

RIGA TECHNICAL UNIVERSITY

Anna ŠUTKA

**TECHNOLOGIES, STRUCTURE AND PROPERTIES OF
LIGNOCELLULOSIC NANOFIBRE BICOMPONENT FILAMENTS**

Summary of the Doctoral Thesis

Riga 2015

RIGA TECHNICAL UNIVERSITY

Faculty of Material Science and Applied Chemistry
Institute of Design Technology

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TECHNOLOGIES, STRUCTURE AND PROPERTIES OF LIGNOCELLULOSIC NANOFIBRE BICOMPONENT FILAMENTS

Summary of the Doctoral Thesis

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The defence of the thesis for scientific degree of Doctor of Science in Engineering will take place at an open session on 18th May of 2015, at 13:00, at Riga Technical University, Institute of Design Technologies, Azenes Street 18, in auditorium No. 117, Riga, Latvia.

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CONFIRMATION

I confirm that I have written this thesis and submitted it for review to Riga Technical University to acquire the Doctoral degree in engineering sciences. The thesis is not submitted to any other university to acquire a scientific degree.

Anna Šutka(signature)

Date:

The doctoral thesis is written in Latvian, comprises an introduction and 3 main chapters: review of published sources, methodology, experimental part and conclusions. The doctoral paper consists of 144 pages containing 85 figures, 17 tables, 26 equations, and a list of 351 references used in the study.

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OVERALL REVIEW OF THE THESIS

Introduction

The studies of manufacturing techniques, modification, properties and applications of nonwoven polymer nanofibre textiles has recently emerged as polymeric materials research of wide interest. In contrast to the already known precursors for textiles, polymer nanofibres have a large specific surface area and small-size pores important in mats for high-performance products such as filters, sensors, tissue engineering, drug delivery and similar developments. Electrospinning technique, in contrast to other methods, allows obtaining polymer mats of micro- and nano-scale fibre diameters. The recent developments of the equipment and facilities for electrospinning allow manufacturing of electrospun nanofibre mats at industrial scale.

Due to a unique set of properties the polyvinyl alcohol (PVA) presently is one of the most commonly used synthetic polymers of a wide range of polymeric materials. PVA is environmentally friendly, biodegradable, biocompatible and easily recyclable hydrophilic water-soluble polymer of good mechanical strength and chemical stability. In addition, PVA and its aqueous solutions provide electrospun nanofibre mats. Instability and weak mechanical properties under conditions of high moisture content in the environment is a notable disadvantage of PVA particularly being displayed by PVA nanofibres because of a large specific surface area. The deficiencies have stimulated efforts to study ways of modifying PVA nanofibres to increase mechanical strength and moisture resistance by chemical and physical techniques such as freeze-drying, irradiation, acid dehydration and crosslinking PVA macromolecules with specific agents - aldehydes, carboxylic acids or anhydrides. At the same time attention is paid to environmentally friendly modification techniques limiting the use of chemical reagents.

Studies indicate that mechanical strength and moisture resistance of PVA can be improved by adding macromolecular compounds of natural origin, such as lignin or cellulose compatible with polar solvents and polymers due to inherent hydroxyl groups. A possible improvement is related to intermolecular hydrogen bonding between PVA and lignin or cellulose. Mechanical properties of nanocrystalline cellulose (NC) and polymer composites have been shown significantly improved by the NC filler acting as a reinforcing component. The modulus of elasticity of NC is very high - from 80 to 150 GPa in the axial direction and 10 to 50 GPa in the radial direction. Taking into consideration reported possible intermolecular hydrogen bonding between the OH groups of cellulose, lignin and PVA, and the high mechanical strength of cellulose fibrils, nanoparticles of cellulose extracted from the woody parts of hemp stalks are chosen as the reinforcing filler to improve mechanical strength and moisture resistance of electrospun PVA nanofibers in the doctoral studies.

Bast fibres present a rich renewable resource of cellulose. Since cellulose is practically insoluble in commonly used solvents extracting cellulose fibrills from bast fibres is a problem; besides, the bast fibres consist of molecular cellulose chains integrated in microfibrills merged into macrofibrills, fibres, fibre bundles, elementary fibres, and technical fibres each of which in addition to crystalline cellulose contain amorphous areas of lignocellulose, lignin, pectin and/or waxes. A method for obtaining NC from hemp by-products within the biorefinery concept is developed in the progress of research and

described in the thesis. For extraction of nanocellulose from the hemp stalk biomass the processes of treatment are combined with steam explosion auto-hydrolysis providing effective defibrillation of cellulose fibres while maintaining the crystalline structure.

Technologies of extraction of nanocellulose (NC) from lignocellulosic hemp biomass, of electrospinning PVA nanofibres reinforced by NC and optimised spinning parameters and solutions for the electrospinning process of PVA/NC nanofibres of increased strength and moisture resistance have been developed as the result of the doctoral studies presenting a significant step in production of materials for a variety of practical applications.

The aim

Environmentally friendly technologies of extraction of nanocellulose from fiber crops for modifying the properties of electrospun polymer nanofibers.

Objectives

1. Combined eco-friendly treatment based on steam explosion auto-hydrolysis to obtain nanocellulose fillers from hemp fibres and shives;
2. Environmentally friendly and productive techniques for production of nanocellulose-reinforced PVA nanofibers by needle-less electrospinning with cylindrical spinning electrode.
3. Interrelation between the electrospinning parameters and morphology of the PVA nanofiber mats.
4. Roller-type electrospinning process for production of nanocellulose-reinforced PVA nanofibers;
5. Mechanical strength and moisture resistance of PVA nanofiber mats improved by employment of effects of the nanocellulose filler on the structure and properties of the products
6. Assessments of practical applications of the nanocellulose-reinforced PVA nanofiber mats.

Scientific novelty

1. Disclosure of the effects of steam explosion auto-hydrolysis parameters on defibrillation of hemp plant fibres and shives.
2. Techniques for environmentally friendly extraction of nanocellulose from hemp fibres and shives.
3. Techniques converting low-value plant biomass into high added-value nanocellulose for modification of polymer nanofibers.
4. Roller electrospinning techniques for production of PVA nanofibers reinforced by nanocellulose;
5. Improved mechanical strength and moisture resistance of PVA nanofibers.

Thesis to be defended

1. Technology for nano-size cellulose extraction from hemp shives;
2. The sequence of processes combined with steam explosion auto-hydrolysis, micro-milling and ultrasonic treatment providing the necessary degree of nanofibre defibrillation and removal of undesired chemical components;

3. Technology for electrospinning of reinforced nanofibers comprising three macromolecular components (PVA-cellulose-lignin).
4. Statement: The lignin and cellulose components contribute to crosslinking of PVA macromolecules in nanofibers improving stability of the product under conditions of high moisture.

Practical significance

The practical importance is determined by the know-how of extracting nanocellulose and manufacturing reinforced PVA nanofibers by environmentally friendly technologies and by the established interrelations between technological parameters and fibre properties allowing for modifying the nanofiber structures required for particular applications. As a result of the studies, sustainable environmentally friendly nanostructured materials are obtained for a wide range of possible applications. Laboratory methods and technology can serve as the basis and prototypes for industrial technological processes.

Approbation of the results

Articles in journals:

1. Putniņa A., Kukle S., Grāvītis J. STEX Treated and Untreated Hemp Fiber Comparative Structural Analysis// Scientific Journal of Riga Technical University Material Science and Clothing Technology – 2011. – Nr. 9. – 36.-42. lpp. ISSN 1691-3132.
2. Kukle S., Gravitis J., Putnina A. Processing Parameters influence on disintegration intensity of technical hemp fibres. Innovative natural fibre composites for industrial applications// Journal of Biobased Materials and Bioenergy – 2012. – Nr. 6. – 440.-448. lpp. ISSN 1556-6560.*
3. Putniņa A., Kukle S., Gravitis J. Steam Explosion as the Pretreatment Method of Lignocellulosic Biomass. Scientific Journal of RTU. 9. series., Materiālzinātne – 2012. – Nr. 7. – 80.-83. lpp. ISSN 1691-3132
4. Putniņa A., Kukle S., Grāvītis J. Extraction of highly purified microfibrils from the renewable resources by using green technology// Energetika – 2013. – 59. Nr. 1. – 20.-25. lpp. ISSN 0235-7208.
5. Sutka A., Kukle S., Gravitis J., Milašius R., Malašauskienė J. Nano-fibre electrospinning poly-(vinyl alcohol) and cellulose composite mats obtained by use of a cylindrical electrode// Advances in Materials Science and Engineering – 2013. – 2013. – Article ID 932636 – 1.-6. lpp. ISSN 1687-8434.*
6. Sutka A., Kukle S., Gravitis J., Milašius, R., Malašauskienė J. Electro-spinning derived cellulose-PVA composite nano-fibre mats// Fibres & Tekstiles in Eastern Europe – 2014. – 22. – Nr. 3. – 105. – 43.-46. lpp. ISSN 1230-3666.*
7. Sutka A., Timusk M., Kisand V., Sutka A., Dauksta E. Fabrication of Lead Titanate PbTiO₃ Nanofiber Mats Via Electrospinning// Int. J. Appl. Ceram. Technol. – 2014. – Nr. 12. – 1.-5. lpp. ISSN 1744-7402.*
8. Sutka A., Gravitis J., Kukle S., Sutka A., Timusk M. Electrospinning of poly(vinyl alcohol) nanofiber mats reinforced by lignocellulose nanowhiskers// Soft Materials – 2015. – Nr. 13. – 1. – 18.-23. lpp. ISSN – 1539-4468.*
9. Vahtrus M., Šutka A., Vlassov S., Šutka A., Polyakov B., Saar R., Dorogina L., Löhmus R. Mechanical characterization of TiO₂ nanofibers produced by different

electrospinning techniques// Materials Characterization – 2015. – Nr. 100. – 98.–103. lpp. ISSN 1044-5803 *

10. Sutka A., Sutka A., Gaidukov S., Timusk M., Gravitis J., Kukle S. Enhanced stability of PVA electrospun fibers in water by adding cellulose nanocrystals// Holzforschung - International Journal of the Biology, Chemistry, Physics and Technology of Wood – 2015.*

Articles in pceedings:

1. Grāvītis J., Kukle S., Belkova L., Veveris A., Tupciauskas R., Putniņa A., Stikute A. Technical Hemp Fibres Treatment by Steam Explosion// Proceedings of conference „From Forest and Agricultural Biomasses to High Added Value Products: Processes and Materials” – 2011. – 173.-176. lpp. ISBN 9788895688657.
2. Kukle S., Grāvītis J., Putniņa A., Stikute A. The Effect of Steam Explosion Treatment on Technical Hemp Fibres// Proceedings of the 8th International Scientific and Practical Conference „Environment. Technology. Resources” – 2011. - 230.-237. lpp. ISSN 1691-5402.**
3. Putnina A., Kukle, S., Gravitis, J. Morphological and structural characterization of steam-exploded hemp fibres// Proceedngs of 9th International Conference of Young Scientists on Energy Issues – 2012. –515.-524. lpp.
4. Putnina A., Kukle S., Gravitis J. Effect of steam explosion treatment on hemp fibres microstructure// Proceedings of 12th World Textile Conference AUTEX – 2012. – Nr. 1. – 871.-875. lpp. ISBN 9789537105471.
5. Gravitis J., Abolins J., Dobele G., Tupciauskas R., Veveris A., Andzs M., Putniņa A., Kukle S. Composites of Steam Exploded Biomass// Proceedings of Annual IAWS Meeting “Wood the Best Material for Mankind” and the 5th International Symposium on the “Interaction of Wood with Various Forms of Energy” – 2013. – 79.-84.lpp. ISBN 9788096886869.
6. Putniņa A., Kukle S., Gravitis, J. An Environmentally Friendly Method for Microfibrillated Cellulose Extraction from Hemp// Proceedings of 10th International Conference of Young Scientists on Energy Issues –2013.– 81.-86. lpp.
7. Putniņa A., Kukle S., Grāvītis J., Grāve L. Characterization of cellulose microfibrills obtained from hemp// Proeedings of International Conference on Natural Fibers – Sustainable Materials for Advanced Applications – 2013. – Nr. 2013. – Article ID 171867. – 1. – 5. lpp. ISSN 2314-5846.
8. Grāve L., Putniņa A., Kukle S., Stramkalne V. Steam Explosion Impact to Technical Hemp Fiber Diameter// Vide. Tehnoloģija. Resursi: IX starptautiskā zinātniski praktiskās konferences materiāli – 2013. – 112.-115.lpp. ISSN 1691-5402.**
9. Sutka A., Kukle S., Gravitis J., Berzins A. Chemical and physical modification of hemp fibres by steam explosion technology// Scientific Journal Proceedings of International Conference Functional Materials and Nanotechnologies: Materials Science and Engineering – 2013. – Nr. 49. (012053) – 1.-4. lpp. ISSN 2304-1862.**
10. Šutka A., Kukle S., Grāvītis J. Electrospinning and Characterization of Cellulose/Polymer Nanocomposite Fiber Mats// Proceedings of the 13th European Workshop on Lignocellulosics and Pulp – 2014. – Nr. 1. – 815.-818.lpp. ISBN 978-84-616-9842-4.

