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NEW METHODS IN THE STUDY OF ROLLER ELECTROSPINNING MECHANISM

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SUMMARY OF THE THESIS

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Abstract

Needleless roller electrospinning is a new technique when compared with needle electrospinning; therefore, parameters of needleless electrospinning have not yet been fully identified and defined. Some dependent parameters were defined in previous works. Relations between selected independent and selected dependent parameters were studied, as it is shown in theoretical part, both experimentally and theoretically. Not all the parameters were defined and studied yet, such as: spinner geometry, roller properties, roller velocity. Only few dependent parameters were defined (throughput, fiber diameter and diameter distribution, quality of nanofiber layer and some others).

It is the aim of this work to continue in study of relations between independent and dependent parameters of needleless electrospinning and to enlarge the knowledge of its mechanism. To reach the goal, further independent and dependent process parameters will be defined and the methods of their measurement developed. The relations between selected parameters will be studied.

In this work, the parameters such as current, current per jet, rotating roller speed, force acting on a jet, distance between jets, spinning area on the roller surface, length of jets and launching time of jets were studied for the aqueous polymer solution of polyethylene oxide (PEO) and for the non-aqueous solution of polyurethane (PU). Two various kinds of salts such as tetraethylene ammonium bromide (TEAB) and lithium chloride (LiCl) were used to determine the effects of salts on the process.

The experimental part of this thesis consists of three chapters. In the first chapter, the relations between the current measurements in the needle-, rod- and roller electrospinning are studied. In the needle electrospinning process, the current does not depend on the relative humidity of the surrounding air within broad limits of 20–80%. In the case of roller electrospinning, the relative humidity inside the spinning device affects the spinning performance, especially the number of jets per spinning area, and therefore also the total current. It was also found that in the needle electrospinning, the current increases with increasing needle protrusion length due to more intensive creation of plasma particles. The relations for current per one jet and for the distance between jets were determined.

In the second chapter, the limits of polymer concentrations and salt concentrations in the polymer solutions were determined for the main group of experiments in the chapter three.

6 wt. % was selected as optimum concentration of PEO solution. In the case of PU, the optimum polymer concentration 17.5 wt. % was accepted from literature. In this case, the amount of salt was determined. 0.056 mol per liter LiCl was chosen as the upper limit for PU because the viscosity of PU solution as well as the diameter of produced fibers increases with increasing salt content. For this reason, low amounts of salt were used for PU solutions.

In the third part, the relations between selected independent and dependent electrospinning parameters described in theoretical part are studied. The velocity of spinning roller and the content of salts in the solutions were chosen as independent process parameters. It was found that the velocity of rotating roller which is related to the feed rate, effects the spinning performance as well as the quality of fibers. The spinnability and spinning behavior of PU and PEO solutions depending on the salt content were also studied. It was found that adding salt decreases spinning performance of PEO solution whereas it increases spinning performance of PU solution. These differences were explained by interactions of polymers with salts and by the "leaky" dielectric model.

Key Words: Needleless roller electrospinning, polyurethane, poly(ethylene oxide), dependent parameters, independent parameters, roller speed, electric current.

Anotace
Ve srovnání s jehlovým elektrostatickým zvlákňováním je bezjehlové zvlákňování novější technologií; z toho důvodu nebyly dosud parametry bezjehlového zvlákňování v celé šíři identifikovány a definovány. Některé závislé parametry byly definovány v předešlých pracích. Teoreticky i experimentálně byly také studovány vztahy mezi vybranými nezávislými a závislými parametry, jak je popsáno v teoretické části práce. Některé parametry však dosud nebyly studovány, jako například: geometrie zvlákňovacího zařízení a vlastnosti a rychlost otáčení válcové zvlákňovací elektrody. Ze závislých parametrů byly definovány pouze některé (zvklákňovací výkon, průměry vláken a jejich distribuce, kvalita nanovlákenné vrstvy

V této práci byly definovány a studovány další parametry procesu elektrostatického zvlákňování, zejména elektrický proud protékající zařízením a jednotlivými polymerními tryskami, rychlost rotace válcové zvlákňovací elektrody, síla působící na polymerní trysku, vzdálenost mezi polymerními tryskami, zvlákňovací plocha na elektrodě, délka polymerních trysek a čas jejich formování, přičemž tyto parametry byly studovány na dvou různých polymerních roztocích – vodném roztoku polyetylenoxidu (PEO) a nevodném roztoku polyuretanu (PU). Byly použity dva typy solí – tetraetylamoniumbromid (TEAB) a chlorid lithný (LiCl).

Experimentální část práce sestává ze tří dílů. V prvním dílu jsou studovány vztahy mezi elektrickými proudy při jehlovém, tyčovém a válcovém elektrostatickém zvlákňování. Při jehlovém elektrostatickém zvlákňování elektrický proud nezávisí na relativní vlhkosti okolního vzduchu v širokém intervalu 20-80 %. U válcového zvlákňování ovlivňuje relativní vlhkost vzduchu v zařízení zvlákňovací výkon, zvláště četnost polymerních trysek na zvlákňovací ploše, a tím i celkový elektrický proud. Bylo rovněž zjištěno, že při jehlovém zvlákňování se elektrický proud zvyšuje s rostoucí délkou vysunutí jehly z nabité elektrody vlivem intenzivnější tvorby plasmových částic na delším úseku jehly. Byly stanoveny vztahy pro proud připadající na jednu polymerní trysku a pro vzdálenost mezi tryskami.

V druhém dílu experimentální části byly stanoveny hranice koncentrací polymeru a solí pro hlavní experimenty. Pro PEO byla vybrána koncentrace polymeru 6 %. U PU byla akceptována optimální koncentrace 17.5 % popsaná v literatuře. Stanovena zde však byla maximální koncetrace LiCl 0.056 mol na litr. Vzhledem k tomu, že obsah solí zvyšuje viskozitu roztoku polyuretanu a tím i průměr vytvořených vláken, byla volena takto nízká maximální koncentrace.

Ve třetím dílu experimentální části byly studovány vztahy mezi vybranými nezávislými a závislými parametry elektrostatického zvlákňování. Z nezávislých parametrů byly vybrány rychlost rotace zvlákňovací válcové elektrody a obsah solí v polymerních roztocích. Bylo zjištěno, že rychlost rotace zvlákňovací elektrody a tím daná rychlost dávkování roztoku do zvlákňovacího pole ovlivňuje produktivitu procesu i kvalitu vytvořených vláken. Dále byla studována zvláknitelnost roztoků PU a PEO a jejich chování při zvlákňování s ohledem na obsah solí. Bylo zjištěno, že přídavek solí snižuje zvlákňovací výkon PEO, zatímco zvyšuje zvlákňovací výkon u roztoku polyuretanu. Tyto rozdíly byly vysvětleny na základě interakcí jednotlivých polymerů se solemi a na základě “leaky” dielektrického modelu.

Klíčová slova: elektrostatické zvlákňování, bezjehlové zvlákňování, polyuretan, polyetylenoxid, závislé parametry, nezávislé parametry, rychlost otáčení válce, elektrický proud.

Content

1. Introduction

The European commission defined the nanomaterials as those containing particles with one or more external dimensions in the size range 1 – 100 nm. One of the aims of researchers is to use nanofibers in the industrial application area. Nanotechnology has gained an interest of the global research and development support over the last few years. Nanotechnology literally means any technology performed on a nanoscale that has applications in the real world. It has also a vast application area in the textile field.

Nowadays, the electrospinning remains the most convenient and scalable technique for nanofiber production. There are many factors affecting the electrospinning process and fiber properties. In this work different than needle electrospinning system, a roller electrospinning system was used. Hundreds of jets can be formed simultaneously in the roller spinning electrode. Parameters of the roller electrospinning process will be discussed in theoretical part.

2. Purpose and the aim of the thesis

The aim of this work is to define key parameters of the roller electrospinning process. The ES parameters are divided into two groups, namely independent and dependent ones. In the group independent parameters, primary and secondary independent parameters are distinguished, for instance: kind of polymer, its molecular weight, kind of solvent, type and amount of additives and concentration of polymer solution are primarily independent parameters, whereas viscosity, conductivity and surface tension as a result of above parameters, directly influencing the electrospinning process, are secondary independent parameters.

3. Theoretical Part

There are two groups of parameters described in the following chapter, namely these described and studied in the previous works and the new parameters defined by the author. The author hopes that it will be possible to understand the electrospinning process when using and studying her new defined and measured parameters which potentially yield more detailed insight into the process (Table 3.1).

Table 3.1. Dependent and independent parameters of needleless electrospinning system (described in literature)

Independent Parameters	Dependent Parameters
• Polymer solution properties (concentration, viscosity, composition, surface tension, conductivity, molecular weigth) • Applied voltage • Distance between electrodes • Velocity or rotating roller* • Velocity of take-up fabric • Geometry of electrode • Geometry of collector	• Number of cones, density of jets • Life time of jets • Spinning performance, spinning performance/per jet • TotaL avr. current , current/jet* • Thickness of polymer solution layer on the surface of the roller* • Force acting on a jet* • Spinning area* • Distance between neighboring jets*

• Ambient conditions (temperature, relative humidity)	• Jet length in stable zone • Fiber diameter and distribution • Non-fibrous area • Launching time of jets

*The parameters defined or studied by the author

Some of these parameters were studied before and all the results show and explain the relation between dependent and independent parameters [1-9].

3.1. The New Parameters Introduced by Author

Until now many researchers have tried to explain mechanism and parameters of electrospinning system. Many of them concentrate on needle electrospinning system while some on roller system. The aim of this work is try to enlarge the number of parameters and to clarify spinning mechanism. The parameters studied up to now are not sufficient to explain experimental results. We found that suggested parameters affect our spinning performance and fiber morphology excessively. For instance, the roller speed which is affecting spinning area and number of jets determine spinning performance and fiber and nanoweb quality.

