The Influence of Conductive Additives on the Mechanical Properties of Electrospun Mats

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology, has not been submitted for doctoral or equivalent academic degree.

Tiia Plamus

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Juhtivate lisandite mõju elektrokedratud nanokiuliste lausmaterjalide mehaanilistele omadustele

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Contents

List of Publications

List of the author's publications, on the basis of which the thesis has been prepared:

I   Savest, N., **Plamus, T.**, Tarasova, E., Viirsalu, M., Krasnou, I., Gudkova, V., Küppar, K.-A., Krumme A. (2016) The effect of ionic liquids on the conductivity of Electrospun polyacrylonitrile membranes. *Journal of Electrostatics,* 83, 63-68.

II   Savest, N., **Plamus, T.**, Kütt, K., Kallavus, U., Viirsalu, M., Tarasova, E.,Vassiljeva, Krasnou, I., Krumme, A. (2018). Electrospun conductive membranes from PANi-ionic liquid blends. *Journal of Electrostatics,* 96, 40-44.

III **Plamus, T.**, Savest, N., Viirsalu, M., Tarasova, E., Krasnou, I., Vassiljeva, V., Kallavus, U., Krumme, A. (2018). The effect of ionic liquids on the mechanical properties of Electrospun polyacrylonitrile membranes. *Polymer Testing,* 71, 335-343.

Author's Contribution to the Publications

Contribution to the papers in this thesis are the following:

I   The author participated in solution preparation, electrospinning, characterisation of mats, data analysis, and writing the paper.

II   The author participated in solution preparation and electrospinning. The author carried out mechanical and morphological characterisation of electrospun mats, developed experimental procedures for mechanical testing, carried out data analysis, and participated in writing the paper.

III The author participated in solution preparation and electrospinning, developed experimental procedures for mechanical testing, and carried out mechanical and morphological characterisation of electrospun mats. The author analysed the experimental results and wrote the paper.

Introduction

Nanofibres are known for their superior properties, such as a high surface-to-volume ratio and generally excellent mechanical properties, such as higher elastic modulus and strength in comparison to other materials. Electrospinning is an efficient and simple method to produce various types of nanofibres with diameters in the nanometre to micrometre scale. In recent years, the fibrous polymeric materials with improved physical and chemical properties produced by electrospinning are of great interest. Such materials have been successfully used in many applications, such as filtration, protective clothing, optical electronics, and tissue engineering scaffolds.

The properties of electrospun mats are dependent on various aspects, such as the polymers, solvents, and additives used for the electrospinning solution as well as the solution and process parameters. This makes the electrospinning technique complex, because the variation of several parameters can determine the properties of the obtained material. During the past decade, researchers have proposed various polymers, solvents, and additives for electrospinning. For example, conductive polymers, such as polyaniline (PANi), have been used to improve the conductivity of mats. Also ionic liquid-based (IL-based) additives have been proven to increase the conductivity of electrospun mats.

Such conductive electrospun mats can be applied as electrospun electrodes inside supercapacitors, as wires and nanowires, and in protective clothing applications and wearable electronics. Besides conductivity, several other properties, such as mechanical behaviour determine the suitability of conductive mats for certain applications.

There have been no studies published on the electrospinning of conductive mats from polyaniline (PANi) salt–ionic liquid (IL) blends. Also, the effect of ILs on the mechanical properties of electrospun mats has not been fully assessed. Therefore, the aim of this research was to produce mats not only with enhanced electrical properties but also with sufficiently good mechanical properties to make them more attractive for application in the field of smart technology.

For this purpose, a variety of additives, such as ILs, conductive polymer PANi, and various solvents were used for the preparation of electrospinning solutions. The process parameters were varied to realize a stable electrospinning process. Various methods were used for the physical, structural, and mechanical characterisation of the obtained mats.

The knowledge gained through this research can provide insight into the effects of various additives and parameters on the properties of electrospun mats and pave the way to new applications for these materials.

In addition, the results of the thesis have been presented at several scientific conferences:

Plamus, T.; Savest, N.; Kallavus, U; Krumme, A. (2017). Electrospun conductive membranes form PANi-ioniq liquid blends. Baltic Polymer Symposium 2017. Tallinn, Estonia 20-22 September 2017, 41.

Plamus, T., Savest, N., Krumme, A., Viirsalu, M. (2017). The effect of ioniq liquids on the properties of electrospun polyacrylonitrile membranes. Proceedings of Nanofibers, Applications and Related Technologies – NART 2017: NART 2017, Liberec, Czech Republic, September 25-September 27, 2017. Liberec: Technical University of Liberec, 45–50.

Plamus, T.; Savest, N.; Viirsalu, M., Kallavus, U; Krumme, A. (2018). The effect of ionic liquids on the properties of electrospun membranes. Baltic Polymer Symposium 2018. Jurmala, Latvia 12-14 September 2018, 98.

Abbreviations

1-D	One-dimensional
[BMIm]Cl	1-butyl-3-methylimidazolium chloride
[C$_{12}$MIm]Cl	1-dodecyl-3-methylimidazolium chloride
(C$_2$MIm)$_3$PO$_4$	1-ethyl-3-methylimidazolium phosphate
CA	Cellulose acetate
CNT	Carbon nanotubes
CSA	Camphorsulfonic acid
DC	Direct current
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EB	Emeraldine base
[EMIm]Br	1-ethyl-3-methylimidazolium bromide
[EMIm][TFSI]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
ES	Emeraldine salt
IL	Ionic liquid
NMP	*N*-Methyl-2-pyrrolidone
PAc	Polyacetylene
PAN	Polyacrylonitrile
PBI	Polybenzimidazol
PCL	Polycaprolactone
PEDOT	Poly(3,4-ethylenedioxythiophene)
PI	Polybenzimidazol
PPV	Poly(para-phenylene vinylene)
PPy	Polypyrrole
PT	Polythiophene
PVC	polyvinyl chloride
PVDF	Polyvinylidene fluoride
SEM	Scanning electron microscopy
SWNT	Single-walled carbon nanotubes
wt%	Weight percent

1 Literature review

1.1 Introduction

Materials in fibre form are of great practical and fundamental importance. The advantages of fibres, such as high specific surface area, flexibility, and superior directional strength, makes them preferred base materials for many applications (Ko and Wan, 2014), such as smart textiles, technical and industrial textiles, and apparel and interior textiles (Kadolph, 2010). Products can range from clothing to reinforcements for aerospace structures. There are various methods to produce textile materials. For example, from fibres, yarns and other nonwoven materials can be produced, and from yarns, woven and knitted fabrics can be manufactured (Kadolph, 2010). The wide range of methods for producing nanofibres has opened a vast variety of new novel applications for textile fibres.

Nanofibres are a class of one-dimensional (1-D) nanomaterials (Roso et al., 2016). (Nano)fibres should have an aspect ratio greater than 1000:1. Nanofibres are usually defined as fibres with a diameter equal to or less than 100 nm. In general, all fibres with diameters smaller than 1 μm can be categorised as nanofibres (Ko and Wan, 2014). The advantages of nanofibres are the following:

- high surface-to-volume ratio;
- generally superior mechanical properties, such as higher elastic modulus and strength in comparison to other materials. These properties are achieved mainly due to the high molecular orientation of polymer molecules (Reneker and Chun, 1996);
- high porosity, excellent pore interconnectivity, and small diameters (Roso *et al.*, 2016).

Methods for the fabrication of nanofibres include conjugate spinning, chemical vapour deposition, phase separation, drawing, template synthesis, self-assembly, meltblown technology, and electrospinning. Electrospinning is a convenient method for producing nanofibres because of the simplicity of the process (Ko and Wan, 2014). Electrospinning is the easiest and most versatile method for producing aligned or randomly distributed nanofibres of various materials, such as synthetic and natural polymers (Huang *et al.,* 2003), composites (Sahay *et al*., 2012), ceramics (Dai *et al*., 2011), and metals (Wu *et al.,* 2007).

Electrospun materials can be categorized as nonwoven; they are fibrous structures fabricated directly from textile fibres (Ko and Wan, 2014). There are several methods for bonding the fibres together, including chemical, mechanical, spinning, and stitch bonding methods. Electrospun materials could be classified as spun-bonded materials (Ko and Wan, 2014).

1.2 Electrospinning method

Electrospinning is a method of continuous formation of fibres composed of a broad range of insulating, conducting, and semiconducting polymers, or even multi-component fibres, with diameters ranging from a few tens of nanometres to several micrometres (Luzio *et al.*, 2014; Baji *et al*., 2010; Reneker and Chun, 1996). The polymer to be used in electrospinning is dissolved in a solvent to create a homogeneous spinnable solution. Because electrostatic force is used to draw the fibres, the term "electrospinning" is used (Wei, 2012).

In the electrospinning process, a high-voltage electric field is applied to the polymer solution or melt (Pillay et al., 2013). This aspect differentiates electrospinning from other conventional fibre spinning techniques (melt, dry, or wet spinning). Those spinning techniques use mechanical forces to produce fibres by extruding the polymer melt or solution through a spinneret, after which the resulting filaments are drawn as they solidify and/or coagulate (Ko and Wan, 2014). In electrospinning, the polymer mixtures to be used are dissolved in a solvent to make homogeneous spinnable solutions. The polymer solution or melt is pumped at a controlled feeding rate through a thin nozzle (see Figure 1). The nozzle functions as an electrode. High direct current (DC) voltages of 10 to 50 kV are typically applied between the nozzle (one electrode) and counter electrode (collector), the distance between two electrodes is usually 10 to 30 cm. The current is in a range from a few hundred nanoamperes to microamperes. A drop of polymer solution is stretched to a Taylor cone by the applied voltage. A solution jet is ejected from the cone when the repulsion force exceeds the surface tension of the pending droplet. On the way to the counter electrode, the solvent evaporates or the melt solidifies. Solid fibres are precipitated on the counter electrode (collector) (Yao *et al.*, 2014; Greiner and Wenderff, 2007).

To conclude, the electrospinning process comprises the following steps:
- charging of the fluid;
- formation of the cone-jet;
- thinning of the jet in the presence of an electric field;
- instability of the jet;
- collection of the jet on an appropriate collector (target) (Rutledge and Fridrikh, 2007).

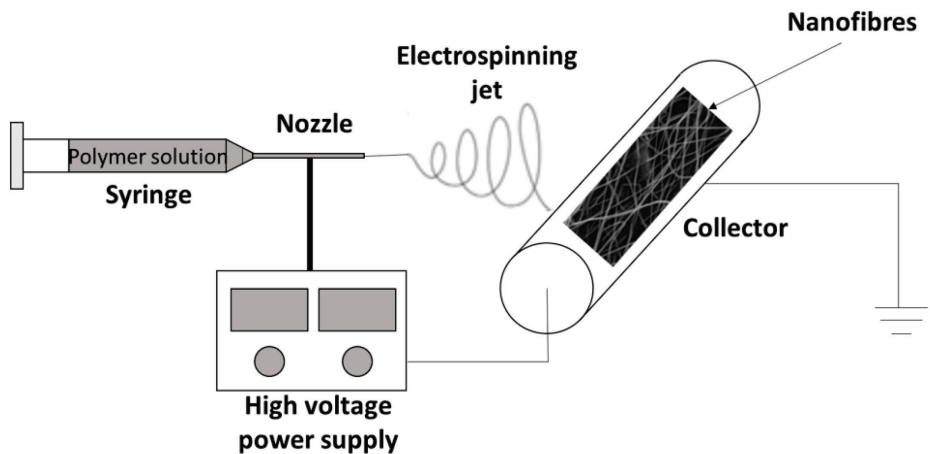Simple schematic process of electrospinning is shown in Figure 1.

Figure 1. Typical electrospinning set-up.

The main components of a simple electrospinning set-up are the following:
- high-voltage power supply;
- flow-control pump;
- syringe that contains polymer solution and is equipped with a metallic needle;
- collector (Wei, 2012; Haider *et al.*, 2015).

Various methods are used to produce fibrous materials with micro- and/or nanoscale structures. They include solution electrospinning, melt electrospinning, and blowing electrospinning. Melt electrospinning produces fibres from melt polymers. Solution electrospinning was described above. Blowing electrospinning uses compressed air combined with an electrical field as the driving force to form fibres (Guarino and Varesano, 2018).

Fibres can also be collected on specially designed collectors, which can influence the alignment of the fibres. Collector types include the following:

- rotating drum collector,
- rotating disk collector,
- static parallel electrodes (Baji *et al.,* 2010).

It has been noted, that the nature of the collector (counter electrode) has an effect on the morphological and physical characteristics of spun fibres (Liu and Hsieh, 2002). The most commonly used collector is a conductive metal plate, which collects fibres in nonwoven form. Liu and Hsieh (2002) discovered that the type of collector used influences the arrangement and packing density of the fibres.

1.2.1 Effects of various parameters on electrospinning

Finding suitable parameters for electrospinning is essential to obtain desirable nanofibres with suitable morphology and properties instead of droplets or beaded morphologies (Pillay *et al.*, 2013). The solution, process, and ambient parameters have an effect on the nanofibre morphology. By varying these parameters, nanofibres with the desired properties can be produced (Bhardwaj and Kundu, 2010). It is also essential to understand the effects of those parameters on the electrospinning process (Haider *et al.*, 2015).

Ambient parameters include relative humidity and temperature (Bhardwaj and Kundu, 2010). Relative humidity can cause changes in the nanofibre diameter. Humidity controls the solidification process of the charged jet. This effect is also dependent on the type of polymer used (Haider *et al.*, 2015). Humidity can also have an effect on the appearance of small circular pores on the surface of the fibres (Haider *et al.*, 2015; Bhardwaj and Kundu, 2010). Solution and process parameters are thoroughly described in Table 1.

Table 1. Solution and process parameters.

Solution parameters	
Concentration	At very low concentrations, electrospray will occur instead of electrospinning. At slightly higher concentrations, a mixture of beads and fibres will occur. At suitable concentrations, smooth nanofibres will be obtained (Bhardwaj and Kundu, 2010; Li and Wang, 2013). Usually, with increasing solution concentration, the fibre diameter will also increase (Li and Wang, 2013).
Molecular weight	Describes the number of entanglements of polymer chains in a solution (Bhardwaj and Kundu, 2010; Li and Wang, 2013). Molecular weight also has an effect on the morphology of electrospun fibres. A high-molecular-weight solution gives fibres with larger average diameters (Bhardwaj and Kundu, 2010).
Viscosity	Optimal viscosity for electrospinning is important to obtain continuous and smooth nanofibres. With very low viscosity, there is no continuous fibre formation. With very high concentration, it is difficult to eject jets from a polymer solution (Bhardwaj and Kundu, 2010; Li and Wang, 2013).
Surface tension	Plays an important role in electrospinning. Smooth fibres can be obtained by reducing the surface tension of a nanofibre solution. High surface tension can inhibit the electrospinning process. Different solvents and surfactants contribute different surface tensions (Bhardwaj and Kundu, 2010).
Conductivity/surface charge density	Solution conductivity is dependent on the polymer type, the solvent used, and the availability of ionisable salts. It has been found that with increasing electrical conductivity of the solution, the diameter of electrospun nanofibres decreases (Bhardwaj and Kundu, 2010).
Processing parameters	
Applied voltage	There are diverse opinions about the influence of the applied voltage on the fibre diameter. Overall, it can be concluded that the voltage influences the fibre diameter, but it is also dependent on the polymer solution concentration and the distance between the tip and the collector (Yördem *et al.*, 2008).
Feed rate/Flow rate	The feed rate/flow rate influences the jet velocity and the material transfer rate. It is important for the solvent to evaporate, and for that purpose, a lower feed rate is preferable (Bhardwaj and Kundu, 2010).
Types of collectors	Fibre alignment is dependent on the type of the collector and its rotation speed (Kumbar *et al.*, 2008). A rotating drum has been used in several studies to obtain aligned fibres (Bhardwaj and Kundu, 2010).
Tip to collector distance	It is important to use the optimum distance between the tip and the collector to avoid beads in the structure of nanofibres. There should be sufficient distance to promote evaporation of the solvent (Bhardwaj and Kundu, 2010).

1.3 Various polymers used for electrospinning

A wide range of polymers are used in electrospinning. Nanofibres have been electrospun from various synthetic polymers, natural polymers, or a blend of both, including proteins (Ohgo *et al.*, 2003; Wnek *et al.*, 2003), nucleic acids (Fang and Reneker, 1997), and polysaccharides (Son *et al.*, 2004). According to Huang *et al.* (2003), more than 50 different polymers have been used successfully for electrospinning; as a result, fibres with diameters ranging from less than 3 nm to over 1 μm have been obtained. Polymers used in electrospinning include carbon precursors (for example PAN), biocompatible polymers [for example polycaprolactone (PCL)], and piezoelectric polymers [like polyvinylidene fluoride (PVDF)] (Levitt *et al.*, 2018).

PAN is the most extensively used polymer in electrospinning. Some of the advantages of PAN include high hydrophobicity and insolubility in a wide range of solvents (Khan *et al*, 2015; He *et al*, 2008; Yun *et al.*, 2007). PAN fibres are chemically resistant and thermally stable with low flammability and good mechanical properties (Mokhtari-Shourijeh *et al.*, 2018). Electrospun PAN fibres are been thoroughly studied by many researchers. Heikkilä and Harlin (2009) explored PAN solution electrospinning with salt as the conductive additive and carbon nanotubes (CNT) as a conductive filler. He *et al.* (2008) explored the effect of concentration on electrospun PAN nanofibres. It was found that the fibre diameter linearly increases with increasing solution concentration, and increasing solution concentration has an effect on solution viscosity. Zhang *et al.* 2011 has pointed out that if PAN concentration is too high it is very difficult to control and maintain a stable flow rate because the viscosity of the polymer solution is high (Zhang *et al.*, 2011). Electrospun PAN materials can be applied, for example, as filters (Yun *et al.*, 2007), supporting materials and substitutes for Pt catalyst (Shi *et al.*, 2015), or as alternative energy devices.

1.4 Various conductive additives for electrospun materials

Various additives have been used to improve the electrospinnability and electrical properties of electrospun materials. Additives also have an effect on electrospinning solution properties, such as conductivity, viscosity, and surface tension (Cheng *et al.*, 2013).

According to their electrical properties, materials are divided into four types: insulators, semiconductors, conductors, and superconductors. Materials with a conductivity less than 10^{-8} S/cm are insulators, semiconductor conductivity is in a range of 10^{-8} to 10^3 S/cm, and materials with the conductivity greater than 10^3 S/cm are conductors (Wan, 2008; Yanilmaz and Sarac, 2014).

Before conducting polymers were developed, polymers were known as excellent electrical insulators. However, conducting polymers are now of growing interest in material science (Wan, 2008). Conductive polymers are favoured for smart applications because of their flexibility and light weight. Usually, conductive polymer products are formed as fibres and cables (Ko and Wan, 2014).

Electrical conductivity is a desirable property for nanofibres (Ko and Wan, 2014). The most commonly available conductive fibres are a blend of nonconductive polymer and conductive additives. Conductive fibres that contain metallic components are easily damaged when they are subjected to long-term exposure to moisture and continuous fatigue. This disadvantage can be overcome when materials are produced in nanoscale or when conductive polymers and other conductive additives are used instead of metallic particles (Ko and Wan, 2014).

Conductive polymers can be described as the cationic and anionic salts of highly conjugated polymers (Miao *et al*., 2010). Some important conjugated polymers are polyaniline (PANi), polypyrrole (PPy), polythiophene (PT), polyacetylene (PAc), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(para-phenylene vinylene) (PPV) (Yanilmaz and Sarac, 2014). The mechanism of conduction in conductive polymers is very complex. It involves the concepts of solitons, polarons, and bipolarons. In the neutral state, conductive polymers are insulative (conductivity is approx. 10^{-10} S/cm). Higher conductivity values can be achieved with the formation of charge carriers upon oxidation or reduction of their conjugated backbone. Conductivity values can increase up to 10^2 S/cm (Yanilmaz and Sarac, 2014).

Various conductive additives, such as carbon nanotubes (Gudkova *et al.*, 2015; Saeed *et al*., 2006; Zhang *et al*., 2011), carbon black (Hwang *et al*., 2007; Li and Wong, 2009), graphene (Peng *et al.,* 2013; Li *et al*., 2016), and ionic liquids (Li *et al*., 2016; Lu *et al*., 2008; Savest *et al*., 2016) are suitable for use in electrospun materials.

1.4.1 Polyaniline

PANi has some unique properties, such as doping/redoping properties, low cost, ease of synthesis, and good compatibility with other polymers. The use of PANi has been explored in a wide range of applications, such as actuators, rechargeable batteries, sensors, separation membranes, electrochemical devices, smart fabrics, plastic microelectronics, and so forth (Ko and Wan, 2014; Ucar *et al.* 2015).

PANi can be found in one of five oxidation forms: leucoemeraldine, protoemeraldine, emeraldine, nigraniline, and pernigraniline. Emeraldine is the most useful form of PANi because of its high stability at room temperature in comparison to other forms. The emeraldine form of PANi is classified into two types: emeraldine base (EB) and emeraldine salt (ES). EB (insulator) cannot be dissolved in common organic solvents due to the conjugated structure. EB can be doped with a suitable strong protonic acid, and then it can be transferred into ES form, which has quite high electrical conductivity up to 1 to 100 S/cm (Qavamnia and Nasouri, 2015).

The low molecular weight and poor solubility of PANi limits its use in electrospinning. Various methods have been introduced to improve the processability of PANi. Ucar *et al.* (2015), for example, examined the effects of various solvents [dimethyl sulfoxide (DMSO), *N*-Methyl-2-pyrrolidone (NMP), dimethylformamide (DMF)] and their mixtures, application of dispersion and mixing techniques during solvent preparation and redoping process on PAN and camphorsulfonic acid (CSA) doped PANi composite nanofibres. On the other hand, since PANi is quite difficult to electrospin, researchers often electrospin it with other polymers (Razak *et al*., 2015).

1.4.2 Ionic liquids

Ionic liquids are salts that are liquid at low temperature (<100 °C) (Wasserscheid and Keim, 2000). ILs are usually composed of an organic cation and weak anions (Dupont, 2011). ILs show good compatibility and solubility in organic polymer solutions. Their unique properties, such as negligible vapour pressure, excellent chemical stability, high thermal stability, and high ionic conductivity (Olivier-Bourbigou *et al.*, 2010; Kubisa, 2009; Tsuda and Hussey, 2007; Savest *et al*., 2016; Gudkova *et al*., 2014) make them ideal to use as additives in polymer solutions for electrospinning. ILs are also called "green solvents". One of the beneficial properties of ILs in use is their miscibility with substances

that have a very wide range of polarities and the ability to dissolve many organic and inorganic compounds (Marsh, 2004).

Cheng *et al.* (2013) studied the effects of adding various ILs to 6 wt% PAN/DMF solutions. Four ionic liquids, (1-butyl-3-methylimidazoliumchloride [BMIm]Cl, 1-dodecyl-3-methylimidazolium chloride [C_{12}mim][Cl], 1-ethyl-3-methylimidazolium bromide [EMIm]Br, and 1-ethyl-3-methylimidazolium phosphate ($C_2MIM)_3PO_4$) were used separately as additives with concentrations ranging from 0.1 to 1.0 wt%. It was concluded that the conductivity significantly increased in comparison to the initial PAN/DMF solution. The conductivity decreased in the following order: ($C_2MIM)_3PO_4$, [EMIm]Br, [BMIm]Cl, [C_{12}mim][Cl]. The diameter of the PAN/DMF solutions with different ILs first decreased and then increased as the ionic liquid content increased.

1.5 Solutions in electrospinning

Solution properties, including conductivity, have an enormous effect on the electrospinning process and the obtained materials. Angammana *et al.* (2011) concluded that, in general, fibres with smaller diameters can be produced from solutions that are more conductive due to the surface charge of electrospinning jet.

1.5.1 Solvents used for electrospinning

Solutions electrospinnability and the properties of the obtained nanofibres are greatly influenced by the choice of solvent (Ucar *et al.,* 2015). Polymers should be completely soluble in the selected solvents, which should have a moderate boiling point. The boiling point determines the volatility of a solvent. Volatile solvents are preferred for electrospinning, but highly volatile solvents are usually avoided because their high evaporation rate can cause evaporation from the nanofibres to occur too quickly during their flight from the needle tip to the collector. Also, less volatile solvents are avoided because of their high boiling point, which impedes their drying (Haider *et al.*, 2015).

