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FAKULTA TEXTILNÍ

THE ROLE OF RHEOLOGICAL PROPERTIES OF POLYMER SOLUTIONS IN NEEDLELESS ELECTROSPINNING

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AUTOREFERÁT DISERTAČNÍ PRÁCE

Název disertační práce:	**THE ROLE OF RHEOLOGICAL PROPERTIES OF POLYMER SOLUTIONS IN NEEDLELESS ELECTROSPINNING**
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1. Aims of the work

The use of electric charge to break up liquids into small particles has been well known and extensively studied for over a century, but commercial applications have been constrained by difficulties in surmounting glow rate limitations associated with the underlying physics of the process. This is true for both electrospraying, in which low viscosity liquids can be atomized into droplets, and electrospinning, in which viscoelastic liquids can be transformed into filaments of nanometer dimensions. With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue enegineering, biosensors, filtration, wound dressings, drug delivery and enzyme immobilization [1]. Using the keyword 'electrospining' for a search on internet will return a thousand scientific papers, but almost of them concerned on needle electrospinning technique includes many aspects as mechanism of electrospinning, materials for electrospinning, properties of nanofibers, factors effect to spinning process and to products properties …etc, as summarize by Anthony L.Andrady [2] or Jon Stanger and his co-workers [3]. Up to now, Nanospider is the unique commercial equipment to produce nanofibers-web via needleless electrospinning technology. This equipment, which is first patented by Jirsak [4], enable to produce membranes collected fibers in a range from 100 to 600 nm of diameter.

It has been seen that, needleless electrospinning is a quite new technique, therefore parameters of needleless electrospinning have not yet been fully identified and defined. It is the aims of author to define independent and dependent parameters of needleless electrospinning. Also, the methods to measure the parameters will be suggested and/or developed. This is understood as necessary step before experimental study of electrospinning process is started. Parameters of needleless electrospinning whether described in literature or suggested by author, are described in this thesis. The central point of experimental work will be rheological properties of polymer solutions. Rheological properties result from type of polymer, type of solvent, molecular weight, polymer concentration, temperature, additives, etc. On the other hand, electrospinning process and its characteristics as well as properties of produced nanofibers can be studied in relation to rheological characteristics. Thus, relations between selected independent and dependent parameters in needleless electrospinning can be studied and explained using rheological characteristics.

2. Overview of electrospinning

2.1 Parameters in needle electrospinning

Up to now, two popular ways to produce nanofibers using high voltage are known those are needle electrospinning and needle-less electrospinning. The first way has been used popularly by researchers in laboratories. Using the needle electrospinning, spinable polymer solutions are easily spun and controlled to achieve desired products. The second way described above is becoming a commercial technique to produce nanofibers membrane. In the needle electrospinning, there is only one jet per needle and the spinning area is very small (0.5-1 mm^2), whereas in the needle-less electrospinning, there is a number of jets, usually 3,000 – 45,000 jets per one square meter of the surface of spinning roller electrode. There are many works interesting in and concerning on factors which effect on parameters of needle electrosping process. And the researcher found that there are extraordinary many variables influencing the electrospinning process as well as product properties. These can be divided into two big groups as follows:

Material parameters: Type of polymer or copolymer, including polymer blends and additives, molecular weight of polymer, solvent or solvent system including mixture of solvents and/or additives, solution parameters including concentration, viscosity, conductivity, molecular weight, and surface tension etc.
Process parameters: include applied electric field, type of spinning and collector electrodes, distance between electrodes, feeding rate, humidity, temperature. Each of these parameters influences the spinning process and the product properties as fibers diameter, number of beads, size of beads and length of jet.
They can be separated into two groups of parameters which are independent parameters and dependent parameters. Independent parameter is a parameter which we can set and/or adjust for spinning process. And dependent parameter is dependent on the others parameters.
The table below can bee seen as summarization of the parameters in needle electrospinning.