11. Gravitis J., Abolins J., Tupciauskas R., Andzs M., Veveris A., Sutka A. Tvaika sprādziena biorafinērijas pašsaistošos plātņu kompozītmateriāli. Iespējamās attīstības tendences// Valsts pētījumu programmas rakstu krājums: Vietējo resursu (zemes dzīļu, meža, pārtikas un transporta) ilgtspējīga izmantošana - jauni produkti un tehnoloģijas (NatRes) – 2010. – 2013. Nr. 1. – 152.-156. lpp. ISBN 978-9934-14-010-5.

Conference theses:

1. Kukle S., Gravitis J., Putnina A. Processing Parameters influence on disintegration intensity of technical hemp fibres. Innovative natural fibre composites for industrial applications, October 12-15, 2011, Italy, Rome
2. Morphological and structural characterisation of steam-exploded hemp fibres, «International Conference of Young Scientists on Energy Issues, May 24-25, 2012, Kaunas, Lithuania.
3. Putnina A., Kukle S., Gravitis J. Natural hemp fibre as additives to form polymer composites, "XVII International Conference on Mechanics of Composite Materials MCM-2012", May-June 28.-1., 2012, Jūrmala, Latvia.
4. Putnina A., Kukle S., Gravitis J. Effect of steam explosion treatment on hemp fibres microstructure, 12th Autex World Textile Conference, June 13-15, 2012, Zadar, Croatia.
5. Putnina A., Kukle S., Gravitis J. Integrative approaches towards sustainability. „Innovative technologies for products from renewable resources, June 27-30, Jūrmala, Latvia.
6. Grāvītis J., Kukle S., Belkova L., Veveris A., Tupciauskas R., Putniņa A., Stikute A. Technical Hemp Fibres Treatment by Steam Explosion. From Forest and Agricultural Biomasses to High Added Value Products: Processes and Materials, September 5-8, 2011, Italy, Viterbo.
7. Kukle S., Grāvītis J., Putniņa A., Stikute A. The effect of steam explosion treatment on technical hemp fibres, Vide. Tehnoloģija. Resursi. (1. Sējums) Rēzeknes Augstskola, June 20-22, 2011, Rēzekne, Latvia.
8. Putniņa, A., Kukle, S., Gravitis, J. Multifunctional materials from hemp fibres treated with steam explosion technology. Book of abstracts International conference Functional materials and nanotechnologies, Estonia, Tratu, April 21-24, 2013. Institute of Physics University of Tartu, 2013, 259.-259. p. ISBN 9789985407448.
9. Putniņa, A., Kukle, S., Gravitis, J. An environmentally friendly method for microfibrillated cellulose extraction from hemp. Proceedings of 10th International Conference of Young Scientists on Energy Issues: 10th International Conference of Young Scientists on Energy Issues, May 29-31, 2013. Kaunas, Lithuania: Lithuanian Energy Institute, 2013, 81.-86.p.
10. Putniņa, A., Kukle, S., Grāvītis, J., Grāve, L. Characterization of cellulose microfibrils obtained from hemp. Book of abstracts: 1st International Conference on Natural Fibers - Sustainable Materials for Advanced Applications, 9-11 June, 2013, 23.-24.p. Portugal, Guimarães.
11. Grāve, L., Putniņa, A., Kukle, S., Stramkalne, V. Steam explosion impact to technical hemp fiber diameter. IX starptautiskā zinātniski praktiskās konferences materiāli: Vide.Tehnoloģija. Resursi, Latvia, Rēzekne, 20-22 June, 2013, 112.-115.lpp.

12. Putniņa A., Kukle S., Grāve L., Grāvītis, J. Steam Explosion as Pretreatment Method of Hemp fibers, Earth day, 2013. Biomaterials.
13. Šutka A., Kukle S., Gravitis J. Electrospun Nanosized Cellulose/Polymer Fibres. Riga Technical University 54th International Scientific Conference, 14–16 October, 2013, Riga, Latvia.
14. Sutka A., Kukle S., Gravitis J. Electrospun nanofiber composites of microcrystalline cellulose/poly(vinyl alcohol). Conference on Natural Fibre Composites, 17-18 October 2013, Rome, Italy
15. J. Gravitis, J. Abolins, S.Kukle, A.Putnina, M.Andzs, R. Tupciauskas, A. Veveris. Feedstock for biorefineries and advancement of value-added products from biomass, The 8th Pacific Regional Wood Anatomy Conference, Annual Meeting of International Academy of Wood Science, 17-21 October, 2013, Naning, China.
16. Sutka, A., Kukle, S., Grāvītis, J. Electrospinning and Characterization of Cellulose/Polymer Nanocomposite Fiber Mats. Proceedings of the 13th European Workshop on Lignocellulosics and Pulp, Spain, Seville, June 24-27, 2014. Institute of Natural Resources and Agrobiolgy of Seville, 2014, 815.-818.lpp. ISBN 978-84-616-9842-4.

* Scientific articles indexed in the Web of Science, and / or SCOPUS databases

** Articles in scientific proceedings indexed in Web of Science Proceedings Conference Citation Index and / or SCOPUS

Literature review

The literature review includes several topics: (i) environmentally friendly technological solutions for zero emission bio-refinery technologies; (ii) the structure and chemical composition of bast fibre plants (especially hems) and lignocellulosic biomass components; (iii) steam explosion technology for pre-treatment of bast fibre plants to obtain nanocellulose; (iv) polymer nano-composites; (v) electrospinning techniques and electrospun nanofiber materials. The literature on hemp plant structural hierarchy, chemical composition, macromolecular structure as well as properties and applications were reviewed. From the literature review it can be concluded, that shives (the woody part of hemp plant) are considered as hemp fiber by-products, which are found only minor uses and only a few studies demonstrates applications of the shives or their derivatives. Some authors demonstrates shives to be used to improve the properties of polymeric materials [1-3], therefore the research in this direction is especially important. No studies are reported on polymer nanocomposites with shives as filler.

The literature review focused also on the steam explosion auto-hydrolysis (SEA) process and its impact on the physical and chemical properties of biomass structural components. Published studies have shown [4-6] that during the SEA process lignocellulosic fibers undergo various chemical changes - destruction of lignocellulosic structure, hydrolysis of hemicellulose fraction, depolymerisation of lignin, defibrillation and crystallization of cellulose. Due to this reason SEA is usually used as biomass pretreatment method and its components can be easily extracted for further processing. SEA is an environmentally friendly process for treatment of bast fibers, as well as production of nanocellulose fillers.

Further review of the literature focuses on the nanocomposites, which consist of two or more materials with significantly different physical and chemical properties. The attention

has been paid mainly on polymer nanocomposites [7-9], their characteristics and properties. The influencing factors, such as specific surface area of the filler, the degree of filler dispersion and adhesion between the filler and matrix were reviewed. Analysis of published studies leads to the conclusion, that properties of nanocomposites are influenced by matrix material and concentration, size, shape and orientation of the nanofiller. Depending on chemical properties of nanofiller, it can be compatible and incompatible with the polymer matrix [10-12]. Cellulose nanofillers are compatible with hydrophilic polymers, including polyvinyl alcohol, determined by the hydroxyl groups of cellulose.

Further, the properties and preparation of cellulose nanofillers were reviewed [13], because they are biodegradable, biocompatible and has high specific strength. Additionally, high aspect ratio cellulose nanofillers can be obtained from a variety of plants in a specific region [14], providing significant economic benefits. Due to the reasons mentioned above, cellulose nanofillers is the most popular natural origin nanofillers used in polymer nanocomposites. Recently, important advances in the synthesis of cellulose nanofillers by chemical hydrolysis [15], by oxidation process [16], by mechanical treatment [17], enzymatic hydrolysis [18] and steam explosion [19] were performed. Generally to obtain cellulose nanofillers in crystalline form mainly aggressive chemical methods are used [15], which are harmful to the environment.

Review of the literature indicates an increase in research addressing to electrospinning (ES) method, recognizing it as an effective method for obtaining polymer nanofibres with a high surface area to volume ratio. Electrospinning enables to integrate diverse structures of nanofiber in filtration membranes, sensors, tissue regeneration, and elsewhere, with important certain characteristics such as high porosity and specific surface area. The influencing factors of ES process and their role in the nanofiber mats and their morphology are also reviewed. The ES process is affected by strength of applied electric field, the distance between the electrodes, the ambient temperature and partial pressure, and polymer solution properties such as molecular weight of polymer, the concentration of the polymer, conductivity, surface tension and viscosity. The different technological solutions of electrospinning were also reviewed [20]. Electrospinning can be used to produce nanofiber composites where fillers, smaller than electrospun fibers, are embedded [21-23]. It has been demonstrated that needles ES process yields higher productivity.

Overall, development of environmentally friendly techniques for obtaining electrospun polymer nanofibre composites reinforced by crystalline nanocellulose structures is highly important.

Materials and methods

The proposed technological sequence of producing nanofiber composite includes: 1) pre-treatment of fibres and shives by steam explosion auto-hydrolysis; 2) processing of fibres and shives after pre-treatment; 3) fractionation of processed biomass; 4) defibrillation by ultrasound; 5) preparation of spinning solution of the polymer and nanocellulose; 6) electrospinning (Fig. 1).

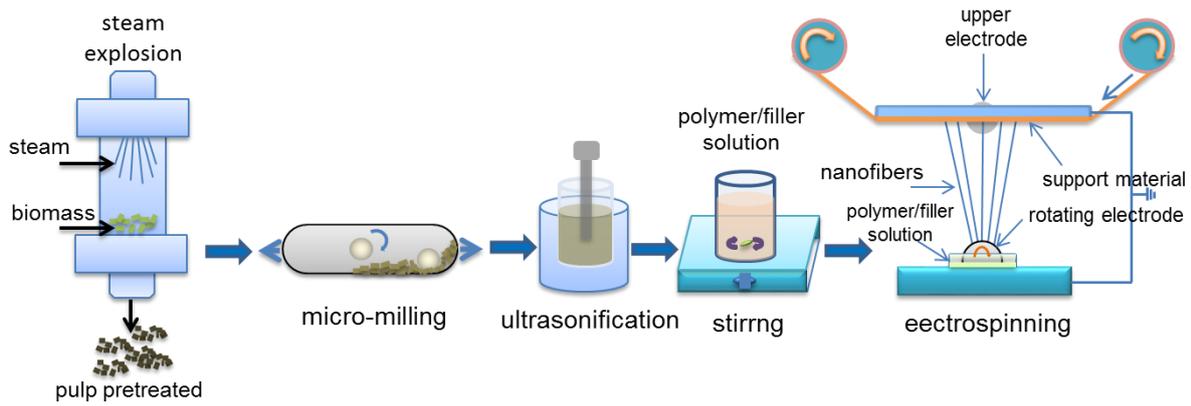


Fig. 1. The sequence of procedures to obtain electrospun nanofiber composites

Nanocellulose (NC) is obtained from fibers (F) and shives (S) of two hemp varieties: "Purini" (P) and "Bialobrzeskie" (B). Samples of purified PF and BF fibers are cut to about 2 mm long segments. Cleaned PS and BS shives are grounded and sifted through a 2 mm mesh sieve.