3.1.1. Independent Parameters

3.1.1.1. Velocity of Rotating Roller and Related Quantities (Secondary Independent Parameters)

The main mechanism of roller electrospinning system is based on a rotating roller which is immersed in a polymer solution tank. The role of roller is feeding to polymer solution to surface of roller by rotational movement as the pump in needle technique. It also relates to the thickness of solution layer on cylinder which is defined clearly below. If there is enough polymer solution fed, fibers are formed on the surface. It is necessary to examine the movement of roller since it determines feeding of polymer solution, number of Taylor cones on the surface and the spinning performance, which will be defined later. The related quantities of roller speed are explained in the next sections which are thickness of layer on the roller surface, spinning area and distance between neighbouring jets.

3.1.1.2. Thickness of Layer on the Surface of Roller

Roller rpm was never optimized and understood. It is one of the aims of experiment to clarify the role of roller rpm. The result should help understanding the electrospinning process as well as optimizing the process parameters.

The effect of roller rotation on the thickness of the polymer solution has been examined in different focuses. When speed (rpm) of roller falls below a critical value, no steady solution layer exists and the fluid drains off. Hereby Taylor's cones are not formed on the surface of roller.

We know that the thickness of solution reduces during rotating and spinning. In this case it is necessary to consider the reduction of thickness of the layer with spinning of solution. Another assumption for calculation of thickness of the layer and the amount of solution on the roller surface were determined using a special experiment and the computer programming in MATLAB. In this way the thickness of the solution layer can be predicted in every point of the roller during spinning.

Many investigators agree that the thickness of the layer on the rotating cylinder depends on the roller speed, polymer solution properties (viscosity, surface tension, molecular weight, and density), gravity, immersion angle and radius of cylinder. Herein, we focused on the roller speed and thickness of layer on the surface and their effects on spinning performance. If the roller speed is too low there is not enough solution on the roller surface for forming Taylor cones. On the other hand, if the roller speed is too high, there is not enough time for Taylor cones to be formed. In both the cases, spinning performance is very low or almost zero. It is necessary to consider roller speed and thickness of layer on the surface for higher production rate.

3.1.1.3. Feeding rate of polymer solution

Feeding rate is another secondary independent parameter depending on the roller velocity. It is well known from the needle electrospinning that the feed rate, here directly set on the syringe pump, influences the spinning mechanism and product quality considerably. The same can be expected in the roller electrospinning. The feed rate depends on the roller velocity in following way:

Let be: h – the thickness of solution layer (m)

ω - angular speed of roller (rpm)

d - roller diameter (m)

ℓ - roller length (m)

Then the linear velocity of the roller surface ν is equal to

$$\nu = \omega*\pi*d/60 \quad (m/s) \qquad \textbf{(3.1)}$$

and the voluminous feed rate ύ

$$ύ = h*\nu*\ell = h*\omega*\pi*d*\ell/60 \quad (m^3/s) \qquad \textbf{(3.2)}$$

The voluminous feed rate of polymer solution per 1 meter length of roller ύ/ ℓ is equal to

$$ύ/\ell = h*\omega*\pi*d/60 \quad (m^3/s/m) \qquad \textbf{(3.3)}$$

3.1.2. Dependent Parameters

3.1.2.1. Average Current and Current per Jet

Under an electrostatic field polymer solution droplet becomes distorted by the induced electrical charge on the liquid surface, and a stable jet of polymer solution is then ejected from the cone. The break-up of the jet depends on the magnitude of the applied electric current. Reneker and Chun characterized the bending instability in a charged jet during electrospinning [10]. Many investigators on electrospraying have focused on the understanding of a current–voltage relationship. Previous attempts to correlate current with electric field and flow rate suggested nonunique linear [11] or power law [12] dependences.

In this work average current was measured by using multimeter. Current per one jet was calculated according to formula 3.4 which was suggested in [2]:

$$CPJ = \frac{TAC}{N} \qquad \textbf{(3.4)}$$

CPJ implies current per one jet, TAC means total average current and N is total number of jets. Cengiz et. al. investigate a strong connection between the current of polymer solution jet and spinnability as well as spinning performance. Measurements were done on rod electrospinning system. They found that electric current of the solution jet increases with PU and TEAB concentrations increase and current indicates the spinning performance [6]. In the previous work [2] we found that the measurement of current/jet on both roller and rod electrospinning system is equal.

3.1.2.2. Parameters Measured Using Camera Records

In the experimental part, the number of jets, spinning area, jet life and position and distance between jets were measured using a camera records.

Spinning Area and Positions of Jets

Spinning area on the roller can be defined as the surface area where the Taylor cones are present. Movement of roller and life time of jet are the main parameters which are directly related to the spinning area. It was assumed in the literature [3] that the spinning area is equal to one the third of roller surface. Experiments showed that spinning area depends on many parameters. Spinning area will be determined by a camera record. For this aim, a special roller which has crosswise and lengthwise lines on the surface will be used. Thus, a net of oblongs is on the roller surface, every oblong has 5.3mm width and 5mm length. The total surface area (TA) of roller is 0.00411075 m^2. The lines on the roller surface will help to determine spinning area.

Spinning area mostly depends on roller velocity. The position of jets vs. velocity of roller is illustrated in Fig. 3.1.

Thickness of polymer solution layer on the roller influences solution flow into Taylor cones. Thickness of layer depends on velocity of roller and viscosity of solution. Simultaneously, polymer solution, when moving out of tank, needs certain time to create Taylor cones. Subsequently, solution from the vicinity of Taylor cones is dragged into the cones and following jets, being consumed gradually of the velocity of roller is small. There is small amount of solution through to the surface and the solution is spun away before it reaches tank again. Thus, only a part of potential spinning area is utilized. On the other hand, if roller velocity is too high, there is not enough time for solution to create Taylor cones and spinning area is small again (Fig. 3.1).

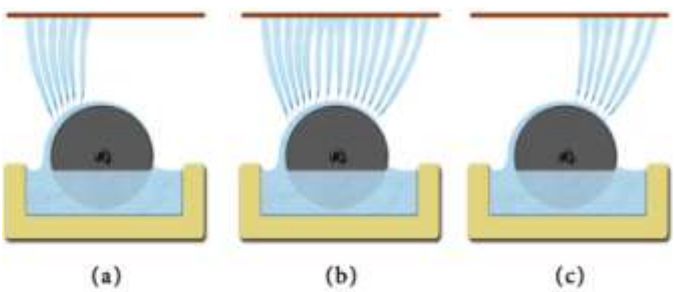

Fig. 3.1. Spinning of low (a), optimum (b) and high (c) roller rpm.

Number of Taylor's cones per spinning area/Distance between neighbouring jets

The average inter-jet distance is described in terms of wavelength (λ) as it was calculated by Lukas et al. [13]. According to this formula, electric field strength, surface tension and density of solution, relative permittivity of the surrounding gas and gravitational acceleration are the main parameters which affect the inter-jet distance. In this work, the distance between neighbouring jets will be calculated using the number of jets (n) and spinning area (A). The spinning area A is supposed to be composed of n identical squares belonging to Taylor's cones.

$$A = n \cdot x^2 \qquad \textbf{(3.5)}$$

x (m) is the length of the square side (and simultaneously the distance between Taylor cones). Then the average distance x between adjoining Taylor cones is

$$x = \sqrt{\frac{A}{n}} \text{ (m)} \qquad \textbf{(3.6)}$$

4. Experimental Methods

4.1. Survey of experiments

In the sub-chapter 4.1.1, the relations between the current measurement in the needle-, rod- and roller electrospinning are studied. As described in the chapter 3. there is a number of studies in literature dealing with the needle ES (electrospinning) whereas no studies were published on the current in needleless ES. It is the aim of this chapter to clarify whether the dependencies of current on the parameters in needle ES can be applied on needleless process.

In the sub-chapter 4.1.2, we determined the limits of polymer concentrations and salt concentrations in the polymer solutions for the main group of experiments described in sub-chapter 4.1.3.

In the sub-chapter 4.1.3, the relation between selected independent ES parameters and dependent parameters described in theoretical part are studied as the independent parameters were chosen;

- Velocity of spinning roller (rpm)
- Content of salts in the solutions

Two kinds of polymers were selected for the experiments, namely PEO soluble in water and PU soluble in DMF as mentioned in the chapter 3.4. These polymers show different, or even opposite dependence of spinning performance on the content of salt. Generally, two systems polymer-solvent-salt were studied, namely

a) PU-DMF-Salt
b) PEO-Water-Salt

Two salts, soluble in both DMF and water were applied in the systems a) and b) namely LiCl and TEAB. These salts differ considerably from each other in the size (and expected movability) of their cations.

4.1.1. On the Measured Current in Needle- and Needleless Electrospinning [2]

The aim of this part of work was to study the effects of various conditions during the electrospinning process on the current and current per jet. For this aim 4% wt PEO with 0.1% wt. KCl and NaCl polymer solution were prepared. Distilled water was used as solvent. Needle, rod and roller electrospinning were used to determine current and current/jet. As a result of the study, suitable quantities should be suggested to characterize the roller electrospinning of polymer solutions and melts [2].

In needle electrospinning, the effects of relative humidity, needle protrusion length, and needle diameter were studied. We found that relative humidity did not affect the current of a jet until 80%. On the other hand needle protrusion length affects the current so much due to intensity of the electric field at the tip of the needle, which grows with increasing needle protrusion length, is responsible for the rise in current. We observed that needle diameter is not so important to change current of jet but feed rate is important. Bhattacharjee et al. [14] found the dependence of the jet current on the voltage, feed rate, and solution conductivity, expressed as $I_{total} \sim E\ Q^{0.5}\ K^{0.4}$,where E is voltage, Q is the feed rate, and K is the solution conductivity. We found that, in all cases, the results obeyed the equation independently of the needle diameter and type of polymer solution.

It was found in both rod and roller electrospinning experiments that the current per jet does not depend on the number of jets. The current can be considered as regularly distributed among the jets present. The numbers of jets were calculated by using camera records. This knowledge gave us small information about mechanisms of spinning system. In the case of rod and roller, current/jet can be comparable. For this reason the jet lengths which is not clear to measure on roller electrospinning system, was measured on rod electrospinning system.

4.1.2. Determining of Optimum Concentration of solutions

For the main purpose of experiments we used two kind of polymers one is water soluble the other is not (PEO and PU). Two kinds of salts (LiCl and TEAB) were used. Before starting to main experiments we tried to determine optimum range for both solution systems. This optimum range is depends on the size of fiber and structure of nanoweb.

