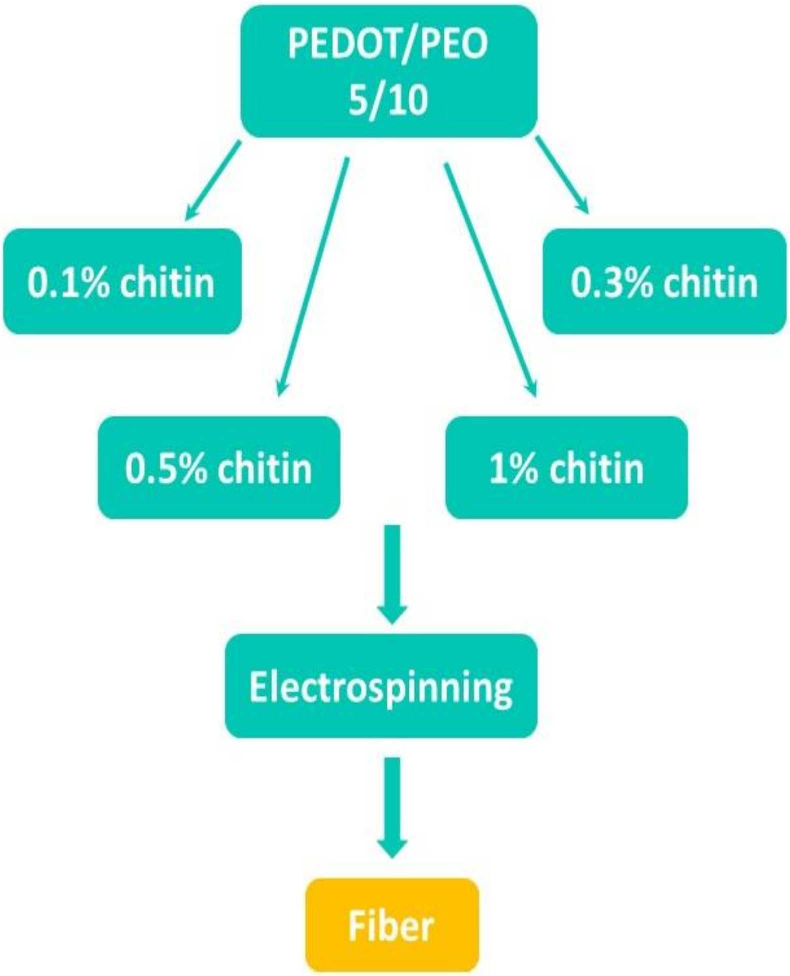

Figure 15. Summarized process of chitin addition to the solution of PEDOT/PEO in ratio of 5/10 with 10% PEO and in 2 M AcAc.

In the case of chitin content at 0.1% - 1%, *PEDOT/PEO*/chitin solutions produced fibers with good morphology. The *SEM* images of the samples and the fiber diameter distribution are available in *fig. 16* and *fig. 17*. All the related data can be seen in *table 5*.