SEA pre-treatment of hemp fibers and shives is made in a laboratory reactor complemented with steam generator (Fig. 2). Reactor loaded with biomass and sealed is filled with saturated steam. 60 seconds (or other chosen time of treatment) after the set treatment parameters have been reached, the biomass is defibrilised by instant decompression and gathered into container (Fig. 2).

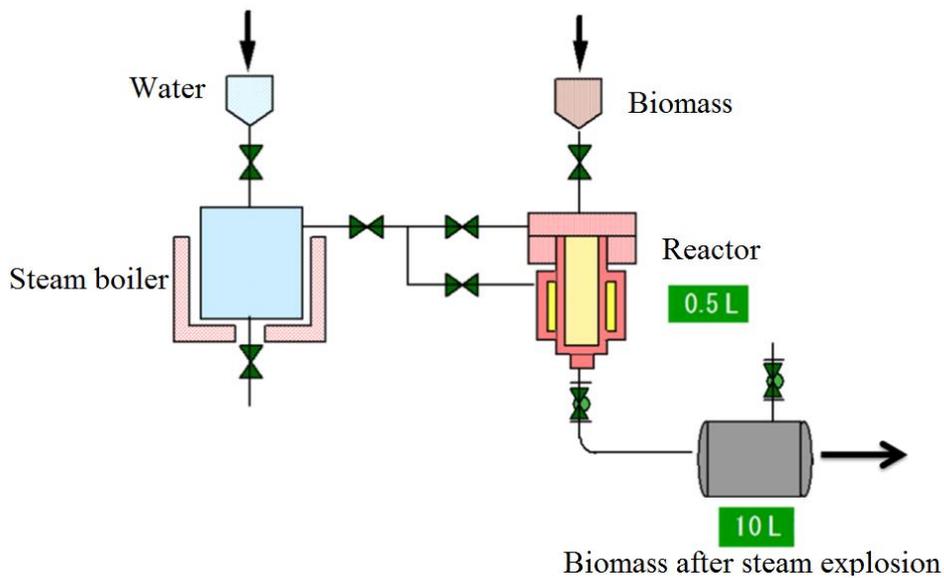


Figure 2. Block diagram of steam explosion treatment [4]

The level of the treatment intensity is defined by severity factor $\log R_0$ [24]:

$$R_0 = t * \exp \frac{(T-100)}{14,75} \quad (1)$$

where, t – treatment time, min;
 T – temperature, °C.

After SEA treatment the biomass is fractionated by methodology developed by "Eco-efficient biomass conversion" laboratory of the Latvian State Institute of Wood Chemistry [25]. The steam exploded biomass is washed in distilled water to remove water-soluble components and in 0.1M NaOH aqueous solution to remove pectin/waxes, lignin, and oils, after which the solution is neutralised with HCl to precipitate lignin, then filtered, washed in water and air-dried at room temperature.

The hemp biomass is homogenised crushing agglomerates in a ball mill for 10 min at frequency of 30 s^{-1} . After ball micro-milling, the powdered biomass is suspended in distilled water and for 30 min treated by ultrasound. The nanocellulose suspension is mixed immediately with PVA solution to concentration between 8 and 10% (wt %) by dissolving the weighed amount of powder in distilled water at $90 \text{ }^\circ\text{C}$ and stirred for 2 hours in a magnetic stirrer. After that the NC is added to PVA solution in the amounts required to obtain the final nanocomposite concentration ranging from 1 to 20% (w/w) relative to the mass of PVA, the stirring being continued for another 2 hours.

The conductivity and viscosity of NC dispersions in PVA aqueous solution is measured before electrospinning.

A needle-less high-voltage Nanospider NS Lab 200 (Elmarco, Czech Republic) electrospinning device equipped with cylindrical spinning electrode is used to produce nanofiber mats of NC dispersed in PVA aqueous solution. Parameters of the electrospinning process are presented in Table 1. Samples of suitable thickness are prepared by electrospinning on nonwoven polypropylene antistatic substrate during 5 min at intervals of 15-30 seconds and feed rate of the substrate being 0.2 m/min.

Table 1

Parameters of electrospinning process

Length of electrode (mm)	145
Diameter of electrode (mm)	20
Rotation speed of electrode (rpm)	4
Distance between electrodes (mm)	120-180
Voltage (kV)	60-70
Relative humidity (%)	~30
Temperature ($^\circ\text{C}$)	$22 \pm 0,5$

The obtained materials are characterised by Fourier Transform infrared spectroscopy (FTIR; ATR-FTIR), X-ray diffraction (XRD), atomic force (AFM) and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM), the optical, calorimetric and mechanical properties and water solubility of nanomats being analysed.

Experimental tests with two types of nanomat samples are made to determine tensile strength (σ_{st}), modulus of elasticity (E) and elongation (ϵ) the test samples being prepared at different spinning parameters: 1) at substrate speed 0.2 m/min and 2) at fixed substrate during 5 min. In the first case tests are made in directions parallel, perpendicular and diagonal with respect to the electrode (Fig. 3.); in the latter case – in the direction parallel to the electrode). The average thickness of the samples is $\sim 100 \text{ }\mu\text{m}$. Each nanocomposite is presented by 10 samples (Fig 4., b).

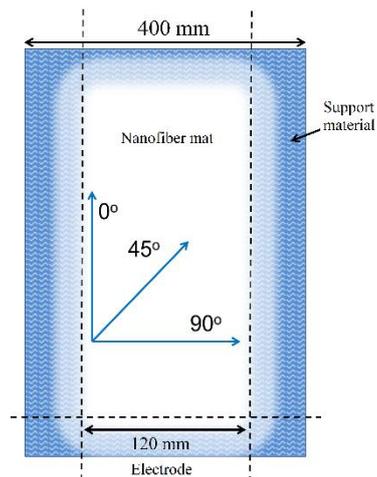


Fig. 3. Cutting directions of sample

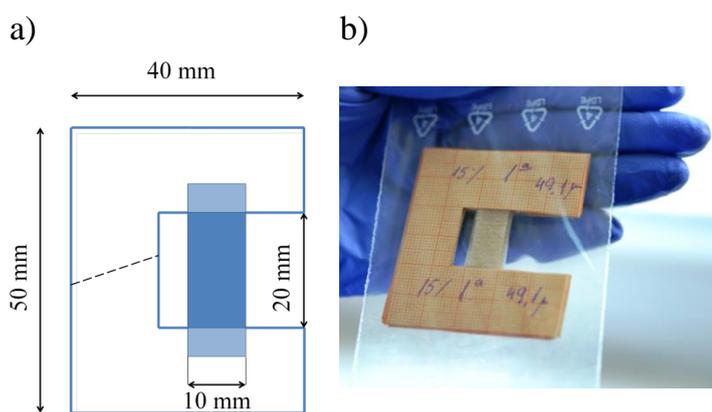


Fig. 4. Size of the sample prepared for testing

Results

The chemical composition of hemp fibres and shives after SEA depends on R_0 . After SEA ($\log R_0=3.53-4.45$) the mass of recovered fibres and shives is 7.3 to 8.8% (fibres) and 6.3 to 13.2% (shives) of the initial biomass. Hemicelluloses and negligible amounts of hydrolysed cellulose and low-molecular phenols are removed by water extraction [26]; the mass recovered after alkaline extraction comprises 4.5 to 7.1% (fibres) and 20.9 to 29.6% (shives) of the initial biomass before SE, the soluble lignin and water-insoluble hemicelluloses being washed out in the NaOH solution [27]. Lignin is precipitated by neutralising the alkali solution with hydrochloric acid [28].

Only 0.75% of the fibre mass SEA at $\log R_0=3.53$ is recovered in lignin, while SEA at $\log R_0 = 3.98$ and $\log R_0=4.45 - 2.5$ and 3.7%, respectively, which is less than a half before SEA (PF 8%). This means that part of lignin is still in the fibres.

The content of lignin ranging from 13 to 17%, after SEA treatment of shives at $\log R_0=3.98$ and from 18.1% to 22.3% – at $\log R_0=4.45$ (close to the lignin content of 22.9% in untreated hemp variety "Purini"). It can be concluded that ~ 97% of lignin can be extracted by SEA treatment and following fractionation of biomass, and control residual lignin content in fibres by conditions of SEA treatment, if necessary.

At SEA severity $\log R_0=3.53$ the cellulose content in fibres is found to be 76.6% of the initial biomass, while the cellulose content in the initial biomass is only 64.2%. At higher SEA treatment severities of $\log R_0=3.98$ and $\log R_0=4.45$ the cellulose content increases from 65.9% to 68.7%. The cellulose content in shives ranges from 43% to 48.4% of the primary biomass at severity parameter $\log R_0=3.98$. At SEA severity $\log R_0= 4.45$ the cellulose content decreases comprising 38% to 43%. This means that lignin still remains in the SEA pulp and is not fully dissolved during alkaline extraction. Components (cellulose and lignin) of the hemp biomass remain while changing their internal structure.

FTIR analysis confirms the changes in the chemical composition of hemp shives and fibres after SE with following water and alkaline extraction (Fig. 5.): characteristic bands of cellulose I (1059 and 1032 cm^{-1}) of increasing intensity after water and alkaline extraction are seen in FTIR spectra of SEA samples [28]. The carbonyl band intensity at 1740 cm^{-1} (C=O stretching in unconjugated cations, carbonyls and in ester groups (frequently of carbohydrate origin)) [29] reducing after SEA indicate destruction of pectin, waxes and hemicellulose components, completely disappears after water and alkaline extraction

(Figure 5). After SE intensity of the characteristic bands of lignin at 1428 cm^{-1} , 1245 cm^{-1} (characteristic to aromatic C-H deformations in syringil units) and 1606 cm^{-1} (C=O stretching) [30] significantly decreases. There is correlation between the drop of lignin band intensity in fibres after water and alkaline extraction ((BS TS E) Fig. 5)

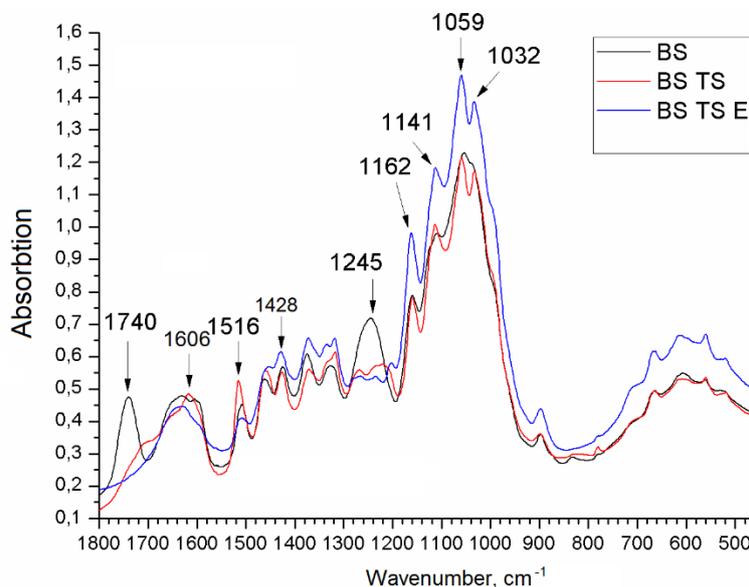


Fig.5. FTIR spectra of shives before (BS) and after steam explosion ($\log R_0=4.45$) (BS TS), and after extraction by water and alkali solution (BS TS E)

SEM micrographs with the main visually detectable changes in hemp shives after SEA and after water and alkali extractions are shown in Figure 6. Untreated fibre structure is monolithic (Fig. 6. a), micrographs after SEA ($\log R_0=4.45$) treatment (Fig. 6. b) show that part of the fibre bundles are decomposed to smaller sizes, still a relatively large proportion of fibre bundles with dimensions of $20\text{ }\mu\text{m}$ or more shows that the intensity of the treatment has not been sufficient to disassemble all fibre bundles; in addition to the fibre/binder surface are visible uneven layers of amorphous components released during SEA. After water and alkaline extraction (Fig. 6. c) the layer on the fibre surface is significantly decreased and the surface has a strong microfibrill structuring, since lignin is mostly removed by water and alkali extractions.