Table 2.1. Effects of needle electrospinning parameters

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

2.2 Electrospinning of poly (vinyl alcohol)

Poly (vinyl alcohol) (PVA) is a water-soluble synthetic polymer. PVA has excellent film forming, emulsifying, and adhesive properties. PVA was discovered in 1915 by F Klatte. The stoichiometric saponification of poly (vinyl acetate) with caustic soda to yield PVA was first described in 1924 by W O Hermann and W Haehnel. Since its discovery, PVA has found many uses and new ones are still being added. Recently, PVA became one of the most popular materials in electrospinning. From many works, it has been seen that, it is very easy when PVA was used as material in electrospinning, and because of its non-toxicity and it can be dissolved easily in water so PVA can be used as a unique material, or PVA can be used in combination with other polymers which are not electrospinnable themselves, but they have special functions for end use purposes [2, 3]. In this section, works relate to electrospinning of PVA will be summarized, and they can be classified into two big groups: effects of properties of PVA solution on electrospinning and additives in electrospinning of PVA.

2.2.1 Effects of properties of PVA solutions on electrospinning

The effects of polymer weight average molecular weight (M_w) on the fiber structure of electrospinning PVA have been studied by Koski and his co-workers [5]. In their work, PVA with a degree of hydrolysis of 98-99% and with molecular weights ranging from 9000 to 186,000 g/mol was dissolved in water. The concentration (c) of the polymer in the solution was varied depending on the molecular weight. It was observed that for each molecular weight, a fibrous structure was stabilized above a minimum concentration, generally corresponding to $[\eta]c > 5$. The average fiber diameter was between 250 nm and 2 µm. The fiber diameter increases with M_w and concentration. At low M_w and/or concentrations ($[\eta]c < 9$), the fibers exhibit a circular cross-section. Flat fibers were observed at high M_w and concentrations ($[\eta]c > 9$). The same purpose has also been studied by Lee and his co-workers [6], they used atactic PVA with number-average degree of polymerization ranging from 1700 to 4000. It is observed that, the molecular weight of a-PVA had a marked influence on the structure and properties of nanofabrics produced. That is, the higher the molecular weight of PVA, the superior the physical properties of PVA nanofabric. Moreover, in their study, a-PVA nanofabrics were prepared by needle electrospinning with controlling the process parameters including electrical field, conductivity, tip-to-tip distance, and they found that, the average diameter of a-PVA nanofiber was slightly decreased with increase in the electrical potential or decreases in solution concentration. Some other researchers have also concerned of polymer molecular weight and polymer concentration of PVA on structure and properties of the products as shown in [7]. Recently, J. Tao [8] has confirmed the effects of polymer molecular weight of PVA on structure and properties of the product via needle electrospinning. In that, the molecular weight of the polymer has a significant role in establishing the structure in the electrospun polymer. The molecular weight dependent concentration regimes for beads, beaded fibers and fibers have been mapped. At a constant concentration, the structure changes from beads, to beaded fibers, to complete fibers and to flat ribbons as the molecular weight is increased. A fully stabilized fibrous structure is obtained for a Berry number of around 9, which corresponds to the onset of significant molecular entanglements. The transition from round fibers to flat ribbons starts at a Berry number of about 12.

Effect of pH on electrospinning of PVA has also been studied by Son [9]. 7 wt% PVA solutions at various pH values from 2.0 to 12.9 were electrospun in order to investigate the effect of pH on the morphology and diameter of electrospun PVA. The average diameter of PVA fibers electrospun at pH 7.2 was 290 nm. Electrospun PVA fibers became straighter and

finer with increasing pH under basic conditions, whereas the electrospinning of PVA solution was not continuous and PVA fibers with beads-on-string structures were obtained due to the protonation of PVA under acidic conditions.
Some results on the rheological properties of PVA have been reported by Kim and et al. who explained that molecular weight of PVA has a significant effect on the rheological properties of PVA/water solutions [10]. In another study, Park and et al have studied the effect of preparation parameters on rheological behavior and microstructure of aqueous mixtures of hyaluronic acid/poly(vinyl alcohol). They found that rheological properties depend on the degree of hydrolysis of PVA [11]. Lee et al. found the rheological responses show time-dependence under low shear rate values and they also observed the chain mobility of molecules decrease as the relaxation time is increase, which is important to spin nanofibres [12].