Several researchers have reported the effects of solvent properties and polymer concentration on the morphology, structure, and mechanical and thermal properties during electrospinning (Bhardwaj and Kundu, 2010). Several solvents are used in electrospinning, such as water as well as organic and inorganic solvents. DMF is a solvent that has been successfully used as a solvent for PAN [Bhardwaj and Kundu, 2010]. It is a dipolar aprotic solvent that has a high dielectric constant and high dipole moment. DMSO is also used to dissolve PAN; it has a high dielectric constant and a high boiling point (Katsogiannis *et al.*, 2015). For DMF and DMSO, the boiling points are respectively 152 to 154 °C and 189 °C (Sigma–Aldrich, 2018).

1.6 Properties and characterisation of electrospun materials

Various characterisation techniques are used to determine the properties of electrospun materials and electrospun fibres. Often it is quite hard to get a single nanofibre for characterisation. Usually, electrospun materials are characterised based on three categories: physical/structural, chemical, and mechanical (Bhardwaj and Kundu, 2010).

1.6.1 Physical and structural characterisation

Physical characterisation of nanofibres is conducted to examine the structure and morphology. The internal structure of nanofibers extensively influences their physical and mechanical properties. Fibre diameter, diameter distribution, orientation, and

morphology (for example cross-section shape and surface roughness) are also known as the geometrical properties of nanofibres (Bhardwaj and Kundu, 2010).

Scanning electron microscopy (SEM) is widely used to measure fibre diameter and to explore the general fibre morphological characteristics (Ko and Wan, 2014). Samples have to be electrically conductive for SEM; therefore, samples of electrospun polymeric fibres must be coated with gold or platinum (Bhardwaj and Kundu, 2010).

Fibre diameter analysis is an important part of the characterisation of electrospun mats. Quite often in other research, the fibre diameter and its distribution is measured from SEM images, but this is not statistically reliable data. An image analysis method should be used instead. This means that a large number of pictures from various points on the mat should be taken. Various image analysis methods have been utilised for this purpose. Shin *et al*. (2008) developed an image analysis processing method for the measurement of nanofibre diameter, which was compared with the traditional manual method. The average diameters and fibre distributions obtained with those two methods were similar. Baheti and Tunak (2017) compared different image analysis methods – specifically Pourdeyhimi and Ziabari method. They have pointed out that both of the methods failed to accurately estimate the fibre diameter during fibre overlapping, cross-overs, beading and co-joined fibres.

1.6.2 Mechanical properties of electrospun materials

Mechanical properties describe a material's characteristic responses to applied loads and displacements. The main applied load in the case of fibres and fibre assemblies is stretching.

It is important to understand the mechanical properties and deformation mechanisms of electrospun nanofibres. It has great impact on the mechanical properties and other characteristics of nanofibre mats. Most mechanical tests have been performed on nanofibrous mats; however, techniques for testing single nanofibres have also been developed (Tan and Lim, 2008).

The mechanical properties of electrospun fibres are particularly important due to their usage for various applications (Richard-Lacroix and Pellerin, 2013). Several studies have shown that electrospun nanofibres have interesting mechanical properties, such as higher Young's modulus in comparison to those of bulk materials (Fennessey and Farris, 2004; Pedicini and Farris, 2003; Cheng et al., 2011) due mainly to the high molecular orientation of polymer molecules.

It is statistically more reliable to measure the mechanical properties of nanofibre mats rather than those of single nanofibres. It gives the assessment of average mechanical properties of the nanofibres. Nanofibrous materials can be tested with a tensile testing machine (Zhang *et al*., 2011).

To characterise the behaviour of fibrous structures, usually two types of curves are used, namely, load–elongation ($F - \Delta l$) and stress–strain ($\sigma - \varepsilon$, where $\varepsilon = \Delta l / l$). From those curves, several useful parameters can be read out: initial modulus E, strength (the stress at failure σ_f), strain at failure, and toughness ε_f (Ko and Wan, 2014).

Usually, two different types of stresses are used to describe the mechanical properties of nonwoven textile materials: tensile stress and specific stress. Tensile stress is defined as the force per cross-sectional area, and it is calculated as

$$\sigma = \frac{F}{A} , (1)$$

where σ is tensile stress MPa; F is the applied force N; A is the cross-sectional area (unit mm^2), which is calculated through the thickness and width of the specimen.

Further, the mechanical properties can be characterised through the specific stress, which takes into account the areal density of the electrospun mats. The specific stress is calculated as (Ko and Wan 2014)

$$\sigma_{sp} = \frac{F}{B \cdot G} \text{ , (2)}$$

where σ_{sp} is the specific stress, N/tex; F in the force, N; B is the width of the specimen, mm; and G is the areal density, g/m^2.

The weight of a planar textile material is usually expressed as areal density (weight per unit area) in grams per square metre (GMS). To determine the areal density, rounded specimens are cut and weighed (Amutha, 2016). The result is calculated by (Amutha, 2016)

$$G = \frac{m \cdot 10\ 000}{A_s} \text{ , (3)}$$

where m is the weight of the sample, g; and A_s is the surface area of the sample, cm^2.

Many researchers have explored the mechanical properties of electrospun mats. Various sample preparation techniques and calculable parameters are being used. Khan *et al*. (2015) studied the effects of solution and electrospinning parameters on the morphology, mechanical properties, and surface characteristics of PAN electrospun nanofibre mats. PAN/DMF solutions at varying concentrations were electrospun under various parameters. Tensile tests were performed using an electroforce instrument. Tests were carried out in accordance with the ASTM D 1822 standard. Samples were cut in a rectangular shape with a gauge length of 15 mm. An increase in the PAN concentration from 6 wt% to 12 wt% resulted in higher tensile stress and failure strength of electrospun nanofibre mats by 346% and 229%, respectively.

Zhang, *et al*. (2011) reviewed the manufacturing process and characterisation methods for the microstructures and mechanical properties of PAN and PAN-based nanofibres. In their study, 5 mm x 20 mm samples were used. Samples cross-section areas were calculated by the weights of the samples, and the densities of PAN and single-walled carbon nanotubes (SWNT-s) were also measured. An electromechanical universal testing machine was used for the tensile tests. It was concluded that the mechanical properties of the PAN nanofibres and PAN/SWNTs composite nanofibres could be further improved by conducting extensive studies of the electrospinning and hot-stretching conditions. This novel electrospinning technique creates aligned and molecularly oriented PAN and PAN-based nanofibres that can be used to prepare carbon nanofibres that possess superior mechanical properties (Zhang *et al*., 2011).

Tarus *et al*. (2016) explored the effects of polymer concentration on the morphology and mechanical characteristics of electrospun cellulose acetate (CA) and poly (vinyl chloride) (PVC) nanofibre mats. Rectangular specimen were prepared with the size of 60 mm x 10 mm. Tensile tests were carried out using MesdanLab strength tester. Specific stress was used to characterise the tensile properties of the mats. It was found that with increasing solution concentration, the specific stress, break strains, and initial moduli of the CA and PVC nanofibre mats increased.

Ucar *et al.* (2015) explored the effects of various solvent mixtures and the application of dispersion and mixing techniques during solution preparation and redoping on PAN and camphorsulfonic acid (CSA)-doped PANi composite nanofibres. Specimen for mechanical testing were prepared with the size of 5 mm x 35 mm. The gauge length was 15 mm. Test were performed with a conventional tensile tester. The nanowebs produced from DMF showed higher breaking elongation values, but the tensile breaking stress values were higher for the nanowebs produced from DMSO and NMP. Mechanical

dispersion with a mechanical homogenisator resulted in higher tensile breaking stress values than magnetic stirring.

According to the literature, there are several factors that influence the mechanical properties of electrospun materials.

Properties that influence single fibre are for example:

- fibre structure (Baji *et al*., 2010),
- molecular orientation (Richard-Lacroix and Pellerin, 2013),

Properties that influence mats are the following:

- geometrical arrangement of the fibres (Baji *et al*., 2010) and alignment of the fibres (Richard-Lacroix and Pellerin, 2013),
- interactions between fibres (Baji *et al*., 2010),
- mat porosity (Richard-Lacroix and Pellerin, 2013),
- microstructure of each individual fibre (Richard-Lacroix and Pellerin, 2013),
- areal density (Ko and Wan, 2014),
- branching of the nanofibres (Ucar *et al.,* 2015)

1.6.3 Electrical conductivity of electrospun mats

Usually, 2-point electrical measurements are used for resistance measurements and current–voltage curve generation. More accurate results can be gained with a 4-point probe if the measured resistance is very low or the resistance of the probes or the contacts is relatively high (Ko and Wan, 2014).

In a study by Ucar *et al*. (2015), PAN/PANi composite nanofibre webs were obtained. Three solvents, namely, DMSO, DMF, and NMP were used. CSA was used as a dopant. The electrical conductivity of the nanofibre webs was around 10^{-6} S/cm when DMSO was used as a solvent. This conductivity value corresponds to the semiconductive material range. Higher conductivity values were achieved with solvent mixtures (CSA–NMP and CSA–NMP/DMF). When redoping was done, the conductivity value increased 10 times and was $1.2 \cdot 10^{-5}$ S/cm.

1.7 Applications and advantages of electrospun materials

Electrospun ultra-fine fibre mats are used in a vast range of engineering, biomedical, and industrial fields, such as energy-related needs (harvesting, transmitting, and storage), membrane technology, filtration media, tissue engineering (scaffolds, dressings for wound healing, drug delivery), medical prostheses, biosensors, cosmetics, and protective clothing applications (Khan *et al*., 2015; Pedicini and Farris, 2003; Bhardwaj and Kundu, 2010).

Conductive nanofibres and their mats can be used in the following areas: electrostatic dissipation, corrosion protection, electromagnetic interference shielding, photovoltaic devices, fabrication of tiny electronic devices (Bhardwaj and Kundu, 2010), electrochemical capacitors or supercapacitors, and flexible energy storage devices for wearable electronics (Liu, 2018). The mechanical properties of those devices are extremely important when considering their applications. Other advantages of electrospun materials for various applications are presented in Table 2.

Table 2. Examples of various applications of electrospun materials.

Application of electrospun material	Unique properties of electrospun materials making them suitable for specific applications
Electrospun insulators, separators, and electrolytes	PAN electrospun mats can be used as separators because of their high porosity, high air permeability, and increased wettability in comparison to conventional separators. Polymer electrolytes have limited internal shorting and low electrolyte leakage (Miao *et al.*, 2010).
Electrospun electrodes	Electrospun electrodes have a porous structure, which can enhance the penetration of a viscous polymer gel electrolyte. For example, $LiCoO_2$ nanofibres have been used as a cathode for Li-ion batteries (Miao, *et al.*, 2010).
Wires and nanowires	Wires and nanowires fabricated by electrospinning have large surface-to-volume ratios and high electron-hole conductivity, which make them good materials for use in ultrasensitive chemical sensors, solar cells, and fuel cell electrodes (Miao, *et al.*, 2010).
Supercapacitors	Carbon nanofibres are a good candidate for electrochemical double-layer capacitors because of their high specific surface area, flexible nature, simple synthesis, and low-cost precursors (Liu, 2018). Activated carbon nanofibres can be produced, for example, from PAN, poly(imide) (PI) and polybenzimidazol (PBI) (Miao, *et al.*, 2010).
Actuators	Actuators take electrical or other energy and transform it into mechanical motion. The most important parameters for actuators are large strain and quick response time. Electrospun materials can provide large strain and good ion mobility. Also, a large amount of electrolyte can be localized in the porous structure of electrospun mats (Miao, *et al.*, 2010).
Protective clothing applications	Lightweight; large surface area; high porosity; great filtration efficiency; resistant to penetration of harmful agents in aerosol form (Gibson *et al.*, 1999; Schreuder-Gibson *et al.*, 2002).
Filtration (air, aerosol and liquid filters)	High surface-to-volume ratio; cohesive properties of polymers nanofibers, high surface cohesion; usage of very small diameter fibres; polymer nanofibres can be electrostatically charged to modify the ability of electrostatic attraction; low air resistance; lower filter mass in comparison to that of conventional fibres; flexibility of adding surface functionality to the fibres by blending or incorporating nanofillers (Pillay *et al.*, 2013; Bhardwaj and Kundu, 2010; Baji *et al.*, 2010).
Tissue engineering applications	Ultra-fine fibres of biodegradable polymers that are produced by electrospinning are good applicants for tissue engineering applications because of their high surface-area-to-volume ratios and high porosity of the fibres as well as flexibility and other mechanical properties (Baji *et al.,* 2010).

1.8 Summary of the literature review and aim of the study

Electrospinning is a simple method to produce nanofibres with versatile properties. It is important to find suitable parameters for electrospinning to produce nanofibres with desirable properties. Electrospinning parameters include solution, processing, and ambient parameters. A wide range of polymers are used for electrospinning. One of the most extensively used polymers is PAN because of its positive properties, such as high hydrophobicity and insolubility in various solvents.

Various additives can be used to enhance the properties of electrospun mats. For example, additives can influence the electrical conductivity of electrospun mats. Electrical conductivity can be increased by adding conductive polymers or conductive additives to the polymer solution. One of the most commonly used conductive polymers is PANi, but the poor solubility of PANi limits its use in electrospinning. Various methods, such as the use of various solvents, the application of dispersion and mixing, as well as doping/redoping, have been proposed to overcome the poor solubility. Also ILs have been explored as conductive additives for electrospinning solutions.

There are several methods for the characterisation of electrospun materials. They include the analysing and examination of single fibres and nanofibrous mats. SEM is widely used for the characterisation of the morphology of fibres and electrospun mats. Several image analysis techniques have been developed for the estimation of fibre diameter distribution.

It is very important to understand the mechanical behaviour of electrospun materials for their application in various fields. Mechanical testing can be performed on single fibres and mats. Mechanical tests of nanofibrous mats are usually performed with a conventional tensile testing machine. Mechanical properties can be evaluated through assessment of tensile or specific stress.

The main aim of this research was to study the influence of various conductive additives (PANi salt and different ILs) on the properties of electrospun mats. It is essential to produce mats with enhanced electrical properties as well as favourable mechanical properties. To achieve the aim of the study, the following objectives were set:

- To develop a proper methodology for testing the mechanical properties of electrospun mats
- To learn the effects of various conductive additives (ILs and PANi salt) on the properties of electrospun materials
- To present a new procedure for producing electrospun conductive nanofibrous mats from a PANi salt solution with ionic liquid and matrix polymer
- To study the influence of fibre morphology and diameter distribution on the mechanical properties of electrospun mats
- To find the optimum amount of conductive additive to produce conductive electrospun mats with the desired mechanical properties

For these objective, the following activities were carried out:

- Various conductive additives were used in the compositions of electrospun mats.
- Various methods were used to evaluate the mechanical properties of the mats.
- Morphology and other characteristics of the mats were studied.

2 Experimental

PAN was chosen as a polymer for the electrospinning process because of its versatile positive properties. DMF and DMSO were chosen as the best solvents for PAN to obtain proper electrospun nanofibres. Various imidazolium-based ionic liquids with various anions were chosen as additives to study their influence on the solution and mat conductivity. Conductive polymer PANi was chosen as a conductive additive in the electrospinning solution to introduce a new solution preparation technique with IL [BMIm]Cl. An overview of the materials and methods used is shown in Table 3. A more thorough explanation of the materials and methods is given in the following chapter.

Table 3. Materials and methods.

Materials	Characterization methods	Aim of the paper	Paper
Polymer: PAN Solvents: DMF or DMSO Additives: [EMIm][TFSI]*, [BMIm]Cl, [EMIm]Br	SEM analysis; conductivity measurements of the solutions and mats	Study the effect of ILs on the PAN mats' conductivity	Paper I
Polymer: PAN Solvent: DMSO Additives: PANi and [BMIm]Cl	SEM analysis; conductivity measurements of the mats; thickness measurements of the mats; mechanical testing	Production of conductive mats from PANi–IL blends by electrospinning	Paper II
Polymer: PAN Solvents: DMF or DMSO Additives: [BMIm]Cl, [EMIm]Br	SEM analysis; conductivity measurements of the mats; mechanical testing; image analysis	Analysis of the dependence of the mechanical properties of electrospun mats on the additives used	Paper III

*1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

2.1 Materials

PAN powder was purchased from Polysciences Inc. with a molar mass of 150,000 g/mol. PAN solutions were prepared in two different solvents: DMF (with purity ≥99.8%) and DMSO (with purity ≥99.9%). DMF and DMSO were purchased from Sigma–Aldrich. Various conductive additives were used: PANi and ILs. PANi (emeraldine salt) was purchased from Sigma–Aldrich with an average molar mass >15,000 g/mol in powder form. PANi was used for preparing the blend of PAN–PANi salt with IL in a solvent for electrospinning. IL, 1-ethyl-3-methyl bis(trifluoromethylsulfonyl)imide ([EMIm][TFSI]), was purchased from Sigma–Aldrich.

[BMIm]Cl and [EMIm]Br, were synthesised in the laboratory according to the methods described in the literature (Cull *et al.*, 2000; Zhang and Liu, 2012). To synthesize [BMIm]Cl, 164 g 1-methylimidazolium (Merck) and 260 g chlorobutane (Merck) were placed in a round-bottom flask fitted with a reflux condenser system and mixed at 75 °C

for 72 h until two phases were formed. Then the colourless viscous liquid was cooled and washed with ethyl acetate (Merck) three times using a separation funnel. The ready ionic liquid was dried under vacuum for 3 h. [EMIm]Br was synthesized by mixing 326 g bromoethane (Merck) and 164 g 1-methylimidazolium in a round-bottom flask fitted with a reflux system at 40 °C for 24 h. Then the viscous liquid was washed with ethyl acetate three times in a separation funnel and dried under vacuum for 3 h.

2.2 Methods

2.2.1 Solution preparation for electrospinning
Solution preparation (paper I and III)
1. The concentration of PAN in solvents was fixed at 10 wt%. Two different solvents, DMF and DMSO, were used. PAN was dissolved in the solvents by mechanical stirring with a magnetic stirrer at 40 °C for 24 h (Figure 2, Step 1).
2. IL as a conductive additive was added to the polymer solution at concentrations ranging from 1 wt% to 10 wt%. The solution was stirred at 40 °C for 90 minutes to achieve a homogeneous solution for electrospinning. Three different ILs [EMIm][TFSI] (this IL was only used in Paper I), [BMIm]Cl, and [EMIm]Br were used (Figure 2; Steps 2a, 2b, 2c).
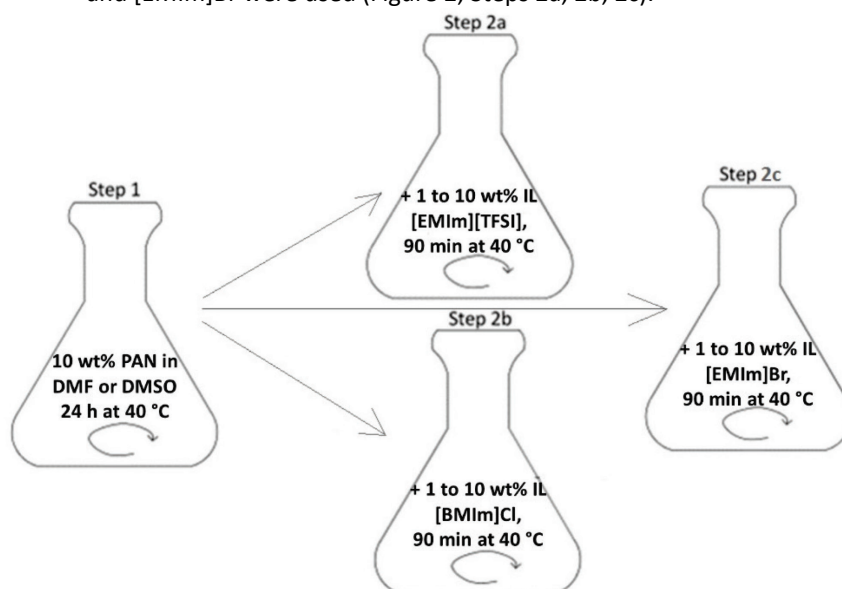
Figure 2. Solution preparation process, Papers I and III (*IL [EMIm][TFSI] was only used in Paper I).

The solutions prepared and their abbreviations are shown in Table 4.

Table 4. Solutions prepared in Papers I and III and their abbreviations.

IL concent-ration, %	DMF + [EMIm][TFSI]*	DMSO + [EMIm][TFSI]*	DMF + [BMIm]Cl	DMSO + [BMIm]Cl	DMF + [EMIm]Br	DMSO + [EMIm]Br
0	F-0	SO-0	F-0	SO-0	F-0	SO-0
1	F-TFSI-1	SO-TFSI-1	F-Cl-1	SO-Cl-1	F-Br-1	SO-Br-1
2	F-TFSI-2	SO-TFSI-2	F-Cl-2	SO-Cl-2	F-Br-2	SO-Br-2
3	F-TFSI-3	SO-TFSI-3	F-Cl-3	SO-Cl-3	F-Br-3	SO-Br-3
5	F-TFSI-5	SO-TFSI-5	F-Cl-5	SO-Cl-5	F-Br-5	SO-Br-5
8	F-TFSI-8	SO-TFSI-8	F-Cl-8	SO-Cl-8	F-Br-8	SO-Br-8
10	F-TFSI-10	SO-TFSI-10	F-Cl-10	SO-Cl-10	F-Br-10	SO-Br-10

*IL [EMIm][TFSI] was only used in Paper I.

PANi solution preparation (Paper II)

- PANi was mechanically dispersed in DMSO solvent by magnetic stirring at 40 °C for 48 h (Step 1 in Figure 3).
- PAN as a binder polymer was added and the PANi–PAN blend in DMSO was mixed mechanically by a magnetic stirrer for 24 h at 40 °C. The concentration of PANi (from 3 to 40 wt%) in blended solution was calculated on the dry matter of binder polymer PAN. The concentration of the binder polymer was 9 wt% in solution and did not change (Step 2a and 2b, in Figure 3).
- Next, 10 wt% of IL [BMIm]Cl was added to the blended solution by mechanical mixing for 1 h at 40 °C (Step 3a in Figure 3).
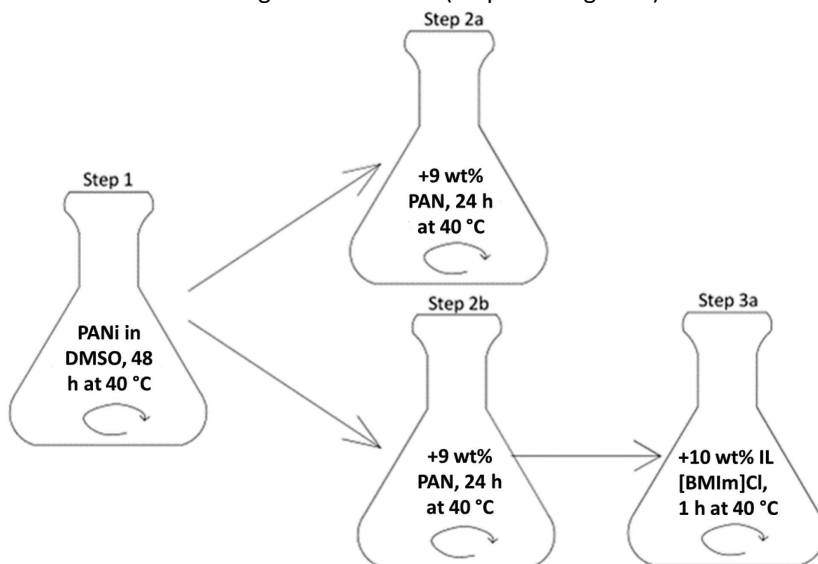
Figure 3. Solution preparation process in Paper II.

The solutions prepared and their abbreviations are shown in Table 5.

Table 5. Solutions prepared and their abbreviations (Paper II).