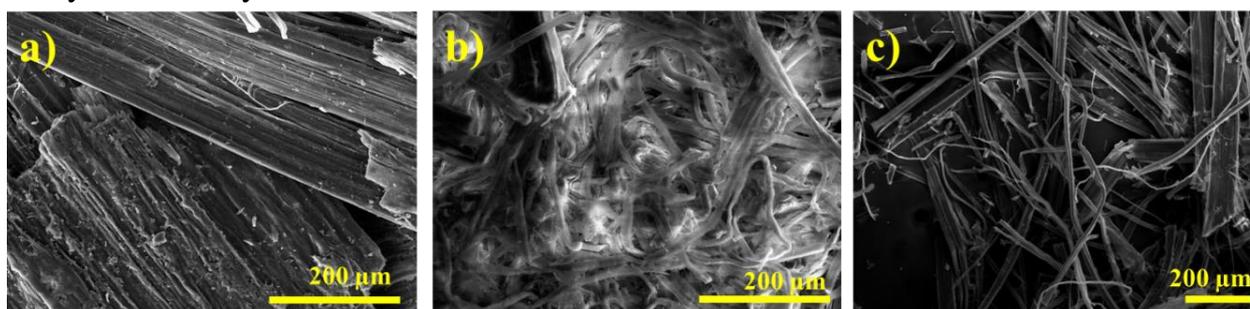


Fig. 6. SEM micrographs of PF before SE (a), after SE ($\log R_0=4.45$) (b) and after extractions by water and alkali (c)

The structure of shives (PS) is disrupted during mechanical separation, parallel fibres and container elements being made visible on the surface (Fig. 7. a). After SEA at

$\log R_0=4.45$ the complexes are disrupted to a deeper level revealing fibre defibrillation into individual fibres and fragments of them (Fig.7, b). Immediately after SEA the fibre bundles are flexible and fragile, adhesion between individual fibres occurring after drying (Fig 7., b). At larger magnification uncovered fragments are observed (Fig. 7. c).

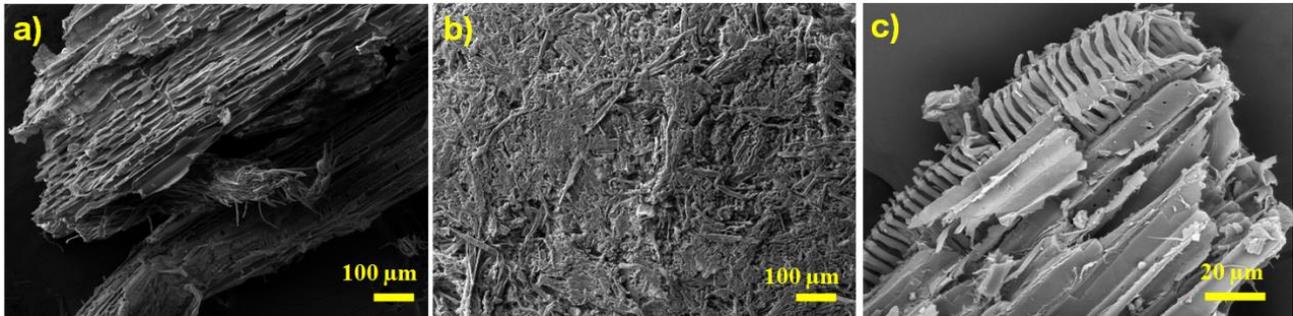
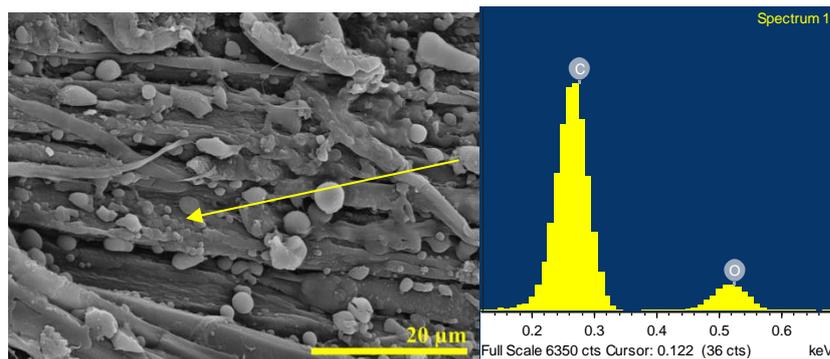


Fig.7. SEM micrographs of hemp shives before SEA (a) and after SEA ($\log R_0=4.45$)

After SE spherical domains are visible on the fibre surface (Fig. 8). As can be concluded from the EDX analysis, the spherical domains mainly contain carbon present in the chemical structure of lignin and hemicellulose. During SEA lignin tends to decompose and resides in the form of spherical particles on the internal and external cell surface and inside the cell walls.



8. Fig. SEM micrograph of hemp shives and EDX analysis of the sample (SEA: $\log R_0=4.45$)

Mechanical grinding of shives before SEA increases content of fine particles in samples, fragments of them and also content of small fibres (Fig. 9., b and c).

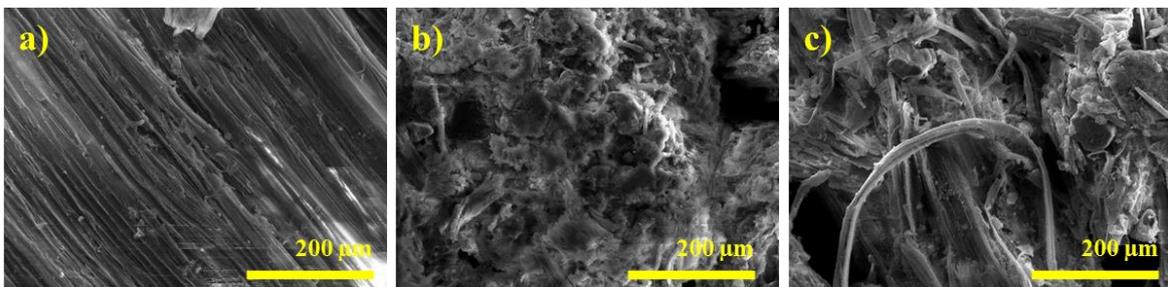


Figure 9. SEM micrographs of ground hemp shives before SEA (a), after SEA ($\log R_0=4.45$) (b) and after water and alkali extractions (c)

The best results provide hemp fibres and shives treated by SEA at $\log R_0=4.45$ and washed by water and alkaline solution to remove lignin from fibre surface. At lower severity parameters fractionation of the components is less efficient while destruction of the natural fibre products is observed to occur at higher severity parameter values. The porous structure and chemical composition (higher lignin content effectively released by SEA) explain the better results with hemp shives. Grinding before SE improves the treatment efficacy of hemp shives. Variety of hemp is not a significant for the outcome of SEA. Milled shives are found being more advantageous for nano-sized fillers.

For farther studies the shives of the "Purini" hemp variety have been used, being a local culture and suitable for agro-climatic conditions in Latvia.

Micro-milling and dispersion of shives by ultrasound (US) before preparing solution for electrospinning improves colloidal stability of the system and reduces the size of shives. As seen from micrographs (Fig. 10), nano-size linear structures are formed after US treatment.

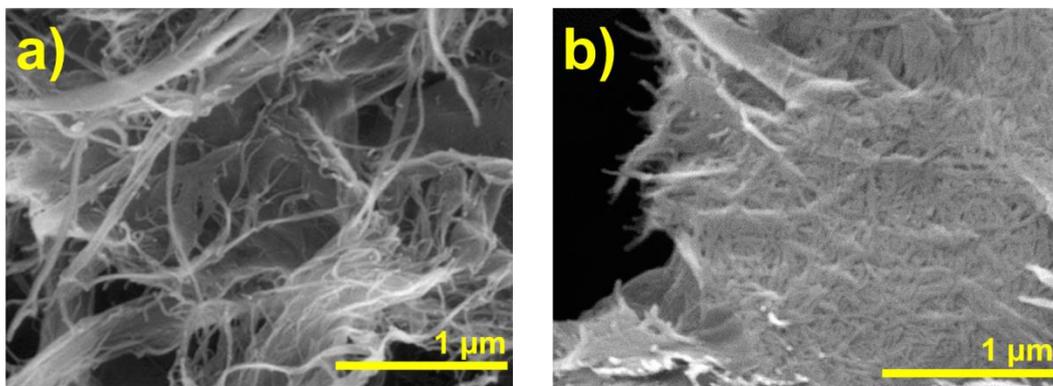


Figure 10. SEM mikrographs of steam exploded and ultrasound treated hemp fibers (a) and shives (b)

The NC obtained from shives for characterization of which TEM and AFM images have been taken exhibit tendency to agglomeration (Fig. 11).

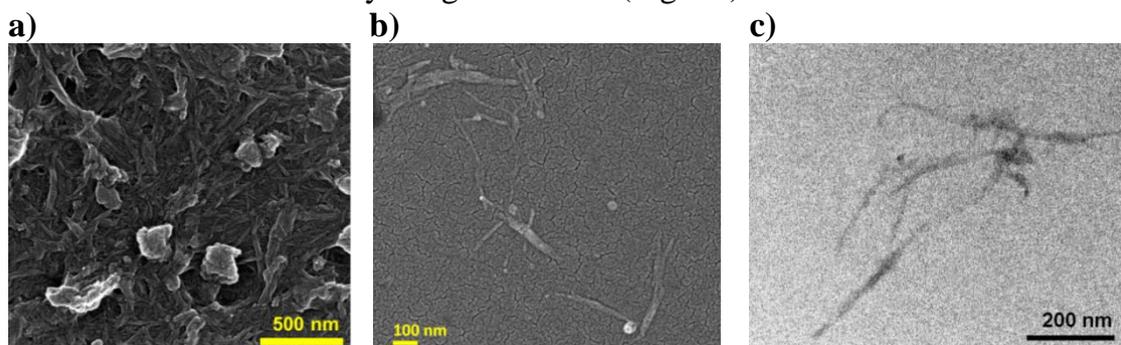


Fig. 11. SEM (a, b) and TEM (b) micrographs of nanocellulose from hemp shives

The XRD pattern of the crystalline NC obtained after SEA, micro-milling and ultrasound treatment comprises intense diffraction peak at 22.5° typical to cellulose I structure (Fig. 12). Degree of crystallinity is found to be 79.2%.

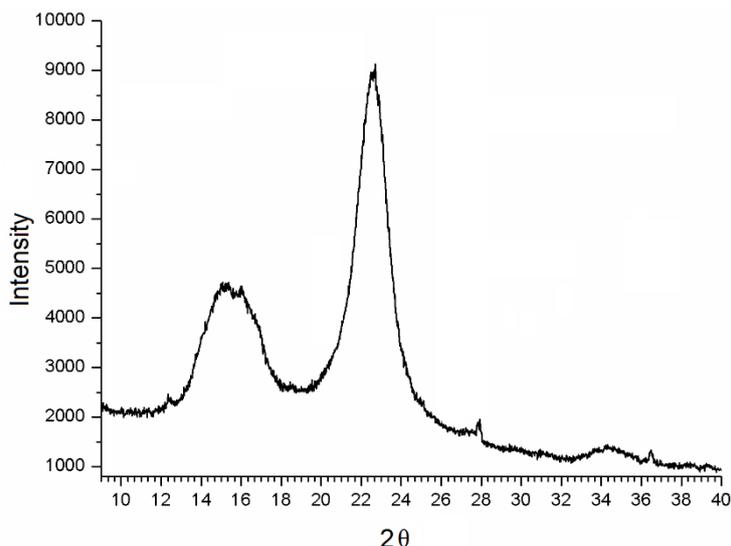


Fig. 12. XRD diffraction pattern of NC from hemp shives

Diameters of NC from hemp shives and fibres after US treatment are in the range from 24 to 400 nm (Fig 13, a), 60% of the total count do not exceed 100 nm in diameter, the mean arithmetic being 115 ± 8 nm is slightly shifted to the side of larger diameter values since a small amounts (~22%) of insufficiently defibrillated fibre complexes with diameters ranging from 250 to 400 nm remain. Diameters of NC fibers obtained from shives (Fig. 13, b) are in the range of 9 to 40 nm, 80% being less than 30 nm and the mean arithmetic diameter value – 25 ± 1 nm. Because of a significantly smaller average diameter relatively narrow diameter variation interval of shive fibers they are more suitable for electrospinning.