Conductivity (conductivity meter), surface tension (Krüss), and viscosity (Haake RotoVisco1 at 23°C) of the polymer solutions were measured. Images of the fibres were taken by SEM (Phenom FEI), and the diameters of the fibres were calculated using the NIS Element AR (NIKON) computer software. A digital camera (Sony Full HD NEX-VG10E Handycam, 14.2 megapixel-E18-200 mm Lens) was used to measure number of jets.
We can divide this part into two subtitles:

Polyethylene Oxide

Polyethylene oxide which is a water-soluble synthetic polymer and has a molecular weight 400.000 Da. PEO is purchased from Scientific Polymers. Distilled water was used as solvent. tetraethyleneammonium bromide was used as salt in a constant molar ratio (0.062mol/L). The interaction between salts and polymer solutions were explained in theoretical part. The results were shown in Table 4.1. It seems that viscosity increase due to increasing concentration of PEO as known in literature however we observed that conductivity decrease with increasing PEO concentration. Even all the solutions have the same amount of salt conductivity decreases slightly. It could be because of mobility of ions are restricted by macromolecules. The surface tension did not change significantly. All measurements were done at stable temperature.

Table 4.1. Properties of PEO solution in various concentrations

Sample Name	Content of salt in Molar ratio	Viscosity (Pa.s)	Conductivity (mS/cm)	Surface Tension (mN/m)
5%PEO	0.062M TEAB	0,19	4,98	61,98
6%PEO	0.062M TEAB	0,32	4,74	59,88
7%PEO	0.062M TEAB	0,48	4,33	61,79
8%PEO	0.062M TEAB	0,72	4,18	62,02
9%PEO	0.062M TEAB	0,96	4,11	60,92
10%PEO	0.062M TEAB	1,23	4,12	60,45

We can say that in this experiment we only changed the viscosity and observed its effects on dependent parameters. All solutions were spun in the same condition.

Polyurethane

In the case of PU we know the spinning range from literature which 17.5% wt. PU with 0-0.4-0.8-1.24% wt. TEAB. Aim of this primarily work is to determine amount of LiCl salt. In case of PU, the salt has bonds with polymer and solvent on the contrary to PEO. It is very important to arrange amount of salt. Salt is not affects only conductivity but also viscosity. The result of polymer solution is tabulated in Table 4.2. Firstly, we determined proper concentration range of LiCl salt and then we selected proper molar ratio of salt in this range for main part of experiment.

Table 4.2. Polymer solution properties of PU.

Sample	Viscosity (Pa.s)	Conductivity (mS)	Surface Tension (mN/m)
17.5% PU+ 0 mol/L LiCl	0.857	0.038	38.49
17.5% PU+ 0.056 mol/L LiCl	1,182	0.824	39.10
17.5% PU+ 0.14 mol/L LiCl	1.457	1.400	45.7
17.5% PU+ 0.28 mol/L LiCl	1.969	1.880	45.7
17.5% PU+ 0.45 mol/L LiCl	1.993	2.800	47.3
17.5% PU+ 0.56 mol/L LiCl	2.340	3.000	47.8

As we mentioned before viscosity and conductivity of polymer solution increased with adding salt. All solutions were spun under the same conditions.

The main purpose of both experiments is to determine proper solutions for main experiment and to see if there is correlation between independent and dependent parameters.

4. 1.3. Effect of Roller Velocity and Salt on Electrospinning System

For experiments two polymers are used. First one is polyethylene oxide and we determined 6% of PEO is optimum for main part of work. Tetraethyleneammonium bromide (from Fluka) and LiCl (from Lach-Ner s.r.o Czech Republic) were used as salt. Salts were added according to their molar ratio and the same amount for both as 0-0.024-0.062-0.124 mol/L. Polymer

solution properties were measured. Polyurethane (Larithane LS 1086 produced by Novotex) was chosen as second polymer. Dimethylformamide, (DMF), purchased from Fluka. 17.5% PU was chosen as optimum concentration. 2.2% distilled water was used in the DMF solvents. Water is a nonsolvent for PU. In the case of solvent/nonsolvent, viscosity increases by adding nonsolvent. Presumably, adding nonsolvent in a fixed PU concentration to PU/DMF solution produced the shrink of polymer chain coils, and hence, to results in more chain entanglements. As a consequence, the viscosity values of PU with PU/DMF present increase consistently with the increasing concentration of water in DMF/water. Adding salt to PU improves spinnability of solution therefore spinning performance [3, 15].
The same salts (TEAB and LiCl) as in PEO were used. Both of the salt has effect on viscosity of solution which means PU is better soluble in the presence of salt as explained in literature [8, 16]. In the case of PU, the molar ratio of each salt was determined and used according to range which the fibers are in nanometer. The molar ratios of TEAB salt in 17.5% PU polymer solutions were 0-0.022-0.044-0.071 mol/L and the molar ratios of LiCl salts were 0-0.014-0.028-0.056 mol/L.

5. Evaluation of Results

Nomenclature and Symbols of Solutions

PEO solutions in the water, polymer concentration 6 wt. % ;

-0 concentration of salts (PEO-▷)

-0.024 mol/L TEAB (tetraethylammonium bromide) (PEOT1-□)

-0.062 mol/L TEAB (tetraethylammonium bromide) (PEOT2-○)

-0.124 mol/L TEAB (tetraethylammonium bromide) (PEOT3-△)

-0.024 mol/L LiCl (lithium chloride) (PEOL1 -▽)

-0.062 mol/L (lithium chloride) (PEOL2-◇)

-0.124 mol/L (lithium chloride) (PEOL3-◁)

PU solutions in the DMF, polymer concentration 17.5 wt. % ;

-0 concentration of salts (PU-▶)

-0.022 mol/L TEAB (tetraethylammonium bromide) (PUT1-■)

-0.044 mol/L TEAB (tetraethylammonium bromide) (PUT2-●)

-0.071 mol/L TEAB (tetraethylammonium bromide) (PUT3-▲)

-0.014 mol/L LiCl (lithium chloride) (PUL1-▼)

-0.028 mol/L LiCl (lithium chloride) (PUL2-◆)

-0.056 mol/L LiCl (lithium chloride) (PUL3-◀)
Spinning conditions of PEO and PU are shown in Table 5.1 and 5.2:

Table 5.1. Spinning conditions of PEO solutions on roller ES

Sample	Voltage(kV)	Distance(mm)	Roller speed(rpm)	RH (%)	Temp.(C°)	Roller Length (mm)	Roller Diameter (mm)
6% PEO+ salt series	42	150	1-1.5-2-3	28.5	23	145	20

Table 5.2. Spinning conditions of PU solutions on roller ES

Sample	Voltage(kV)	Distance(mm)	Roller speed(rpm)	RH (%)	Temp.(C°)	Roller Length (mm)	Roller Diameter (mm)
17.5%PU+ salt series	62	130	1-3-5-7-9-14-62	24.5	16	145	20

In the case of PEO it is impossible to increase roller speed over 3 rpm, otherwise the fiber bundles starts to fly in the surround and fabric surface become hairy.

All dot and dash lines indicate the connection of the points.

- Measurement of surface tension: The measurement done on KRÜSS Tensiometers and their software LabDesk by using plate method and illustrated in Fig. 5.1.

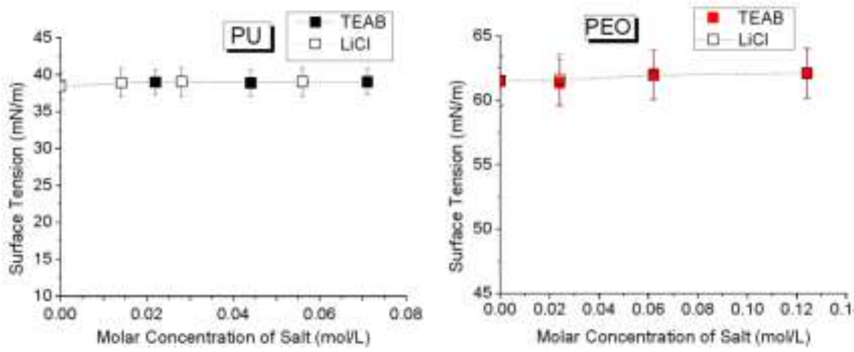

Fig. 5.1. Surface tension of polymer solutions

- Measurement of viscosity: The zero-shear viscosities of solutions were measured by Haake RotoVisco1 at 23 ^{0}C and illustrated in Fig. 5.2.

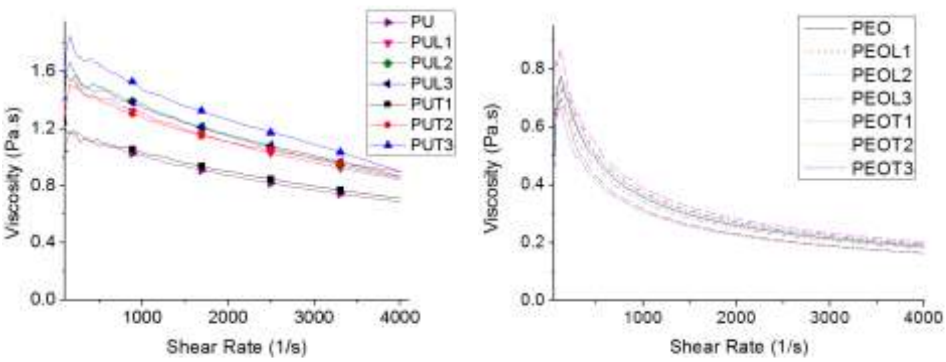

Fig. 5.2. Viscosity of polymer solutions

- Measurement of conductivity: The conductivities of solutions were measured by conductivity meter OK-102/1 branded Radelkis and illustrated in Fig. **5.3**.