PANi concentration	PANi + PAN in DMSO	PANi + PAN in DMSO + 10% IL [BMIm]Cl
0	SO-0	SO-Cl-0
3	SO-PANi-3	SO-Cl-PANi-3
10	SO-PANi-10	SO-Cl-PANi-10
15	SO-PANi-15	SO-Cl-PANi-15
20	SO-PANi-20	SO-Cl-PANi-20
30	SO-PANi-30	SO-Cl-PANi-30
40	SO-PANi-40	SO-Cl-PANi-40

2.2.2 Electrospinning process

Electrospinning was carried out by using a horizontal electrospinning setup with a cylindrical rotating collector covered with aluminium foil at room temperature (Figure 4.). Each spinning solution was placed into a 1 ml syringe with a needle diameter of 0.4 mm, 0.6 mm, or 0.8 mm. The pumping feed rate was set to a certain value. The choice of needle diameter and the pumping feed rate depended upon the solution viscosity. Larger needle diameter was chosen for solutions that were more viscous. The solutions were electrospun at 20 to 25 kV with a distance of 8 to 10 cm between the needle and the collector. The electrospinning parameters are shown in Table 6.
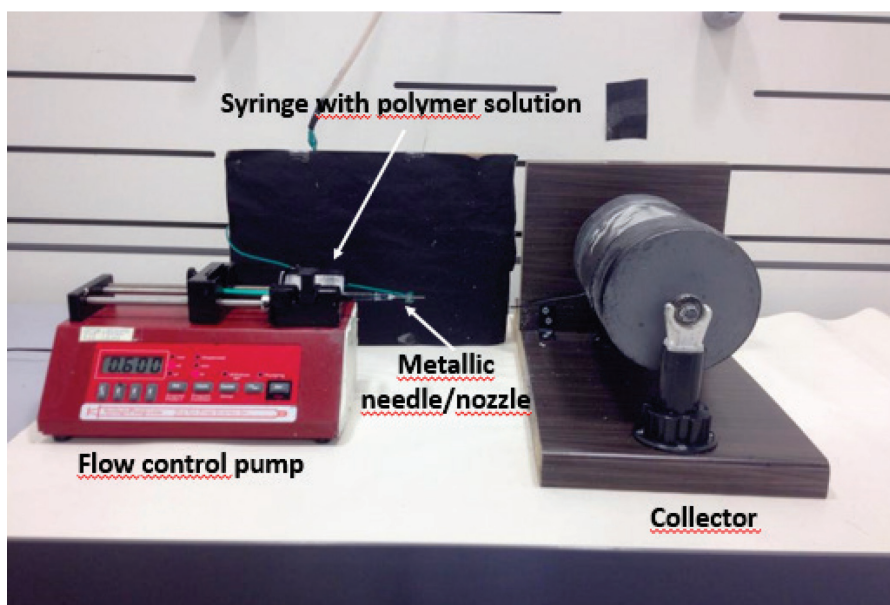
Figure 4. Electrospinning setup.

Table 6. Electrospinning parameters.

Solution used/electrospinning parameter	DMF + [EMIm][TFSI]* or [BMIm]Cl or [EMIm]Br DMSO + [EMIm][TFSI]* or [BMIm]Cl or [EMIm]Br (Papers I and III)	PANi + PAN in DMSO or PANi + PAN in DMSO + 10% IL [BMIm]Cl (Paper II)
Syringe volume, ml	1	1
Needle diameter, mm	0.4 or 0.6	0.8
Voltage, kV	20-24	20-25
Distance between the needle and the collector	8-10	8-10
Pumping feed rate, ml/h	between 0.4 and 0,6	0.9

*IL [EMIm][TFSI] was only used in Paper I.

2.2.3 Solution analysis

The conductivity of ILs used and PAN solutions was measured with a conductivity meter (Metler Toledo SevenCompact Conductivity Meter) at room temperature.

2.2.4 Analysis of electrospun mats
Characterisation of mechanical properties
Thickness of the mats. Sample thickness was measured using an Insize digital thickness gauge with an accuracy of 1 μm.
Areal density of the mats. Rounded specimens were cut from the mats with the diameter of 1.5 cm and weighed with analytical balances to an accuracy of 10 μg.
Mechanical testing. Tensile tests of the electrospun mats were carried out using an Instron 5866 tensile testing machine. The samples were cut using a tool that combined two sharp razors. The samples were cut in a rectangular shape with a gauge length of 10 mm and a width of 1 mm. A load cell with a maximum capacity of 2.5 N was used for the tensile tests with a constant test speed of 10 mm/min. Five specimens were used for each sample, and the maximum load (force) and extension data were measured and recorded.

Analysis of mat morphology and nanofibre diameter measurements
In Paper I, the morphology of Electrospun mats was analysed by scanning electron microscopy using a Hitachi TM1000. No conductive coating was deposited onto the samples. The fibre diameter was measured and presented as an arithmetic mean.

In Papers II and III, the morphology of electrospun mats was analysed by using a SEM Zeiss EVO MA 15. An accelerating voltage of 15 kV was applied. The samples were covered with Au/Pt with an ion sputter JFC-1100. In Paper II, the fibre diameter was measured and presented as an arithmetic mean.

In Paper III, software for the geometric characterization of fibre systems based on SEM images was used to measure the diameters of electrospun nanofibres and the diameter distribution inside the mats. The software was developed by Fraunhofer Institute for Industrial Mathematics ITWM, supported by validation through the German Institutes of Textile and Fiber Research (DITF). Before the image analysis, the samples were covered with Au/Pt by ion sputtering, and the electrospun mats were analysed by SEM using a Hitachi TM1000.

Conductivity measurements

In Papers I and II, the conductivity of the mats obtained from PAN solutions was measured by the two-probe method using a conductivity meter (High-Resistance Low-Conductance Meter HR2, AplhaLab Inc.). All mats were prepared for measurement of 1 x 3 cm in Paper I and 1 x 2 cm in Paper II.

3 Results and discussion

3.1 Effects of ionic liquids on the conductivity of PAN solutions

Solution conductivity was thoroughly explored in Paper I (see Figs. 1 and 2 in Paper I Appendix). One of the objectives of the study was to compare the effects of different types of ILs on the electrical properties of polymer solutions. Before the experiments, the conductivity of pure ILs and PAN solutions was measured. The conductivity of pure [BMIm]Cl was 33.4 μS/cm. The conductivity of pure [EMIm]Br was 4510 μS/cm and [EMIm][TFSI] was 8200 μS/cm. Pure DMF solvent conductivity was 3.5 times higher than the conductivity of pure DMSO solvent – 0.719 and 0.253 μS/cm, respectively. The conductivity of pure PAN solution in DMF was also higher than that of PAN solution in DMSO – 48 μS/cm and 21.5 μS/cm, respectively. Both PAN solutions (PAN in DMSO and PAN in DMF) had a similar trend, which showed a linear increase in solution conductivity with increasing IL concentration. Solutions with PAN in DMF showed about 1.5 times higher conductivity values in comparison with solutions with PAN in DMSO. The conductivity of PAN solutions was higher when ILs [EMIm]Br and [EMIm][TFSI] were added instead of IL [BMIm]Cl. It can be concluded that the conductivity of pure solvents and ILs has an effect on the conductivity of the final solutions.

3.2 Effects of various additives on the conductivity of electrospun mats

In the current study, various additives were used to enhance the electrical properties of electrospun mats. First, three different ILs were used, and then the effect of using PANi with and without IL [BMIm]Cl was analysed.

3.2.1 Effects of ionic liquids on the conductivity of electrospun mats

Figures 5 and 6 present the influence of various ILs and solvents on the conductivity of electrospun mats. Logarithmic scale is used to get a more comprehensive overview of the mat conductivity values. Linear scales are presented in Paper I, Fig. 3 and Fig. 4. Conductivity reaches its maximum value at an IL concentration of 8 wt%. The mat conductivity decreases considerably at 10 wt%. In the other words, at a concentration of 8 wt%, the system becomes conductive. This critical concentration can also be called the electrical percolation threshold (Mazinani *et al.*, 2010). It can be assumed that at this concentration, the conductive additive, IL, is evenly distributed within the polymer matrix (Wessling, 2011).
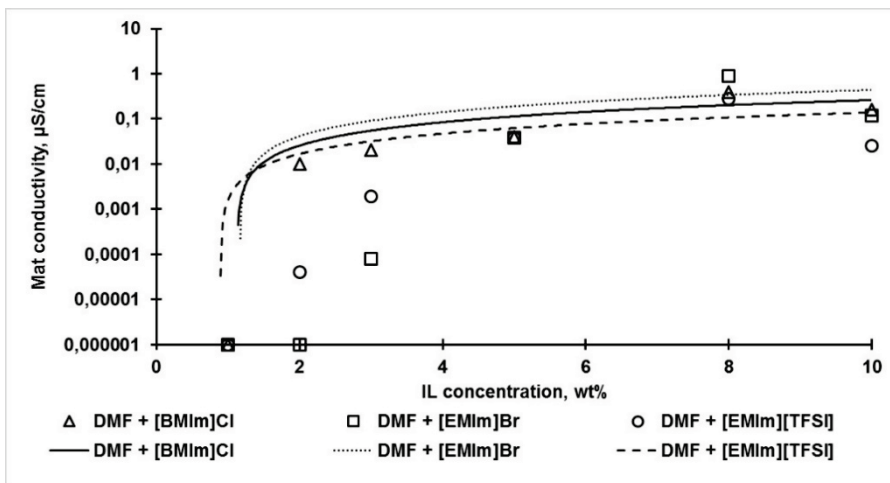
Figure 5. Impact of various ILs in solvent DMF on the conductivity of electrospun mats (Paper I).
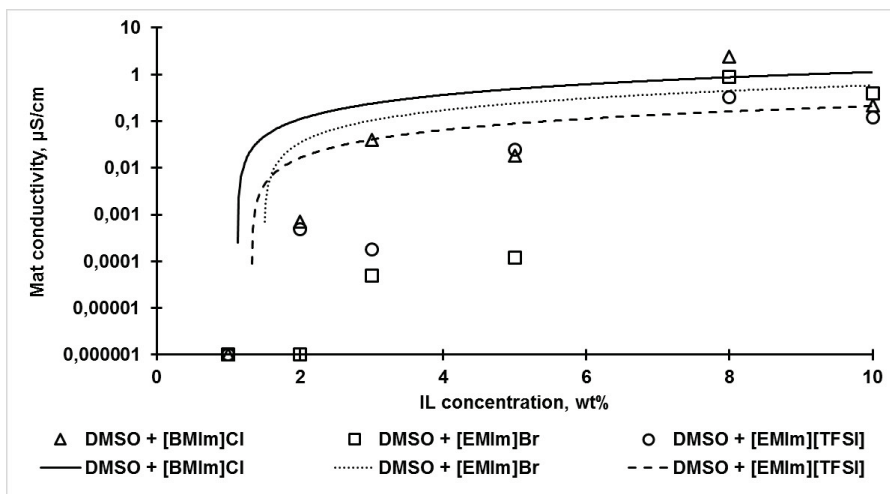

Figure 6. Impact of various ILs in solvent DMSO on the conductivity of electrospun mats (Paper I).

As seen in Figure 5, the most conductive mats (measured conductivity 0.88 µS/cm) obtained from the solution of PAN in DMF were produced by using [EMIm]Br. The two other ILs, [BMIm]Cl and [EMIm]TFSI, showed smaller increases in mat conductivity. The conductivity of the mats changed from high to low in the following order: [EMIm]Br, [BMIm]Cl and [EMIm]TFSI.

The most conductive mats (measured conductivity 2.39 µs/cm) were obtained from the solution of PAN in DMSO, and they were produced by using 8 wt% [BMIm]Cl. The conductivity with IL [EMIm]Br was 0.88 µS/cm. The conductivity of the mats obtained with solvents DMF and DMSO and with [EMIm]TFSI, was within the same range, 0.28 to 0.30 µS/cm. The conductivity of the mats obtained with the solvent DMSO changed from high to low in the following order: [BMIm] Cl, [EMIm]Br, and [EMIm]TFSI.

3.2.2 Effects of PANi salt and IL [BMIm]Cl on the conductivity of electrospun mats

In the second approach to achieve conductive mats, conductive additive PANi was used. One of the focuses of this approach was to present a new procedure for producing electrospun conductive nanofibrous mats from PANi salt solution with IL [BMIm]Cl and matrix polymer PAN. IL was proposed as the additional solvent to improve the solubility of PANi salt and to increase the conductivity of the mats. IL can also maintain lower conductivity when an insulator polymer is used as a matrix in electrospinning.

Figure 7 (and Fig. 1. in Paper II) presents the influence of PANi content on the electrical conductivity of nanofibrous mats obtained from PAN–PANi blended solutions. From Figure 7 and Fig. 1. in Paper II, it can be seen that the conductivity of the mats obtained from the solutions without adding ionic liquid is much lower than that of the mats obtained from the blend solution with 10 wt% IL. Without the addition of IL to PANi-PAN solutions, an increase in the mats' conductivity with increased PANi concentration could be observed. The highest conductivity value was achieved at 10 wt% of PANi, which was 0.79 µS/cm. Higher concentrations of PANi did not increase the mat conductivity. A possible explanation for that could be that there was a lack of complete homogeneous dispersion of PANi salt in the solution; consequently, PANi particles could only be partly transferred into the electropsun mat.

On the other hand, higher conductivity with IL is seen in Fig. 6 and Fig. 1 in paper II. The conductivity starts to increase already from 0 wt% of PANi. The highest value of electrical conductivity was achieved at 10 wt% PANi; at this level, the mat conductivity was 2.62 µS/cm. This mat conductivity is three times higher than without using IL in the blend solutions. In comparison to the results of the literature data, the achieved conductivity was higher than that of the electrospun mats obtained from the solution of doped PANi, for which the conductivity was 0.18 µS/cm (Castagna *et al*., 2016). As seen in Fig. 6 and Fig. 1 in Paper II, the conductivity of the mats electrospun from PAN–PANi–IL solutions decreases with increased PANi concentration above 12 wt%. However, it is still much higher than the conductivity of the mats obtained from the solution without using IL. Such results confirm the role of IL in a PAN–PANi blend to improve the dispersion of PANi particles by creating more conductive pathways.

The experimental results showed that there is a limited concentration of PANi salt at which it is possible to perform electrospinning of PAN–PANi-blend solutions. At a PANi concentration of 30 wt%, the mats were very fragile. At a concentration of 40 wt%, electrospinning was almost impossible to perform. This can be explained by the high viscosity and non-homogeneity of the solution due to the large amount of non-dispersed particles of PANi salt in the solution. Figure 7 demonstrates that the optimum concentration of PANi salt to achieve the most conductive mats in both solutions with and without IL was 10 wt%. This evidence can be interpreted by considering the electrical percolation threshold. According to the percolation theory, a remarkable increase in conductivity occurs when the concentration of a conductive additive exceeds its critical value. The percolation threshold is the optimum conductive additive content in the polymer matrix above which there are no significant changes in the conductivity (Wessling, 1991; Pan *et al*., 2011; Kalaitzidou *et al*., 2010).
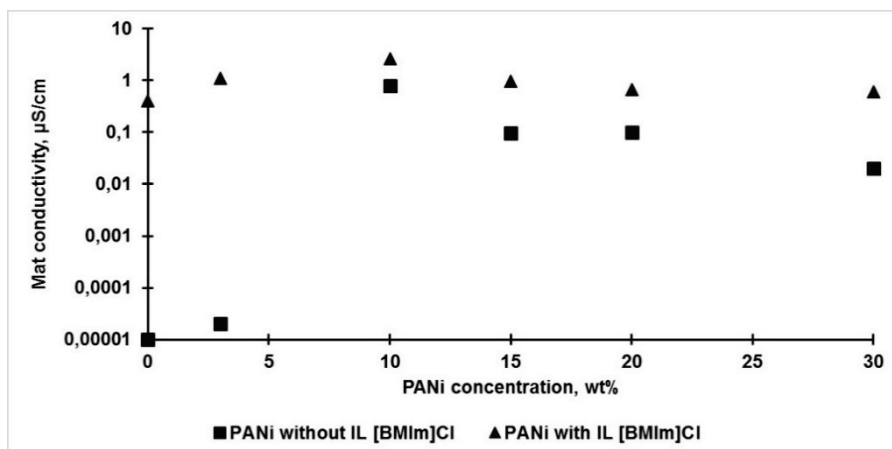
Figure 7. Impact of PANi salt and IL [BMIm]Cl on the conductivity of electrospun mats (Paper I).

In conclusion, more stable conductivity values were obtained with mats containing PANi and IL [BMIm]Cl. The highest mat conductivity values were comparable for the mats obtained with three different ILs (the highest value was achieved with the mat obtained from solution SO-Cl-8, 2.39 µs/cm) and with PANi and IL [BMIm]Cl (the highest conductivity value was achieved with the mat obtained from solution SO-Cl-PANi-10, 2.62 µS/cm). When comparing the conductivity of mats with IL [BMIm]Cl with and without PANi then, it can be concluded that the addition of PANi has an effect on the mat conductivity. The mat conductivity from solution SO-Cl-10 was 0.22 µs/cm, and that from solution SO-Cl-PANi-10 was 2.62 µS/cm.

3.3 Mechanical properties

3.3.1 Mechanical properties of the mats with ILs
The influence of various ILs and solvents on the mechanical properties of electrospun mats are presented in Figures 7 and 8. By increasing the IL concentration, the specific stress started to increase at the lower concentrations (1 and 2 wt%) of ILs with the exception of mats F-Cl-1, F-Cl-2, and F-Br-2. This could be due to the use of solvent DMF. When 3 wt% and higher concentrations of ILs were used, the specific stress decreased. According to Meli *et al.* (2010) fibres with higher additive contents will aggregate, intertwine, and fuse. Electrospun mats prepared from PAN solutions in DMF and DMSO without ILs showed the specific stress values of 56.68±2.76 mN/tex and 51.98±4.40 mN/tex, respectively. The highest specific stress with IL [BMIm]Cl was observed for mat SO-Cl-1 (74.32±3.85 mN/tex) and lowest for the mat SO-Cl-8 (9.09±1.00 mN/tex). The highest specific stress of the examined mats was gained with IL [EMIm]Br with mat F-Br-1 (87.93±5.15 mN/tex). The lowest specific stress value with IL [EMIm]Br was obtained with the mat F-Br-10 (14.95±1.44 mN/tex). Higher specific stress values were achieved with IL [EMIm]Br.

Mats obtained from solutions with solvent DMF, especially with IL [BMIm]Cl, showed the most stable specific stress values. The specific stress values ranged from 34.28 mN/tex (mat F-Cl-1) to 27.01 mN/tex (mat F-Cl-10). Mats obtained from solutions with solvent DMSO showed higher values of specific stress. It can be concluded that

mechanical properties are strongly dependent on the IL type and the solvent used for the preparation of the polymer solution.
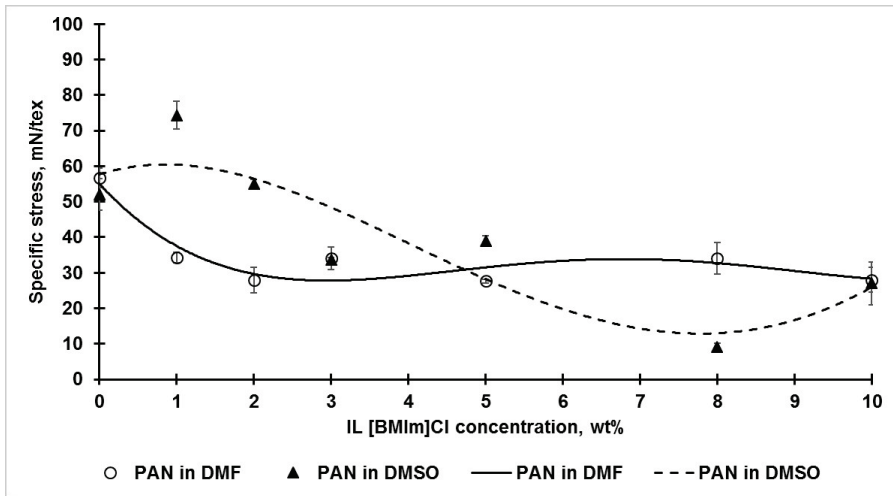

Figure 8. Impact of IL [BMIm]Cl and various solvents on the specific stress of the mats (same as Fig. 2. in Paper III).
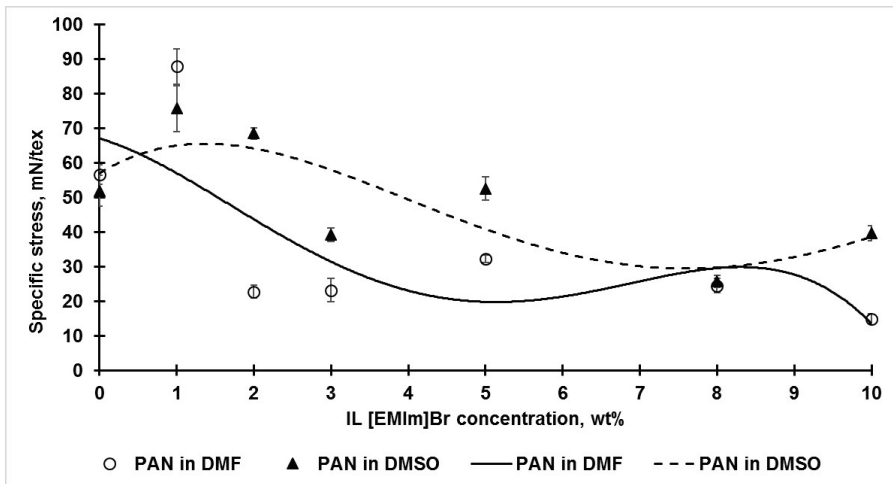

Figure 9. Impact of IL [EMIm]Br and different solvents on the specific stress of the mats (same as Fig. 3. in Paper III).

3.3.2 Mechanical properties of the mats with PANi salt and IL [BMIm]Cl

The tensile properties of the mats obtained from solutions with various amount of PANi salt are presented in Fig. 3. of Paper II and Figure 10. In Figure 10, the areal density of the mats was also taken into account, and specific stress values were calculated. Overall, it can be concluded that the specific stress values decreased with the increasing PANi concentration. More extensive decrease was observed with mats with IL. Decreased specific stress values could be obtained due to the nonhomogeneous dispersion of PANi salt at higher concentrations, which in turn leads to morphological changes of

electrospun fibres. Kizildag *et al*., 2016 also studied the effect of PANi with various dopants and solvents on the breaking stress of electrospun mats. It was concluded that PANi in the electrospun solution decreased the breaking stress. This could be explained by the incompatibility between PAN and PANi in the solutions, which could have led to nonhomogenous dispersion of the PAN and PANi in the structure.

In the current study, PANi mats with IL showed the highest tensile stress value at the concentration where the conductivity was the highest, that is, 10 wt% of PANi. The highest specific stress and tensile stress values were measured for the mat SO-PANi-10, 64.18 mN/tex and 13.62±1.39 MPa (Fig. 3. Paper II), respectively. The highest specific stress and tensile stress values with IL was achieved with the mat SO-Cl-PANi-3, 32.51±3.85 mN/tex and 13.42±1.11 MPa (Fig. 3. Paper II) respectively. According to other researchers, the maximum breaking stress values of PANi-containing electrospun mats are slightly lower, 10.58±2.04 MPa according to Ucar *et al*. (2015) and 7.09±1.56 MPa according to Kizildag *et al*. (2016).

When the results of tensile stress and specific stress were compared, then the specific stress values were moderately lower in case of the mats with IL (with the exception of the mats SO-Cl-PANi-12.5 and SO-Cl-PANi-30). This could be attributed to the influence of areal density on the stress values.
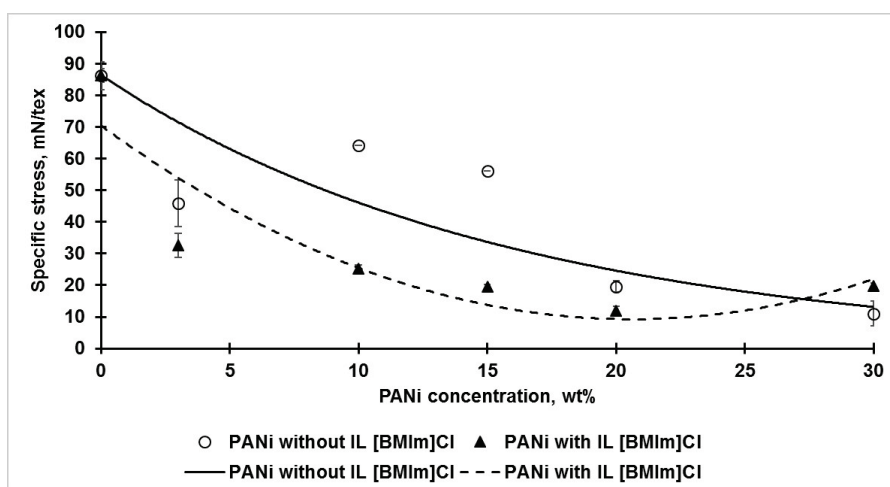
Figure 10. Impact of PANi and IL [BMIm]Cl on the specific stress of the mats.