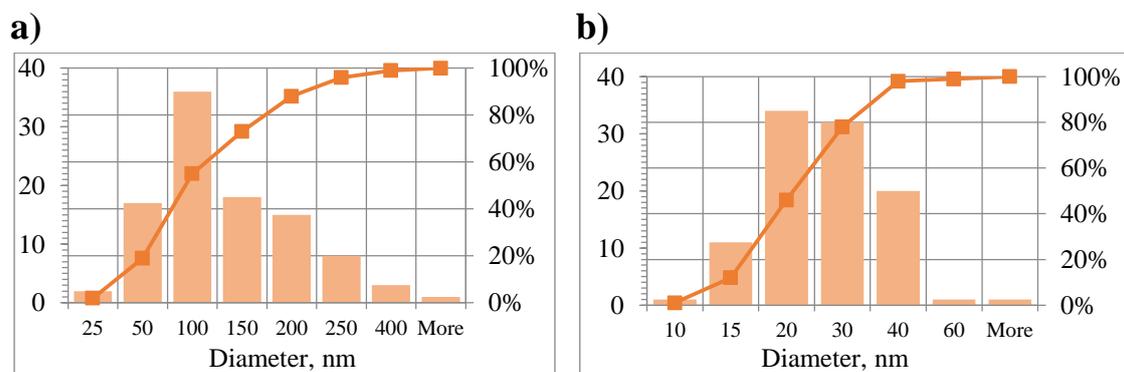


Fig. 13. Histograms of diameter distribution of hemp fibers (a) and shives (b)

Length of the NC particles obtained from shives after US treatment varies within the range from 142 to 319 nm with the mean arithmetic of 216 ± 16 nm the aspect ratio being 9, complying with the TAPPI standard for pulp nano-fibrils [31].

Further the studies refer to electrospinning of PVA and PVA reinforced with NC nanofibers. The effects of concentration of the PVA solution, the distance between electrodes and the concentration of NC on fiber morphology are presented in Figs. 14 and 15. If the concentration of PVA in spinning solution is less than 6 wt%, the electrospinning process does not go on and fibers are not formed.

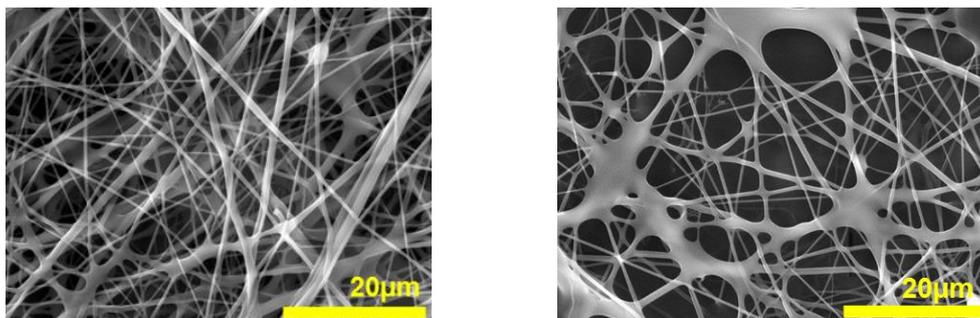


Fig. 14. PVA nanofibre mat morphology depending on the distance between electrodes: 16 cm (a) and 12 cm (b)

A steady electrospinning proceeds at PVA concentrations from 8 to 10 wt% the optimal distance between the electrodes being 16 cm at which a homogeneous nanofiber web is formed (Fig. 14, a). Reducing the distance to 12 cm provides defected (beaded fibers, thickenings and films) nanofibre webs (Fig. 14, b). At distances above 16 cm breakages of the electrospinning flow of fibers occur.

The effects of the NC concentration on the morphology of nanofiber mats are seen in SEM micrographs (Fig. 15.). PVA mats without the NC filler are significantly coarser and smoother. Increasing the concentration of NC in the solution reduces diameter and the number of defects.

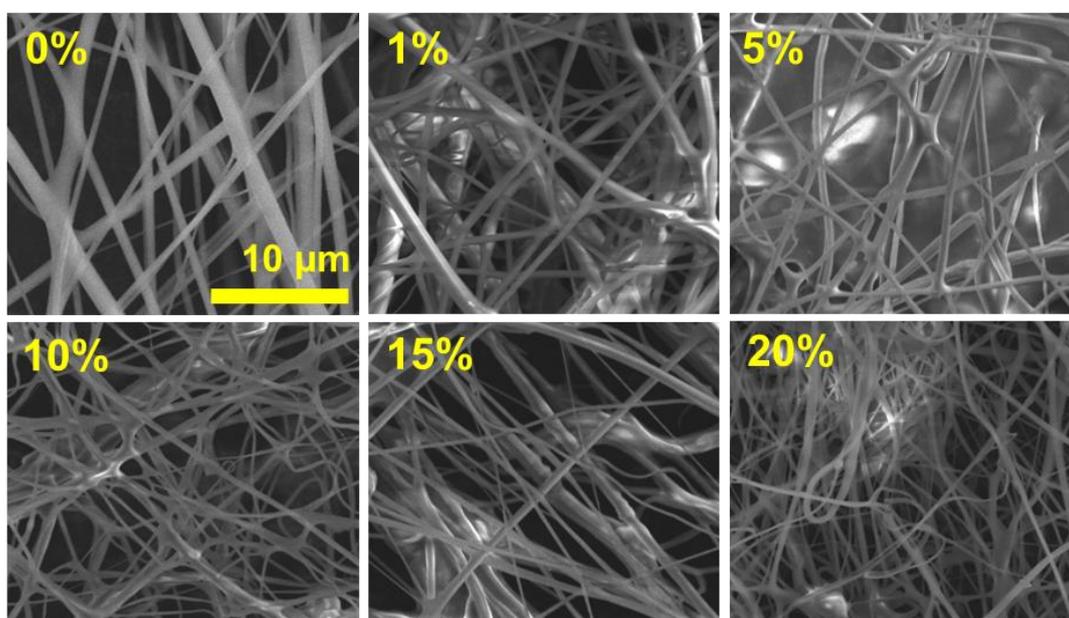


Fig. 15. Morphology of nanomats at different contents of NC (0-20 wt%).

The histograms of nanofiber diameter size distribution are obtained from at least 100 measurements of five SEM micrographs are presented in Figs. 16, 17 and 18. Diameters of PVA fibres range between 211 and 1108 nm (Fig. 16, a) 50% of the measured diameters exceed 500 nm, the modal diameter of 600 nm exceeds the mean arithmetic value of 505 ± 23 nm, indicating a large proportion of fibre diameters in the range of 500 to 1108 nm. This means that PVA fibres are relatively coarse. Blurred fibres formed on the surface shift the

centre of the diameter distribution toward larger diameter values. Addition of even a little amount of NC to the spinning solution significantly affects the characteristics of the diameter distribution (Fig. 16., b): at NC content of 1 wt % diameters are in the range from 196 to 985 nm, the modal diameter shifts from 600 nm to 400 nm being less than the mean arithmetic diameter of 471 ± 17 nm and indicates that distribution is centred at smaller fibre diameters 62% of which are less than 500 nm.

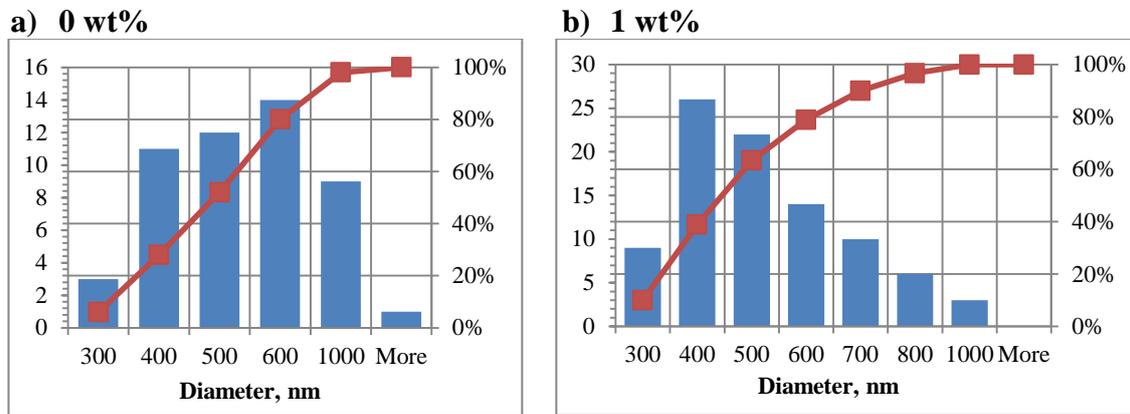


Fig. 16. Histograms of fibre diameter distribution: PVA (a) and PVA/NC of 1 wt% (b)

At NC content of 5 wt% (Fig. 17., a), the upper limit of fibre diameter is 868 nm, 40% of fibres having diameter less than 400 nm and 77% – less than 500 nm, the mean arithmetic diameter value being equal to 440 ± 21 nm – by 13% less compared with PVA.

At 10 wt% of NC (Fig. 17, b) diameter distribution is shifted more to smaller diameters within the range of 181 to 651 nm, 58% of fibres having diameter below 300 nm. Diameter of 82% fibres does not exceed 350 nm, the average mean arithmetic diameter of 304 ± 14 nm is within the modal range indicating that diameter distribution approaches to the Gaussian pattern. Diameters exceeding 500 nm belong to a very small percentage of fibres.

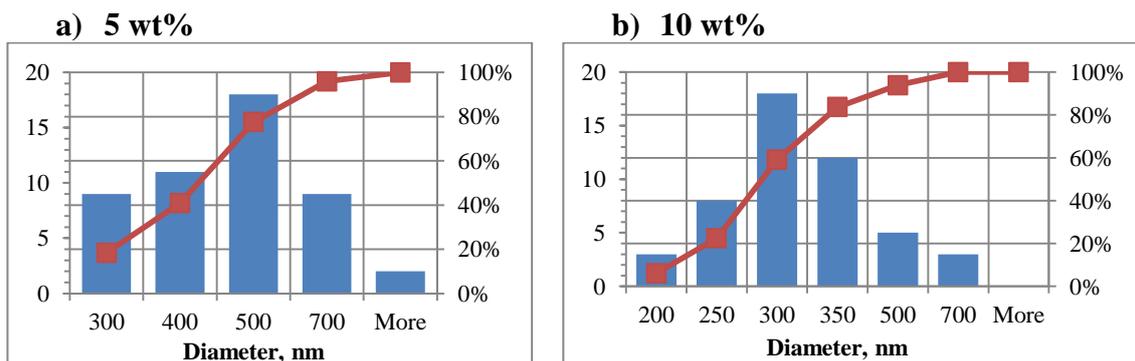


Fig. 17. Histograms of diameter distribution of PVA/NC 5 wt% (a) and PVA/NC 10 wt% (b) fibers

Increasing the NC content up to 15 wt %, the range of diameter values (179-730 nm) does not change (Fig. 18, a), but the proportion of the three central intervals around the mean arithmetic diameter of 305 ± 18 nm being within the modal range increases; 63% of fibres have diameters below 300 nm, diameter of 83% of the fibres being less than 350 nm.

The fibre diameter distribution in mats obtained from PVA/NC spinning solution of the NC content of 20% wt. is shown in Fig. 18., b. Diameters of 78% of fibres are in the range of 83 to 250 nm, the mean arithmetic diameter equal to 225 ± 10 nm is in the modal range being decreased by 55% or 2.44 times compared with fibre diameter of PVA mats, a negligible proportion of fibres being of diameter above 400 nm.