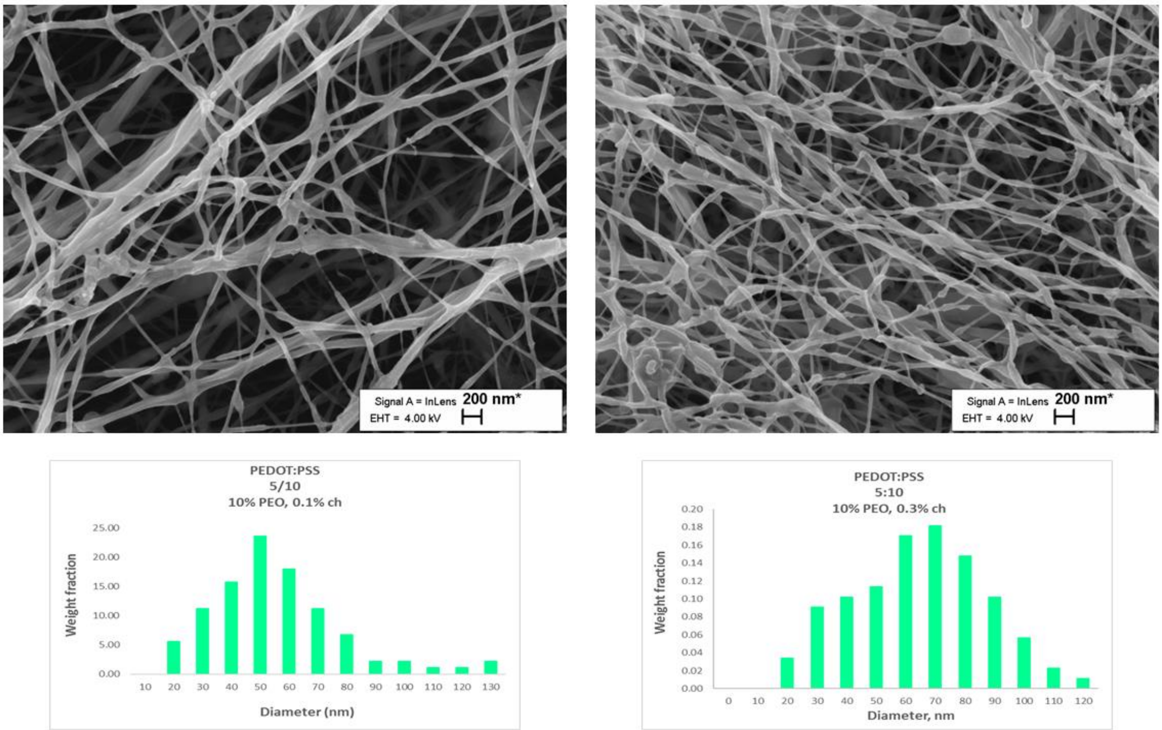

Figure 16. 50000x magnified SEM images and fiber diameter distribution of the solution of 10% PEO and the ratio of PEDOT/PEO 5/10 with different amount of chitin in 2 M AcAc with the related fiber diameter distribution.