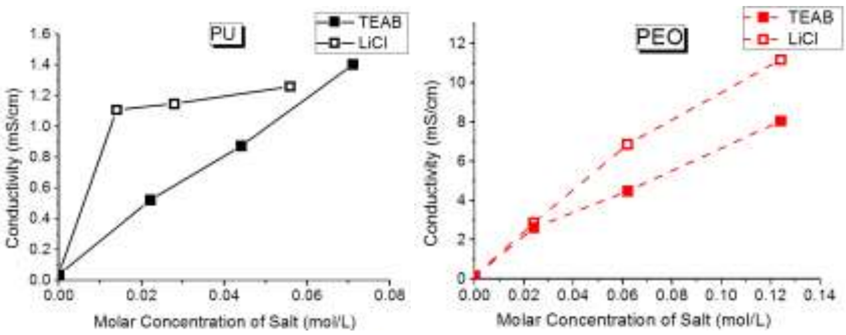

Fig. 5.3. Conductivity of polymer solutions

-Measurement of launching time of jets: Launching time of jets is the time between switching on the voltage and the moment when the first jet appears on the surface of spinning roller. Launching time was measured using two methods:

-the first jet was indicated on the camera record

-the first jet was indicated as the jump on the current-time record.

The results of both the methods were identical.

The launching time was measured in two different electrospinning arrangements:

-the device (roller electrospinning)

-the device with a grounded wire (roller electrospinning).

The latter arrangement was studied based on the experience gained in previous experiments. The grounded wire placed close to the spinning electrode deforms the electric field. This many times helped to create Taylor's cones of polymer solutions with a difficult spinnability.

Camera and current measurement were used simultaneously. At the time we replaced wire between collector and roller for PU solutions, suddenly cones were formed in a few seconds and it started to spin on the middle of roller. Two unstable solutions were chosen for this experiment.

Measurement of number of jets and spinning area: A Sony Full HD NEX-VG10E Handy cam (14.2 megapixels)-E18-200 mm Lens camera was used in the experiments. Spinning area was determined by taking image from camera and using NIS-elements software (Figures 5.4-5.5).

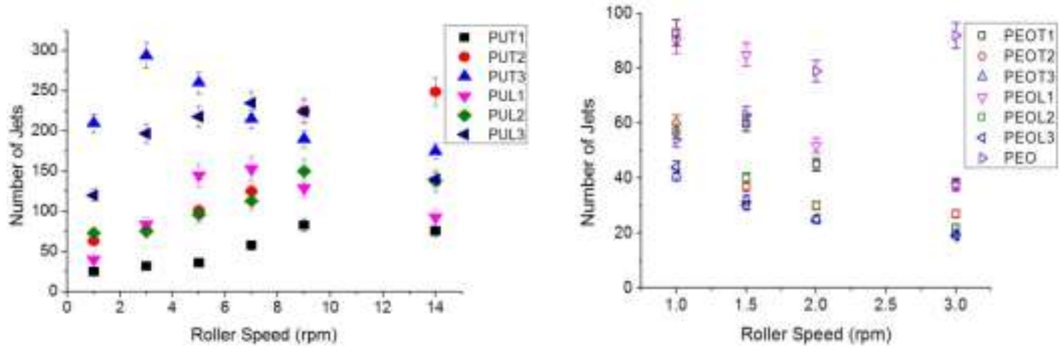

Fig. 5.4. Number of jets on the roller

At 62 rpm; the number of jets of PUT1 solution was zero and the other solutions (PUT2-PUT3-PUL1-PUL2-PUL3) had fewer number of jets on the surface than 14 rpm.

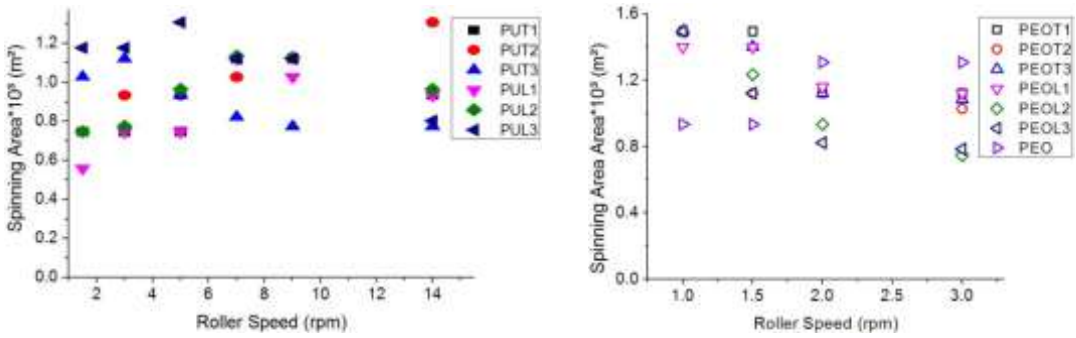

Fig. 5.5. Spinning area

At 62 rpm ; the spinning area of PU solutions was smaller than that at 14 rpm.

- Measurement of current and current/jet: Roller electrospinning technique used for spinning. The current is evaluated by measuring the voltage on the resistor R placed between the collector electrode and earth. Resistance R is equal to 9811 Ω. The voltage is measured by a 33401A digital multimeter produced by Agilent and the values are stored in a computer at selected points on the time axis (typically 20 records per second) (Figures 5.6-5.7).

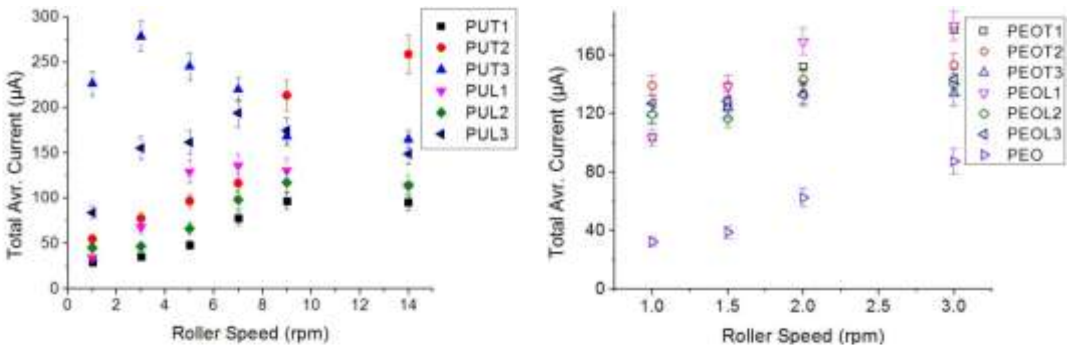

Fig. 5.6. Total current vs. roller speed

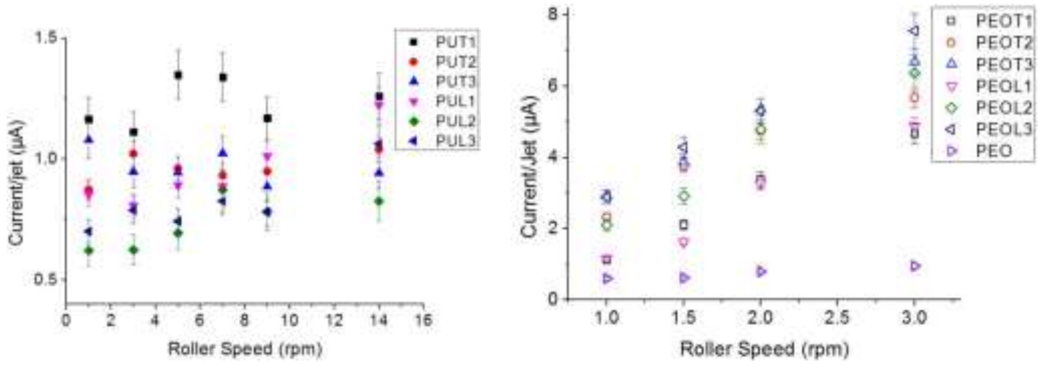

Fig. 5.7. Current/jet vs. roller speed

- Measurement of distance between neighboring jets: It was determined by taking image from camera and then calculating spinning area. Number of jets were determined and illustrated in Fig. 5.8. At 62 rpm; the distance between jets of PUT1 solution was zero and the other solutions (PUT2-PUT3-PUL1-PUL2-PUL3) had the same distance of jets with 14 rpm.

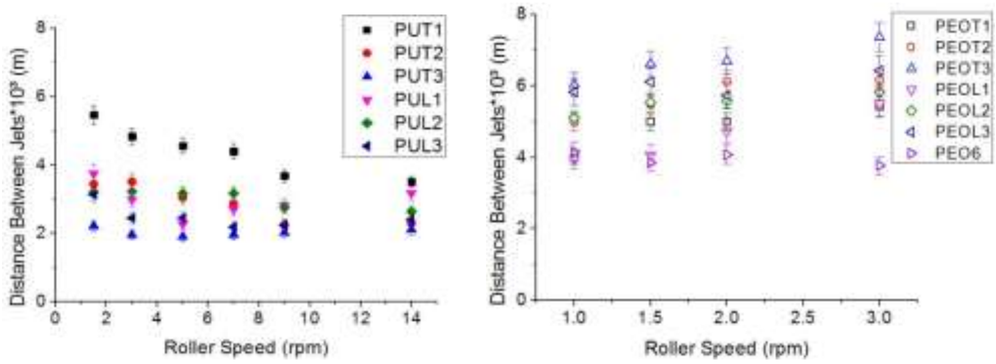

Fig. 5.8. Distance between jets vs. roller speed

- Measurement of spinning performance and performance/jet: 10x10 cm^2 nanofiber webs were prepared and measured on a balance. The calculations were done and results are in Figures 5.9.-5.10. At 62 rpm; the SP of PUT1 solution was zero and the other solutions (PUT2-PUT3-PUL1-PUL2-PUL3) had fewer SP than 14 rpm.

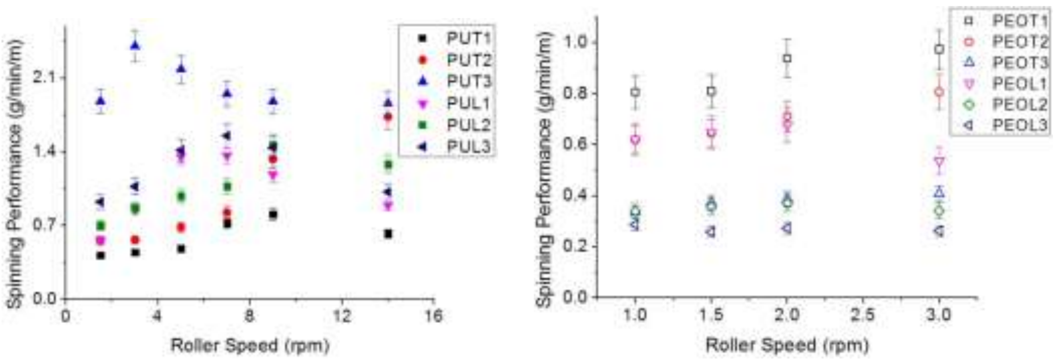

Fig. 5.9. Spinning performance of PU and PEO nanofibers in various rpm.

