Additives influence on spinning solution and nano web properties

S Kukle¹, S Jegina¹, A Sutka¹ and R Makovska¹
¹Riga Technical University name, Faculty of Material Science and Applied Chemistry, Department of Design and Material Technologies, Kipsalas Street 218, LV-1028 LATVIA

E-mail: Silvija.kukle@rtu.lv

Abstract. Needleless electrospinning operated as a one-stage process producing nanofibres webs from spinning solutions with the corresponding to the final use properties seems has a good future prospects. Complicated spinning solution designing started with the selection of composition and components proportion, pre-processing sequence and parameters establishing for every component and for their mixing. Spinning solution viscosity and electro conductivity together with the spinning distance and intensity of electromagnetic field are main parameters determined spin ability and properties of obtained nanofibers. Influence of some pre-processing parameters of components, combinations of organic and non-organic components and their concentration influence on spinning solution viscosity and conductivity, as well on fibres diameters are under discussion.

1. Introduction

By integrating nanoparticles or other functional materials, the cellulose-based webs can achieve tailored properties. Optionally, low density and large specific surface area of nanofibers, small pore size and high porosity, excellent mechanical properties in proportion to the weight, possibility to incorporate different additives are attractive features for use cellulose based nano-nonwovens in a wide range of intermediate and final products. Morphology of nanofibers produced by needleless electrospinning influences a wide range of factors classified in three groups: 1) solution properties – polymer types and molecular weight, concentration, solvent properties, viscosity, conductivity, surface tension, dipole moments, dielectric constants; 2) controlled processing variables such as flow rate, electric field strength, distance between spinning electrode and collector, geometry of spinning electrode, collector composition and geometry; 3) ambient parameters temperature, humidity, air velocity.

Complicated spinning solution designing started with the selection of composition and components proportion, pre-processing sequence and parameters establishing for every component and for their mixing. Every component included could change solution viscosity and electro conductivity, as a result spin ability, fibres and web quality.

The solution for electrospinning should be in the semi-conducting range. An absolutely non-conductive solution cannot be electrospun because no electric charges could be transferred to the droplet surface. However, if the solution is highly conductive, extra charge could not be accumulated on the droplet surface. As a result, fluid could not be drawn into fine filaments because of the very small stretching force [1].
Polymer types and concentration are the most important factors affecting an electrospinning process, because they also affect many other solution properties such as viscosity, conductivity, and surface tension. For a polymer with a reasonable molecular weight, concentration changes can result in different types of fibres morphology. Higher polymer concentration tends to result in coarser fibres. For the same polymer solution system, a higher viscosity suggests stronger entanglement between the polymer chains, which makes stretching more difficult. For some polymers, with the polymer concentration increase, the charge density in solution also increases. This will lead to a stronger stretching force hence with increased polymer concentration, as fibres stretched under two opposing forces. Reasonable number of studies has shown the presence of defects such as beads and droplets instead of fibres at low polymer concentrations [2, 3].

For some polymers, beaded fibres collected even the concentration is very high. In this case, the solution conductivity increase via the addition of other chemicals to the solution found to be an effective approach to stop the formation of beaded fibres. Additives such as inorganic salts, surfactants, and other polymers have been added into proposed polymer solutions to increase conductivity [4, 5]. With the increase in solution conductivity, uniform nanofibers can be obtained, and fibres diameters are even reduced with the increase in additive concentration. Some of these additives can also decrease the solution surface tension, which facilitates the electrospinning process.

Therefore, solution properties such as viscosity, conductivity, surface tension affect the ability to form fibres, as well as alter the morphology of spun fibres. Solution viscosity alone is one of the most important property found to alter the fibres size and morphology. Solutions having viscosity above 2000 and below 100 mPa s could not be spun. If polymer molecular weight is comparative low (>60 000 g/mol) fibres could not be obtained [6].

Solvent in solutions also affects fibres morphologies. Dry fibers are collected only when solvent evaporates completely from the filaments, before they deposit on the collector. For some solvents of low volatility, wet fibers would be collected, which merge together to form an interconnected web structure [7].