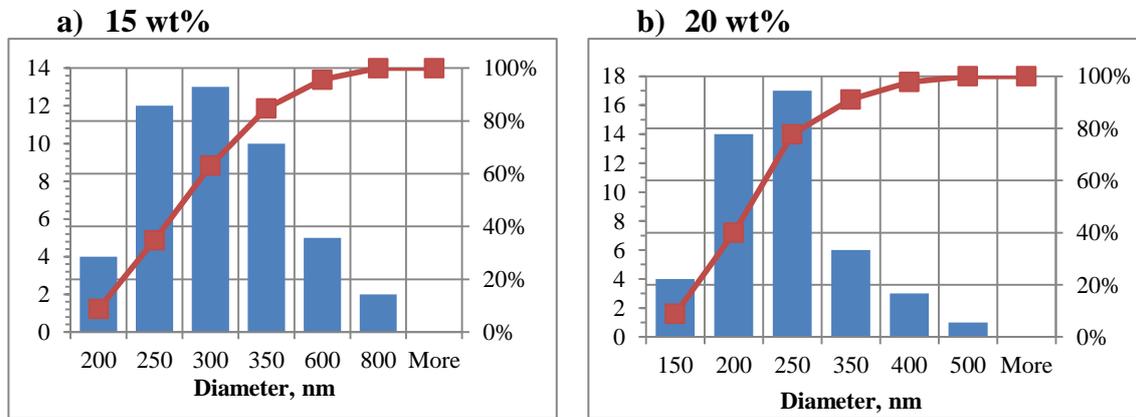


Fig. 18. Histograms of diameter distribution of PVA/NC 15 wt% (a) and PVA/NC 20 wt% (b) fibers

The characterising parameters (modal diameter, median, mean arithmetic and quartiles (Q3) of fibre diameter distribution is shown in Fig. 19. All curves show the trend of decreasing diameter values with growing the concentration of NC in the PVA solution and stabilising at concentrations within the range of 10 to 20 wt%

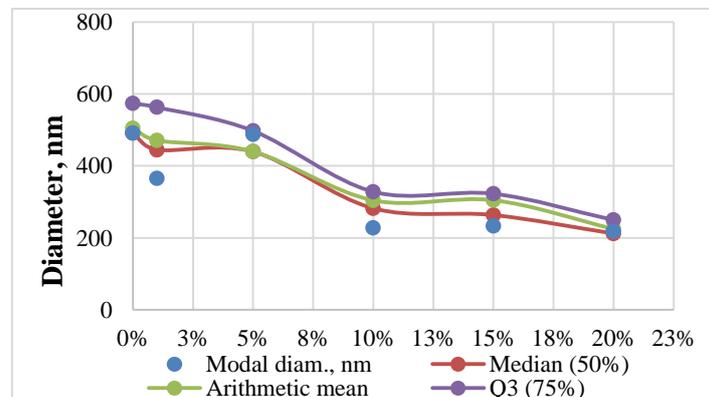


Fig. 19. Characteristic fiber diameters of electrospun PVA/NC mats at different NC concentrations

On the basis of the determined characterising parameter values of fibre diameters in the obtained mats and taking into account that fibre diameter is one of the most important indicators of the electro-spun fibre mats end applications, the optimal NC concentrations of the PVA/NC spinning solutions for the roller type electrospinning equipment are in range from 10 wt % to 20 wt %.

As seen from the FTIR spectra (Fig. 20), the increase of the NC concentration in the PVA solution changes chemical bonding and molecular configuration, resulting in

differences of the intensity and position of the absorption bands providing the evidence of the presence of NC in PVA nanomats. Observed absorption at 1034 and 1059 cm^{-1} belong to CO vibrations of cellulose (Fig. 20, a). Particularly strong intensity is observed in PVA/NC at 20 wt % (Fig. 20, b). The bands in the range of 1733-1713 cm^{-1} attributed to the acetyl C-O and C=O vibrations in the PVA matrix [23] present equally intense absorption in all samples (Fig. 20, a).

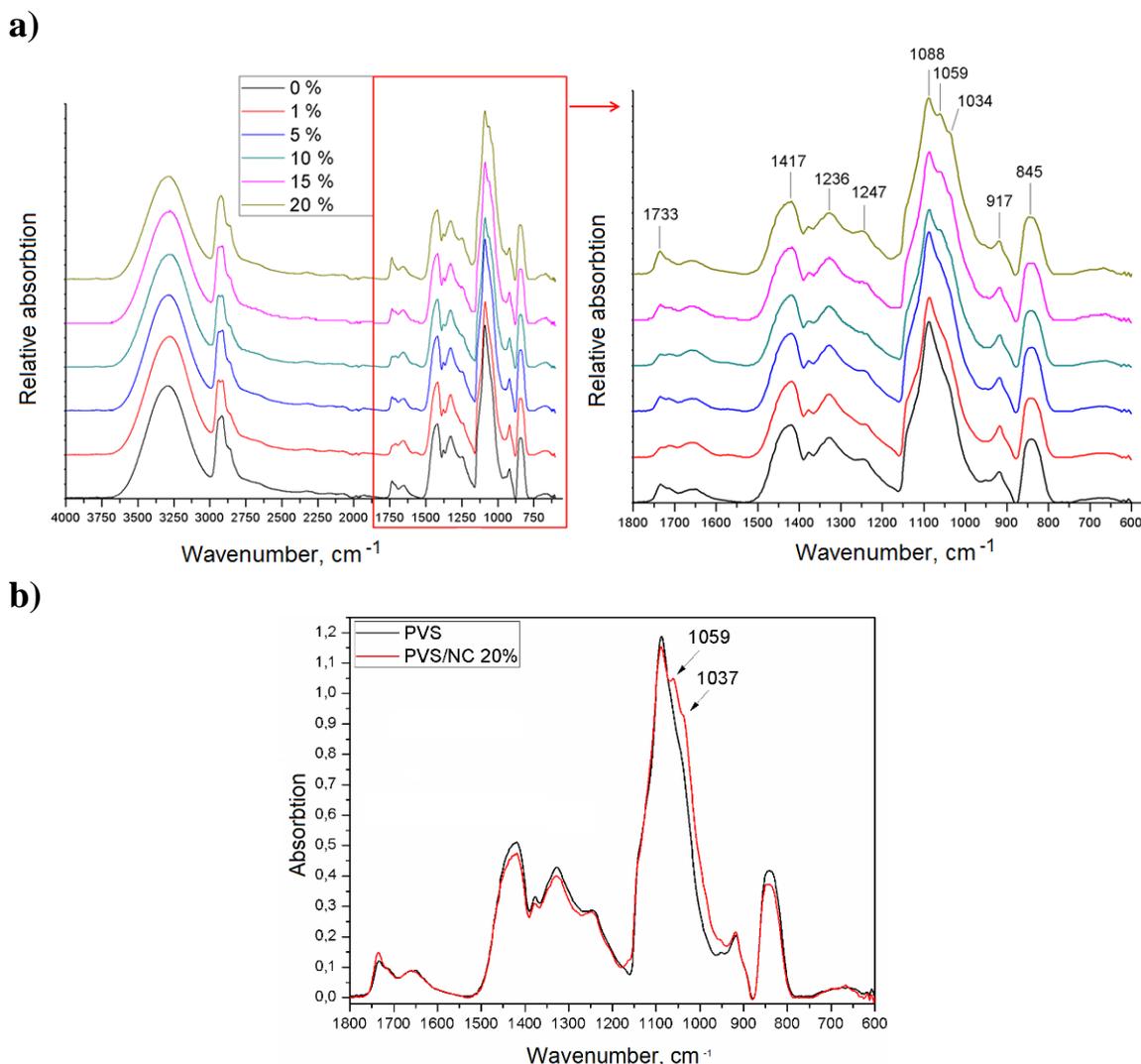


Fig. 20. ATR-FTIR spectra of PVA nanomat and PVA/NC nanofibre composites (a) and PVA/ 20 wt % NC nanofibre composite (b)

Absorption in the UV and visible range increases with increasing of the content of NC in the PVA/NC nanomats (Fig. 21), which can be attributed to presence of a small amount of lignin residue in NC (Fig. 22.). The peak at 280 nm observed UV-vis absorption spectra corresponds to a residue of the catalyst used for hydrolysis of the vinyl acetate group and also can be assigned to residual lignin remaining in the hemp lignocellulose even after the various treatments.

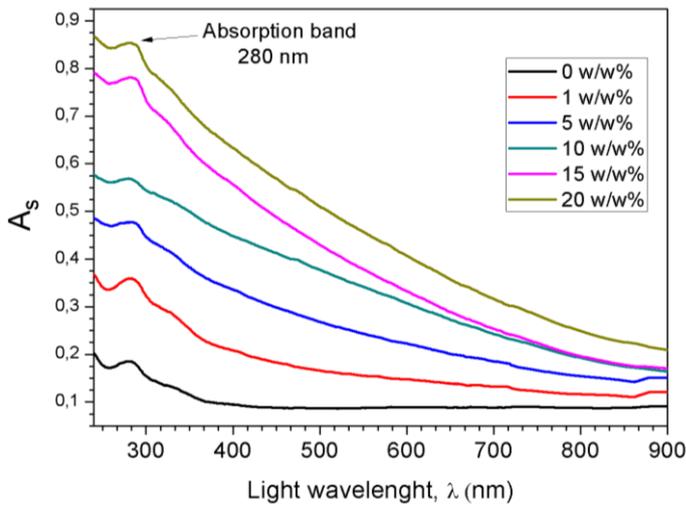


Fig. 21. UV-vis absorbance of PVA nanofiber mat and of PVA/NC nanofiber composite mats

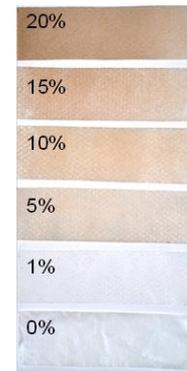


Figure 22. Photos of PVA and PVA/NC nanofibre composites mats

XRD patterns of PVA and PVA/NC nanofiber composite mats (0-20 wt%) in Fig. 23 contain a peak at $2\theta = 19.8^\circ$ characteristic to PVA [32] and a peak around $2\theta = 22.5^\circ$ (in PVA/NC 1-20 wt%) typical to the structure of cellulose I [33] the peak intensity increasing with increasing the NC content. intensity of the peak characteristic to PVA decreases relative to the rest of the background spectrum becoming almost fully equal with the intensity of the NC the peak at $2\theta = 22.5^\circ$ when NC concentration reaches 20 wt%.

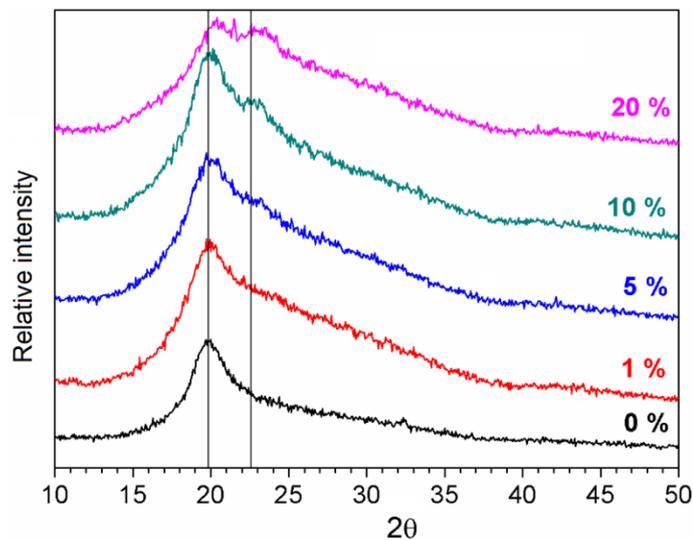


Figure 23. XRD patterns of PVA and PVA/NC nanofibre composite mats (0- 20 wt%)

The broad endotherm peak on the DSC curve between 40°C and 120°C associated with water in the samples visible in the first heating cycle disappears in the second heating cycle (Fig. 24). The second endotherm peak is related to the melting of PVA. The same behaviour is observed with all compositions. Cooling cycle was performed at similar rate over the same temperature interval to remove prehistory of the specimens the second heating cycle being conducted for analysis of differences. Thermal behaviour of the electrospun fibres is affected by the orientation of polymers during electrospinning and by

water content in the fibres being the reason of difficulties to interpret the DSC transition temperatures from the first heating cycle. The second heating cycle is better suited for estimation of the glass transition (T_g) and melting (T_m) temperature, as well as the degree of crystallinity of the PVA/NC composites [35]. The crystallisation temperature (T_c) of different samples was estimated from the exothermic curve of the cooling experiment.