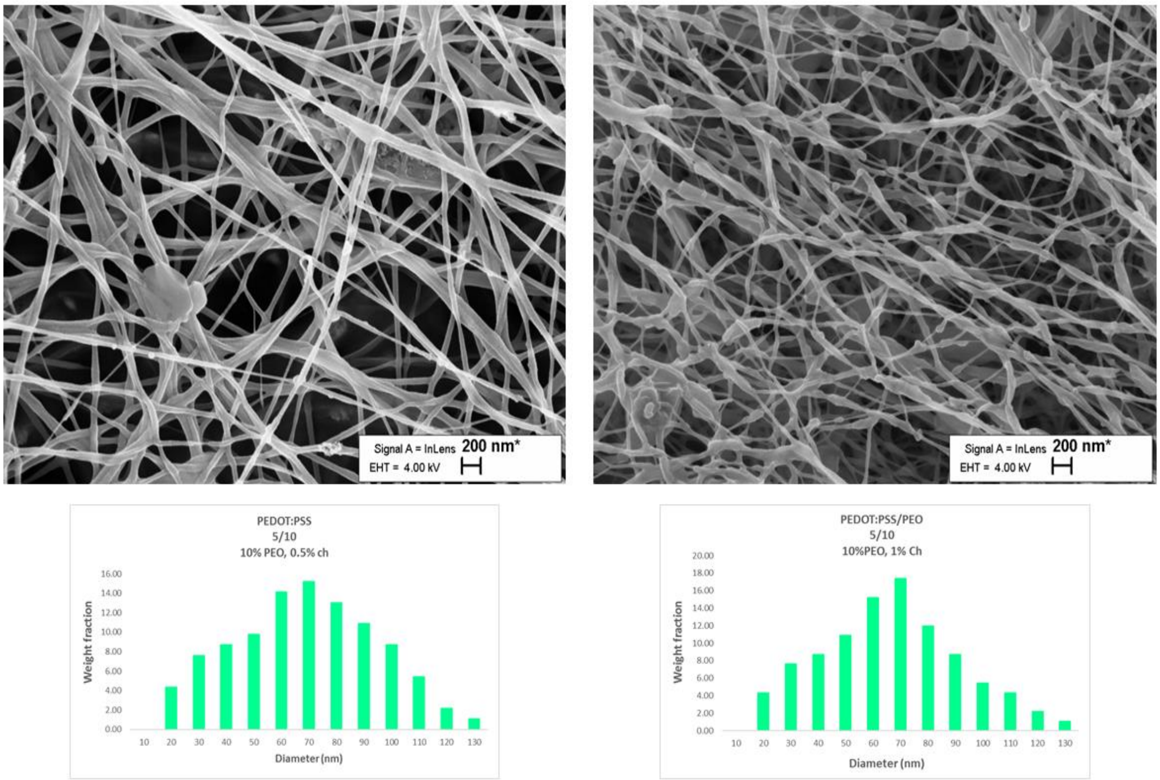

Figure 17. 50000x magnified SEM images and fiber diameter distribution of the solution of 10% PEO and the ratio of PEDOT/PEO 5/10 with different amount of chitin in 2 M AcAc with the related fiber diameter distribution.

Table 5. Summary of preparing solutions with PEDOT/PSS, PEO, and chitin.

Sample	Carrier Polymer	Cons of PEO in AcAc, %	PEDOT/PEO	Chitin conc. in solution, %	Viscosity in cP; (40 RPM)	Conductivity mS/cm	Mean fiber Diameter (nm)	Conductivity of membrane, µS/cm	PEdot/PEO/ Chitin
11	PEO	10	5/10	0.1	1572	6.61	56	0.41	33/66/1
12	PEO	10	5/10	0.3	1573	6.59	63	0.43	33/65/2
13	PEO	10	5/10	0.5	1587	6.60	64	0.44	33/64/3
14	PEO	10	5/10	1	1610	6.59	67	0.45	32/62/6

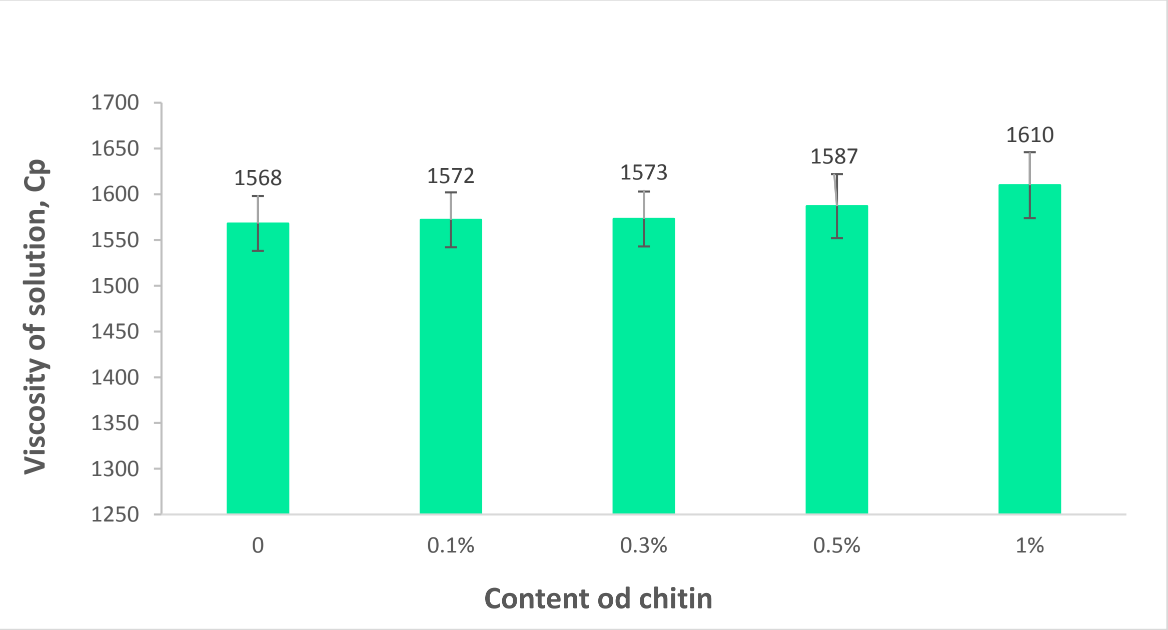

Figure 18. Viscosity changes of the solution of PEDOT + PEO + Chitin. PEDOT/PEO=5/10, 10% PEO in 2 M AcAc.