For some highly volatile solvents, rapid evaporation of the solvent cools the filament and moisture could froze on the filaments surfaces, resulting in the formation of nano/micro-sized pores on the fiber surface [8].

Most of conclusions discussed above based on empirical studies of specific spinning solutions and obtained fibres properties. The goal of this study is to truck influence of functionalizing additives to the poly(vinyl alcohol) (PVA) based spinning solution and electrospun nanofibers diameters produced by needleless electrospinning process.

2. Materials and methods
Needle free nanofibres electrospinning lab equipment (Nanospider LAB 200) from Nanospider™ production line developed by ELMARCO were used to estimate and compare influence of composition and proportion on spinning solution main parameters. Three compositions with the polyvinyl alcohol PVA (Moviol 28-99, Mw ~ 145 000 from Sigma Aldrich) used as a matrix are under discussion. Variants of spinning solution:

1) PVA composite with herbal extract from the spruce (Picea abies) needles sodium chlorophyllin with the concentrations in a range from 1 wt% to 15 wt% [9, 10];
2) PVA composite with cellulose nanofibers (NC) extracted from hemp shives (mean D 25+/− 1 nm; 80% with D less than 30 nm) in a range from 0.1 wt% to 2 wt% in water solution or 1 to 20 wt% in composite fibres [11, 12];
3) PVA 9 wt% composites with the cellulose nanofibers extracted from hemp shives 1 % in solution (or 10 % in composite) fibres and titanium dioxide (TiO₂) nanoparticles (nanopowder: ca.21 nm) [2].

Viscosity of spinning solution measured by HAAKE Viscotester 6 plus, electro conductivity measured with the WinLab Data Line Conductivity meter, fibres diameters measured by atomic force microscopy (AFM Dimension Edge, non-contact regime).
3. Discussion
With the sodium chlorophylin added to the 8 wt% PVS water solution in a range from 1 to 5 wt% viscosity ($V_1$) of spinning solution drops down fast decreasing by 16.5 % (Figure 1, left). This tendency describe linear equation (1):

$$V_1 = 668.63 - 22.39 \text{SChl} \ (R^2 = 0.98) \quad (1).$$

Viscosity ($V_{II}$) decrease rate (Figure 1, left) become slow (2.8 %) with the additives concentrations in a range from the 5 wt% to 15 wt% (0.5-1.5 wt% in spinning solution) and descriptive linear equation for this range (equation 2):

$$V_{II} = 569.57 - 16 \text{SChl} \ (R^2 = 0.99) \quad (2).$$

Fibres diameters ($D$) with the SChl concentration in a range from 0.1 to 0.5 wt% drop down from 507 nm (neat PVA) to 339 nm (with the 0.5 wt% SChl) following equation (3):

$$D = 507.51 - 33.51 \text{SChl} \ (R^2 = 1) \quad (3).$$

![Figure 1. Influence of SChl additive on spinning solution viscosity (left) and electroconductivity (right) [9, 10]](image)

Conductivity of the spinning solutions increase fast started from neat PVA ($C_{PVA}$) solution conductivity 324 μS cm$^{-1}$ and following proportionally to the increase of SChl content from 0.1 wt% to 1.5 wt% corresponding to the equation (4):

$$C_{PVA} = 656.35 + 544.91 \text{SChl} \quad (4).$$

As solution conductivity with 1.0 wt% and 1.5 wt% SChl additive correspondingly 5830 and 8870 μS cm$^{-1}$ exceed upper electro conductivity limit, it become too high for the normal fibres formation process. Rapid conductivity increase with the SChl concentration increase originated by the high conductivity of SChl. Conductivity of PVA 8 wt% solution in water 565 μS cm$^{-1}$ (Figure 1, right) combined with the SChl additive in result of intensive compound mixing pre-treatment growth proportionally with the growth of SChl concentration.