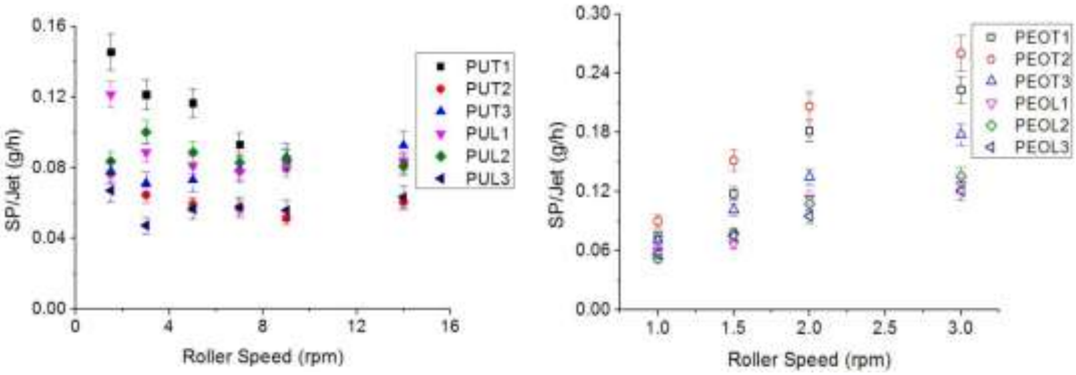

Fig. 5.10. SP/jet of PU and PEO nanofibers in various rpm.

At 62 rpm ; the SP/jet of PU solutions were almost the same with the result of 14 rpm.

-Measurement of fiber diameter and diameter distribution: Images of microstructure of nanofibers membrane were taken by scanning electron microscope (SEM) branded by Feico. NIS-elements software was used to determine fiber diameter and diameter distribution (Fig. 5.11). At 62 rpm; the fiber diameter and diameter distribution of PU solutions were very high.

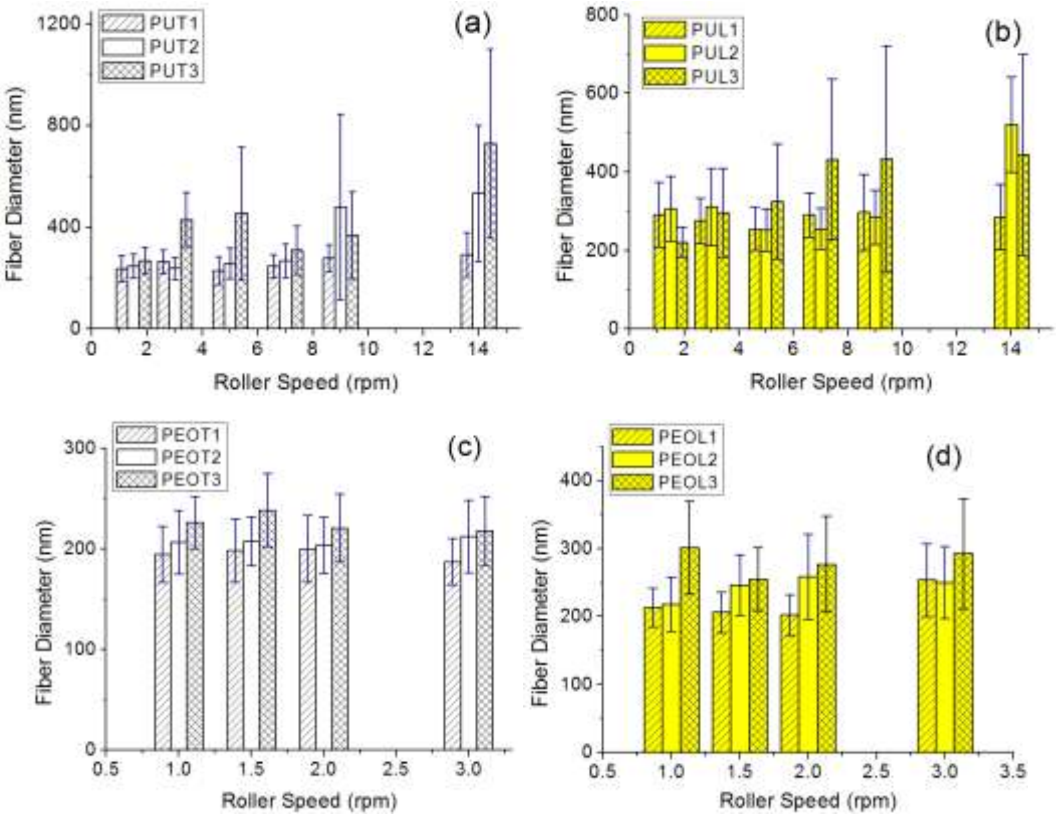

Fig. 5.11. Fiber diameter vs. roller speed (a) PU with TEAB salt, (b) PU with LiCl salt, (c) PEO with TEAB salt, (d) PEO with LiCl salt.

- Measurement of non-fibrous area: Using SEM images and NIS-elements software, non-fibrous areas were calculated. At 62 rpm, the non-fibrous area of PU solutions was extremelly high.

- Measurement of length of jets: A Sony Full HD NEX-VG10E Handy cam (14.2 megapixels)-E18-200 mm Lens camera was used in the experiments. For measurement of jet length a rod with 10 mm diameter electrospinning system was used. The length of jet was measured on the record of camera (Fig. 5.12).

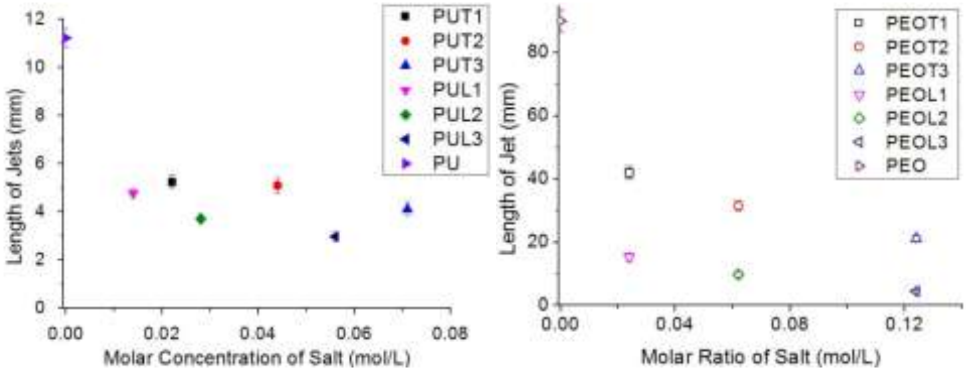

Fig. 5.12. Length of jets vs. molar ratio of salt

6. Discussion

6.1. On the Measured Current in Needle- and Needleless Electrospinning

In the needle electrospinning, the effects of relative humidity, needle protrusion length, and needle diameter were studied. Relative humidity does not influence the value of current except for extremely high humidity (over 80%), when the air becomes conductive. The current increases with increasing needle protrusion length. Undoubtedly, the intensity of the electric field at the tip of the needle, which grows with increasing needle protrusion length, is responsible for the rise in current. In the roller electrospinning, the electric field intensity at the places of origin of the jets is probably rather low, close to that at a zero value of needle protrusion length. It corresponds with the generally lower spinnability of any polymer solution on the roller compared with needle spinning. The results of the roller electrospinning process show that the current as well as the number of jets is rather constant during the spinning process. The values of current per jet in the studied spinning systems are similar: 1–10 µA in the needle spinning process, 5–7 µA in the rod spinning process, and ca. 11 µA in the roller electrospinning process.

6.2. Determining optimum concentration of solutions

Polyethylene Oxide

The results illustrated in Table 4.1 show that the differences in electric conductivity and surface tension of studied solutions are not significant. Conditions of electrospinning were the same for all the materials. Therefore, only the concentration of solutions and related solution viscosity influenced the spinning performance and fiber diameters.

Polyurethane

The results illustrated in Table 4.2 show that the differences in surface tension of studied solutions are not significant while the viscosity and conductivity are affected by addition of salt. Conditions of electrospinning were the same for all the materials. We can assume that viscosity and conductivity of solutions are responsible for significant differences in spinnability, throughput and fiber quality. Solution viscosity shows an important effect on the fiber diameter and morphology of nanofiber layer.

6.3. Effect of roller velocity and salt on electrospinning process

Solutions of PU in DMF and of PEO in water containing salts TEAB and LiCl were employed in the experiments in the part 4.1.2. These solutions and their concentrations were chosen for following reasons:

1. PU and PEO show considerably different behaviour in ES process, namely opposite influence of added salts on their spinnability;
2. The solutions allow a comparison between the aqueous and non-aqueous systems;
3. Concentration limits of polymers and salts in the solutions were determined in the chapter 4.1.2.

Basic properties of the solutions measured and described in the chapter 4.3. show that:

1. Surface tension of the solutions corresponds to that of used solvents and is not significantly dependent on the content of salts. Thus, the surface tension was not an influencing independent parameter in the experiments;

2. Viscosity of the solutions as a function of share rate shows considerably different character of both the polymers: Effective viscosity of PEO strongly depends on share rate, that of PU shows only moderate dependence. Thus, the macromolecules of PEO 400 kDa show high degree of mechanical entanglement and highly macromolecular character. The strength of PEO jets as a necessary requirement for spinnability is satisfactorily high at relatively low polymer concentration and corresponding viscosity. On the other hand, spinnability of PU requires rather high polymer concentration and corresponding viscosity. Viscosity of PU solutions grows with content of salts which is not the case in PEO solutions.