3.4 Effects of various additives on the fibre diameter and morphology

3.5 Fibre diameter and morphology of electrospun mats with ionic liquids

The morphology of electrospun mats with ionic liquids was thoroughly studied in Papers I and III. In Paper I, fibre diameters were measured manually from SEM images. In Paper III, software for the geometric characterization of fibre systems was used. In Paper I, the fibres were not coated with Pt/Au, but in Paper III they were. All that caused the inaccuracies of the measurements in Paper I. Depending on the image quality, some uncertainties can be involved in the measuring processes. In Paper I, clearly the image quality influenced the final measurement results.

The impact of various ILs and solvents on the median fibre diameter of the mats is presented in Figures 11 and 12. The median diameter of nanofibres obtained from solutions without ILs were 476 nm (mat SO-0) and 324 nm (F-0). Overall, it could be concluded that mats from the solutions with solvent DMSO showed much larger median diameters than those produced with solvent DMF. The mats with the smallest median diameter were obtained from solution F-Br-2 (222 nm), and those with the highest value were obtained from the solution SO-Br-5 (542 nm).

Mats from solutions with IL [BMIm]Cl consisted of fibres with larger median diameters than those produced with IL [EMIm]Br. The diameters of the mats from solutions with [BMIm]Cl ranged from 231 nm (mat F-Cl-3) to 542 nm (mat SO-Cl-5). Mats from solutions F-Cl-3 and F-Cl-8 consisted of fibres with median diameters smaller than 300 nm. Most even diameters were obtained with solvent DMF and IL [EMIm]Br.
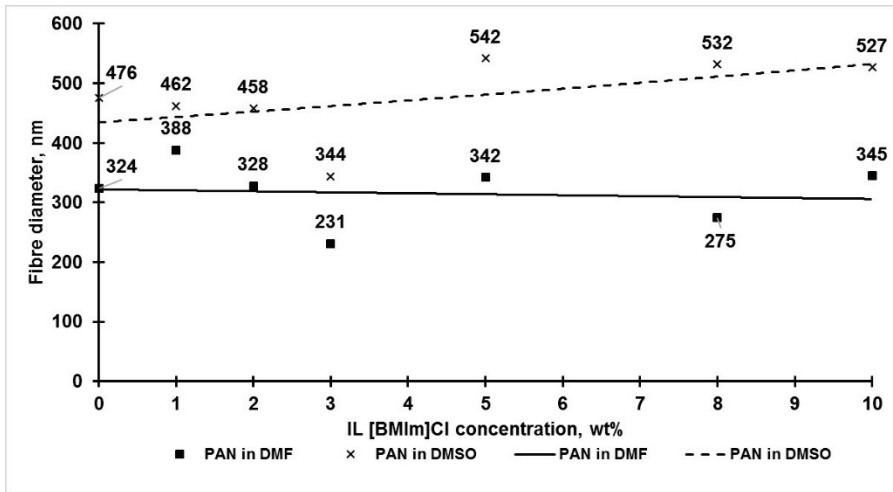
Figure 11. Impact of IL [BMIm]Cl and various solvents on the median fibre diameters of the mats (same as Fig. 4. in Paper III).
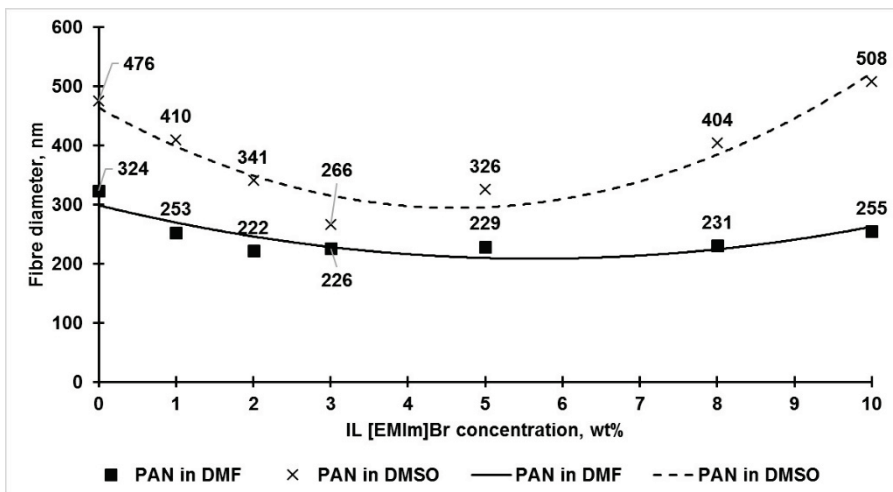
Figure 12. Impact of IL [EMIm]Br and various solvents on the median fibre diameters of the mats (same as Fig. 5. in Paper III).

Because median diameter does not entirely characterise the diameters in the mats, the fibre diameter distribution was also studied. The fibre diameter distributions of mats F-0 and SO-0 are presented in Figure 13. Mats obtained from solution F-0 showed bimodal fibre distribution. However, mats obtained from solution SO-0 showed larger median diameters, and the diameter values were not so dispersed.
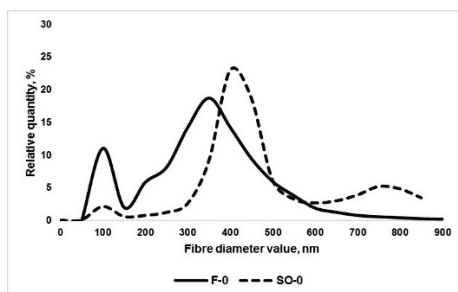
Figure 13. Fibre diameter distributions for the mats obtained from pure solutions F-0 and SO-0 (same as Fig. 6. in Paper III).

The fibre diameter distributions for other mats are presented in Figure 14. Mats obtained from the solutions with solvent DMSO with IL also showed larger median diameters, similar to mats from solutions F-0 and SO-0. At higher concentrations of IL, the fibre diameters were more dispersed. As the solution conductivity measurements showed, there is an increase in conductivity values with increasing IL concentration. The charged polymer solution is less stable, which could be the cause of more dispersed fibre diameter values (Pan, 2011). Mats with the highest specific stress (F-Br-1, Figure 14h) and the lowest specific stress (F-Br-10, Figure 14m) have different fibre diameter distributions. Mat F-Br-10 has very dispersed distribution, which is opposite to that of mat F-Br-1. Multimodal distributions of fibre diameter can be seen for the mats from solutions SO-Br-5 (Figure 14k), SO-Cl-8 (Figure 14e), and F-Br-8 (Figure 14l).
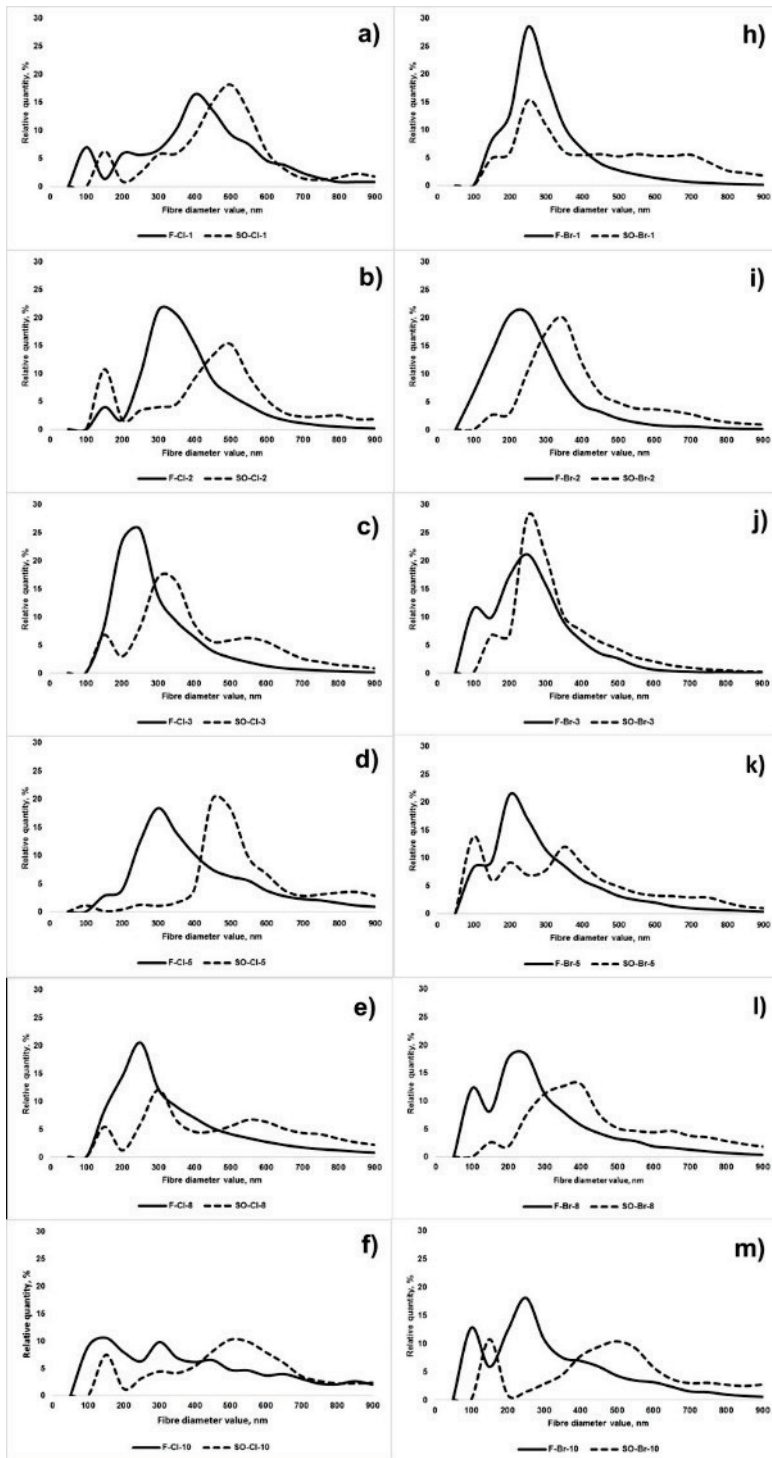
Figure 14. Fibre diameter distributions for mats from different solutions (same as Fig. 7. in Paper III).

Mats obtained from the solutions with solvent DMSO showed slightly higher specific stress values in comparison to the mats obtained from the solutions with DMF as a solvent (Figures 8 and 9). According to other researchers, solvents have a great effect on nanofibre diameter and morphology (Kizildag et al., 2016), which in turn affects the mechanical properties (Richard-Lacroix and Pellerin, 2013; Cheng et al., 2011). For example, for fibres produced at an IL concentration of 10 wt% the following observations were done (Figure 15). Comparing the morphologies of mats obtained from solutions F-Br-10 and SO-Br-10, beads can be noticed in mat F-Br-10. This morphological aspect could be the reason for the lower specific stress value.
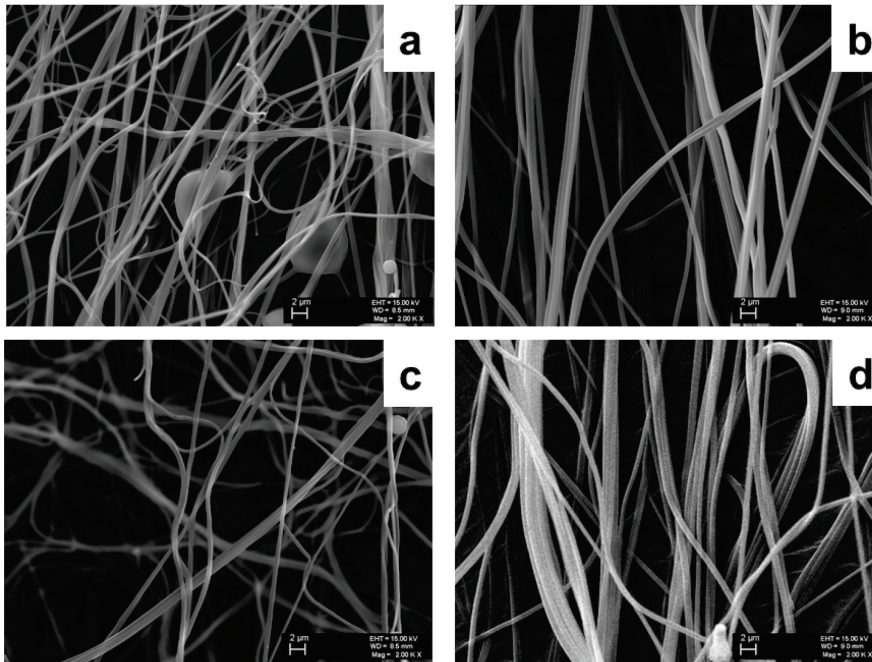
Figure 15. SEM images of mats obtained from solutions F-Br-10 (a), SO-Br-10 (b), F-Cl-10 (c) and SO-Cl-10 (d).

As discussed before, the specific stress values were slightly lower at higher concentrations of ILs (8 wt% and 10 wt%). As seen in Figure 16a, the mat obtained from solution SO-0 consisted of quite smooth nanofibres. Addition of IL [BMIm]Cl at concentrations of 8 wt% and 10 wt% influenced the fibre morphology. The fibres no longer had smooth surfaces (Figures 16b and 16c); surface roughness could be observed. The specific stress of the mats also decreased at higher concentrations, from 51.98±4.40 mN/tex (mat SO-0) to 9.09±1.00 mN/tex (mat SO-Cl-8), and 27.01±5.99 mN/tex (mat SO-Cl-10). Because the diameters did not drastically change at those concentrations, it could be concluded that morphology plays a major role in determining the specific stress. It could also be concluded that the morphology of the nanofibres was not influenced much by the addition of IL [EMIm]Br because the fibres obtained had smooth and even surfaces (Figures 16d and 16e). Also, the diameter did not drastically increase compared to mat SO-0. Specific stress values also did not drastically decrease (mat SO-Br-8's specific stress was 25.69±1.74 mN/tex, and mat SO-Br-10's specific stress was 39.73±2.16 mN/tex).
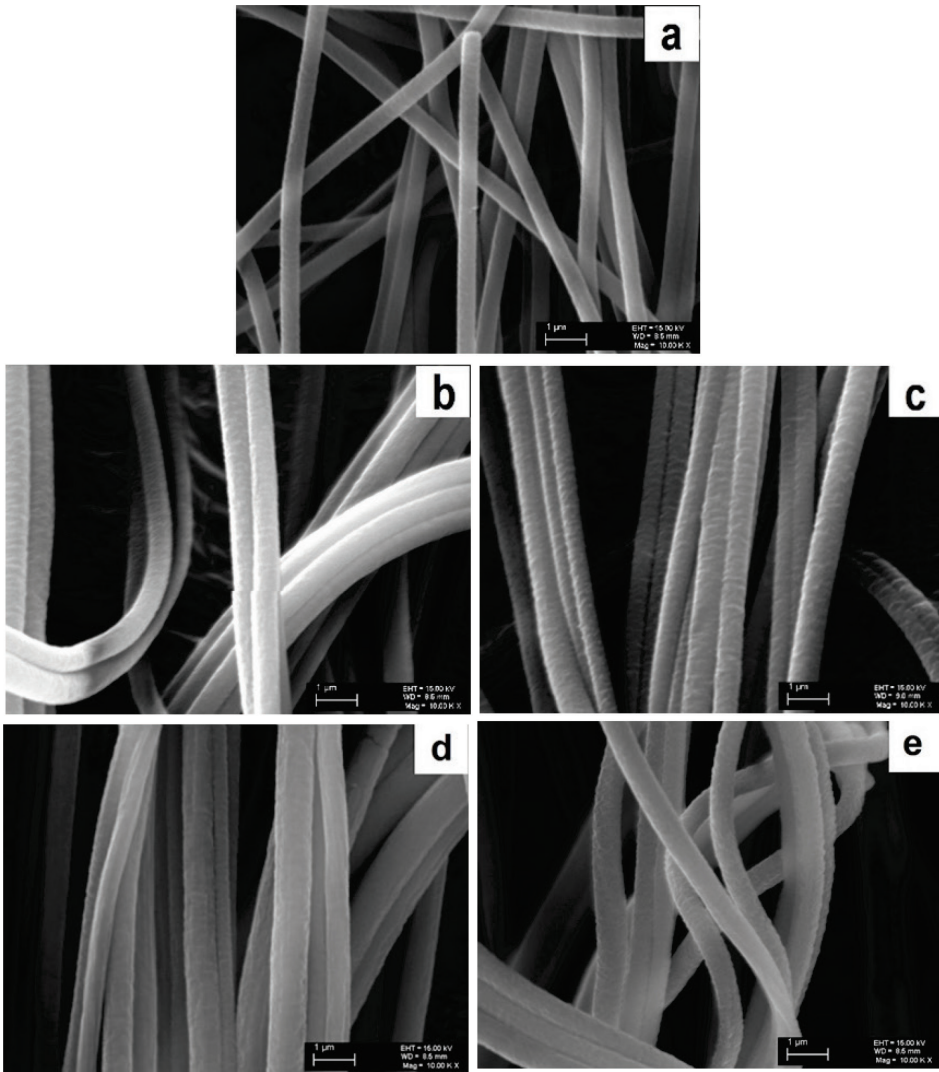
Figure 16. SEM images of mats obtained from solutions SO-0 (a), SO-Cl-8 (b), SO-Cl-10 (c), SO-Br-8, (d) and SO-Br-10 (e) (same as Fig. 8. in Paper III).

3.5.1 Fibre diameter and morphology of electrospun mats with ionic liquid and PANi salt

The effect of PANi concentration on the mats fibre diameters is presented in Figure 17. It can be seen that with increasing PANi concentration, the average fibre diameter increased. The most conductive mats (at 10 wt% PANi) showed quite moderate average fibre diameters. The finest fibres were produced from solutions without PANi. This shows the effect of fibre fineness on the mechanical properties of electrospun mats. On the other hand, with higher PANi concentrations the fibres were thicker, and the specific stress also decreased. At lower concentrations (0, 3, and 10 wt% of PANi), fibres with IL showed larger fibre diameters. With higher concentrations (15, 20 and 30 wt% of PANi), fibres without IL showed larger fibre diameters.
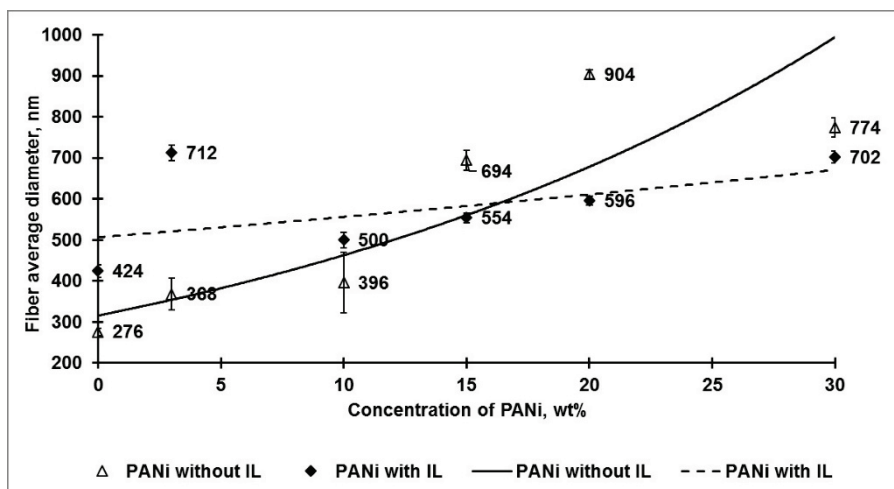
Figure 17. Effect of PANi concentration on the mat fibre diameter (same as Fig. 2. in Paper II).

The influence of IL on the morphology of electrospun mats from PAN–PANi–IL blends is shown in Figure 18, where two mats with 30 wt% of PANi are presented. In Figure 18a (mat from solution SO-PANi-30), PANi particles are clearly seen on the fibre surface. However, in Figure 18b (mat from solution SO-Cl-PANi-30) the surfaces of the electrospun fibres are smooth and without any extra particles. This evidence could explain the higher conductivity and higher specific stress of the mats obtained from solution SO-Cl-PANi-30 mats (mat conductivity was 0.60 µS/cm, and specific stress was 19.64±5.99 mN/tex) in comparison to those obtained from SO-PANi-30 (mat conductivity was 0.02 µS/cm, and specific stress was 11.06±0.55 mN/tex).
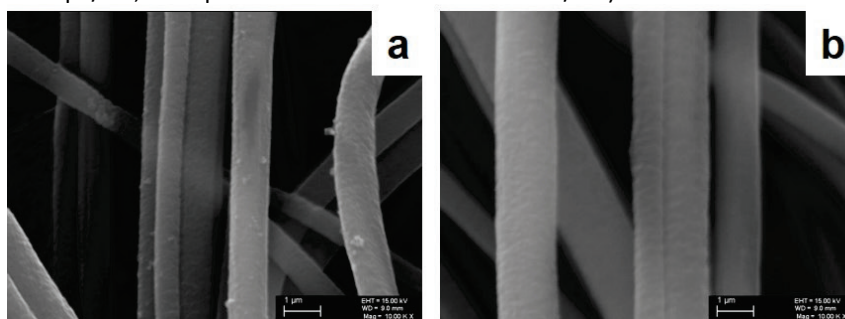
Figure 18. SEM images of mats obtained from solutions SO-PANi-30 (a) and SO-Cl-PANi-30 (b).

3.6 Mat conductivity versus mechanical properties

One essential goal of this study was to find the amount of conductive additive to produce electrospun mats with the best mechanical properties within the explored additive concentration range. In Figs. 19, 20, and 21 the influence of various conductive additives (ILs and PANi salt) and their concentrations on the mechanical properties and conductivity of electrospun mats is presented.
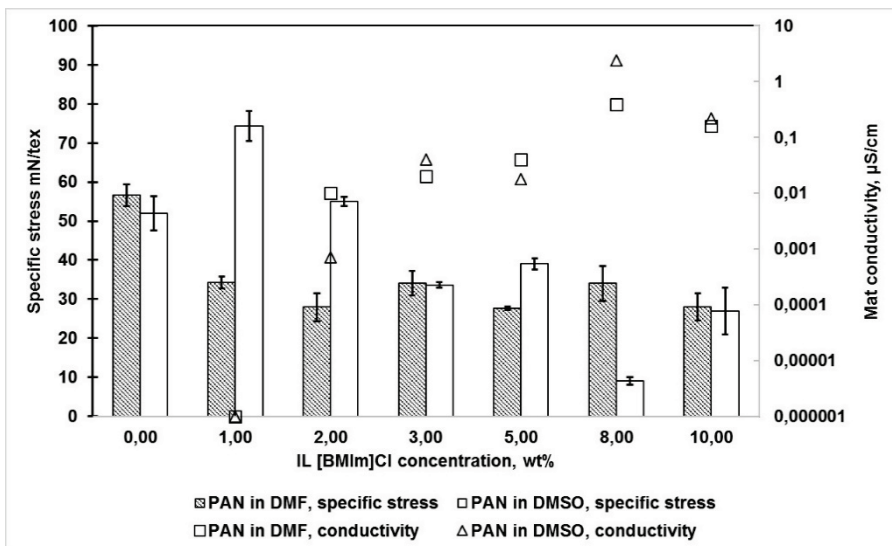
Figure 19. Impact of IL [BMIm]Cl and various solvents on the specific stress and conductivity of electrospun mats (same as figure 9, Paper III).
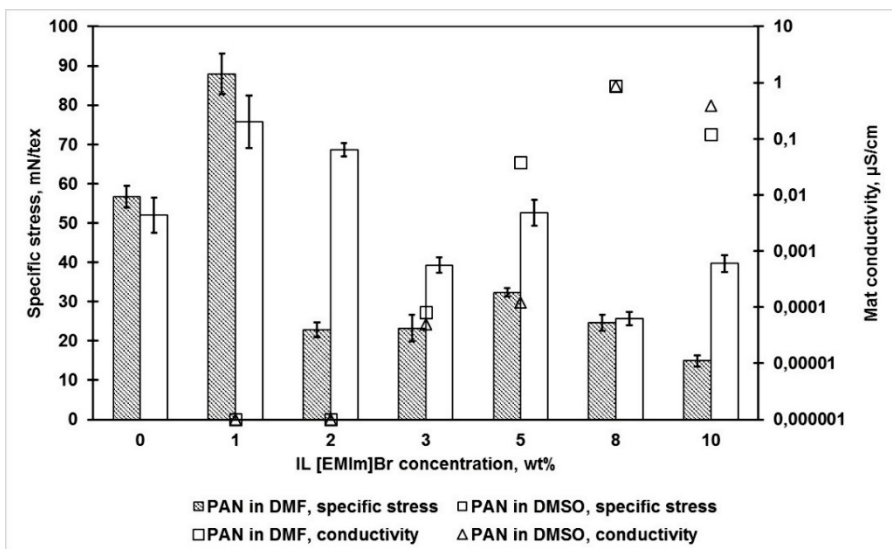

Figure 20. Impact of IL [EMIm]Br and various solvents on the specific stress and conductivity of electrospun mats (same as figure 10, Paper III).
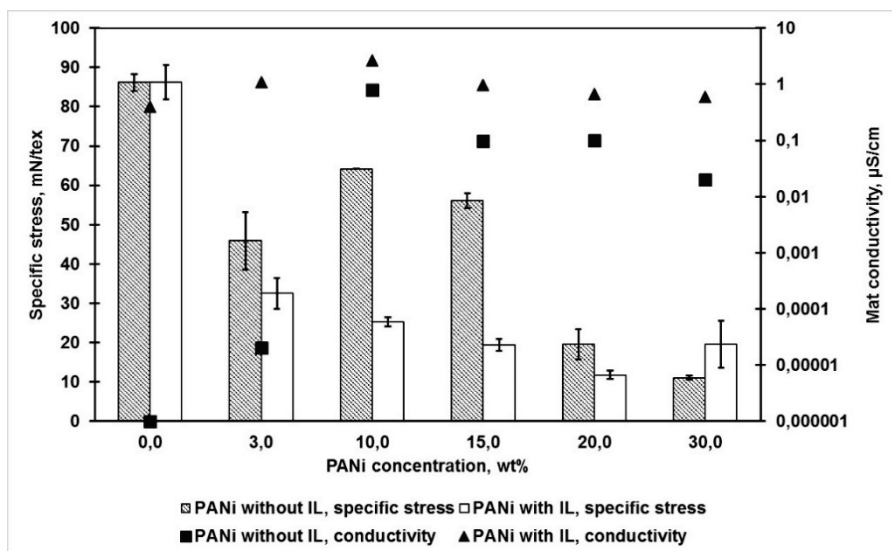
Figure 21. Impact of PANi salt and IL [BMIm]Cl on the tensile stress and conductivity of electrospun mats.