2.2.2 Additives in electrospinning of PVA

As said above, PVA can be used as a unique material, or PVA can be added by many different kinds of additives to change PVA solutions properties. One of the most important purposes of using additives is to improve spinnability of PVA solutions and their products properties also. For this reason, Qin [13] had added into PVA solution by vitriolic acid which was used as a catalyst activator during cross-linking. The result shows that the filtration efficiency increases sharply when crosslinked PVA nanofibers layer were added to the sublayers. In another work, Xinsheng Zhu and his co-workers [14] had done via dialysis and complexation pretreatment to improve electrospinnability of PVA. In advance, Kostakova and her co-workers [15] have shown the effects of the additives on spinnability of PVA and on morphology of product via needleless electrospinning.
For another important purpose, PVA can be used in combination with other polymers which are not or poor electrospinnable themselves, but they have special functions for end use purposes. For example, the blend between PVA and chitosan (CS) was concerned by many researchers. This blend has been fabricated successfully by the electrospinning process [16]. Many other works have also studied about PVA blends.

2.3 Objective setting

Parameters of needleless electrospinning have not yet been fully identified and defined as the technology is rather young. It is the aim of author to define independent and dependent parameters of needleless electrospinning based on his own experiments. Also, the method to measure the parameters will be suggested and/or developed. This is understood as necessary step before experimental study of electrospinning process is started. So works in this thesis include:

- Parameters of needleless electrospinning whether described in literature or suggested by author. The method to measure the parameters will be suggested and/or developed in this chapter also.
- The effects of polymer molecular weight and concentration of PVA solutions on some dependent parameters (as life time of jets, length of jets, throughput, and throughput per cone) will be studied.
- Relations between Berry number and needleless spinnability will be detected.
- Relationships between rheological properties and throughput of needleless electrospinning product will be studied also.
- Rheological properties of PVA solutions will be used to explain the effects of polymer molecular weight and concentration of PVA solutions.
- Effects of solvent quality on changing microstructure of spinning solution and dependent parameter in needleless electrospinning will be studied.

- Effect of cross linking agent as time dependent on throughput parameter will be tested and detected by rheological properties.
- Relationship between conductivity parameters and some dependent parameters as throughput, density of cone in needleless electrospinning process will be studied.

3. Used methods

3.1. Parameters in needleless electrospinning

The independent and dependent parameters in needleless electrospinning will be defined and the methods to determine them will be also described by the author. These parameter definitions and method descriptions based on the author's works with laboratory electrospinning apparatus in Technical university of Liberec.

3.2. Experimental

This part describes materials and methods used in the experiments focused on relations between selected independent and dependent parameters of needleless electrospinning.
Four groups of experiments will be carried out:
1. Poly (vinyl alcohol) with different polymer molecular weights and solution's concentration will be used as materials for the experiments. The aims of these experiments are to explore relationships between polymer molecular weight; concentration of solution and some dependent parameters such as throughput, fiber diameter and length of jets.
2. Effect of solvent quality on needleless electrospinning will be studied. Water – n-propanol mixtures in various ratios will be used as the solvent of PVA. Water is a good solvent of PVA and n-propanol is not the PVA solvent, whereas it is soluble in water. Thus, the more n-propanol is admixed into water, the poorer PVA solvent is prepared. Effect of the solvent quality on selected dependent parameters such as throughput, fiber diameter and non-fibrous area is studied.
3. The time-dependent effect of crosslinking agent on needleless electrospinning of PVA will be studied. At the laboratory temperature, the crosslinking agent slowly reacts with the polymer, increasing its molecular weight. So, the results can be compared with those in paragraph 1 above. Simultaneously, the experiments serve as information for the production technology where PVA solutions with crosslinking agent are spun and it is necessary to know what changes in solution and product quality are to be expected depending on ageing of solutions.
4. Effect of solution conductivity on some parameters of needleless electrospinning will be studied. Sodium chloride will be used as additive to change conductivity of PVA solution. The relationships between solution's conductivity and some dependent parameters as throughput, throughput per cone, density of cones, the life time of jet and fiber diameter will be studied in this group of experiments.
For all groups of experiments, rheological properties (such as viscosity, complex modulus, elastic modulus and elastic component) of the experimental materials will be measured to understand the differences and/or the change in solutions microstructure of the materials and also to explain studied relationships between independent and dependent parameters.