3. Conductivity of the solutions of the both TEAB and LiCl in water as well as in DMF is generally high and all the values are surprisingly close to each other. TEAB shows the same conductivity in water as LiCl does in spite of its evidently bigger ions. The values of conductivity in DMF are, again surprisingly, close to those in water which refers to a high degree of dissociation of the salts in DMF. On the other hand, the conductivities of polymer solutions containing salts differ from each other to some extent. The PEO solutions show higher conductivity than PU solutions due to their lower viscosity and corresponding greater movability of ions in direct electric field. The PU solutions containing LiCl are more conductive than those with TEAB as their ions are more movable in the highly viscous liquid.

4. The other basic properties of the solutions were not measured but there are probably a number of differences between the solutions which may cause their different behaviour in the ES process. For instance, the kind and concentration of polar groups in polymers, solvents and in the systems polymer-solvent-salt are certainly responsible for interactions of the solutions of their components with the electric field. Character and content of polar groups influences dielectric constant of materials.

The launching time of jets depends significantly on the content of salts in the polymer solutions. With increasing salt concentration the launching time decreases in the case of PU as well as PEO. If the electric field is deformed by the grounded wire, launching time also decreases significantly due to high local concentration of electric field.

Measurement of the ***jet length*** shows significant differences between PU and PEO behaviour. The jets of electrospun PEO are much longer than those of PU. These are probably caused by considerably greater interactions of PEO with electric field when compared with those of PU due to more polar character of PEO. Stronger interactions lead to a faster jet deformation and resulting jet length.

In ES, PU and PEO show essential differences in their behaviour, namely in ***the number of jets*** on the spinning roller (and in the spinning performance as discussed below).

First, the number of jets is considerably larger at PU. Two attempts have been done to explain this difference:

-The theory of shielding effect of conducting lightning rods was taken into account [18]. According to this theory, the electric field is screened out in the conical space having a tip at the end of conductor and a top angle about 45^{o} to 60^{o} [19-25]. We supposed that the distance between cones is proportional to the length of jets and only one jet can be formed within the area of this cone base.

- Lukas [13, 26-27] calculated the distance between jets by calculating inter-jet distance called the critical wavelength. This parameter allows estimation of the relative productivity of the electrospinning process. Calculation of the critical wavelength λc can be done using the equation $\lambda_C = 2\pi\alpha$, where α denotes the capillary length.

Second, the number of PU cones grows with the content of salt in the solution. On the contrary, the number of PEO cones falls with growing salt concentratrion. This effect seems to be difficult to explain as the role of salts is multiple:

1. Salt (TEAB more than LiCl) creates complex structures with PU which leads to changes in the interactions macromolecule – macromolecule and macromolecule – solvent. This causes an increase in viscosity, related entanglement number and stronger jets. Thus, the effect of salts in the PU solutions is following:

-stronger jets result in longer average life of jets [8];

-the jets are shorter due to higher content of ions and greater viscosity [1], the number of jets grows.

These effects of salts do not occur in the PEO solutions as the salts do not create complex structures with PEO.

2. Salts increase the conductivity of the polymer solutions. Increase in the conductivity changes the character of the polymer solution from a semi-conductor to a conductor so that the solution is losing the character of a „leaky model“ . This leads to the loss of ability to create Taylor's cones.

Apparently the effect of salts according to 2. works against that in 1. In the case of PU, the effects described in 1. predominate those in 2. In the case of PEO, only effects according to 2. apply.

The differencies between the PU and PEO behavior are also based on different polymer characteristics, namely:

1. PEO 400 kDa has the molecular weight high enough to create strong jets even at the low concentration and corresponding viscosity. It is not the case of PU. PU needs an increase in entanglement level using a salt.

2. PEO contains strongly polar groups so that it shows strong interactions with electric field. This is expressed by a high value of dielectric constant. Again, this is not the case of PU. PU needs an increase in polarity via creating complexes with salts.

The spinning performance shows in principle the same tendencies as the number of jets. Nevertheless ***the spinning performance per jet*** is not an independent quantity. The amount of polymer solution flowing through one Taylor's cone depends on the viscosity of solution, on the thickness of solution layer and on the drawing force of electric field, dependent on dielectric properties of the polymer or polymer solution.

The total average current shows the same tendencies as the spinning performance does does (Fig. 6.1). On the other hand, the plot of the current per jet vs. spinning performance per jet does not show clear relation (Fig. 6.2). When a jet breaks up into secondary jets, the additional ions are transfered from the polymer solution into the air in the vicinity of the jet [28]. Several reports have suggested that charge carriers are transported in the atmosphere surrounding fluid jet [14, 29-30]. Therefore, measured current grows with spinning performance and with the amount of salts in the polymer solutions. The current is probably not transported from one to the other electrode primarily with the polymer or solvent. The mechanism of current in ES was studied separately in more detail [18] and the results are not a part of this work.

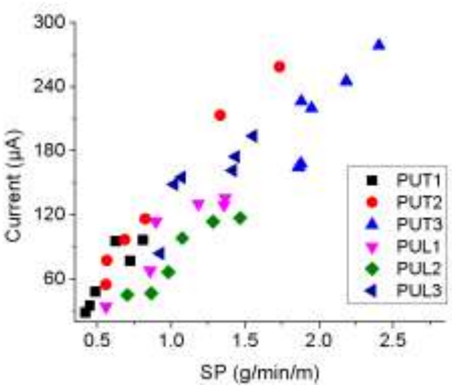

Fig.6.1. Average total current vs. spinning performance (PU)

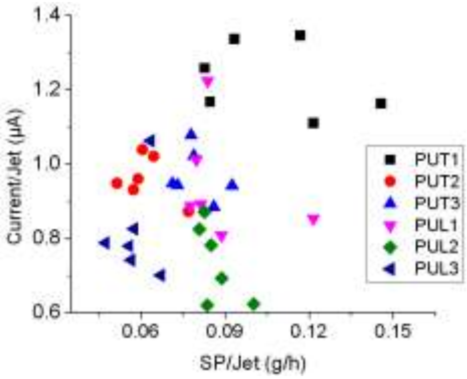

Fig. 6.2. Current per jet vs. spinning performance per jet (PU)

To explain rather complex and non-monotonous dependencies of studied dependent ES parameters on the ***spinning roller velocity***, the video records of the spinning process were carefully studied and following velocities compared:

$\vec{v}$ - velocity of roller surface (ms^{-1})

$\vec{v}_{j1}$ - velocity of jets against static collector electrode

$\vec{v}_{j2}$ - velocity of jets against the surface of moving roller electrode.

The situations depending on the movement of roller are shown in Fig. 6.3.

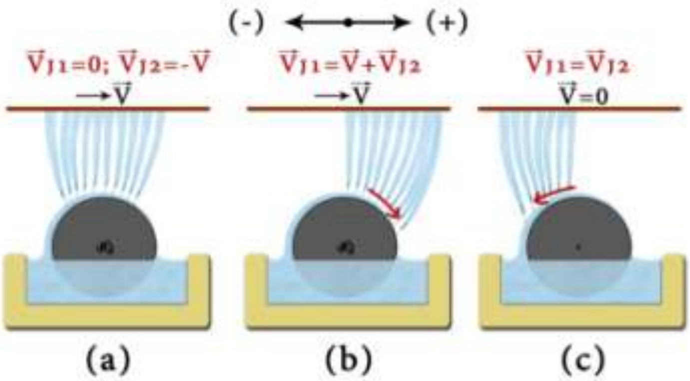

Fig. 6.3. Movement of roller and position of jets.

A. Low roller velocity (Fig. 6.3.a): The jets move against the moving surface of roller and keep stable positions against the collector electrode.

$$\vec{v}_{j2}' = -\vec{v} \quad \text{and} \quad \vec{v}_{j1} = 0 \qquad (6.1)$$

B. High roller velocity (Fig. 6.3.b): The jets move in the direction of $\vec{v}$ and reach the solution bath.

$$\vec{v}_{j1} = \vec{v} + \vec{v}_{j2} \quad (\vec{v}_{j2} \text{ being negative}) \qquad (6.2)$$

C. Roller stops suddenly (Fig. 6.3.c): The jets start moving against the former direction of roller movement.

$$\vec{v} = 0 \text{ and } \vec{v}_{j1} = \vec{v}_{j2} < 0 \qquad (6.3)$$

The case C illustrates crucial importance of the strength of jets in the ES process. It also shows that the jets have their „roots“ inside the solution layer, the „roots“ being moving, partially oriented macromolecules of dissolved polymer.

The border velocity $\vec{v}$ separating the cases A and B depends on movability of jets against the surface of spinning roller is a complex function of solution viscosity, thickness of solution layer and drawing electric force F.

Using the above described observations, the dependencies of measured ES parameters on the roller velocity can be explained as follows:

Generally, the dependence of the number of jets, spinning area and spinning performance on the roller velocity is non-monotonous for following reason:

If the roller velocity is low, then the solution feed and the thickness of solution layer on the roller are small. This is limiting the values of above mentioned dependent parameters. Also, the jets move against the surface of the roller and keep stable positions against the static collector electrode. If the roller velocity exceeds a critical value, the limited movability of jets leads to their movement towards the solution bath. This causes a reduction in spinning area and number of jets but not necessarily that of spinning performance. Spinning performance can be kept more or less constant or even slightly grow with increasing roller velocity as the loss of the number of jets is compensated by greater throughput per jet due to increase in the thickness of solution layer. The critical value of the roller velocity depends on the viscosity of polymer solution and probably on some other properties of polymer solution such as its spinnability. In the case of PEO, the critical value is lying at the low roller velocity (below 1 rpm) as the movability of jets is limited due to rather thin solution layer. Therefore, the non-monotonous character of above mentioned dependencies is not apparent from the experimentally found data.

Quality of produced nanofibers and nanofiber layers was tested in the experiments, namely fiber diameters and non-fibrous area, though this was not an important part of the work. In the PU ES, the highest content of salts leads to an increase in viscosity and bigger fiber diameters connected with it. High salt content also leads to lower quality of PU nnanofiber layers. On the contrary, PEO nanofiber diameters and quality of nanofiber layers do not significantly depend on the content of salt if this lies above a certain limit.

There are some dependencies found in the experimental results which were not explained by performed experiments and their explanation requires specific studies. The dependence of jet lengths on the roller velocity is one of examples.