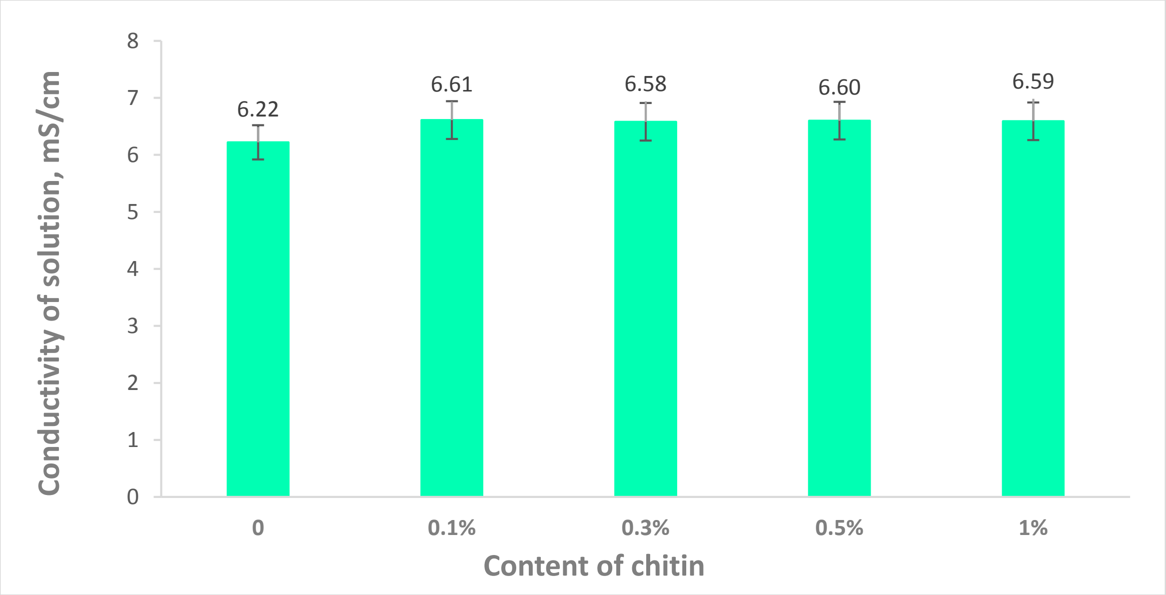

Figure 19. Conductivity changes of the solution of PEDOT/PEO/Chitin. PEDOT/PEO=5/10, 10% PEO in 2 M AcAc.

As can be understood from *fig. 18* and *fig. 19*, by addition of chitin to the solution, Viscosity of solution increased; while the conductivity of solution practically does not change since the amount of conductive polymer remained the same. Regarding the importance of these two factors on the morphology of the electrospun membrane, we can infer that viscosity has the strongest effect on fiber diameter of the final composite which results in slightly thicker fibers (67 *nm*) electrospun from more viscous solution. Also, comparing sample 9 (without chitin) introduced in *table 4* with samples with chitin, we can state that the addition of chitin, results in a slight increase in conductivity of solution from 6.22 *mS/cm* (no chitin) to 6.60 *mS/cm* (in average).

The electric conductivities of membrane follow roughly the same trend as the electric conductivity of solutions and have not changed significantly with the addition of chitin content as is obvious from *table 5.*

The achieved value of electric conductivity of *PEDOT + PEO +* chitin fibers is 0.43 *µS/cm* on average, which can be considered as having a semiconductive level of conductivity.