4. Results

4.1. Parameters in needleless electrospinning

In contrast to the needle electrospinning technique, many parameters of needleless electrospinning have not yet been defined. Up to now, not many researchers studied this technology. In this work I suggest definition of process parameters of the needleless electrospinning technique. Some of them are similar to the parameters of needle electrospinning techniques, some of them are completely new. These parameters are separated into two groups: independent parameters which can be adjusted and controlled and dependent parameters which depend on independent parameters. The table below is a summarization of parameters in needleless electrospinning which have been defined and described.

Table 3.1 Summarization of electrospinning parameters

Independent parameters	***Dependent parameters***
Concentration of polymer solution (%)	Density of cones (m^{-2}) [A]
Molecular weight of polymer (g/mol)	Life time of jets (s) [A]
Viscosity of polymer solution (Pas)	Throughput (g/min/m) [A]
Conductivity of solution (mS/cm)	Throughput per cone (g/h) [A]
Surface tension of solution (mN/m)	Non-fibrous area (%) [A]
Applied voltage (kV)	Fibers diameter (nm)
Velocity of cylinder (rpm)	Fibers diameter distribution [A]
Distance between electrodes (mm)	
Velocity of collected fabric (m/min)	
Relative humidity (%)	
Temperature (^{0}C)	

[A] Suggested by Author.

4.2. Overview results from the experiments

- There is a significant difference between mechanisms of needle and needleless electrospinning technique. In the needle electrospinning, material is supplied by mechanical forces from a syringe whereas in needleless electrospinning material is pulled out of free surface of polymer solution by the electrical force. In this process, the intermolecular interaction or/and polymer net strength is very important, in fact this is a necessary condition of a stable polymer jet and electrospinning process. Relevant characteristic of polymer solution can be detected from shear thinning behaviour of the solution. The number of entanglement and Berry number do not help to predict spinnability in this case.
- From literature, it is obvious that polymer molecular weight and concentration of solution have significant effects on some dependent parameters of needle electrospinning such as fiber diameter and morphology of fiber. Once again, they play an important role in needleless electrospinning and strongly affect some dependent parameters of needleless electrospinning such as throughput and fiber diameter. The results of experiments show that throughput and fiber diameter increase with increasing polymer molecular weigh and/or its concentration in solution. The differences in these dependent parameters and in microstructure of polymer solution can be expected from the differences in rheological properties of polymer solution such as viscosity, complex modulus, elastic modulus and elastic component. For example, the lower is elastic component, the higher is throughput.
- The higher is the viscosity of polymer solution (no matter whether caused by higher molecular weight or polymer concentration) the longer are jets. Explanation of the phenomenon was offered in the part discussion.
- Quality of solvent effects strongly on shape of macromolecules in diluted solution. The poorer is the quality of solvent, the lower is intrinsic viscosity. In concentrated solutions, the effect of non-solvent is opposite. The poorer is the solvent, the higher value of viscosity is found. Corresponding change in the structure of polymer solution leads to

higher complex modulus and to reduction of elastic component, which causes increase in throughput.

- Rheological properties of poly (vinyl alcohol) solutions containing a cross-linking agent (Sequarez 755) are time dependent at laboratory temperature. The results show that viscosity, viscous modulus and elastic modulus continuously increase in time, but elastic component decreases in the first period of time, after that it increases in time like other rheological properties. These changes also affect spinnability of the solution. As presented above, throughput parameter relates to the elastic component. Polymer solution is not spinnable if the elastic component is too high. The results of this study also find their application in production technology where the crosslinking agents are frequently used.
- Conductivity of spinning solution affects strongly needleless electrospinning dependent parameters, especially the throughput and density of cones. On the contrary, it almost does not affect the throughput per cone. Throughput parameter and density of cones decrease strongly with increasing conductivity of spinning solution. It is a phenomenon to be explained by physicist and other experiments. Described experimental results are not sufficient to work out such explanation.