From the graph of Figure 2 (left) is seen that viscosity of neat PVA spinning solution increase non-linearly with the PVS concentration increase from 8 to 10 wt%. With the extracted from hemp shives nanocelulose additives (NC) to the PVA solution viscosity of spinning solution drops down rapidly by 49 % till 1.0 wt% NC. Then in a NC range from 1.0 to 2.0 wt% do not changes substantially more. At the same time, mean diameter of fibres decrease from 505+/−23 nm of PVA 8 wt% spinning solution to 225+/−10 nm from spinning solution with 2 wt% cellulose aditive (80 % of fibres diameters do not exceed 250 nm).
Conductivity of the neat PVA spinning solution increase from 323 to 385 μS cm⁻¹ (by 19 %) in concentration range from the 8 to 10 percent (Figure 3, left). Although cellulose is non-conductive with NC additives conductivity of solution increase by 22 percent, compare to the neat 8 %wt PVA solution (Figure 3, right). It seems that the dispersion of cellulose nanofibres by ultrasound in PVA solution results in the charged NC particles generation imparting optional conductivity to the spinning solution.

All additives to the PVA matrix spinning solution [14] increase viscosity of spinning solution compare to the 9 wt% PVA solution (Figure 4). 1 wt% cellulose additive increase PVA/ and PVA/B solution viscosity to compare with neat PVA correspondingly by 95% and 173%. Differences in pre-processing time of cellulose nanofibers (PVA/A ball milling 10 minutes, ultrasonification 30 minutes and PVA/B 20 minutes ball milling, 60 minutes ultrasonification) lead to the substantial increase (40%) of PVA/B viscosity to compare with PVA/A. It could be explained, that more severe milling and ultrasonic treatment results in a higher cellulose fibrils dispersion intensity producing a great amount of even distributed in solution smaller particles. 2 wt% TiO₂ additive to the PVA solution increase viscosity 1.6 times, but this ratio a little (6%) decrease with 10% TiO₂. In result of addition to the PVA/B 2 wt% TiO₂ viscosity of the composition drops down by 40 % (Figure 4).
Figure 4. Spinning solution viscosity of samples with 1 wt% NC (PVA/A and PVA/B), TiO$_2$ additive (2 wt% and 10 wt%) and three component solutions PVA/B/TiO$_2$ [14]

Influences on samples electro conductivity are not so dramatically (Figure 2). Imparting cellulose nanofibres increase conductivity of spinning solution by 12.3 % independently from pre-processing time (samples PVA/A, PVA/B).

Figure 5. Spinning solution conductivity of samples with 1 wt% NC (PVA/A and PVA/B), TiO$_2$ additive (2 wt% and 10 wt%) and three component solutions PVA/B/TiO$_2$

Electro conductivity of composite solution with TiO$_2$ increases correspondingly by 3.9% and 7.2 % compare to the neat PVA solution. Increase of TiO$_2$ content from 0.2 wt% to 1.0 wt% do not increase substantially conductivity (3.2%) as specific conductivity of the 0.2 wt% TiO$_2$ water solution is 9.3 and 1 %wt TiO$_2$ 67.7 μS cm$^{-1}$.
Nanofibres web from 9 wt% PVA spinning solution functionalized with 1 wt% TiO$_2$ (10 wt% TiO$_2$ in fibres) seen in Figure 6 consist of fibres varying in diameters and some defects in form of films. From the graph of Figure 7 seen that with the functional additive TiO$_2$ mean diameters of fibres vary quite close to the corresponding neat PVA value. With added 1 wt% cellulose mean diameters of fibres drop down by 38 and 35 % compare to the corresponding values of two component composite fibres.

4. Summary

Viscosity of net PVA spinning solution in a concentration range from 8 to 10 wt% increase non-linearly, especially rapid in the range from 9 wt% to 10 wt%, at the same time conductivity grow moderate linearly.

Conductive organic additive SChl in PVA based spinning solutions increase rapidly solution conductivity with the increase of additive concentration limiting its maximal spin able concentration. Conductivity of PVA 8 wt% solution in water 565 μS cm$^{-1}$ combined with the SChl additive in result of intensive compound mixing pre-treatment growth proportionally with the growth of SChl concentration.