5.5 Mechanical testing

Several samples Pure *PEO* (*Sample 1*), *PEO* + chitin (*Sample 3*), *PEDOT* + *PEO* (*Sample 9*) and *PEDOT + PEO* + chitin (*Sample 12*) have been chosen for tensile testing. Content of chitin in samples was fixed at 0.3% (to the weight of solution) and 2% to the weight of the whole membrane (*Table 5*), *PEDOT/PEO* ratio was 5/10, and *PEO* concertation in 2 M *AcAc* was 10% in all solutions. The tensile stress-strain curves were evaluated for ten specimens of each membrane and the average graph of all the electrospun membranes is presented in *fig.20*. The first factor which is explained is Young's modulus of the electrospun membranes, and it is the initial slope of the tensile stress-strain graph. As it is known, Young's modulus is a measure of material stiffness.

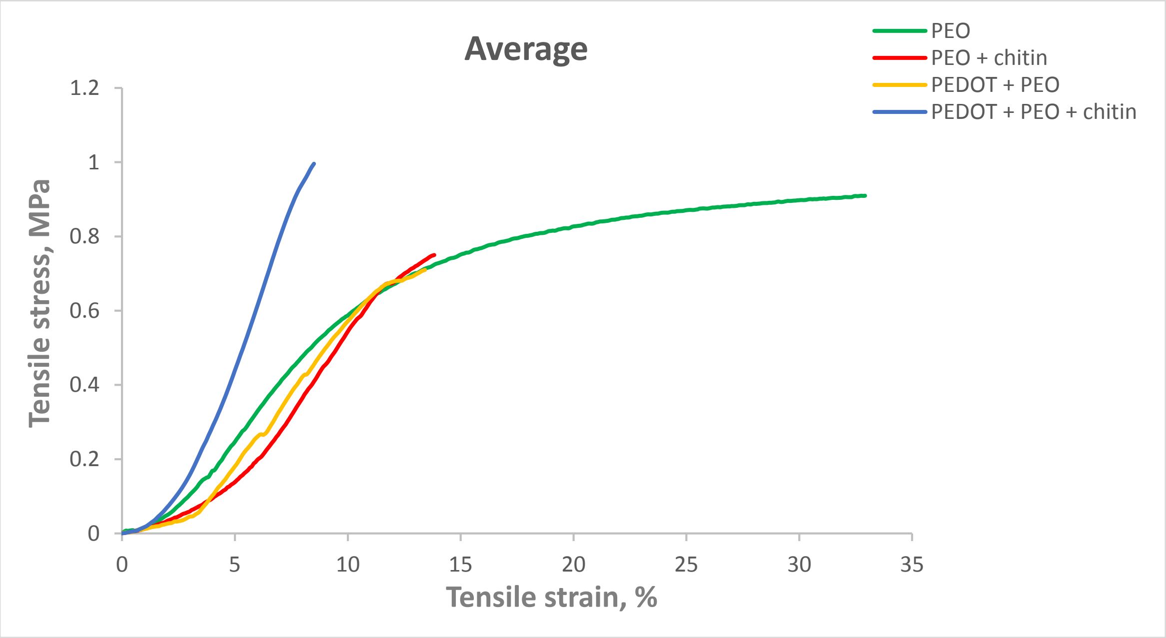

Figure 20. Average tensile stress-strain graphs for different specimens.

Considering the graph, Young's modulus of the *PEO +* chitin sample is very close to that of pure *PEO*. Moreover, it can be seen, the addition of *PEDOT* to *PEO* also produced a membrane with the mechanical properties similar to that of PEO concerning Young's modulus. The final composite behaved the best in terms of stiffness (rigidity) and represented the highest value of Young's modulus. As the conclusion in this step, we can infer that the addition of chitin or *PEDOT* to *PEO* did not change the stiffness of the membrane significantly. Meanwhile, the membrane of *PEDOT+ PEO* represents slightly less rigidity than the others. However, the final composite, *PEDOT + PEO +* chitin, is the stiffest material among all others. The diagrams of tensile stress at maximum load and energy (taken as an area under the curve) for the samples are presented in *fig. 21* and *fig. 22*.