The mats with the best conductivity values were obtained from the solutions of PAN–PANi blend with IL [BMIm]Cl in DMSO. IL [BMIm]Cl also showed better conductivity in solutions without PANi.

The optimum concentration of conductive additive to achieve an adequate combination of conductivity and mechanical properties depends on the solvent and conductive additive used. It can be concluded that the best value for the mats without PANi salt was achieved with IL [BMIm]Cl and solvent DMF at an IL concentration of 8 wt%; thus, the mat conductivity was $3.90 \cdot 10^{-1}$ µS/cm and specific stress was 34.03 mN/tex. For mats with PANi salt and IL, the optimum concentration of PANi was found to be 10 wt%, with which the highest conductivity (2.62 µS/cm) and good mechanical properties (specific stress was 25.28±1.14 mN/tex) were achieved.

In the case of adding various ILs (Figures 19 and 20), it could be concluded that the mats with higher conductivity showed quite poor specific stress values. The most conductive mats with IL [BMIm]Cl were obtained from solutions SO-Cl-8 and F-Cl-8 (respectively, 2.39 and $3.90 \cdot 10^{-1}$ µS/cm), and with IL [EMIm]Br, the best conductivity was achieved with solutions F-Br-8 and SO-Br-8 ($8.80 \cdot 10^{-1}$ µS/cm). Among these mats, the best specific stress was shown by the mat from solution F-Cl-8, 34.03 mN/tex, and the worst specific stress was shown by the mat from solution SO-Cl-8, 9.09 mN/tex.

Conclusions

The aim of this study was to explore the effects of various conductive additives on the properties of electrospun mats. For that purpose, several additives, such as ILs ([BMIm]Cl; [EMIm]Br; [EMIm][TFSI]) and conductive polymer PANi were used. In the analysis part, various methods, such as SEM, mechanical tensile testing, conductivity measurements, and image analysis were carried out. Based on the study the following conclusions can be made:

1. The conductivity of the mats obtained from PAN in DMF with three different ILs changed from high to low in the following order: [EMIm]Br, [BMIm]Cl, and [EMIm][TFSI]. The conductivity of the mats obtained from PAN in DMSO with three different ILs changed from high to low in the following order: [BMIm]Cl, [EMIm]Br, and [EMIm][TFSI]. The most conductive mat was produced by using [BMIm]Cl at an IL concentration of 8 wt% with PAN in DMSO; the conductivity reached was 2.39 μs/cm.

2. A novel approach for preparing solutions containing PANi salt was proposed. IL [BMIm]Cl was introduced as an additive in PAN–PANi blended solutions to improve mat conductivity and PANi salt dispersibility in solution. The most conductive mat was obtained from a solution with 10 wt% of PANi with IL [BMIm]Cl (conductivity was 2.62 μS/cm); the mat conductivity achieved with the same PANi concentration without ILs was 0.22 μs/cm.

3. A suitable mat preparation process for mechanical testing was proposed. The results of mechanical testing were expressed as a dependence on the areal density of the mats – specific stress. This parameter was found to characterise the mats in the most applicable way.

4. According to the current research, mechanical properties are strongly dependent on the IL type and the solvent used for the preparation of polymer solution. Higher specific stress values were achieved with IL [EMIm]Br and with solvent DMSO.

5. Morphological studies confirmed the suitability of IL as an additive in PANi containing solutions. The obtained membranes were smoother and without any nondispersed particles. This evidence could explain the higher conductivity and higher specific stress at the higher concentrations of PANi. PANi mats with IL showed higher tensile stress at the concentrations where the conductivity was the highest (10 wt% to 15 wt% of PANi). The highest specific stress and tensile stress value was achieved with the mat SO-PANi-10, 64.18 mN/tex.

6. Studies confirmed the influence of fibre morphology, diameter distribution, and median diameter on the mechanical properties of electrospun mats. For example, at higher concentrations of IL, fibre diameters were more dispersed. The mat with the lowest specific stress (F-Br-10) showed a very dispersed fibre diameter distribution, which was the opposite of the mat with the highest specific stress (F-Br-1).

7. The amount of conductive additive needed to produce electrospun mats with the best mechanical properties within the explored concentration range with IL and PANi as additives was found. The best conductivity for the mats without PANi salt was achieved with IL [BMIm]Cl and solvent DMF at IL concentration 8 wt% where the mat conductivity was $3.90 \cdot 10^{-1}$ μS/cm and specific stress was 34.03 mN/tex. For mats with PANi salt, the optimum concentration of PANi was found to be

10 wt%, where the highest conductivity and good mechanical properties were achieved.

8. The obtained membranes can be categorized as semiconductors and applied in a wide range of energy-related applications.

The results of the current study pave the way to many further explorations to achieve satisfying properties of electrospun mats for various applications. There is a need to further explore techniques to improve the mechanical properties of conductive electrospun mats. Moreover, it is essential to study the dependence of mechanical properties on the molecular orientation of single nanofibres and fibre alignment inside the mat.

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Abstract
The Influence of Conductive Additives on the Mechanical Properties of Electrospun Mats

Obtaining conductive electrospun mats with good mechanical properties is essential for various applications in energy-related fields. The main aim of the current research was to study the influence of various conductive additives on the properties of electrospun mats. There is no published information about electrospinning conductive mats from polyaniline (PANi) salt–ionic liquid (IL) blends; also the effect of various ILs on the mechanical properties of electrospun mats has not been fully assessed. To fill in this gap, the effect of PANi and various ILs on the properties of electrospun mats was explored.

The influence of three different ILs, 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), 1-ethyl-3-methylimidazolium bromide ([EMIm]Br), and 1-ethyl-3-methyl bis(trifluoromethylsulfonyl)imide ([EMIm][TFSI]), on the properties of electrospinning solutions and electrospun mats was studied. Polyacrylonitrile (PAN) solutions in solvents dimethylsuloxide (DMSO) and DMF were prepared. ILs were added at concentrations up to 10 wt% (weight percent). The conductivity of the mats obtained from PAN in DMF with three different ILs changed from high to low in the following order: [EMIm]Br, [BMIm]Cl, and [EMIm][TFSI]. The conductivity of the mats obtained from PAN in DMSO with three different ILs changed from high to low in the following order: [BMIm]Cl, [EMIm]Br, and [EMIm]TFSI. The most conductive mat was produced by using [BMIm]Cl at an IL concentration of 8 wt% with PAN in DMSO. The conductivity reached was 2.39 µs/cm. A suitable mat preparation process for mechanical testing was also proposed. Specific stress was used to characterize the mechanical properties. According to the current research, mechanical properties are strongly dependent on the IL type and the solvent used for the preparation of the polymer solution. Higher specific stress values were achieved with IL [EMIm]Br and with solvent DMSO (highest specific value achieved was 87.93±5.15 mN/tex with 1 wt% of IL).

The studies confirmed the influence of fibre morphology, diameter distribution, and median diameter on the mechanical properties of electrospun mats. For example, at higher concentrations of IL, fibre diameters were more dispersed. The mat with the lowest specific stress (mats from solution PAN in DMF with 10 wt% of IL [EMIm]Br) showed a very dispersed fibre diameter distribution opposite to that of the mat with the highest specific stress (mats from solution PAN in DMF with 1 wt% of IL [EMIm]Br).

Also, the addition of conductive polymer PANi to the electrospinning solution was explored. The effect of adding 0 to 40 wt% of PANi salt to PAN electrospinning solutions in solvent DMSO with and without IL [BMIm]Cl was observed. According to the study, IL [BMIm]Cl in PANi salt-PAN solutions improved the dispersion of PANi particles. The obtained membranes were smoother and without any nondispersed particles. The most conductive mat was obtained from solution 10 wt% PANi with IL [BMIm]Cl (conductivity was 2.62 µS/cm); the mat conductivity achieved with the same PANi concentration without IL was 0.22 µs/cm. Morphological studies confirmed the suitability of IL as an additive in PANi containing solutions. This evidence could explain the higher conductivity and higher specific stress at the higher concentrations of PANi. PANi mats with IL showed higher values of tensile stress at the concentrations where the conductivity was the highest (10 wt% PANi). The highest specific stress value was achieved with the mat with 10 wt% PANi salt without IL (64.18 mN/tex).

The amounts of conductive additive needed to produce electrospun mats with the best mechanical properties within the explored concentration range with IL and PANi as additives was found. The best conductivity for the mats without PANi salt was achieved with IL [BMIm]Cl and solvent DMF at an IL concentration of 8 wt%, where the mat conductivity was $3.90 \cdot 10^{-1}$ µS/cm and the specific stress was 34.03 mN/tex. For mats with PANi salt, the optimum concentration of PANi was found to be 10 wt%, where the highest conductivity and good mechanical properties were achieved.

To conclude, a proper methodology was developed for testing the mechanical properties of membranes. A novel approach for preparing solutions containing PANi salt was proposed. IL [BMIm]Cl was introduced as an additive in PAN–PANi blended solutions to improve the mat conductivity and PANi salt dispersibility in the solution. Both PANi salt and the ILs enhanced the conductive properties of electrospun mats. The obtained conductive electrospun mats can be categorized as semiconductors that can be applied in a wide range of energy-related applications.

The results of the current study pave the way to many further explorations to achieve satisfying properties of electrospun mats for various applications. In further research, the dependence of mechanical properties on the molecular orientation of single nanofibers and fibre alignment inside a mat should be observed. According to the results, various techniques should be applied to improve the mechanical properties of conductive electrospun mats.

Lühikokkuvõte

Juhtivate lisandite mõju elektrokedratud nanokiuliste lausmaterjalide mehaanilistele omadustele

Heade mehaaniliste omadustega juhtivad nanokiulised lausmaterjalid leiavad laialdast kasutust erinevates elektrilistes rakendustes. Käesoleva doktoritöö põhieesmärgiks oli erinevate juhtivate lisandite mõju uurimine elektrokedratud nanokiuliste lausmaterjalide omadustele. Seni pole kirjanduses kirjeldatud elektroketrust polüaniliini (PANi) soola ja ioonvedelike segude lahustest, samuti pole põhjalikult hinnatud erinevate ioonvedelike mõju elektrokedratud nanokiuliste lausmaterjalide mehaanilistele omadustele. Täitmaks seda tühimikku, uuriti käesolevas doktoritöös PANi soola ja erinevate ioonvedelike mõju elektrokedratud nanokiuliste lausmaterjalide omadustele.

Uuriti kolme erineva ioonvedeliku, 1-butüül-3-metüülimidasoolium kloriidi ([BMIm]Cl), 1-etüül-3-metüülimidasoolium bromiidi ([EMIm]Br) ja 1-etüül-3-metüülimidasoolium bis(trifluorometüülsulfonüül)imiidi ([EMIm][TFSI]), mõju elektroketruslahuse ja elektrokedratud nanokiuliste lausmaterjalide omadustele. Esmalt valmistati polüakrüülnitriili (PAN) lahused erinevates lahustites, milleks kasutati dimetüülsulfoksiidi (DMSO) ja dimetüülformamiidi (DMF). Ioonvedelikke lisati lahustele kuni 10 massiprotsendi ulatuses. PAN-DMF-is lahustest saadud nanokiuliste materjalide elektrijuhtivus vähenes järgmises järjekorras [EMIm]Br, [BMIm]Cl and [EMIm][TFSI]. PAN-DMSO-s lahustest saadud nanokiuliste materjalide elektrijuhtivus vähenes järgmises järjekorras [BMIm]Cl, [EMIm]Br ja [EMIm][TFSI]. Kõige kõrgema elektrijuhtivusega materjal saadi lahusest, mis sisaldas 8% ioonvedelikku [BMIm]Cl PAN-DMSO-s. Saavutatud elektrijuhtivuse väärtus oli 2,39 µS/cm. Antud doktoritöö käigus arendati välja nanokiuliste lausmaterjalide ettevalmistusprotsess mehaaniliste katsetuste läbiviimiseks. Mehaaniliste omaduste iseloomustamiseks kasutati suhtelist katkekoormust. Antud katsetuste tulemusena selgus, et mehaanilised omadused sõltuvad suuresti kasutatud ioonvedelikust ning lahustist. Kõrgemad suhtelise katkekoormuse väärtused saadi ioonvedelikuga [EMIm]Br ja lahustiga DMSO (kõrgeim suhtelise katkekoormuse väärtus oli 87,93±5,15 mN/tex 1%-lise ioonvedeliku kontsentratsiooni juures).

Katsetuste tulemused kinnitasid, et kiudude morfoloogia, kiudude diameetrite jaotuvus ning mediaandiameetri väärtus mõjutavad oluliselt elektrokedratud nanokiuliste materjalide mehaanilisi omadusi. Näiteks ioonvedelike kõrgema kontsentratsiooni puhul olid kiudude diameetrite väärtused laiema jaotusega. Kõige madalama suhtelise katkekoormuse väärtusega nanokiuliste lausmaterjalide (valmistatud lahusest PAN-DMF-is 10%-lise [EMIm]Br-i sisaldusega) puhul olid kiudude diameetrite väärtused hajusamad võrreldes materjaliga, mille suhteline katkekoormus oli kõrgeim (valmistatud lahusest PAN-DMF-is 1%-lise [EMIm]Br-i sisaldusega).

Käesolevas doktoritöös uuriti ka juhtiva polümeeri PANi lisamist elektroketruslahustele. Täpsemalt uuriti PANi soola lisamist vahemikus 0-40% PAN-DMSO-s lahustele koos ioonvedeliku [BMIm]Cl lisamisega ning ilma ioonvedeliku lisamiseta. Tulemused näitasid, et ioonvedelik parandab PANi osakeste dispersiooni lahuses. Saadud nanokiud olid siledamad ning ilma koaguleerunud osakesteta. Kõige kõrgema juhtivusega materjal saadi lahusest, mis oli valmistatud ioonvedeliku [BMIm]Cl lisamisega 10 %-lisele PANi lahusele. Antud lahuse juhtivus oli 2,62 µS/cm, samas kui ilma ioonvedelikuta valmistatud materjali juhtivus oli 0,22 µS/cm.

Kiudude morfoloogilised uuringud kinnitasid samuti ioonvedeliku sobivust PANi-t sisaldavate lahuste lisandina. Sellele annavad kinnitust näiteks kõrgema juhtivuse ja suhtelise katkekoormuse tulemused PANi kõrgematel kontsentratsioonidel. Ioonvedeliku lisamisega valmistatud elektrokedratud materjalid näitasid suhtelise katkekoormuse kõrgemaid väärtusi nendel kontsentratsioonidel, kus ka juhtivus oli kõrgeim. Kõrgeim suhteline katkekoormus (64,18 mN/tex) saavutati materjali puhul, mis oli elektrokedratud lahusest, kus oli 10% PANi soola ilma ioonvedeliku lisamiseta.

Doktoritöö käigus leiti optimaalne juhtivate lisandite hulk, mis võimaldab elektrokedrata parimate mehaaniliste omadustega materjale uuritud lisandite (erinevad ioonvedelikud ja PANi sool) kontsentratsioonide vahemikus. Parim juhtivus ilma PANi soolata materjalide puhul saavutati ioonvedeliku [BMIm]Cl ja lahusti DMF kasutamisel ioonvedeliku kontsentratsioonil 8%. Antud kontsentratsioonil mõõdeti materjali elektrijuhtivuseks $3{,}90 \cdot 10^{-1}$ µS/cm ja suhtelise katkekoormuse väärtuseks $34{,}03 \pm 4{,}47$ mN/tex. PANi-t sisaldavate materjalide puhul leiti optimaalseimaks PANi sisalduseks 10%, mille juures mõõdeti elektrijuhtivuse väärtuseks 2,62 µS/cm ja suhtelise katkekoormuse väärtuseks $25{,}28 \pm 1{,}14$ mN/tex.

Kokkuvõttes võib järeldada, et antud doktoritöö raames töötati välja sobiv metoodika elektrokedratud lausmaterjalide mehaanilisteks katsetusteks. Pakuti välja uudne lahendus PANi soola sisaldavate elektroketruslahuste valmistamiseks. Selleks kasutati ioonvedelikku [BMIm]Cl kui lisandit PAN-PANi lahustes, et ühelt poolt tõsta juhtivust ning teisalt parandada PANi soola dispergeeritavust lahuses. Katsetuste tulemusel saab öelda, et nii PANi sool kui ka erinevad ioonvedelikud parandasid elektrokedratud nanokiuliste lausmaterjalide elektrijuhtivust. Saadud juhtivad elektrokedratud lausmaterjalid võib liigitada pooljuhtideks ning neid saab kasutada erinevates elektrilistes rakendustes.

Käesoleva doktoritöö tulemused loovad eeldused uutele uuringutele tootmaks sobivaimate omadustega elektrokedratud materjale erinevaks otstarbeks. Edasises uurimistöös võiks keskenduda üksiku kiu makromolekulaarse ehituse ja makromolekulide orienteerituse ning kiudude endi orienteerituse mõju uurimisele lausmaterjali mehaanilistele omadustele. Vastavalt saadavatele tulemustele tuleks rakendada erinevaid meetodeid juhtivate lausmaterjalide mehaaniliste omaduste edasiseks parendamiseks.

Appendix

Paper I

Savest, N., **Plamus, T.**, Tarasova, E., Viirsalu, M., Krasnou, I., Gudkova, V., Küppar, K.-A., Krumme A. (2016) The effect of ionic liquids on the conductivity of Electrospun polyacrylonitrile membranes. Journal of Electrostatics, 83, 63-68.

The effect of ionic liquids on the conductivity of electrospun polyacrylonitrile membranes

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ARTICLE INFO

ABSTRACT

Adding conductive additives to electrospinning solutions has been proven to increase the conductivity of electrospun membranes. The aim of this study was to learn the effect of ionic liquids (ILs) on the polyacrylonitrile membranes conductivity. Three different ionic liquids were used with concentration to 10 wt%. The conductivity of the membranes increases from picoS range without using IL to microS range with adding IL. At concentration 8 wt% ILs the percolation threshold was observed with maximum conductivity of the electrospun membranes. The maximum conductivity was measured to be 2.39 μS/cm.

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1. Introduction

In recent years, the fibrous polymeric materials with improved electrical properties produced by using electrospinning method are of great interest. Such materials have successfully found the application in filtration, protective clothing, optical electronics, and tissue engineering scaffolds [1–4].

Electrospinning is an efficient and simple method that is able to generate different types of fibers with diameter in the nanometer to micron scale. The fibers are produced from polymer solution or melt [5–7]. By adding conductive additives such as carbon nanotubes (CNT), carbon black (CB), graphite [8] or ionic liquids (ILs) the conductivity of polymeric electrospun materials can be improved. There are a lot of research works presenting the data on using CNT and CB, but there are little data on influence of ILs on the conductivity of electrospun membranes [3,9,10]. In the work by Wei Cheng et al. the effect of ILs on the morphology of polyacrylonitrile (PAN) membranes was investigated [11]. E. Kowsari and M. Mallakmohamadi used adding IL as an electrolyte to PAN solution to reduce electrospun fiber size [9]. No data were found by us on the effect of ionic liquids as additives on the conductive properties of polyacrylonitrile membranes. Thus, the focus of this study was to investigate the effect of three different ionic liquids on the conductivity of electrospun polyacrylonitrile fibrous membranes with the aim to propose one more alternative perspective conductive additive for electrospun materials.

Ionic liquids (ILs) are organic salts that consist entirely of ions. ILs are mainly found in the liquid state at room temperature [12,13] and show good compatibility and solubility in organic polymer solutions. The properties of IL can be modified by adjusting the structures of its anion or cation or both [14]. Their unique properties such as negligible vapor pressure, excellent chemical stability, high thermal stability and high ionic conductivity [12,13,15] make them ideal for using as fillers in polymer solutions for electrospinning.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN) powder purchased from Polysciences Inc. with molecular weight of 150,000 was used as polymer matrix for solutions preparation. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solvents were purchased from SigmaAldrich. 1-etyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide EMImTFSI was purchased from SigmaAldrich. 1-buthyl-3-methylimidazolium chloride BMImCl and ethyl-3-

* Corresponding author.
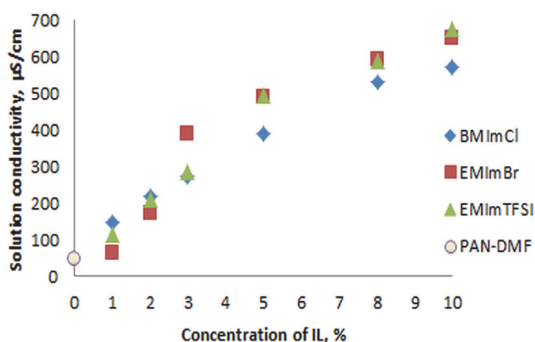*E-mail address:* natalja.savest@ttu.ee (N. Savest).

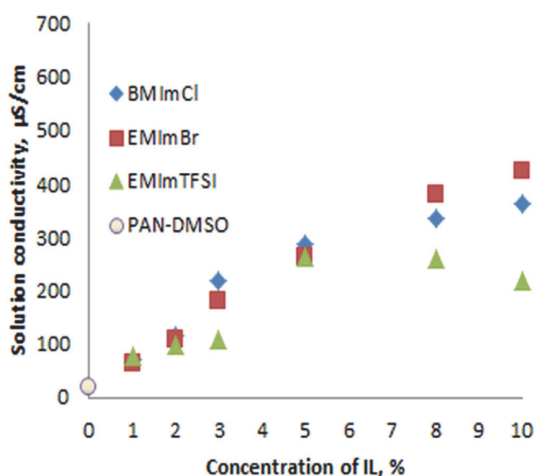**Fig. 1.** The effect of ionic liquid on the conductivity of PAN solution in DMF.