With the increase of SChl concentration till 0.5 wt% viscosity of spinning solution drops down decreasing fast by 16.5 %, further SChl concentration increase till 1.5 wt% do not change viscosity substantially. Nanofibres diameters decrease with the SChl concentration increase.

Cellulose additive 1.0 wt% to the PVA 9 wt% solution decrease viscosity by 45 percent, and in a range from 1.0 to 2.0 wt% by 6.0 percent only. Conductivity of spinning solution increase moderate by 22 percent with cellulose additive 2.0 wt% to compare with the mean diameters of fibres decrease from the 505+/-23 nm of PVA 8 wt% spinning solution to 225+/-10 nm spun from solution with 2 wt% cellulose additive, 80 % of fibres diameters do not exceed 250 nm.

Increase of plant cellulose pre-processing severity leads to the higher spinning solution viscosity. Cellulose 1 wt% additive to the two component (PVA/TiO2) spinning solution allow to decrease mean diameters of nanofibres by 35 % compare to the mean diameters of fibres spun from PVA/TiO$_2$ solution.

References

[1] T L Xungai Wang. Needleless electrospinning of nanofibres. Technology and Applications 13: 978-981-4316-84-2 (eBook - PDF). 2013, Taylor & Francis Group, LLC

[2] Ki CS, Baek DH, Gang KD, Lee KH, Um IC, Park YH. Characterization of gelatine nanofiber prepared from gelatine–formic acid solution. Polymer. 2005 46(14):5094-102.
[3] Jiang H, Fang D, Hsiao BS, Chu B, Chen W. Optimization and Characterization of Dextran Membranes Prepared by Electrospinning. *Biomacromolecules*. 2004, 5(2):326-33

[4] Wu D, Huang X, Lai X, Sun D, Lin L. High throughput tip-less electrospinning via a circular cylindrical electrode. *Journal of Nanoscience and Nanotechnology*. 2010 10(7): 4221–4226.

[5] Cengiz F, Jirsak O. The effect of salt on the roller electrospinning of polyurethane nanofibers. *Fibers and Polymers*. 2009 10(2): 177–184

[6] Dao A.T. The role of rheological properties of polymer solutions in needleless electrostatic spinning. *PhD Thesis, Technical University of Liberec, Czech Republic* 2011

[7] Hsu C-M, Shivkumar S. Nano-sized beads and porous fiber constructs of poly(vepsilon-caprolactone) produced by electrospinning. *Journal of Materials Science*. 2004 39(9): 3003–3013.

[8] Casper CL, Stephens JS, Tassi NG, Chase DB, Rabolt JF. Controlling surface morphology of electrospun polystyrene fibers: effect of humidity and molecular weight in the electrospinning process. *Macromolecules*. 2004 37(2): 573–578.

[9] Jegina S, Sutka A, Kukle S, Zelca Z. The Effect of Sodium Chlorophyllin on Polyvinyl Alcohol Electrospun Nanofiber Diameters 2015, *Conference Paper* (PDF Available, Riga Technical University Press)

[10] Sandra Jegina, Silvija Kukle, Anna Sutka. Potential of nanofibers webs with sodium chlorophyllin for the skin care. DOI: 10.5593/sgem2016HB63

[11] Sutka A, Kukle S, Gravitis J Electrospinning and Characterization of Cellulose/Polymer Nanocomposite Fiber Mats 2014 *Proceedings of the 13th European Workshop on Lignocellulosics and Pulp* Spain, Sevilja, pp.815-818. ISBN 978-84-616-9842-4.

[12] A Sutka, S Kukle, J Gravitis, R Milasius, J Malasauskiené Electro-Spinning Derived Cellulose-PVA Composite Nano-Fibre Mats. *Fibres & Textiles in Eastern Europe*, 2014, Iss.3, 43.-46.lpp. ISSN 1230-3666

[13] Sutka A, Kukle S, Gravitis J, Loca D, Makovska R Lignocellulose nanofibrils and titanium dioxide nanoparticles impact on PVA/NF/TiO2 nanofibers web morphology and mechanical properties 2016 *Abstracts Eco-Bio* P1.32