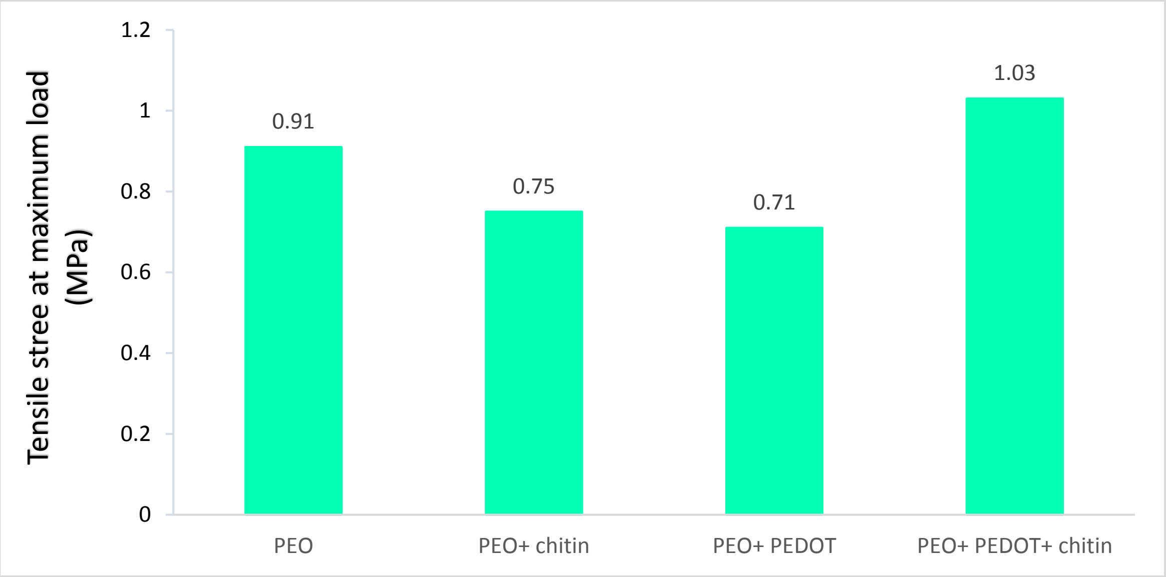

Figure 21. Tensile stress at maximum load dependence on the various solution compositions.

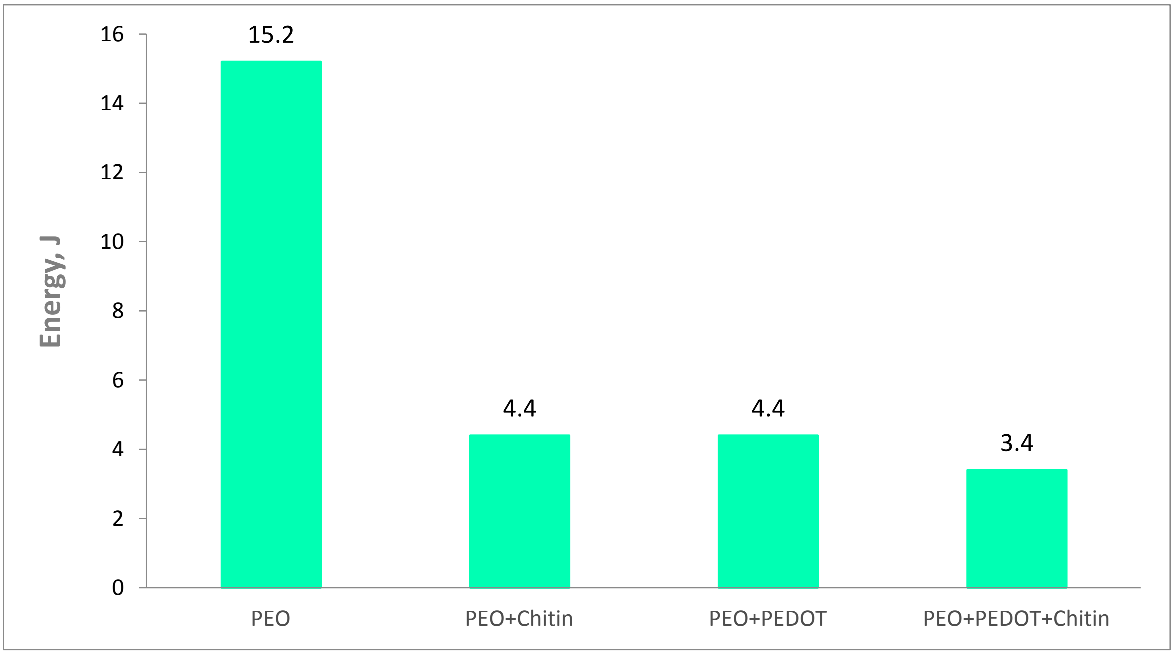

Figure 22. Membrane toughness dependence on the various solution compositions.