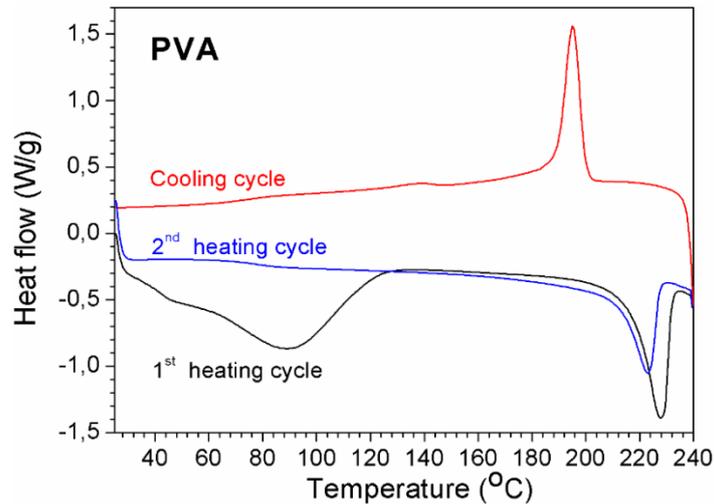


Figure 24. DSC thermograms of the electrospun PVA nanomats

DSC curves of the second heating cycle of samples with the different NC contents are presented in Fig. 25, a. The characteristic temperatures T_g , T_m , and T_c of PVA/NC are summarised in Table 2. Adding of NC does not change the shape of the endothermic transition moving to higher temperatures. As seen from Fig. 25 b and Table 2, both the T_g and T_m temperatures increase with the increase of the NC content. The glass transition interval of the PVA/NC, in which the relaxation processes proceed, is noticeably extended, which is attributed to the restrictions in conformation mobility of the polymer chains due to interactions at the interface of the polymer matrix and nano-size fillers [36].

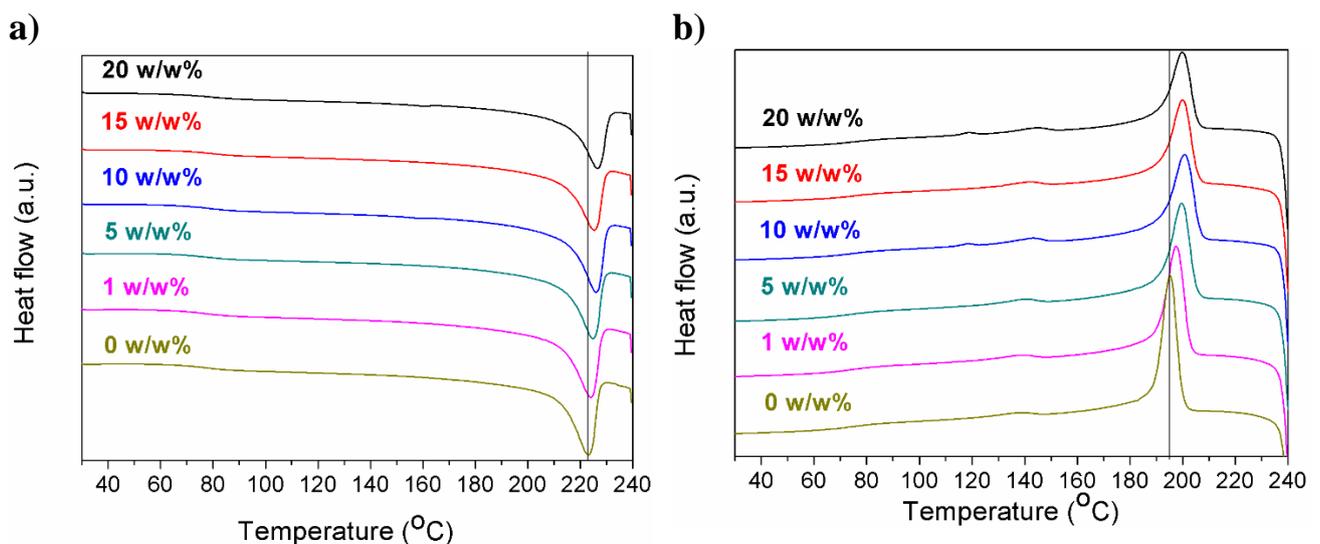


Fig. 25. DSC thermogrammes of PVA and PVA/NC nanomats at second heating (a) and cooling (b) cycles

Table 2

Effects of the NC content on the glass transition (T_g), melting (T_m) and crystallisation (T_c) temperatures and the degree of crystallinity (χ_c) of nano-composite mats*

NC, wt%	First heating cycle					Second heating cycle						Cooling cycle		
	$T_m, ^\circ\text{C}$			χ_c		$T_m, ^\circ\text{C}$			$T_g, ^\circ\text{C}$			$T_c, ^\circ\text{C}$		
	T_{ms}	$T_{m\text{ vid}}$	T_{mb}			T_{ms}	$T_{m\text{ vid}}$	T_{mb}	T_{gs}	$T_{g\text{ vid}}$	T_{gb}	T_{cs}	$T_{c\text{ vid}}$	T_{cb}
0	198	228	235	0.39	0.30	188	223	230	64	83	102	207	195	167
1	181	227	236	0.36	0.31	183	224	230	63	82	106	212	198	162
5	199	226	235	0.31	0.28	189	225	232	62	84	103	208	200	161
10	194	224	233	0.33	0.28	193	226	233	59	86	113	210	201	159
15	195	225	233	0.31	0.24	194	226	232	57	83	107	210	200	159
20	198	224	233	0.27	0.23	195	227	234	57	80	102	211	197	164

* $\chi_c = (\Delta H_m)/((\Delta H_m^0 * w))$, where $\Delta H_m^0 = 158 \text{ J/g}$ (heat of fusion of the crystalline phase of 100% crystalline PVA) [37], w – polymer weight

In addition, the cooling curves (Fig. 25, b) indicate that the crystallisation temperature (Tab. 2) of PVA/NC also increases. The calculated T_c of different samples shifts to higher temperatures (Tab. 2). Complete crystallization of PVA/NC takes place at higher temperatures as compared with the temperature of neat PVA nanofibers and is assigned to decreasing polymer chain mobility at the interface. NC can also act as nucleating agent changing the polymer crystallinity. The crystallinities of PVA and PVA/NC nanomats were calculated from DSC curves of the second heating cycle (Table 2). Obviously, the crystallinity decreases with increasing of the NC content because of replacement of PVA with NC counterparts, of interaction between PVA and NC, or because of formation of an interphase polymer layer. The improved crystalline quality after incorporation of NC well fits the observed increase of T_m .

Solubility of the mats was tested by immersion/washing in water at vigorous stirring. Samples were electrospun from neat PVA aqueous solutions, gelatinized, and disintegrated in water in < 30 min (Fig. 26).

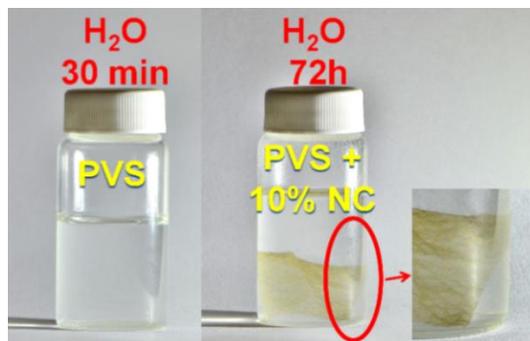


Fig. 26. Photographs of glass vessels containing neat PVA fibre mat (left), which was fully dissolved in water in < 30 min and the PVA fibre mats containing 10 wt% NC (right) retaining integrity after being immersed in water for 72 h at continuous stirring

PVA/NC mats have a superior integrity when immersed in water, although the best results were observed with samples containing 10 wt % and 15 wt % of NC. Figure 26 illustrates that the PVA sample loaded with NC retains its integrity even after being exposed to water for 72 h.

The ATR-FTIR spectra of the PVA, PVA/NC and PVA/NC W (after water treatment) samples are shown in Fig. 27, a. The maximum of the 1732 cm^{-1} band (C=O stretching in PVA), the 1092 cm^{-1} band, and 840 cm^{-1} band decrease with the increase of the NC content and after immersion and stirring in water. The 840 cm^{-1} band (C=O stretching in PVA) is possibly due to the interaction between NC and PVA [38]. Bands at 1055 and 1031 cm^{-1} , corresponding to the typical C-O stretching of cellulose are also present in the samples. The 850 to 1500 cm^{-1} region is sensitive to crystal structure of the cellulosic material.

The XRD patterns (Fig. 27, b) reveal the characteristic peak of PVA at $2\theta = 19.8^\circ$ [32] the intensity of which decreases either at adding NC or after being immersed in water for 72 h at constant stirring. The PVA/NC composites also have a peak around $2\theta = 22.5^\circ$ being typical to native cellulose-I structure [33] the intensity of which increases with addition of NC and after immersion in water, indicating the presence of NC in nanofiber mats.

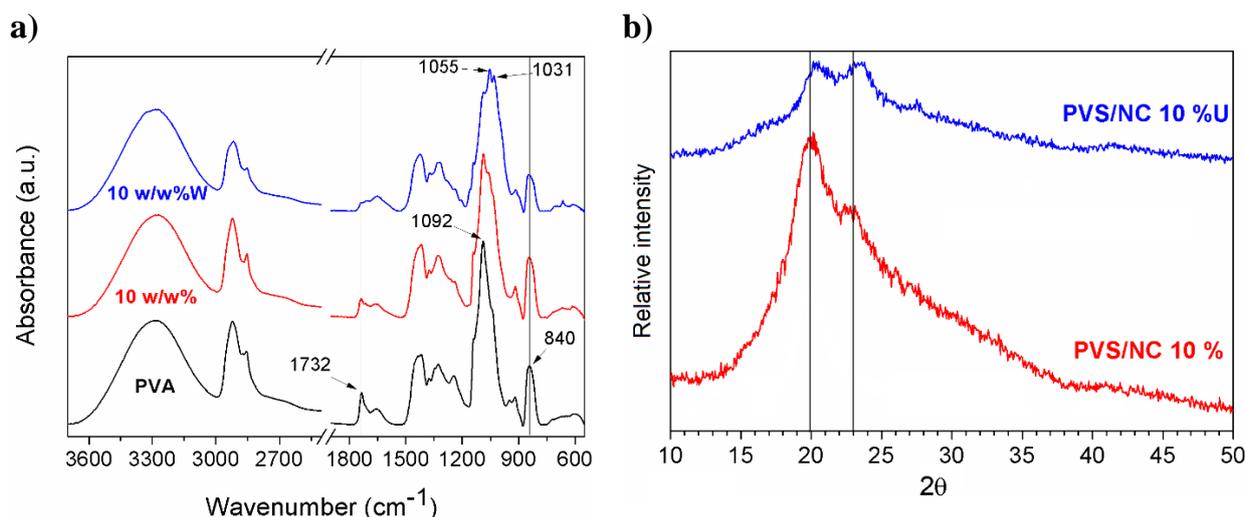


Fig. 27. ATR-FTIR spectrograms (a) and XRD patterns (b) of PVA, PVA/NC 10 wt% and PVA/NC 10 wt% U nanomats

The stress-deformation curves of nanofiber mats (Fig. 28. a.) suggest that integration of NC improves the tensile strength of the PVA nanomats and reduces the flexibility, as seen from comparing the relative elongation (ϵ) of PVA PVA/NC composites (Fig. 28., b). The elongation of nanofiber mats decreases with increasing of the NC content of up to 15 wt %, slightly increasing at 20 wt %. Changes can be described by a second order polynome (2).