5. Evalution of the results

Needleless electrospinning is a technique using electrical forces to tear and push spinning materials from free surface liquid toward electrode collector. Up to now, Nanospider is the unique commercial equipment to produce nanofibers-web via needleless electrospinning technology. This work mostly use the apparatus based needleless technique to produce nanofibers membrane.

There are two main groups of scientific contribution done in this thesis are presented below.

- The first contribution is definitions of process parameters and methods to measure the parameters in needleless electrospinning. Some completely new parameters in needleless electrospinning such as throughput, density of cones, throughput per cone, non-fibrous area have been described, defined and methods to measure the parameters were developed.
- The second is that this thesis also brings the results of studies of the relations between some selected parameters, for example, relationships between polymer molecular weight, solution’s concentration and throughput, length of jets, fiber diameter and some others

6. Publications

6.1 Tuan Anh DAO, Oldrich JIRSAK, *Contribution to study of needleless electrospinning mechanism*, Nanofibers for the 3rd millennium – Nano for life conference, Prague Czech Republic, 11th-12th March 2009.

6.2 Oldrich JIRSAK and Tuan Anh DAO, Production, Properties and End-uses of Nanofibers, 3rd International Symposium on Nanotechnology in Construction, Prague, Czech Republic, 31st May- 2nd June, 2009. ***(http://apps.isiknowledge.com/summary.do?product=WOS&doc=1&qid=1&SID=W2KM@OdG8cj1le4hodH&search_mode=AdvancedSearch).***

6.3 Anh Tuan DAO and Oldrich JIRSAK, Effect of Sodium Chloride on the needle electrospinning of poly (vinyl alcohol), Nanocon 2009 – 1st Conference with International Participation, Roznov, Czech Republic, EU 20th – 22nd October 2009. ***(http://apps.isiknowledge.com/summary.do?product=WOS&doc=1&qid=1&SID=W2KM@OdG8cj1le4hodH&search_mode=AdvancedSearch).***

6.4 Anh Tuan DAO and Oldrich JIRSAK, The life of Jets in the roller electrospinning, 16th International Conference Strutex, Liberec Czech Republic, 3rd – 4th December 2009.

6.5 Cengiz Funda; Tuan DAO; Oldrich JIRSAK, Influence of solution properties on the roller electrospinning of poly(vinyl alcohol), Journal of Polymer Engineering and Science. (Accepted on 29th September 2009 in "Decision on PES-09-0035.R2"). ***(http://apps.isiknowledge.com/summary.do?product=WOS&doc=1&qid=1&SID=W2KM@OdG8cj1le4hodH&search_mode=AdvancedSearch).***

6.6 Anh Tuan DAO and Oldrich JIRSAK, Improve spinning ability of poly (vinyl alcohol) via needleless electrospinning, AUTEX2010 World textile conference, Vilnius, 21 – 23 June, 2010.

6.7 Anh Tuan DAO and Oldrich JIRSAK, Effect of cross-linking agent on electrospinning of poly (vinyl alcohol), 7th International conference – TEXSCI2010, Liberec, Czech Republic, 6 – 8 September, 2010.

6.8 Anh Tuan DAO and Oldrich JIRSAK, Roller electrospinning in various ambient parameters, Nanocon2010 conference, Olomouc, Czech Republic, EU, 12-14, October, 2010.

7. Literature

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8. Summary

The results of this thesis should be seen as initial works focused on definitions of parameters of needleless electrospinning and on development of methods to measure these parameters. This thesis also brings the results of studies of the relations between some selected parameters, for example, relationships between polymer molecular weight, solution's concentration and throughput, length of jets, fiber diameter and some others. In future, I suggest continued studies focused on:

- Full understanding of relations between independent and dependent parameters
- Theoretical studies leading to full explanation and complete description of electrsospinning process involving effects of viscosity, conductivity and other material characteristics.

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