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Published in refereed journals, technical notes, letters to the editor, discussion, case reports and a summary of publications other than the type of article

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12. O. Jirsak, K. Farana, F. Yener, ‘Electrospinning Studies: Jet Forming Force’, **19th Strutex**, Liberec-Czech Republic, 2012.
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14. F. Yener, B. Yalcınkaya, O. Jirsak, ‘Roller Electrospinning System: A Novel Method to Producing Nanofibers’, **The International Istanbul Textile Congress**, ISBN: 978-605-4057-37-5, pp. 917-922, Istanbul, Turkey, 2013.
15. B. Yalçinkaya, F. Yener, F. Cengiz Callioglu, O. Jirsak, ‘Relation between number of Taylor Cone and life of jet on the roller electrospinning', **The International Istanbul Textile Congress**, ISBN: 978-605-4057-37-5, pp. 213-218,Istanbul, Turkey, 2013.
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1. F. Yener, O. Jirsak, R. Gemci, ‘Effect of Polymer Concentration on Electrospinning System’, **Fiber Society**, Bursa, spring 2010.
2. F. Yener, B. Yalcinkaya, O. Jirsak, ‘Effect of Jet Electric Current on Jet Regimes in Electrospinning of Polyvinyl Butyral Solutions’, **Fiber Society**, St. Gallen, Spring 2012.
3. F. Yener, O. Jirsak, ‘A Study on Physical Principles of Roller Electrospinning’, Advanced Material World Congress, 16-19 September, Izmir, 2013.

National conference posters presentations

1. F. Yener, O. Jirsak, R. Gemci, ‘Effect of Concentration on Roller Electrospinning’, **6th Nanoscience and Nanotechnology Conference**, Izmir, Turkey, 2010.
2. F. Yener, B. Yalcinkaya, O. Jirsak, M. Kumalo,’ Increasing Fabric Performance of Electrospun Nano Mat’, **8th Nanoscience and Nanotechnology Conference**, Abstract 0111, pp. 393, Ankara, Turkey, 2012.
3. B. Yalçınkaya, F. Cengiz Callıoglu, F. Yener, O. Jırsak, Effect of Polymer and Salt Concentration on Jet Electric Current in Electrospinnig, **8th Nanoscience and Nanotechnology Conference**, Abstract 0162, pp. 401, Ankara, Turkey, 2012.

Supported by national organizations to take part in the project

1. ‘Set up of Needle Electospinning System’ BAP Project, Kahramanmaraş Sutcu Imam University (Project Manager Asistant).
2. ‘Development of new methods for study of mechanism of electrospinning’ Ministry of Education, Youth and Sports of the Czech Republic (Student’s grant competition TUL in specific University research in 2012 - Project No. 4866).
3. ‘Study of mechanism of electrospinning’ Ministry of Education, Youth and Sports of the Czech Republic (Student’s grant competition TUL in specific University research in 2013 - Project No. 48004).

Awards

4. Swiss National Science Foundation (SNSF) for the conference **Fiber Society**, Empa, St. Gallen, 2012.
5. Honorable mention Poster Award in **Nanocon**. Brno, 2013.

9. Conclusion

New independent and dependent ES parameters were introduced and studied by author, namely:

-velocity of rotating roller and related quantities – secondary independent parameters (thickness of solution layer, feeding rate of polymer solution, time available for Taylor's cones formation). The relations between the roller velocity and secondary independent parameters were calculated and/or measured;

-average electric current in roller ES and current per jet;

-spinning area and positions of jets;

-number of Taylors‘s cones per spinning area and the average distance between neighboring cones;

-polymer solution throughput per Taylor's cone was calculated.

Above mentioned parameters were introduced and studied with the aim of better understanding the ES mechanism. In the previous studies focused on a limited number of parameters such as molecular weight of polymer, solution concentration and viscosity, spinning performance), some ES phenomena remained unexplained.

Curriculum Vitae

Surname: Yener

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Education :

Ph.D. (2011-2014) Technical University of Liberec, Textile Faculty- Nonwoven Dept. /Czech Republic

Master (2007-2010) Kahramanmaras Sutcu Imam Universty Textile Eng. Department

Degree: 95.8/100

2009 (4.5 months) Technical University of Liberec (Czech Republic)-Erasmus Programe Nonwoven Dept.

Undergraduate

2002-2006 Gaziantep University Textile Eng. Department

Degree: 78.3/100

2006 (6 months) Akademia Techniczno-Humanistyczna (Poland)-Erasmus programe Textile Eng. Department

Other Languages : **English** (Good at reading, writing and speaking)

Master Thesis: "Comparision of Needle and Needless Electrospun Nanofibers and Effect of System Parameters on Electrospun Nanofibers", August 2010 Kahramanmaraş.

Work Experiences:

1. Internship in **Sanko Holding** (yarn production stage), 2003 (1 month)
2. Internship in **Sanko Holding** (knitting and weaving), 2004 (1 month)
3. Production and quality control engineer in **Adil Hali Iplik San. Ldt. Sti**. (2007-2009)
4. Research assistant in **Kahramanmaras Sutcu Imam University** (2009-2010)
5. Research assistant in **Bilkent University-National Nanotechnology Research Center** (2010-2011, 6 months).

Record of the state doctoral exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktoranda:	**Ing. Fatma Yener**
Datum narození:	**1. 1. 1983**
Doktorský studijní program:	**Textilní inženýrství**
Studijní obor:	**Textilní technika**
Termín konání SDZ:	**13. 3. 2014**

prospěla ✓ ~~**neprospěla**~~

Komise pro SDZ:

		Podpis
Předseda:	prof. RNDr. David Lukáš, CSc.	
Místopředseda:	prof. Ing. Jiří Militký, CSc.	
Členové:	prof. Ing. Jaroslav Šesták, DrSc., Dr.h.c.	
	doc. Ing. Eva Košťáková, Ph.D.	
	prof. Ing. Ivan Stibor, CSc.	

V Liberci dne 13. 3. 2014

O průběhu SDZ je veden protokol.

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Reccomendation of the supervizor

Stanovisko školitele k doktorské dizertační práci

New Methods in the Study of Roller Electrospinning Mechanism

Autorka: Fatma YENER, MSc

Předložená dizertační práce se zabývá studiem mechanismu elektrostatického zvlákňování. Navazuje na několik předchozích prací zaměřených na přípravu nanovláken tímto postupem. Charakter práce je dán tím, že zpracovávané téma je relativně nové a vzhledem k velkému počtu nezávislých i závislých proměnných procesu elektrostatického zvlákňování poměrně málo popsané. Je tedy nemožné zabývat se studiem pouze jednoho či dvou vybraných parametrů, pokud není podrobně znám vliv ostatních. To dává předložené práci poměrně velký rozsah daný potřebou brát v úvahu vliv různých okrajových podmínek.

Autorka v teoretické části práce dosti podrobně mapuje dosud studované parametry elektrostatického zvlákňování a jejich vliv na proces a jeho výsledky. Na základě toho navrhuje, definuje, vyvíjí a analyzuje další nezávislé a závislé proměnné, od jejichž studia lze očekávat hlubší porozumění studovanému problému.

V rozsáhlé experimentální části podrobně studuje vzájemné souvislosti vybraných nezávislých parametrů (obsah solí v polymerních roztocích a rychlost otáčení zvlákňovací elektrody) a závislých parametrů. Výsledky jsou podrobně diskutovány a přinášejí nové poznatky využitelné teoreticky i přímo v technologii výroby nanovláken.

V průběhu studia autorka úspěšně publikovala. Web of Science uvádí 6 jejich prací, z toho 5 časopiseckých. Kromě toho prezentovala 14 příspěvků a 5 posterů na mezinárodních konferencích.

Dizertační práce uchazečky je zpracována na solidní úrovni s ohledem na jazykovou i věcnou stránku. Práci

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k obhajobě.

V Liberci, 1. dubna 2014

Školitel: Prof. RNDr. Oldřich Jirsák, CSc

Rewievs of the opponents

Oponentský posudek

doktorské disertační práce

"New Methods in the Study of Roller Electrospining Mechanism"

kterou podává

MSc. Fatma Yener

Fakultě textilní Technické univerzity v Liberci

oboru Textilní materiálové inženýrství

Předložená disertační práce vznikla na půdě Katedry netkaných textilií Fakulty textilní Technické univerzity v Liberci. Tato katedra je známá u nás i v zahraničí originální metodou přípravy polymerních nanovláken metodou elektrostatickým zvlákňováním. Na počátku současných úspěchů je patent, který už před deseti lety obdržel Profesor Oldřich Jirsák se spolupracovníky. Na tento výchozí patent pak navázala celá řada dalších experimentálních i teoretických studií v rámci Technické univerzity v Liberci a také úspěšný vývoj komerčního zařízení na kontinuální přípravu nanovláken, které pod názvem Nanospider nyní vyrábí a dodává liberecká firma Elmarco. Fatma Yener se prací na své disertaci zařadila do tohoto plodného úsilí. Mohla na dosavadní výzkum logicky navázat už proto, že profesor Jirsák je jejím školitelem.

Vlastní disertační práce má standardní členění, které zahrnuje teoretickou část, charakteristiku experimentálních materiálů a přehledné shrnutí výsledků. Dobře napsaný úvod prokazuje, že autorka pronikla do celé problematiky elektrostatického zvlákňování. To prokazuje i rozsáhlý soubor celkem 176 odkazů, na některých vystupuje jako autorka nebo spoluautorka. Po literárním úvodu následuje popis experimentálních materiálů a část „Výsledky". Autorka své výsledky odborně a zasvěceně komentuje. Podstatné je, že autorce se podařilo vzájemně porovnávat teoretické vztahy a modely s praktickými experimenty. Poznatky, kterých dosáhla, tak mají bezprostřední praktický význam. Umožní ovládat a optimalizovat celý složitý proces úpravou nezávislých parametrů. Hlavní výsledky své práce, které jsou přínosné pro teorii a techniku elektrostatického zvlákňování autorka přehledně popsala na str. 107. Zamýšlí se také nad dalším směrem výzkumu, který by vedl k lepšímu porozumění vztahům mezi nezávislými a závislými parametry procesu.