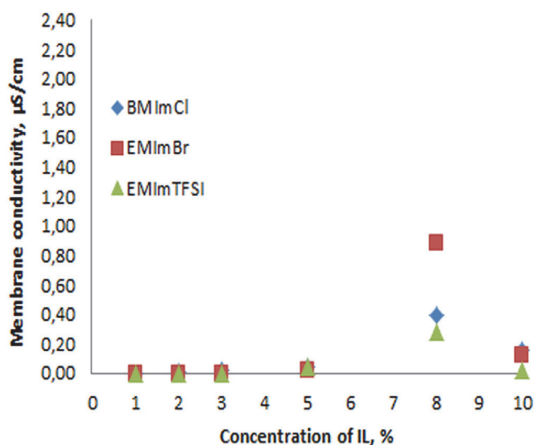**Fig. 2.** The effect of ionic liquid on the conductivity of PAN solution in DMSO.

Fig. 3. The effect of ionic liquid on the conductivity of electrospun membranes obtained from the solution PAN in DMF.
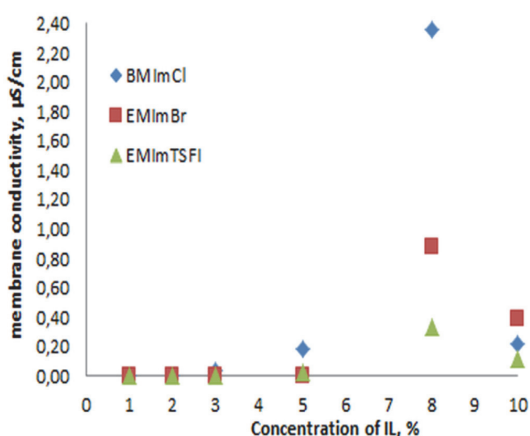

Fig. 4. The effect of ionic liquid on the conductivity of electrospun membranes obtained from the solution PAN in DMSO.

methylimidazolium bromide EMImBr ionic liquids (ILs) were synthesized in the laboratory according to the methods described in the literature [16,17]. Shortly, to synthesize 1-buthyl-3-mthylimidazolium chloride 164 g 1-methylimidazolium (Merck) and 260 g chlorobutane (Merck) were placed into round bottom flask fitted reflux condenser system and mixed at 75 °C for 72 h until two phases formatted. Then the colorless viscous liquid was cooled and washed with ethyl acetate (Merck) three times by using separation funnel. The ready ionic liquid was dried under vacuum for 3 h. EMImBr was synthesized by mixing 326 g bromoethane (Merck) and 164 g 1-methylimidazolium in the round bottom flask fitted with reflux system at 40 °C for 24 h. Then the viscous liquid was washed with ethyl acetate three times in a separation funnel and dried under vacuum for 3 h.

2.2. Solution preparation for electrospinning

Two PAN solutions were prepared in DMF and DMSO solvent. Two different solvents were chosen to investigate their influence on the conductivity of solution and electrospun membranes. The concentration of PAN in solvents was fixed at 10 wt%. To obtain homogeneous solution the polymer was dissolved in solvent and stirred mechanically with magnetic stirrer at 40 °C for 24 h. Then the ionic liquids were added to polymer solutions at concentration from 1 wt% to 10 wt% and the solution was stirred at 40 °C for 1.5 h to achieve homogeneous solution for electrospinning. 10 wt% of ILs was the maximum in PAN solutions to be able to carry out the electrospinning process at room temperature.

Electrospinning was performed by using horizontal electrospinning setup with cylindrical rotating collector covered with the aluminum folium at room temperature. The spinning solution was placed into 1 ml syringe with the needle diameter 0.4 and 0.6 mm. The choice of the needle diameter depended on the solution viscosity. The solution was electrospun at 23 kV with the distance 8–10 cm between the needle and the collector, and the pumping feed rate 0.6 ml/h. The electrospinning process was performed at room temperature. The influence of the humidity was not investigated in this study.
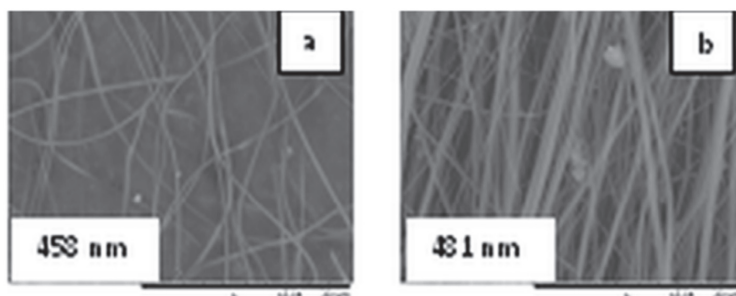
Fig. 5. SEM images of nanofibrous membranes prepared from the pure solutions PAN in DMF (a) and DMSO (b).

2.3. Conductivity measurement

The conductivity of ILs used and PAN solutions was measured with the conductivity meter (Metler Toledo SevenCompact Conductivity Meter) at room temperature. The conductivity of pure BMImCl was measured to be 33.4 μS/cm. The conductivity of pure EMImBr was 4510 μS/cm and EMImTFSI was about 8200 μS/cm.

The conductivity of the membranes obtained from PAN solutions was measured with two-point method by using High Resistance Low Conductance Meter HR2. All membranes were prepared for measurement of one size of 1 × 3 cm. Before conductivity measurement the membranes were pressed.

2.4. Analysis of membrane morphology

The morphology of electrospun membranes was analysed by Scanning Electron Microscope (SEM) (TM1000, Hitachi High-Technologies Europe GmbH, Germany).

3. Results and discussion

3.1. Effect of ionic liquids on PAN solution conductivity

Ionic liquids are salts comprising organic cations associated with inorganic or organic anions. In this study we used three imidazolium-based ionic liquids with different inorganic anions in PAN solutions as additives to influence the conductivity of elecrtospun membranes. The objective of the work was to compare the effect of different types of IL with different inions on the electrical properties of polymer solutions and electrospun fibrous membranes obtained from these solutions. The results are presented in Figs. 1 and 2.

Figs. 1 and 2 demonstrate the general trend of increasing of solution conductivity with ionic liquid concentration increasing in both PAN solutions, in DMF and DMSO. The noticeable increase of conductivity is already observed at small amount of added IL, at concentration of 2%. The linear dependence of solution conductivity with the increase of IL amount can be clearly observed. Comparing the tendency of IL influence on solutions conductivity it can be seen from Figs. 1 and 2 that the conductivity of PAN solution in DMF is higher 1.5 times with all three ILs used than in the solution PAN in DMSO. This can be explained with the possibility of ionic liquids to ionize to free ions in DMF solvent. The conductivity increases when the quantity of free ions in the solution increases [11]. The conductivity of pure solvents also affects the results of solution conductivity. The measured conductivity of DMF solvent was 0.719 μS/cm that is 3.5 times higher than the conductivity of pure DMSO solvent, 0.253 μS/cm, respectively. The conductivity of pure PAN solution in DMF was also measured to be higher, 48 μS/cm than of PAN solution in DMSO, 21.5 μS/cm. By adding EMImBr and EMImTFSI the conductivity of PAN solution in DMF (Fig. 1) is higher than with added BMImCl.

3.2. Effect of ionic liquids on electrospun membrane conductivity

Figs. 3 and 4 shows that there is only small increase in the conductivity of the membranes obtained from both PAN solutions with added ILs in concentration up to 8 wt%. At 8 wt% of ILs the conductivity of electrospun membranes increases sharply and then decreases considerably at 10 wt%. This evidence can be explained with electrical percolation threshold. In the case of electrical percolation the conductivity increases remarkably (sometimes by several orders of magnitude) when the concentration of conductive filler exceeds its critical value. Percolation threshold is the minimum of filler content in polymer matrix after which there is no significant changes in the conductivity [18—20].

Fig. 3 demonstrates that the most conductive membranes obtained from the solution PAN in DMF were produced by using EMImBr. The conductivity was measured to be 0.88 μS/cm. Two others ILs, BMImCl and EMImTFSI show lower increase in membrane conductivity. Depending on IL used the conductivity of membranes changes from high to low in the following order: EMImBr, BMImCl and EMImTFSI. In the case of the membranes obtained from the solution PAN in DMSO (Fig. 4), it is seen that the maximum conductivity, 2.39 μs/cm, was measured when 8 wt% of BMImCl was added to polymer solution as a conductive additive. Much smaller effect on membrane conductivity was detected when 8 wt% EMImBr was used. The conductivity was measured to be 0.88 μS/cm, which is the same that with the solution PAN in DMF (Fig. 3). The conductivity of the membranes obtained from both solutions, in DMF and DMSO, with added EMImTFSI, was fixed at the same range, 0.28—0.30 μS/cm. The influence of used three ILs in the solution PAN in DMSO on the membrane conductivity can be put in the following order, from high to low: BMImCl, EMImBr and EMImTFSI.

From Figs. 3 and 4 it can be seen that the percolation threshold was observed with all tree ILs with larger or smaller extent at the content of IL of 8 wt%. Basing on the "percolation theory" [21] it can be assumed that at this concentration the conductive additive, IL, is evenly distributed within the polymer matrix. Then, with increasing ILs concentration to 10 wt% the membranes conductivity decreases showing only insignificant influence on the electrical properties of the electrospun material.
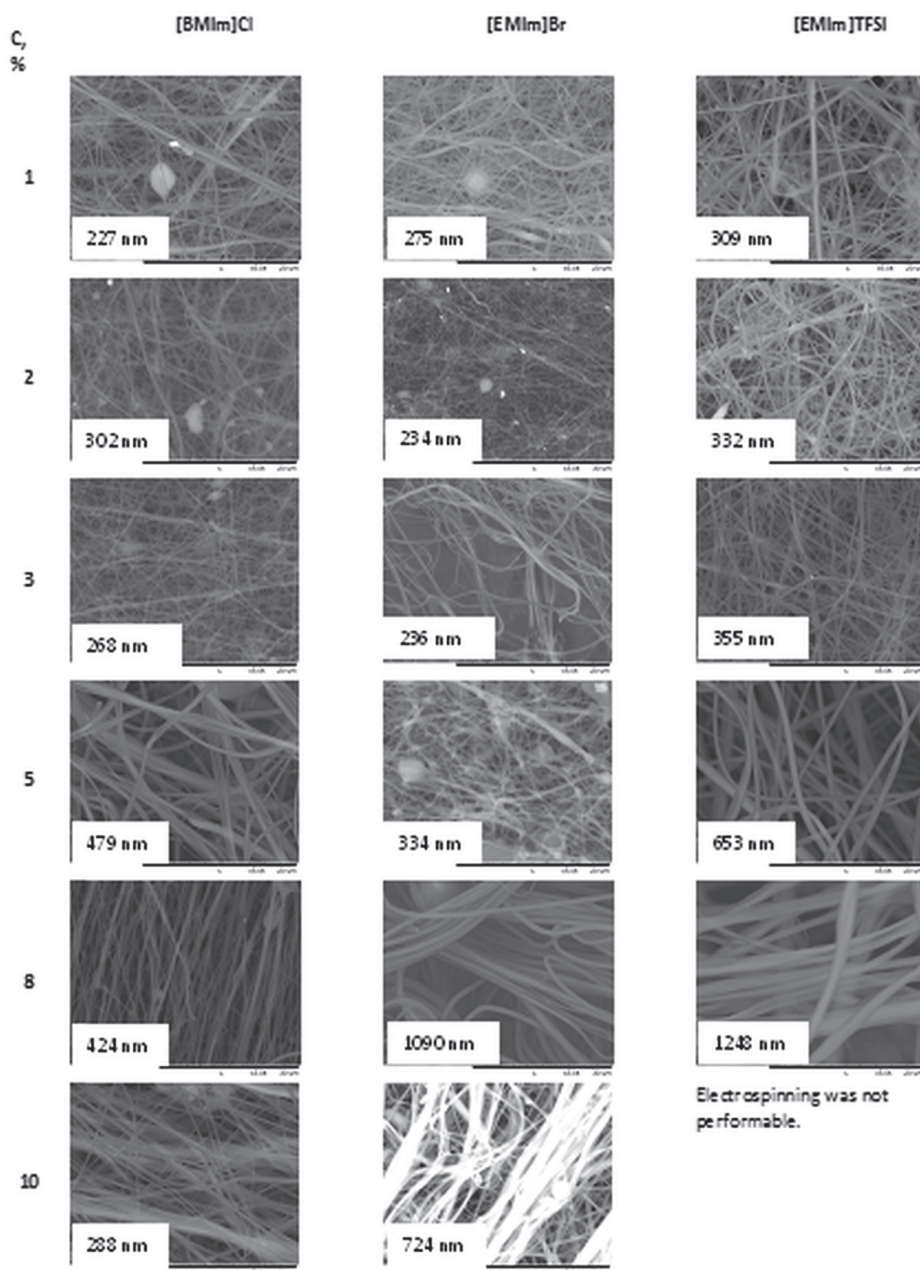
Fig. 6. SEM images of nanofibrous membranes prepared from the pure solutions PAN in DMF with different content of ILs.

3.3. Morphology of electrospun membranes with added ionic liquids

The changes in the morphology of electrospun membranes with using ILs as additives in polymer solutions are presented in Figs. 6 and 7. For comparison the morphology of the fibers obtained from the pure polymer solutions without adding IL is demonstrated in Fig. 5. The fibers produced from the pure PAN solutions were observed to be uniform with the average diameter 460 nm. It can be also seen from Fig. 5 that all of the pure PAN
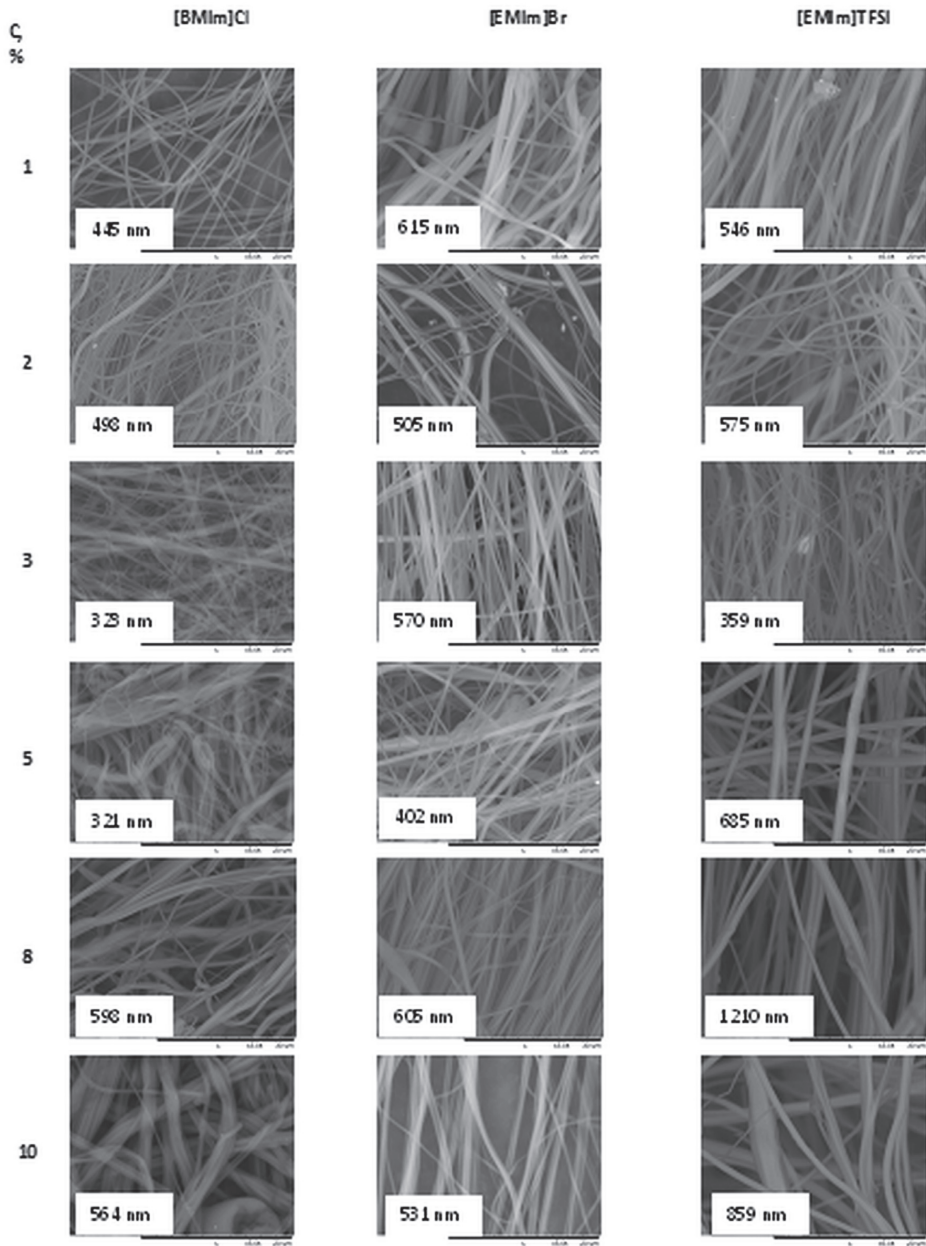
Fig. 7. SEM images of nanofibrous membranes prepared from the pure solutions PAN in DMSO with different content of ILs.

fibers had smooth surfaces that shows full evaporation of the solvents in the nanofibers before the fibers had reached the collector. From Figs. 6 and 7 it is seen that the fibers morphology depended not only on the ILs added but also on the solvent. It can be also observed that three ILs affected the morphology in different way at the same concentration. Fig. 6 shows that the morphology of the composite nanofibers obtained from the blend PAN-ILs in DMF with the content of ILs up to 3 wt% was similar to that of PAN fibers. The fibers produced were smooth without any detectable beads. The fiber diameter decreased. This

can be explained with the evidence that the adding of even small amount of IL increases the solution conductivity, thus there are much more free charge carries in the solution and the spinning jet stretches more during the process [11]. From the concentration 5 to 10 wt% of ILs added to the solution PAN in DMF (Fig. 6) the produced nanofibers became inconsistent with diameter changing in range from 334 nm to 1248 nm. This evidence could be mainly caused by the increasing electric charge that was introduced by the ionic salts, ILs, to the electrospinnable PAN solutions [22]. In addition, the surface of the fibers obtained from the solutions with larger ILs content (Fig. 6) was rougher; the fibers shape became more ribbon-like. The surface roughness may be attributed to the slower evaporation of DMF that was hindered by adding ILs. The mixing of IL with solvent and polymer matrix leads to the interactions with each other preventing the enough evaporation. From Fig. 7 it can be seen that comparing with pure PAN fibers there was not noticed the decrease in the diameter of the nanofibers produced from the blend of PAN-ILs in DMSO solvent, especially with adding EMImBr and EMImTFSI ionic liquids. Most significantly the fiber diameter increased when ILs content was increased from 8 to 10 wt% in the solution PAN in DMSO. This can be explained with worth evaporation of DMSO solvent comparing with DMF. The solution further conductivity increase causes the increase in the electrostatic force that can shorten the stretching of the jet with the result of larger fiber diameter [22].

4. Conclusions

Using ionic liquids BMImCl, EMImBr and EMImTFSI as the additives in PAN solutions has been shown to improve the electrical properties of electrospun membranes. With small increasing of the concentration of ILs the membrane conductivity has significantly increased comparing to the membranes obtained from the pure PAN in DMF and PAN in DMSO solutions. At concentration 8 wt% of all three ILs the percolation threshold has been fixed with maximum achieved conductivity of 2.39 μS/cm of the membrane when [BMIm]Cl was added to PAN in DMSO solution. The adding ILs to PAN solutions influences the morphology of electrospun membranes. At higher concentration of ILs fibers with thicker diameter were produced.

Acknowledgements

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Paper II
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Electrospun conductive mats from PANi-ionic liquid blends

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ARTICLE INFO

ABSTRACT

The study is focused on the production of conductive mats from polyaniline - ionic liquid (IL) blends by electrospinning. PAN was used as a binding matrix in blends. The effect of adding 3 to 40 wt.% of polyaniline salt to PAN blend was investigated on the electrical and mechanical properties of the mats. 10 wt.% of IL was used in PAN blends for improving the dispersion of PANi particles. IL increased the conductivity of the material three times, comparing with the materials without IL. The optimum concentration of polyaniline in blend was 10–12.5 wt.% to produce mechanically strong mats.

1. Introduction

Intensive development of nanotechnology and active use of nano-devices put the scientists to look for the more attractive material combinations. Electrospinning is well known method that is used to produce nanomaterials with enhanced properties from polymer solutions [1–3]. Electrospun materials have already found the applications in various fields such as tissue engineering, optoelectronics, supercapacitors, pressure sensors [4–7]. The advantage of electrospinning method is the possibility to produce nanofibrous materials with high surface area-to-volume ratio, good mechanical and enhanced electrical properties. Incorporating conductive fillers into non-woven mats provides the possibility to electrospin fibrous materials in nanosize with improved conductive properties. Conductive fillers such as carbon nanotubes [8–10], carbon black [11,12], and graphene [13,14], ionic liquids [14–16] are approved additives in electropsun materials.

For the last time conjugated polymers, also called conductive polymers, have been of great interest as good candidates for being conductive additives in electrospinning solutions due to their superior properties [17]. Conductive polymers have very good electrical properties and their conductivity can be increased from 10^{-10}–10^2 S/cm by doping. One more advantage of using conductive polymers is easy synthesis and the potentiality to tune up the properties by synthesis methods [18].

Among the organic conjugated polymers, polyaniline (PANi) is one of the most investigated because of its easy synthesis, the cheapness of the monomer aniline and simple doping/dedoping process. There are

five different forms of polyaniline. Emeraldine form is in the greatest request due to very good environmental stability comparing to other forms. PANi emeraldine form is classified into two ones, emeraldine base (EB) and emeraldine salt (ES). Both EB (insulator) and ES (conductive form) are insoluble almost in all common organic solvents due to the conjugated structure. By doping EB with a suitable acid it can be transferred into ES form and made soluble in several solvents. The interest to use PANi as alternative conductive filler is increasing due to the sufficient conductivity of PANi, 1-100 S/cm [19]. However, the small molecular weight and poor solubility of PANi limits its application to be used in pure form of PANi solutions to produce the nanomaterials with enhanced electrical properties by electrospinning method. Different efforts such as coating electrospun mats with conducting polymers, using functional dopans or introducing side chains have been done to improve the processability of PANi [20,21]. The most widely used technique to prepare electrospun mats based on PANi is electrospinning of solution blends with adding binder polymer [22–25].

Most of the results of the literature data report the using doped PANi in binder polymer solutions. Usually, EB is doped with acid to be transferred into ES conductive form either before adding into solution or within preparing the solution. The works in literature present very various results achieved with increasing the conductivity of the electrospun materials based on doped PANi. The range of the conductivity of the produced mats was from insulating to conductive [17,22]. But there are several disadvantages to use doped PANi instead of pure conductive filler. The process of the solution blend preparing is longer

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combining several steps to get enough conductive ES doped. The filtration of the doped PANi is usually needed before it using in electrospinning solution that makes the estimation of the real content of PANi in final solution more complicated [26]. The transferring EB into ES by doping can influence the conductivity value of the prepared conductive PANi form PANi [27].

To eliminate these obstacles the focus of the present research study is to present a new procedure for producing electrospun conductive nanofibrous mats from PANi salt solution with added ionic liquid and blended with binder polymer. IL has been proposed by us as the additional solvent to improve the solubility of PANi salt. First of all, the using of ionic liquid (IL) will help to overcome the problem of poor solubility of PANi salt in common solvents. Secondly, the adding IL can maintain the decreased conductivity when insulator polymer is used as a binder in electrospinning PANi solution for being able to perform electrospinning process. Thirdly, there is no need to use filtration step as it is done after PANi base doping procedure.

Ionic liquids (ILs) have become popular due to their unique properties such as negligible vapour pressure, excellent chemical stability, high thermal stability and high ionic conductivity [28,29]. Room temperature ionic liquids are the salts in liquid state at room temperature. They are also called as "green solvents". The liquid range of ILs is up to more 400 K and their density is higher than water one. One of the beneficial properties of ILs in use is the miscibility with the substances of very wide range of polarities and the ability to dissolve many organic and inorganic compounds [29]. Owning high ionic conductivity ILs can be used to improve the conductive properties of the electrospun materials that have been demonstrated in our previous research works [16,30].

To the best of our knowledge, there are no studies published in the literature on the electrospinning conductive mats from PANi salt – ionic liquid blends. The aim of this research is to produce the mats not only with enhanced electrical properties but also with enough good mechanical properties to make the material more attractive for the real application in the field of smart technology.