Having considered the diagrams, we can realize that the addition of chitin and *PEDOT* to the pure *PEO* has decreased membrane tensile strength. However, regarding the diagram, it can be concluded that *PEDOT+PEO+Chitin* membrane is the strongest compared to the other studied materials.

Considering the energy data in *fig. 22,* which is the measure of the toughness of the material, we can infer that toughness of the membrane decreased significantly by the addition of chitin and *PEDOT* to the *PEO*. It can mean that stress accumulates at the interfaces between polymeric additives (chitin and PEDOT) and PEO matrix, resulting in lower toughness during tensile extension. To improve this parameter, better bonding between all the components should be done either by chemical modification of polymers or by using various coupling agents/crosslinkers, etc.

Hence, the addition of *PEDOT* and chitin to *PEO* improved the strength of the material as well as its stiffness while the possibility of pulling is reduced.

As a conclusion, we can infer that the *PEO* + *PEDOT* membrane does not show good behavior in terms of mechanical properties. However, the addition of chitin to the mentioned membrane improved the rigidity (Young's modulus) and also had a rising effect on the strength of the membrane from 0.71 to 1.03 MPa. Chitin impact on the toughness of the membrane was not satisfactory and reduced energy from 15.2 *J* in pure *PEO* to 3.4 *J* in the final composite.

6 CONCLUSION

- ✓ Chitin/chitosan was extracted from an Estonian mushroom using an alkaline treatment with the *DA* of 42.52%.
- ✓ Addition of chitin and *PEDOT* to *PEO* solution decreased the fiber diameter of composite, which is affected by the increase in conductivity of the solutions.
- ✓ The electric conductivity of the triple component system, *PEDOT + PEO* + chitin depends on mostly *PEDOT* content. The higher the *PEDOT* content, the higher the membrane conductivity. Chitin does not affect the conductivity of composites. The value of 0.43 *μS/cm* has been obtained in this work.
- ✓ Maximum chitin and *PEDOT* content in membranes achieved in this work were 6% and 33% respectively.
- ✓ Mechanical testing of the membranes showed that the addition of chitin to the *PEDOT/PEO* produced an electrospun membrane with the highest stiffness and tensile strength, but lower toughness compared to pure *PEO* membrane.

7 SUMMARY

The current work aimed to produce a mechanically robust and electrically active fiber material based on chitin. The reason for choosing this topic is to produce a biodegradable composite with the possibilities of medical application.

Following this aim, *PEDOT* was chosen among a variety of conductive polymers because of smooth production and high conductivity and biodegradable properties.

A carrier polymer should be used for spinnability of the solutions; different tests have been done and reveal the best suitable polymer for this project could be *PEO*.

Electrospinning was the main method to produce nanofibers with high surface to volume ratio, which involves the formation of fibers from a solution using high voltage. Different solutions with different components in 2 M *AcAc* were used for electrospinning, and all the membrane were analysed by scanning electron microscopy (*SEM*), the most promising of which were tested mechanically. The tensile strength of the different membranes with or without chitin was tested.

The *SEM* analysis represents that most of the samples prepared by electrospinning had a fibrous structure with the diameter in the range of nanometre, and those membranes containing chitin, showed the good dispersion of polymers.

Tensile strength test of some of the solutions have been done, and the results showed that the final composite of *PEDOT*/*PEO*/chitin had had relatively high Young modulus and tensile stress at maximum load. It means the addition of chitin to the combination of *PEDOT*/*PEO* solution, produced more rigid and stronger fiber material; however, the data for tensile strain at maximum load reveals the addition of chitin reduced this property of the electrospun fiber material.

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