Po formální práce má práce vysokou úroveň. Text je doprovázen velkým množstvím názorných ilustrací. V příloze pak představuje řadu mikroskopických snímků připravených nanovlákených textilií a jejich statistické vyhodnocení. Práce je celá napsána anglicky a angličtina textu je – pokud to mohu sám posoudit – na velmi slušné úrovni. Právě s anglicky napsanou prací předloženou v České republice na české vysoké škole ovšem mohou vzniknout problémy. Tak disertační práce neobsahuje název v češtině ani stručný český souhrn. To by měla autorka ještě před vlastní obhajobou doplnit.

Velmi kladně je třeba hodnotit, že autorka už některé své výsledky publikovala v kvalitních recenzovaných mezinárodních časopisech. Na čtyřech významných mezinárodních publikacích vystupuje v seznamu autorů na prvním místě. To je určitě nadprůměrné, a nejen v rámci samotné liberecké školy.

Tyto připomínky však nechtějí snižovat zřejmé přednosti a přínosy této práce. Autorka shromáždila velké množství původních experimentálních dat a poznatků, které budou jistě užitečné i při dalším navazujícím výzkumu na fakultě. V disertační práci poukázala na další možnosti a cesty, jak metodu elektrostatického zvlákňování dále rozvíjet. Některé výsledky disertační práce byly už publikovány v recenzovaných časopisech. Lze tedy konstatovat, že cíle disertační práce, tak jak byly vytyčeny na str. 21 (Aims of the work), byly splněny.

K práci mám několik otázek, které by se mohly stát podnětem ke krátké diskusi při obhajobě:

(1) Představte přehledně základní možnosti a modifikace elektrostatického zvlákňován, pokud jde o zdroj vláken a typ kolektoru. Jednotlivé prvky popište v anglickém i v českém jazyce.

(2) Shrňte stručně hlavní přínosy své práce vzhledem k dosavadnímu stavu poznatků a dřívějším pracím na katedře netkaných textilií. .

(3) Jaké jsou výhody rotujícího válce jako zdroje nanovláken?

Závěrem chci konstatovat, že není pochyb o tom, že **MSc. Fatma Yener,** autorka předložené práce, se představuje jako vědecká osobnost a plně si zaslouží vědecko-akademickou hodnost *philosophiae doctor*, PhD. **Předloženou disertační práci doporučuji k obhajobě.**

V Praze 25.7. 2014

Prof. RNDr. Miroslav Raab, CSc.

Oponentský posudek

doktorské dizertační práce

Fatmy YENER, MSc

New methods in the study of roller electrospinning mechanism

Oponent: Ing. Ladislav Mareš
NAFIGATE Corporation, a.s.
Praha

Doktorská dizertační práce byla vypracována ve studijním oboru Textilní materiálové inženýrství na katedře netkaných textilií a nanovlákenných materiálů Textilní fakulty Technické univerzity v Liberci.

Práce se týká velmi aktuální oblasti polymerních nanovlákenných materiálů, konkretně jejich přípravy metodou bezjehlového elektrostatického zvlákňování a jejich kvality. Výroba a využití nanovláken se v současnosti rychle rozvíjí, přičemž mechanismus jejich tvorby není dosud plně fyzikálně popsán ani experimentálně prozkoumán. Vyšší stupeň poznání procesu by měl vést ke zvýšení produktivity výroby a tím ke snížení ceny nanovláken. Poznání parametrů dále umožní řízení procesu a tím připravovat materiály se širokou variabilitou jejich vlastností ať už volbou polymerů nebo různými způsoby modifikací. To jsou bezesporu podmínky nutné k širší využitelnosti těchto nových materiálů a jejich specifických vlastností. Tímto směrem je práce dle definice cílů autorkou zaměřena a její nasměrování se proto jeví vysoce užitečné.

Práce je psána anglicky na poměrně slušné jazykové úrovni a v logickém a přehledném členění. Provedení a značení obrazů, grafů a tabulek je správné a jasné a činí práci pro čtenáře srozumitelnou.

V teoretické části autorka výstižně popisuje nezávislé a závislé proměnné elektrostatického zvlákňování a jejich vzájemné vztahy dosud popsané v literatuře. Podle mých znalostí i podle seznamu použité literatury je teoretická část široce a správně pojata. V téže teoretické části pak autorka definuje další, jí navržené parametry. Umístění tohoto vlastního tvůrčího přínosu k problematice vedle literární rešerše je sice poněkud neobvyklé, ale svým způsobem logické a pochopitelné.

V experimentální části zvolila autorka studium vlivu dosud ne plně prozkoumaných nezávislých proměnných – rychlosti rotace válcové zvlákňovací elektrody a obsahu solí v polymerních roztocích. Při sestavování plánu experimentů lze chápat jako pozoruhodnou, i jako výzvu, kterou si autorka před sebe postavila, volbu vodného a nevodného systému, v nichž je, jak známo z předchozích prací, vliv solí na zvlákňovatelnost a zvlákňovací výkon právě opačný. V diskusi je pak přijatelným způsobem tento zdánlivý rozpor vysvětlen. To lze považovat za významný příspěvek k poznání mechanismu studovaného procesu.

Při studiu předložené práce jsem odhalil některé náměty k diskusi:

1. V kapitole 2.2.2. je popsána technologie melt-blown jako jedna z cest k přípravě nanovláken. Tato technologie je známá již více než 30 let a slouží k výrobě útvarů z jemných vláken s typickými průměry 2 – 10 mikrometrů. V čem spočívá modifikace (v textu nazvaná „modified spinning die") umožňující přípravu submikronových vláken?
2. Jaké jsou výhody a nevýhody výroby nanovláken cestou přípravy bikomponentních vláken? Není mi známo, že by se takto nanovlákna průmyslově vyráběla. Dle popisu autorky vede tato metoda k submikronovým vláknům o úzké distribuci průměrů a to s poměrně vysokou výrobností.
3. Vedle vlivu rychlosti posunu podkladové textilie (kap. 2.3.1.1.7) je znám i vliv jejích elektrických vlastností. Tato proměnná není mezi parametry procesu diskutována
4. Jak lze vysvětlit nemonotonní průběh závislosti tloušťky vrstvy roztoku na povrch válce na viskozitě na obr. 2.20 ?
5. Které získané výsledky lze zobecnit a aplikovat na technologii wire spinning?
6. V seznamu nezávislých a závislých proměnných ovlivňujících proces jsou parametry, které ovlivňují vlastnosti vznikajících nanovlákenných materiálů. Doporučuji vytvořit matici popisující vliv jednotlivých parametrů na vlastnosti koncového produktu.

Předloženou doktorskou dizertační práci za přínosnou, značně rozsáhlou a kvalitní. Obzvláště cenná je třetí kapitola experimentální části a příslušná diskuse. Oceňuji také vysoký počet publikací autorky vztahující se k výsledkům dizertační práce, časopiseckých i konferenčních. V průběhu obhajoby očekávám vyjádření ke vzneseným otázkám.

Předloženou práci

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k obhajobě.

V Liberci, 20. srpna 2014

Ing. Ladislav Mareš
NAFIGATE Corporation, a.s.

Report on Fatma Yener's PhD Thesis
"New Methods in the Study of Roller Electrospinning Mechanism"

26/08/2014

I have read the PhD thesis written by Ms.Fatma Yener under the supervision of Prof.Dr.Oldrich Jirsak attentively and evaluated the importance of the thesis for the field of science.

It is understood from the literature part that until now many researchers have tried to explain mechanism and parameters of electro spinning process whereas the researched parameters include velocity of rotating roller and related quantities, surface tension, conductivity and permittivity, applied voltage, distance between electrodes, ambient conditions, velocity of take-up fabric, geometry of electrodes, geometry and conductivity of collector electrode as *Independent Parameters* and number of cones, theoretical considerations concerning the new parameters, jet length, spinning performance and spinning performance per jet, fiber diameter and fiber diameter distribution, non-fibrous area, life time of a jet, measurement of current, launching time of jet as *Dependent Parameters.* Many of the researchers concentrate on the needle electro spinning while only a few on the roller system.

The aim of this work is to contribute to understanding the roller electro spinning mechanism using new measurable independent and dependent process parameters which were not yet investigated and which have the potential, when studied, to bring new information. The new parameters introduced by the author are velocity of rotating roller and related quantities and feeding rate of polymer solution as *Independent Parameters* and average current and current per jet, number of jets, spinning area, jet life, positions of jets and distance between jets as *Dependent Parameters*. Theoretical considerations concerning the new parameters were made.

The aim of the experimental part is to clarify whether the dependencies of current on the parameters in needle electro spinning can be applied on needleless process. In the experimental part, Polyurethane and Polyethylene Oxide were used as materials together with determined salts in the electro spinning process.

As a result of the experimental part, the author has concluded that total electric current in the roller electro spinning is more or less proportional to the spinning performance; the dependence of number of jets and the dependence of spinning performance on the roller velocity in generally non-monotonous; the experimentally found distance between jets depends on the conductivity of polymer solution, spinning area mainly depends on movement of roller; the length of jets mainly depends on the amount of salt which is related with conductivity and the viscosity of solution; the effect of rotating roller on fiber surface morphology shows that increasing roller speed increase the fiber diameter and non-fibrous area, salts may influence entanglement number and polarity of macromolecules when creating complex bonds with them; PEO with its high polarity and high entanglement number (strength of jets) shows high spinning performance; in the case of PU, the salts creating complex bonds with the polymer, increase the low polarity as well as the entanglement number which causes an increase in the spinning performance.

The symbols, list of tables and figures are given clearly within the thesis. The tables and figures represent the results of the experimental work. The results and conclusions are explained clearly and carefully within the text contributing to easily understanding the aim of the scientific work.

Ms. Fatma Yener has made many important publications in serious indexed journals and many oral and poster presentations in mostly international and national conferences concerning the valuable scientific work included in her PhD thesis and thus contributed to the field of electro spinning. The theoretical and experimental parts of the thesis have fulfilled the set aims of the thesis and contributed to better understanding the roller electro spinning mechanism.

Depending on the below evaluation, I consider the PhD thesis on "New Methods in the Study of Roller Electrospinning Mechanism" is a valuable scientific work and I highly recommend it for defence.

Prof.Dr.Telem GÖK SADIKOĞLU

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