2. Materials and methods

2.1. Materials

Polyaniline (emeraldine salt) (Aldrich, average $M_w > 15,000$, in powder) was used for preparing the blend of PAN-PANi salt - ionic liquid in solvent for electrospinning. Polyacrylonitrile (PAN) in powder purchased from Polysciences Inc. with molecular weight of 150,000 was used as a binder polymer in PANi blend solution. Dimethylsulfoxide (DMSO) solvent (with purity ≥ 99.9%) was purchased from SigmaAldrich for preparing the blended solutions. 1-buthyl-3-methylimidazolium chloride [BMIm]Cl ionic liquid (IL) was added to PAN-PANi solution as the additional solvent to improve the dispersion of PANi salt in DMSO. [BMIm]Cl was synthesized in the laboratory according to the method described in the literature [31,32]. Shortly, to synthesize 1-buthyl-3-mthylimidazolium chloride 164 g 1-methylimidazolium (Merck) and 260 g chlorobutane (Merck) were placed into the round bottom flask fitted reflux condenser system and mixed at 75 °C for 72 h until two phases formatted. Then the colourless viscous liquid was cooled and washed with Ethyl Acetate (Merck) three times by using separation funnel. The ready ionic liquid was dried under vacuum for 3 h.

2.2. Preparation of PAN-PANi solution

The solutions with different concentration of PANi, from 3 wt.% to 40 wt.%, were prepared in two steps. Firstly, PANi was dispersed in DMSO solvent mechanically by magnetic stirring for 48 h at 40 °C. In the next step, to make the solution spinnable PAN as a binder polymer was added and PANi-PAN blend in DMSO was mixed mechanically by

magnetic stirring for more 24 h at 40 °C. The concentration of PANi in blended solution was calculated on the dry matter of binder polymer. The concentration of binder polymer was 9 wt.% in solution and did not change. The binder polymer was not removed from the mats by washing after electrospinning. 10 wt.% of IL was added to the ready blended solution using mechanical mixing for 1 h at 40 °C before electrospinning performing.

2.3. Electrospinning

The prepared solutions were electrospun by using the horizontal homemade electrospinning set-up. PAN-PANi blended solution was put to the syringe with needle inner diameter 0.8 mm. The nanofiberous mats were collected on the drum collector at pumping rate 0.9 mL/h with distance of 8–10 cm between the collector and the needle tip. The voltage of 20–25 kV was applied to collect the nanofibers on the drum collector. The electrospinning of PAN-PANi blend solutions was performed at room temperature.

2.4. Analysis of electrospun material

Morphology. The morphology of the nanofibrous PAN-PANi mats was analysed by using Scanning Electron Microscope (SEM) (Zeiss EVO MA 15). No conductive coating was deposited onto the samples. The fibre diameter was measured and presented as an average one ± standard deviation.

Conductivity. The electrical conductivity of the electrospun mats was measured with two-probe method by using the conductivity meter (High Resistance Low Conductance Meter HR2, AlphaLab Inc.). The measured samples were with the same thickness and the same size of 1×2 cm. The conductivity was measured in three points of the mat sample.

Thickness of the membranes. Samples thickness was measured using a micrometer.

Mechanical testing. Tensile tests of electrospun PAN-PANi mats were carried out using a tensile testing set-up Instron 5866. The samples were cut using a tool combined of two sharp razors. The samples were cut in a shape of rectangular with a gauge length of 10 mm and a width of 1 mm. Before cutting, the thickness of the specimens was measured. 2.5 N load cell was used for the tensile test study with a constant strain rate of 10 mm/min. Five specimens were used for each sample. The measured results were expressed as the mean ± standard deviation.

3. Results and discussion

The effect of increasing PANi amount and the using ionic liquid, BMImCL, in PAN-PANi blended solutions is described with regards to the electrospun mats conductivity, morphology and mechanical properties.

3.1. Conductivity

Fig. 1 presents the influence of PANi content on the electrical conductivity of nanofiberous mats obtained from PAN-PANi blended solutions. From Fig. 1 it can be seen that the conductivity of the mats obtained from the solutions without adding ionic liquid is much lower than the conductivity of the mats obtained from the blend solution with adding 10 wt% IL. When IL is not used, no remarkable increasing of the mat conductivity with PANi concentration increasing can be observed, except at 10 wt.% of PANi. At this concentration the maximum rise in mat conductivity, 0.8 μm/cm, has occurred. After that the conductivity drastically decreases and no any increase has been achieved even at the highest concentration of PANi salt at 40 wt.%. It can be explained with not complete homogeneous dispersion of PANi salt in the solution and consequently PANi particles could only partly be transferred into the
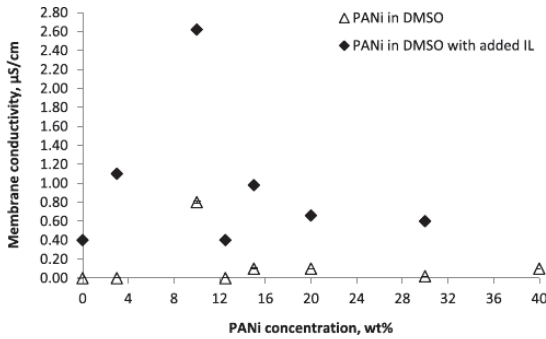
Fig. 1. Electrical conductivity of electrospun PAN-PANi-blend mats.

electropsun mat. The adding IL improves the dispersion of PANi salt that is demonstrated with higher conductivity of the electrospun mats (Fig. 1, full dots). Here, the conductivity increase is demonstrated already from 3 wt% PANi. The highest increase in the electrical conductivity of these mats has occurred when PANi concentration of PAN-PANi-IL blend solution is increased to 10 wt%. The conductivity of the mat was measured 2.62 μS/cm that is three times higher than without using IL in the blend solutions. Comparing to the results of the literature data the achieved conductivity is higher than the conductivity of the electrospun mats obtained from the solution of doped PANi when conductivity was measured 0.18 μS/cm [26]. From Fig. 1 it is seen that the conductivity of the mats electrospun from PAN-PANi-IL blended solutions slightly decreases with increasing the concentration of PANi from 12 wt.%. However, it is still much higher than the conductivity of the mats obtained from the solution without using IL. Such result confirms the role of IL in PAN-PANi blend to improve the dispersion of PANi particles by creating more conductive pathways. The experimental results have shown that there is the limited concentration of PANi salt to be able to perform electrospinning of PAN-PANi-blend solutions. At the amount of PANi salt of 30 wt.% the mats were very fragile. At 40 wt.% the electrospinning was not performable that can be explained with very high viscosity and non-homogeneity of the solution due to possible large amount of non-dispersed particles of PANi salt in the solution. Fig. 1 demonstrates that the optimum concentration of PANi salt in both solutions, with and without IL, is 10 wt% to achieve the most conductive membranes. This evident can be interpreted with electrical percolation threshold. According to the percolation theory, the remarkable increase of conductivity occurs when the concentration of conductive filler exceeds its critical value. Percolation threshold can be named as the optimum conductive filler content in polymer matrix after that there are no significant changes in the conductivity [33–35].

3.2. Morphology

The results of SEM images and the average fibers diameter of the mats are presented in Table 1 and Fig. 2. The analysed morphology of the produced mats with different content of conductive PANi salt can explain the behaviour in the achieved conductivity results. From SEM images demonstrated in Table 1 it is seen that pure PAN based nanofibers ((a) and (b)) are randomly arranged and without beads in the nanowebs. The using of the conductive additive PANi salt and also IL in the electrospinning blend solution improves the alignment of the nanofibers ((c)-(h)). Such behaviour can be explained with the increased net charge density that contributes the higher elongation of the fibres during electrospinning process [22]. The significant change in fibres morphology occurs at the highest PANi concentration of 40 wt% ((g)). From image (g) it is seen that the fibres are thicker with beads. It may be due to not complete dispersion of PANi salt in the electrospinning

solution. Comparing this result (g) with the fibres produced from the blend solution with adding IL (h) the decreasing in fibre diameter in the mat can be seen. Such effect confirms the role of IL in the improvement of the dispersion of PANi salt in the blended solution. The effect of IL was also observed in decreasing of fibres diameter in Fig. 2. It is seen that the diameter of the fibres obtained from the solution with adding IL is smaller. From 10 wt% PANi in blend solution with IL the obtained fibre diameter decreases comparing with the fibres produced from the solution without IL. The adding of the IL to PANi blend solution increases the conductivity of the solution resulting in the formation of the thinner fibres at the highest amount of PANi. It is known from the literature data that conductivity of the solution is the important parameter that can affect the morphology of the fibres [22,36]. The changes in the morphology presented in Fig. 2 can also explain the conductive behaviour of the fibres discussed in the part *Conductivity*. As it is observed from Fig. 2 the fibres with the smallest diameter were obtained from the both blend solutions (with and without IL) with 10 wt% of PANi salt. The most conductive mats were also produced when 10 wt% PANi was used in blend solutions (Fig. 1). Larger fibre diameter the less conductive mats were obtained. This evident may be caused by less contact probability in the thicker fibres in the same mat volume when increase in fibres diameter results in increasing in void space between fibres [37].
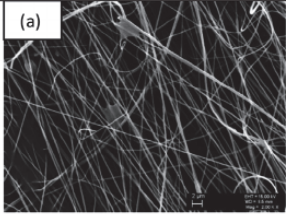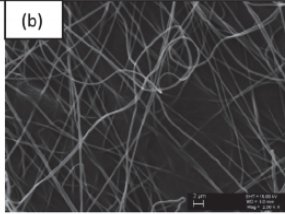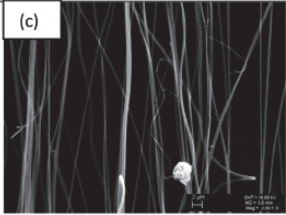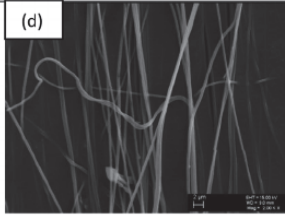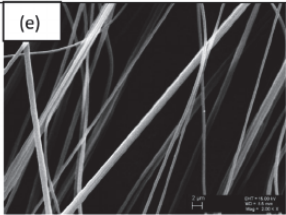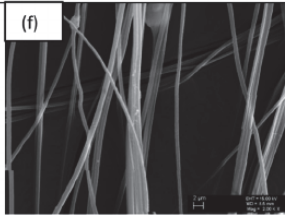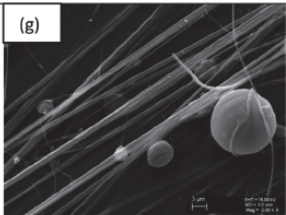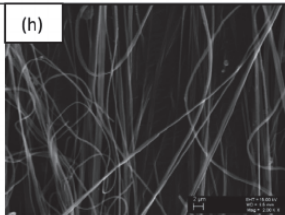
3.3. Mechanical properties

The tensile properties of the mats obtained from the blend solutions with different amount of PANi salt are presented in Fig. 3. It is seen that the tensile stress at maximum load decreases with increasing the concentration of PANi. Decreasing tendency is observed in the mats obtained from both blend solutions with and without adding IL. The decrease in breaking stress values can be the result of nonhomogeneous dispersion of PANi salt at high concentrations that leads to the possible structural deformations. Nuray Ucar et al. in his research study also showed the effect of efficiency of solution homogeneity on tensile breaking stress. The mats obtained from the solutions that are more homogeneous resulted in higher tensile breaking stress [22]. In the present research, Fig. 3 demonstrates that the tensile stress of the mats produced from the blend solutions with adding IL is higher than of the mats obtained from the blend solutions without IL. This evidence can be explained with the improved morphology of the mats with adding IL that was presented in Table 1. From Fig. 3 it can be observed that tensile stress at maximum load drastically decreases in the mats obtained from blend solutions at higher PANi concentration, 20 wt.%, without IL. Here, the parallel between the mat conductivity and the achieved mechanical properties can be made. With adding IL the conductivity of the mats increases improving the elongation of the fibres in the nanoweb that resulted in the increase of the tensile stress at maximum load. This evidence also explains the highest results of tensile stress at maximum load at PANi concentration from 3 wt.% to 10 wt.% that can be observed in Fig. 3. The most conductive mats were produced at these concentrations (Fig. 1).

4. Conclusion

This research was carried out to propose new procedure for producing electrospun materials with enhanced electrical properties by using conductive polymer PANi salt in blend with IL. The results have shown that it is possible to obtain fibrous conductive mats from PANi salt-IL blends by electrospinning. Adding ionic liquid to PANi salt blended solution significantly improves the dispersion of PANi salt making solution electrospinnable. The optimum concentration of PANi from 10 wt.% to 12.5 wt.% in the blend has been investigated to achieve the highest conductivity of electrospun mat with good mechanical properties. The experimental results have demonstrated that the mechanical properties depend on the homogeneity of the solution

Table 1
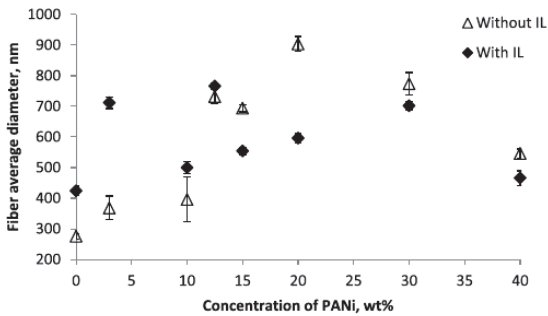SEM analysis of PAN-PANi-blend membranes.

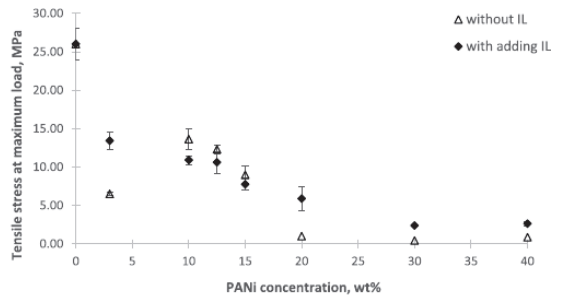Fig. 2. The effect of PANi concentration on the mats fibre diameter.

Fig. 3. The effect of PANi concentration on the mats mechanical properties.

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the mats were electrospun from and on the electrical properties of the got material. The more conductive mats show higher tensile stress at maximum load, from 10 MPa to 14 MPa.

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Paper III
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Material Properties

The effect of ionic liquids on the mechanical properties of electrospun polyacrylonitrile membranes

Check for updates

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ABSTRACT

Obtaining electrospun membranes with good mechanical properties is important for their various applications. Several ionic liquid-based additives (IL-based) for electrospinning solutions have been proven to increase the conductivity of electrospun membranes. The aim of this study was to analyse the dependence of the mechanical properties of electrospun membranes on the additives used. Moreover, the relationship between conductivity, specific stress and the morphology of the membranes was studied. Polyacrylonitrile (PAN) solutions were prepared in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solvents. Two different ILs (1-butyl-3-methylimidazolium chloride [BMIm]Cl and 1-ethyl-3-methylimidazolium bromide [EMIm]Br) were used at a concentration of up to 10 wt%. Overall, it can be said that, with IL [EMIm]Br, higher specific stress values were achieved. Most stable values of specific stress were achieved with membranes obtained from solutions with DMF, especially with added IL [BMIm]Cl. The highest specific stress value achieved was 87.93 ± 5.15 mN/tex.

1. Introduction

Electrospinning is a simple method of producing polymer fibres, enabling continuous formation of fibres that can be composed of a broad range of insulating, conducting and semiconducting polymers, or even multi-component fibres, with diameters ranging from a few tens of nanometres to several micrometres [1–3]. Normally, the polymer to be used in electrospinning is dissolved in an organic solvent in order to create a homogeneous spinnable solution.

Electrospun ultra-fine fibre mats are used in a vast range of engineering, biomedical and industrial fields such as membrane technology, filtration media, energy-related needs (harvesting, transmitting, and storage), tissue engineering, medical prostheses, drug delivery and wound healing [4,7]. The mechanical properties of electrospun fibres are particularly important due to their usage for various applications [5]. Several studies have shown that electrospun nanofibres have interesting mechanical properties such as, for example, increased Young's modulus when compared to bulk materials [6–8], due mainly to the high molecular orientation of polymer molecules. This molecular orientation is produced by the stretching of the polymer jet during electrospinning [3].

Although a number of researchers have explored the mechanical properties of electrospun mats [1–3], no comprehensive studies have been reported in any published literature which cover the effects of the main parameters on the mechanical properties of polyacrylonitrile (PAN) which has been electrospun using ionic liquid (IL). Researchers have found that process parameters, polymer concentration, viscosity and solution conductivity all play an important role in the outcome of electrospinning [10–12].

Khan (2015) [4] explored the effects of solution and electrospinning parameters on the morphology, mechanical properties and surface characteristics of PAN electrospun nanofibre mats. PAN/dimethylformamide (DMF) solutions of varying concentrations were electrospun under various parameters. It was found that the increase in PAN concentration, from a 6–12 wt percent (wt%) in solution resulted in higher tensile strength, failure strength and ductility of electrospun nanofibre mats by 346%, 229% and 504%, respectively. The results showed that the average fibre diameter increased from 208 nm to 881 nm with higher PAN concentration from 6 to 12 wt%.

Zhang (2011) [9] reviewed the manufacturing process and characterisation methods for the microstructurs and mechanical properties of PAN and PAN-based nanofibres. He concluded that the mechanical

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properties of the PAN nanofibres and PAN/SWNTs (single-walled carbon nanotubes) composite nanofibres can be further improved by conducting extensive studies of electrospinning and the hot-stretching conditions. Due to that, this novel electrospinning technique creates aligned and molecularly-orientated PAN and PAN-based nanofibres that can be used to prepare carbon nanofibres which possess superior mechanical properties [9].

Savest et al. (2016) [13] explored the effect of (ILs) on the PAN membranes' conductivity with the aim of proposing one or more perspective conductive additives for electrospinning. Using [BMIm]Cl and [EMIm]Br as the additives in PAN solutions was shown to improve the electrical properties of electrospun membranes. Even a small increase in the concentration of ILs resulted in a significant increase in membrane conductivity when compared to membranes that were obtained from pure PAN in DMF and PAN in dimethylsulfoxide (DMSO).

Although a number of researchers have investigated the mechanical properties of electrospun mats, no comprehensive studies have been reported in published literature which cover the effects of the main parameters on the mechanical properties of PAN which has been electrospun using IL. This work serves to study the effects of the key solution and process parameters on the morphology and mechanical properties of electrospun nanofibre membranes.

2. Materials and methods

2.1. Materials

PAN powder was purchased from Polysciences Inc with a molecular weight of 150,000. PAN solutions were prepared in two different solvents: DMF (with purity $\geq 99.8\%$) and DMSO (with purity $\geq 99.9\%$). DMF and DMSO were purchased from SigmaAldrich. ILs, 1-Butyl-3-methylimidazolium chloride ([BMIm]Cl) and 1-ethyl-3-methylimidazolium bromide ([EMIm]Br), were added in concentrations from 1 wt% to 10 wt% to the polymer solutions as conductive fillers.

[BMIm]Cl and [EMIm]Br ILs were synthesised in the laboratory according to the methods described in Savest et al. (2016) [13].

2.2. Solution preparation for electrospinning

PAN matrix was dissolved in the solvent by means of a magnetic stirrer at 40 °C for 24 h. Two different solvents DMF and DMSO were used. The concentration of PAN in solvents was fixed at 10 wt%. 10 wt % was experimentally found during the present research work to be the optimum concentration for PAN to produce the membranes with enhanced properties. Also, according to the literature, tensile stress will increase in higher concentrations of PAN [4]. On the other hand, if the concentration is too high it is very difficult to control and maintain a stable flow rate because the viscosity of the polymer solution is high [9]. IL as conductive additive was added to polymer solution at concentration from 1 wt% to 10 wt%. The solution was stirred at 40 °C for more than 90 min in order to achieve an homogeneous solution for electrospinning. Two different ILs [BMIm]Cl and [EMIm]Br were used. Solutions prepared and their abbreviations are shown in Table 1 below.

2.3. Electrospinning process

Electrospinning was carried out by using a horizontal electrospinning setup with a cylindrical rotating collector covered with aluminium foil at room temperature. The spinning solution was put into a 1 ml syringe with a needle diameter of either 0.4 mm or 0.6 mm. The pumping feed rate was set between 0.4 ml/h and 0.6 ml/h. The choice of needle diameter and the pumping feed rate depended upon the solution viscosity. The solution was electrospun at 20–24 kV with a distance of 8–10 cm between the needle and the collector.

2.4. The characterisation of mechanical properties

Tensile tests of electrospun membranes were carried out using an Instron 5866 tensile testing machine. The samples were cut using a tool which combined two sharp razors. The samples were a rectangular shape with a gauge length of 10 mm and a width of 1 mm. A load cell of maximum capacity of 2.5 N was used for the tensile tests with a constant test speed of 10 mm/min. Five specimens were used for each sample, and maximum load(force) and extension data were measured and recorded. The specific stress at maximum load was used to characterise the membranes. The specific stress was calculated with the following equation [14].

$$\sigma_{sp}\left(\frac{N}{tex}\right) = \frac{force\ (N)}{width\ (mm)} \times \frac{1}{areal\ density\left(\frac{g}{m^2}\right)} \tag{1}$$

Before calculating the specific stress, areal density of each membrane was calculated. For that, circular specimens were cut from the membranes with a diameter of 1.5 cm and weighed with analytical balances to accuracy of 10 μg.

2.5. Analysis of membrane morphology and nanofibers diameter

The samples were covered with Au/Pt with an ion sputter JFC-1100. The morphology of electrospun membranes was analysed by a scanning electron microscope (SEM) Zeiss EVO MA 15. An accelerating voltage of 15 kV was used.

Software for geometric characterisation of fibre systems based on SEM images was used for measuring electrospun nanofibers diameter and diameter distribution inside the membrane. The software was developed by Fraunhofer Institute for Industrial Mathematics ITWM supported by validation through German Institutes of Textile and Fiber Research (DITF). Before the image analysis, the samples were covered with Au/Pt with an ion sputter and electrospun membranes were analysed by the scanning electron microscope (SEM) TM1000, Hitachi. Different SEM apparatus was used for image analysis to get suitable contrast, magnification and amount of fibres for the images.

3. Results and discussion

3.1. The effect of ILs on the mechanical properties of the membranes

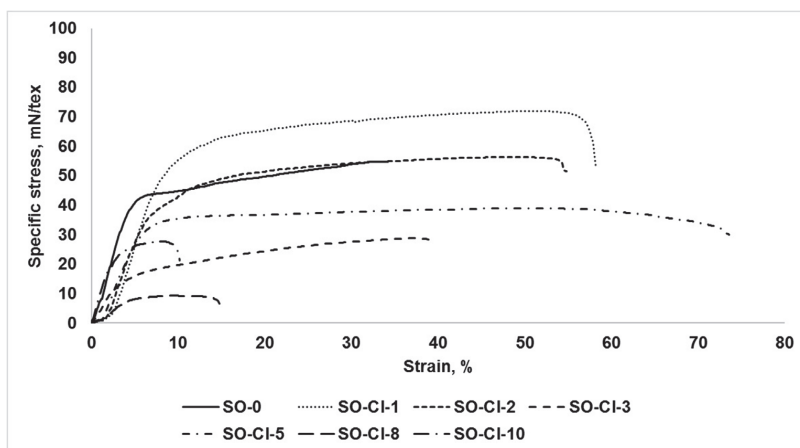The typical specific stess-strain curves of electrospun membranes

Table 1
Solutions prepared and their abbreviations.

IL and solvent used/IL concentration	DMF + [BMIm]Cl	DMSO + [BMIm]Cl	DMF + [EMIm]Br	DMSO + [EMIm]Br
0%	F-0	SO-0	F-0	SO-0
1%	F—Cl-1	SO—Cl-1	F—Br-1	SO—Br-1
2%	F—Cl-2	SO—Cl-2	F—Br-2	SO—Br-2
3%	F—Cl-3	SO—Cl-3	F—Br-3	SO—Br-3
5%	F—Cl-5	SO—Cl-5	F—Br-5	SO—Br-5
8%	F—Cl-8	SO—Cl-8	F—Br-8	SO—Br-8
10%	F—Cl-10	SO—Cl-10	F—Br-10	SO—Br-10

Fig. 1. Specific stress-strain curves for the membranes obtained from solutions with added IL [BMImCl] + 10 wt% PAN in solvent DMSO.

with IL are explained with an example of the membranes from solutions SO-0, SO−Cl-1, SO−Cl-2, SO−Cl-3, SO−Cl-5, SO−Cl-8 and SO−Cl-10 (Fig. 1). It can be observed that the specific stress decreases with the increase of IL concentration. The strain at break increased until the added IL concentration was 5%, showing the greatest strain value of 73.5%. For solutions SO−Cl-8 and SO−Cl-10, the strain at break decreased considerably showing the lowest strain at break 10.2% for the membrane from solution SO−Cl-10. It can be concluded that there is an optimum IL concentration to achieve the higher elongation. The elastic modulus of the membranes is slightly decreasing with the addition of IL.

The influence of different ILs and solvents on the mechanical properties of the electrospun membranes is presented in Fig. 2 and Fig. 3. By increasing the concentration of IL, the specific stress decreased, with the exception of membranes F−Br-1; SO−Br-1; SO−Cl-1; SO−Br-2; SO−Cl-2. This may be caused by the increased solution viscosity and reduced evaporation rate of the solvent in the electrospinning process that, in turn, leads to the changes in the morphology, these being fibre diameter and uniformity [12]. Fibres prepared from PAN solutions in DMF and DMSO without ILs showed specific stress values reaching 56.68 ± 2.76 mN/tex and 51.98 ± 4.40 mN/tex,

respectively. Highest specific stress with IL [EMIm]Br was obtained with membrane F−Br-1 (87.93 ± 5.15 mN/tex) and lowest with the membrane F−Br-10 (14.95 ± 1.44 mN/tex). Highest specific stress with IL [BMIm]Cl was obtained with membrane SO−Cl-1 (74.32 ± 3.85 mN/tex) and lowest with the membrane SO−Cl-8 (9.09 ± 1.00 mN/tex). Overall, it can be said that, with IL [EMIm]Br, higher specific stress values were achieved. Such an effect can be caused by the higher conductivity levels of [EMIm]Br when compared to [BMIm]Cl [13]. It is known that the conductivity of the solution influences the electrospinning process [15&16]. W Cheng et al. [17] describe in their research that even a small amount of added IL increases the conductivity; added IL can also provide an additional fibre stretch. The research by N Kizildag et al. [18] also showed the effects of more orientated fibres on the mechanical properties.

The specific stress of membranes obtained from the solution in DMSO were a little higher when compared to the membranes produced from the solution in DMF. Solvents used have a great effect on the nanofiber diameter and morphology [18], which in turn affects the mechanical properties [5,8]. Most stable values of specific stress were achieved with membranes obtained from solutions with DMF, especially with added IL [BMIm]Cl. Specific stress values ranged from 34.28
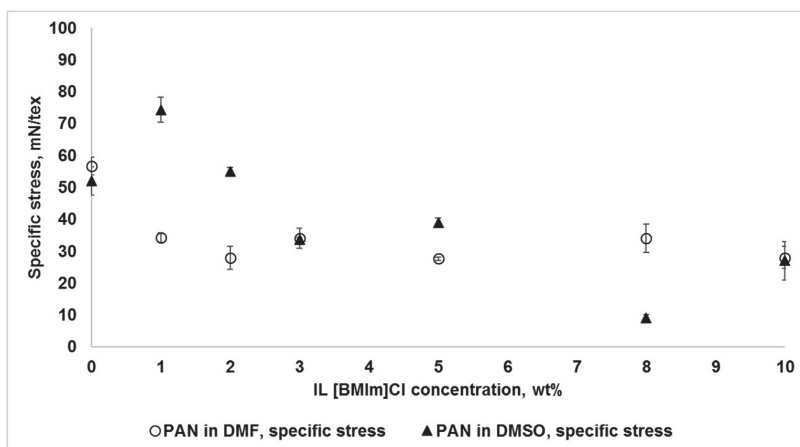

Fig. 2. The impact of IL [BMIm]Cl and different solvents on the specific stress of the membranes.
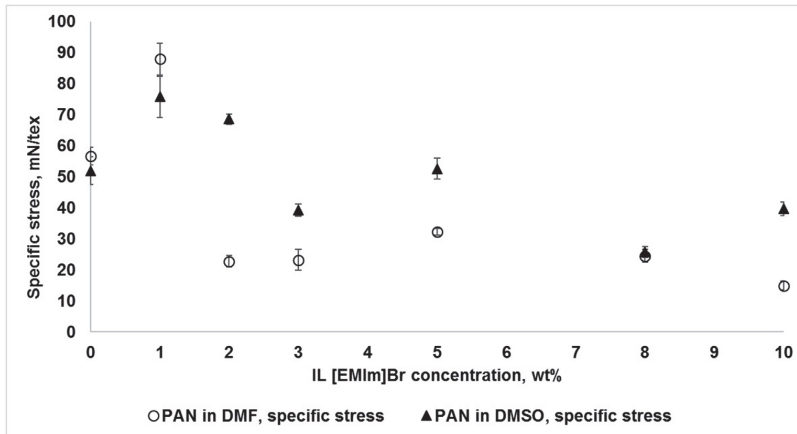
Fig. 3. The impact of IL [EMIm]Br and different solvents on the specific stress of the membranes.

mN/tex for membrane F—Cl-1 to 27.01 mN/tex for membrane F—Cl-10. From the results presented, it can be seen that mechanical properties strongly depend on the added IL and the solvent being used for the polymer solution.

3.2. The effect of ILs on the fibre diameter and morphology

The morphology and fibre diameter of electrospun membranes were thoroughly studied by Savest et al. (2016) [13]. It was concluded from the studies that fibre morphology depended, not only on the ILs being added, but also on the solvent. In this study, a more thorough method was used to estimate the fibre median diameter. In Fig. 4 and Fig. 5, the impact of different ILs and solvents on the median fibre diameter of the membranes is demonstrated. Median diameter of nanofibers obtained from solution SO-0 and F-0 were, respectively, 476 nm and 324 nm. Membranes obtained from the solutions with solvent DMSO showed much higher values of median diameter than with solvent DMF. Membranes with the highest value of median diameter were obtained from solution SO—Br-5 (542 nm). The finest fibres were obtained from solution F—Br-2 (222 nm).

Different ILs also gave different values of median fibre diameter. For example, it can be concluded that membranes from solutions with IL [BMIm]Cl gave higher median diameter values than with IL [EMIm]Br. Diameter values of the membranes obtained from solutions with IL [BMIm]Cl ranged from 231 nm (membranes from solution F—Cl-3) to 542 nm (membranes from solution SO—Cl-5). There were only two membranes in the case of IL [BMIm]Cl that gave median diameter values below 300 nm, these were membranes from solutions F—Cl-3 and membrane F—Cl-8. Most stable diameter values were obtained with solvent DMF and IL [EMIm]Br.

The fibre diameter distribution inside the membranes was also studied. In Fig. 6, fibre diameter distribution inside the membranes obtained from pure solutions F-0 and SO-0 is demonstrated. It can be observed that there is a slight difference in median diameter values and also in diameter distribution. Membrane obtained from solution SO-0 gave higher value of median diameter, also the diameter values were not so dispersed.

In Fig. 7, fibre diameter distribution for other membranes is demonstrated. From the graphs, it can be seen that membranes obtained from the solutions with solvent DMSO gave slightly higher values of median diameter, similar to the membranes from pure solutions. Also, it can be seen that fibre diameters in higher concentrations of IL were
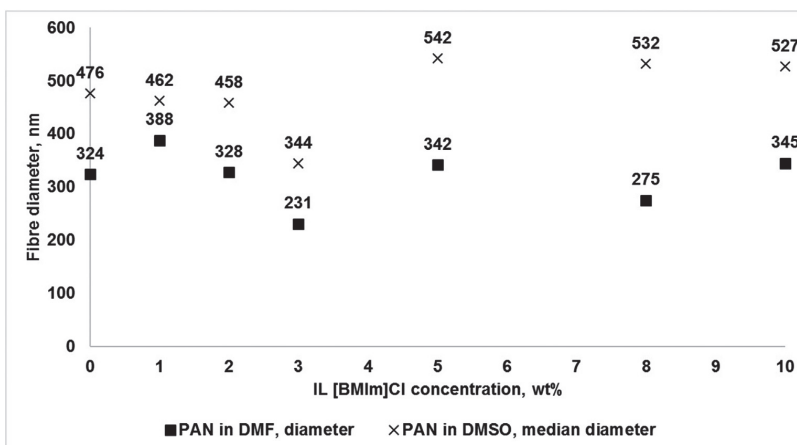

Fig. 4. The impact of IL [BMIm]Cl and different solvents on the median fibre diameter of the membranes.
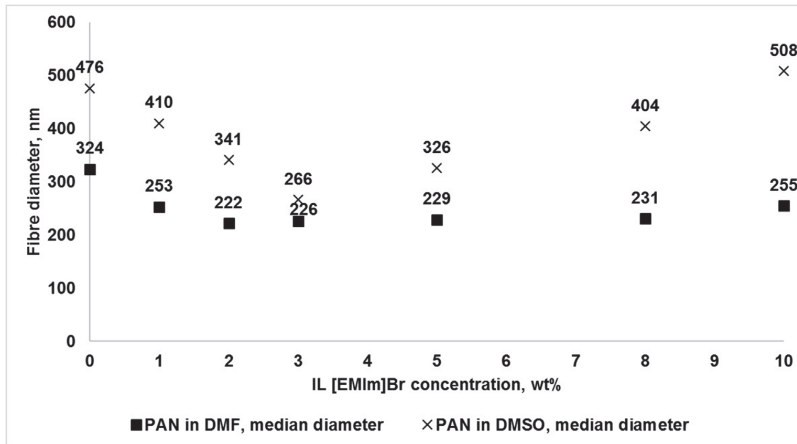
Fig. 5. The impact of IL [EMIm]Br and different solvents on the median fibre diameter of the membranes.

more dispersed. Savest et al. (2016) [13] concluded that there is an increase in solutions conductivity with IL concentration increasing in PAN solutions in both DMF and DMSO. Hence, more dispersed fibre diameter values could be caused by the higher electrical conductivity of the polymer solution, which can make the charged polymer solution less stable [19]. It can also be observed that the membranes with the highest value of specific stress (F–Br-1, Fig. 7h) and lowest value of specific stress (F–Br-10, Fig. 7m) have different fibre diameter distributions. For example, the membrane F–Br-10 has very dispersed distribution opposite to the membrane F–Br-1. For some membranes, multimodal distribution can be seen from the graphs, for example membranes from solutions SO–Br-5 (Fig. 7k), SO–Cl-8 (Fig. 7e) and F–Br-8 (Fig. 7l).

Specific stress values are moderately lower on higher concentrations of ILs (8 wt% and 10 wt%). The SEM image of the membrane which was obtained from solution SO-0 is shown in Fig. 8a, it can be seen that fibres without added IL were quite smooth. When adding a high concentration of IL [BMIm]Cl, at 8 wt% and 10 wt% (Fig. 8b and c), the fibres were not so even. At the same time, the specific stress of the membranes decreased significantly, from 51.98 ± 4.40 mN/tex without added IL to 9.09 ± 1.00 mN/tex (with 8 wt% added IL), and 27.01 ± 5.99 mN/tex (with 10 wt% added IL). According to Fig. 4, the diameter values did not drastically change. Hence, it can be concluded that diameter values do not have a significant impact on specific stress in case of solutions SO–Cl, instead the morphology plays a major role in the values of specific stress. Fig. 8d and e show that the fibres were still quite smooth after adding [EMIm]Br at 8 wt% and 10 wt%, and the diameter also did not drastically increase when compared with those membranes that were obtained from the initial PAN solution (Fig. 8a). Compared the specific stress of the membranes obtained from solutions SO–Br-8 and SO–Br-10 with solutions SO–Cl-8 and SO–Cl-10, the specific stress did not decrease so drastically. The value of specific stress with 8 wt% added IL [EMIm]Br was 25.69 ± 1.74 mN/tex and 39.73 ± 2.16 mN/tex with 10 wt% added IL. Hence, it can be concluded that the morphology of the nanofibers was not influenced so much by adding IL [EMIm]Br, fibres obtained were smooth surface and
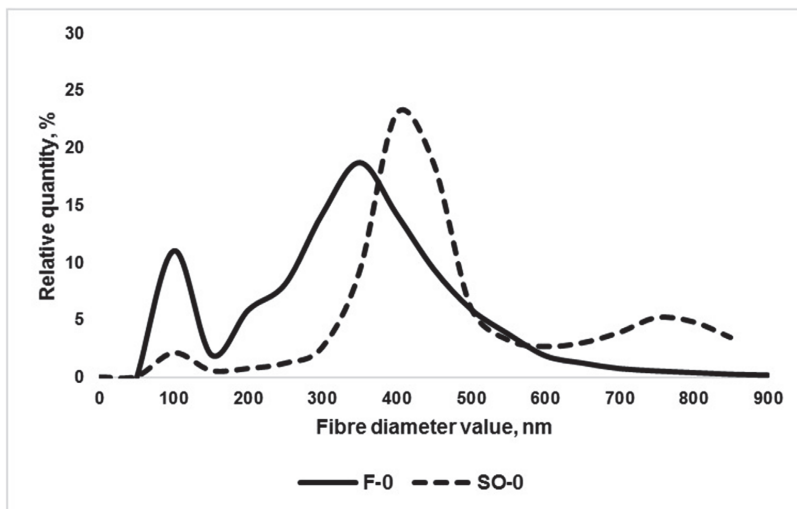

Fig. 6. Fibre diameter distributions for the membranes obtained from pure solutions F-0 and SO-0.
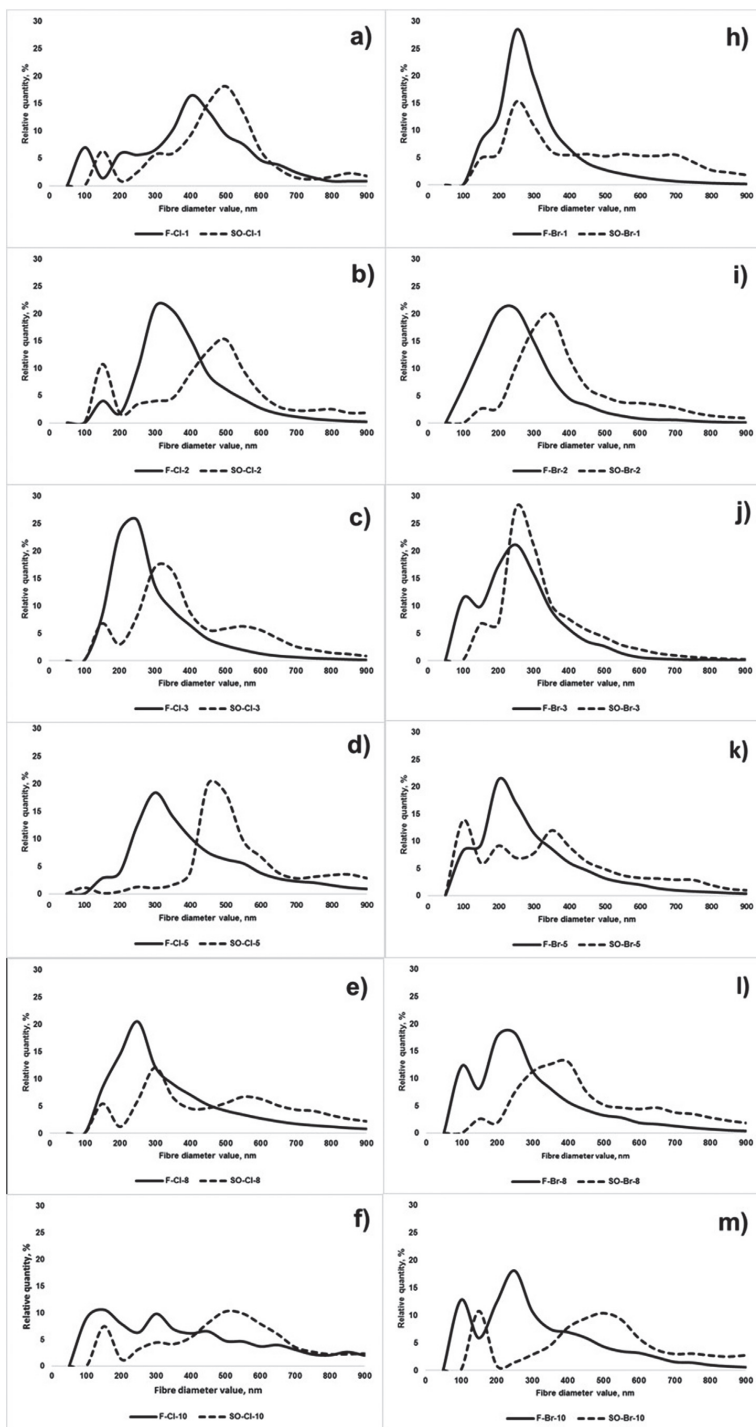
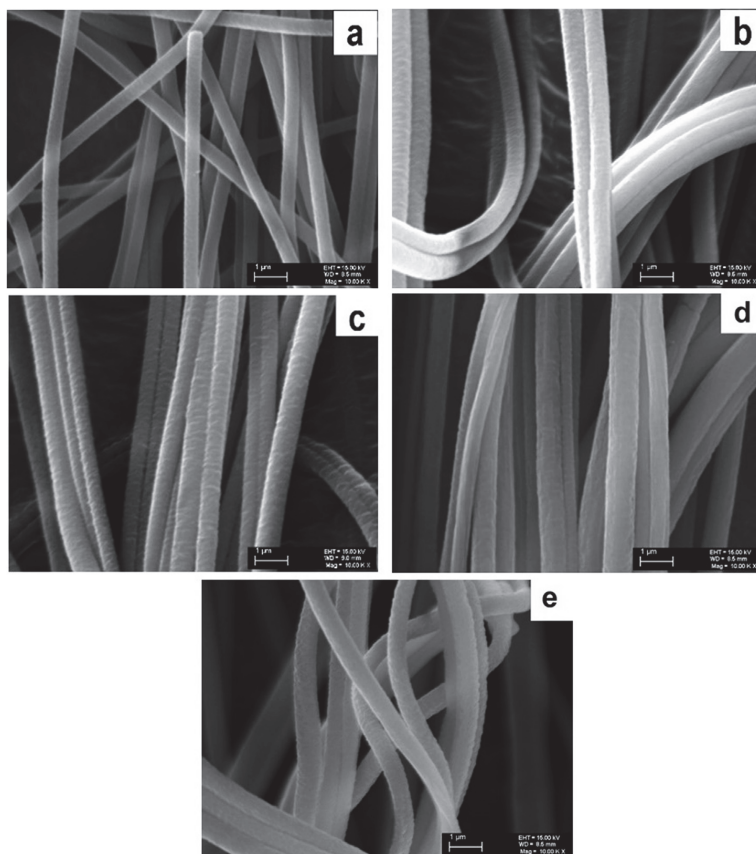**Fig. 7.** Fibre diameter distributions for membranes from different solutions.

Fig. 8. SEM images of membranes obtained from the solutions SO-0 (a), SO—Cl-8 (b), SO—Cl-10 (c), SO—Br-8 (d) and SO—Br-10 (e).
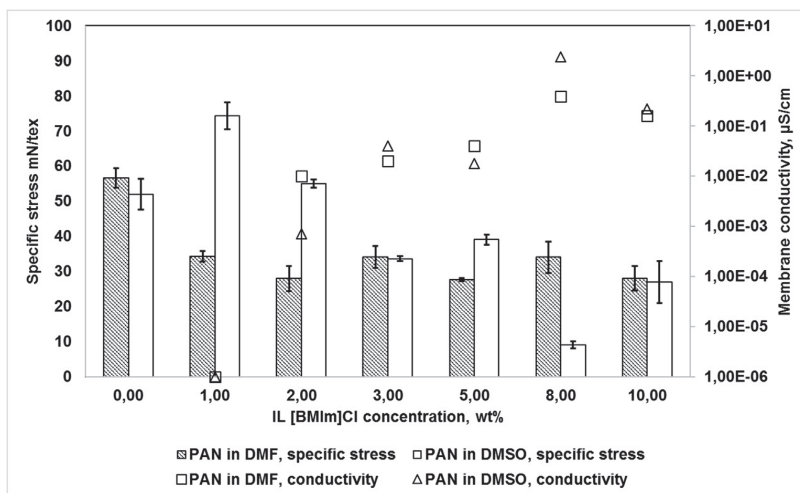

Fig. 9. The impact of IL [BMIm]Cl and different solvents on the specific stress and conductivity of electrospun membranes.
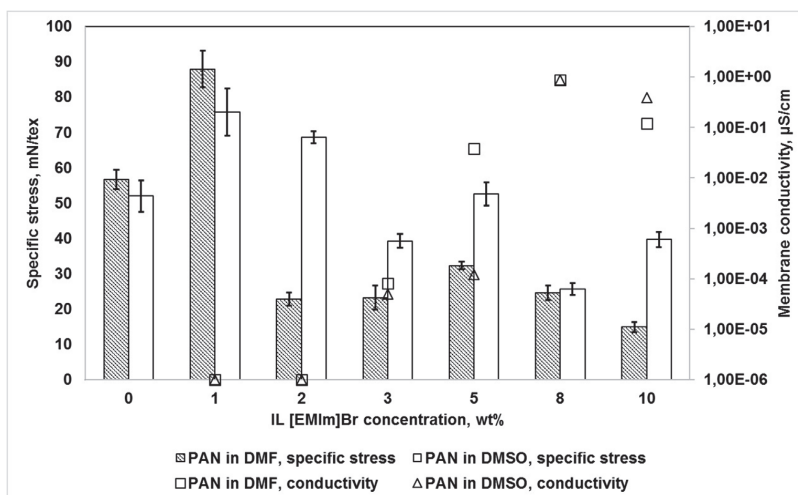
Fig. 10. The impact of IL [EMIm]Br and different solvents on the specific stress and conductivity of electrospun membranes.

even and, due to that, the specific stress of those membranes was also not significantly influenced.

3.3. Membrane conductivity versus mechanical properties

Fig. 9 and Fig. 10 present the influence of different ILs and their concentrations on the specific stress and conductivity of electrospun membranes. Overall, it could be concluded that the membranes with higher conductivity showed quite poor specific stress values. As can be seen from Fig. 9 and Fig. 10, the most conductive membranes with IL [BMIm]Cl were obtained from solutions SO–Cl-8 and F–Cl-8 (respectively, 2.39 and $3.90 \cdot 10^{-1}$ μS/cm), and with IL [EMImBr] from solutions F–Br-8 and SO–Br-8 ($8.80 \cdot 10^{-1}$ μS/cm). Among these membranes, the best specific stress was demonstrated by the membrane from solution F–Cl-8, 34.03 mN/tex and the worst specific stress was demonstrated by the membrane from solution SO–Cl-8, 9.09 mN/tex. Hence, the optimum concentration to achieve adequate combination of different properties for the membrane (type of IL/solvent used, solution concentration, membrane conductivity and specific stress) depends on the solvent and IL used. It can be concluded that the best value was achieved with IL [BMIm]Cl and solvent DMF at 8 wt% concentration where the membrane conductivity was $3.90 \cdot 10^{-1}$ μS/cm and specific stress was 34.03 mN/tex.

4. Conclusions

Two different ILs ([BMIm]Cl and [EMIm]Br) and solvents (DMF and DMSO) were used in order to obtain electrospun membranes with enhanced mechanical properties and conductivity. As a result, it can be said that the mechanical properties of those membranes which had enhanced conductivity depended, not only on the type and concentration of ILs, but also on the solvent being used. Higher specific stress values were achieved with IL [EMIm]Br. The highest specific stress value achieved was 87.93 ± 5.15 mN/tex for the membrane obtained from solution PAN in DMF with 1% added IL [EMIm]Br. Most stable values of specific stress were achieved with membranes obtained from solutions with DMF, especially with added IL [BMIm]Cl. Overall, it can be concluded that the membranes with higher conductivity showed lower specific stress values. Membranes obtained from the solutions with solvent DMSO showed much higher values of median diameter than with solvent DMF. It can also be concluded that the morphology

plays major role in the values of specific stress. Also, it can be seen that fibre diameters in higher concentrations of IL were more dispersed which led to lower tensile stress values of the membranes. Hence, the optimum concentration to achieve adequate combination of different properties for the membrane depends on the solvent and IL used. The best value in this research was achieved with IL [BMIm]Cl and solvent DMF at 8 wt% concentration where the membrane conductivity was $3.90 \cdot 10^{-1}$ μS/cm and specific stress was 34.03 mN/tex.

Declarations of interest

None.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymertesting.2018.09.003.

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