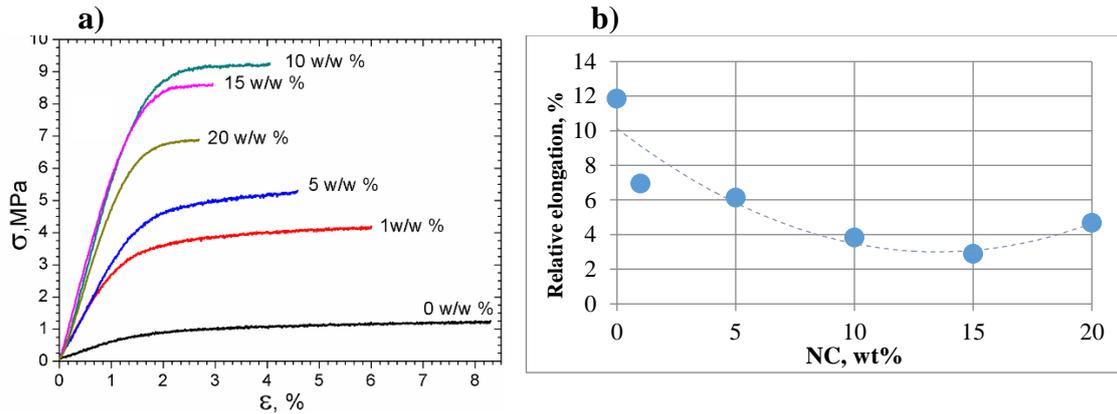


Fig. 28. Relative elongation at the break (a) and relative elongation vs. NC concentration (b)

$$Y_{\epsilon} = 0,0391X_{NC}^2 - 1,0568 X_{NC} + 10,133 \quad (2)$$

where: Y_{ϵ} – relative elongation of nanofiber mats, %;

X_{NC} – NC content in solution, wt %

Coefficient of determination = 0,85.

Tensile strength of composite nanomats containing 10 wt % of NC is significantly lower compared to PVA nanofiber mat containing 1 wt % of NC (Fig. 29, a). The correlation is described by equation (3). Increasing content of the NC up to 10 wt % the tensile strength increases from 1.58 to 8.81 MPa (458%). Ability of nanofiber mats to resist elongation and the modulus of elasticity as function of the NC content are presented in Fig. 29. The modulus of elasticity as a function of NC content is fairly well described by non-linear equation (4). The value of the modulus increases by 671% (from 0.07 to 0.54 GPa at increasing the content of NC in the composite to 10 wt %).

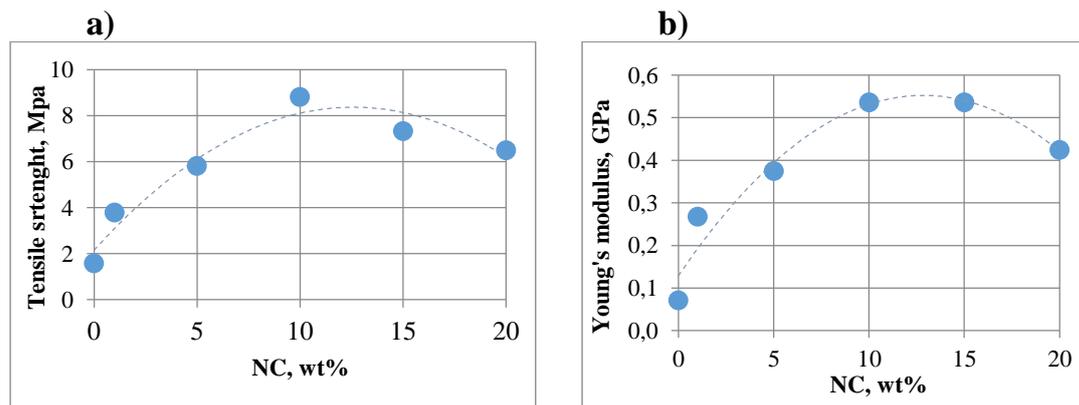


Fig. 29. Tensile strength (a) and modulus of elasticity of the nanomats (b) as functions of NC content.

$$Y_{ost} = -0,0393X_{NC}^2 + 0,9893 X_{NC} + 2,1559 \quad (3)$$

where: Y_{ost} – tensile strength of nanomats, MPa;

X_{NC} – NC content in solution, wt %

Coefficient of determination = 0.94.

$$Y_E = -0.0026 X_{NC}^2 + 0.0659X_{NC} + 0.129 \quad (4)$$

where: Y_E –modulus of elasticity, GPa;
 X_{NC} – NC content in solution, wt %
Coefficient of determination = 0.94.

CONCLUSIONS

- The crystalline nanocelullose is obtained by combined biorefining comprising steam explosion auto-hydrolysis, micro-milling and ultrasonic treatment of hemp shives.
- The best results are obtained by steam explosion treatment of hemp fibres and shives at severity parameter $\log R_0 = 4.45$, followed by water and alkaline extraction to remove lignin from fibre surfaces;
- The impact of steam explosion auto-hydrolysis on the defibrillation efficiency of shives increases if milled hemp shives are subject to processing providing deeper penetration of high-temperature water vapour in the structure of shives;
- Comparative analysis of the size of fibres and shives shows the nanocelullose from shives of mean diameter of 25 ± 1 nm and length of 216 ± 16 nm being most suitable for electrospinning;
- Viscosity of PVA/NC spinning solution decreases with increasing the concentration of NC. Analysis of the interaction of PVA and NC shows that viscosity of the spinning solution is affected by the ratio of PVA and NC concentration and by the concentration of each of the components separately, which must be taken into account at preparation of the solution.
- Electrical conductivity of the PVA/NC spinning solution increases with increasing the concentration of PVA and NC the NC determining factors being the concentration of NC and the ratio of PVA to NC concentrations. To increase conductivity of the spinning solution by increasing the concentration of NC the concentration of PVA should be reduced and vice versa;
- The optimum NC mass concentrations of the PVA/NC spinning solutions are within the range from 10 wt% to 20 wt% for roller type electrospinning equipment to allow obtaining composite fibres of smaller average diameter within the range of 225 to 304 nm;
- From the analysis of the nanomat tensile strength follows that even at low concentrations of NC (1 wt%) mechanical properties of the nanomat are significantly improved reducing the large elongation typical of PVA nanofiber mats;
- The highest mechanical strength and elasticity are achieved in compositions with NC concentrations in the range of 10 to 15 % by mass;
- Adding nanocelullose to PVA matrix favours crosslinking of the nanofibers by intermolecular hydrogen bonding between cellulose, lignin and PVA. Modification of the structure improves resistance of PVA nanofiber mats to moisture;
- NC is effectively spun into the nanofiber mat by electrospinning, as evidenced by more intense IR peaks at 1059 and 1037 cm^{-1} specific to cellulose I structure;
- The X-ray diffraction maximums around $2\theta = 22.5^\circ$ of the PVS/NC nanofiber

- composites are typical to the structure of cellulose I. Intensity of the maximums increases with increasing the NC content, pointing to NC content in the nanofibers;
- With adding of NC to the PVA matrix the shift of the DSC endotherm signal to higher temperatures is associated with macromolecular interactions between PVA and NC and lessening of the macromolecular mobility resulting in the increase of PVA melting point;
 - As a result of the studies, a new type of reinforced electrospun three-component (PVS-cellulose-lignin) macromolecular nanofiber mat of significantly higher mechanical strength is obtained. The tensile strength compared with PVA is increased by 458% from 1.58 to 8.81 MPa, and the modulus of elasticity by 671% from 0.07 to 0.54 GPa indicating to a very efficient reinforcing effect of NC.

REFERENCES

1. Elfordy S., Lucas F., Tancret F., Scudeller Y., Goudet L. Mechanical and thermal properties of lime and hemp concrete ('hemcrete') manufactured by a projection process// *Constr Build Mater* – 2008. – 2117-2123. lpp.
2. Stevulova N., Kidalova L. Lightweight Composites Containing Hemp Hurds// *Procidea engineering* – 2013. – Nr. 65. – 69.-74. lpp.
3. Bruijna P.B., Jeppsona K.H., Sandinb K., Nilssona C. Mechanical properties of lime–hemp concrete containing shives and fibres// *Biosyst Eng* – 2009. – Nr. 103. – 474.-479. lpp.
4. Gravitis J. Theoretical and applied aspects of steam explosion of plant biomass. Review// *Wood Chemistry* – 1987. – Nr. 5. – 3.-21. lpp.
5. Sudo K., Shimizu K., Sakurai K. Characterization of steamed wood lignin from beech wood// *Holzforschung* – 1985. – Nr. 39. – 281.-288. lpp.
6. Mason W.H. Pulp and board from steam exploded wood// *Paper Trade J* – 1927. – Nr. 84. – 131.-136. lpp.
7. Zhanhu G., Park S., Hahn H. T., Wei S., Moldovan M., Karki A. B., Young. P. D. Magnetic and electromagnetic evaluation of the magnetic nanoparticle filled polyurethane nanocomposites// *J Appl Phys* – 2007. – Nr.101. – 09M511.
8. Cadek M., Coleman J.N., Barron V., Hedicke K. Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites// *Appl Phys Lett* – 2002. – Nr. 81. – 5123.-5125. lpp.
9. Nguyen T.T.T., Tae B., Park J. S. Synthesis and characterization of nanofiber webs of chitosan/ poly(vinyl alcohol) blends incorporated with silver nanoparticles// *J Mater Sci* – 2011. – Nr. 46. – 6528.-6537. lpp.
10. Ruiz M. M., Cavaille J. Y., Dufresne A., Gerard J. F., Graillat C. Processing and characterization of new thermoset nanocomposites based on cellulose whiskers// *Compos Interfaces* – 2000. – Nr. 7. – 63.-68 lpp.
11. Roohani M., Habibi Y., Belgacem N. M., Ebrahim G., Karimi A.N., Dufresne A. Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites// *Eur Polym J* – 2008. – Nr. 44. – 2489.-2498. lpp.

12. Peresin M.S., Habibi Y., Vesterinen A. H., Rojas O.J., Pawlak J. J., Seppala J. V. Effect of moisture on electrospun nanofibre composites of poly(vinyl alcohol) and cellulose nanocrystals// *Biomacromolecules* – 2010. – Nr. 11. – 2471.-2477. lpp.
13. Eichhorn S. J. Cellulose nanowhiskers: promising materials for advanced applications// *Soft Matter* – 2010. – Nr. 7. – 303.-315. lpp.
14. Sjöström E. *Wood chemistry fundamentals and applications*. New York: Academic Press, 1993. 293. lpp.
15. Bondeson D., Mathew A., Oksman K. Optimization of the Isolation of Nanocrystals from Microcrystalline Cellulose by Acid Hydrolysis// *Cellulose* – 2006. – Nr. 13. – 2. – 171.-180. lpp.
16. Miyawaki S., Katsukawa S., Abe Y. Process for oxidation of cellulose and catalyst for oxidation of cellulose// *JP2010209510A* – 2010.
17. Wang S.Q., Cheng Q.Z., J. A novel process to isolate fibrils from cellulose fibers by high-intensity ultrasonication, Part 1: Process optimization// *Appl Polym Sci* – 2009. – Nr. 113. – 1270.-1275. lpp.
18. Satyamurthy P., Jain P., Balasubramanya R.H., Vigneshwaran N. Preparation and characterization of cellulose nanowhiskers from cotton fibers by controlled microbial hydrolysis// *Carbohydr Polym* – 2011. – Nr. 83. – 122.-129. lpp.
19. Deepa B., Abraham E., Cherian B.M. Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion// *Biores Technol* – 2011. – Nr. 102. – 1988.-1997. lpp.
20. Agarwala S., Greinera A., Wendorff J. Functional materials by electrospinning of polymers// *Prog Polym Sci* – 2013. – Nr. 38. – 6. – 963.-991. lpp.
21. Huang J., Liu L., Yao J.M. Electrospinning of Bombyx mori Silk Fibroin Nanofiber Mats Reinforced by Cellulose Nanowhiskers// *Fiber Polym* – 2011. – Nr. 12. – 8. – 1002.-1006. lpp.
22. Peresin M.M.S., Vesterinen A.H., Habibi Y., Johansson L.S., Pawlak J. J., Nevzorov A.A., Rojas O. J. Crosslinked PVA nanofibers reinforced with cellulose nanocrystals: water interactions and thermomechanical properties// *J Appl Polym Sci* – 2014. – Nr. 131. – 40334. – 1.-12. lpp.
23. Peresin M.S., Habibi Y., Zoppe J.O., Pawlak J.J., Rojas O.J. Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: Manufacture and characterization// *Biomacromolecules* – 2010. – Nr. 11. – 674.-681. lpp.
24. Overend R.P., Chornet E. Fractionation of Lignocellulosics by steam aqueous pretreatments// *Philos Trans R Soc Lond Ser A Math Phys Eng Sci* – 1987. – Nr. 321. – 1561. – 523.-536. lpp.
25. Grāvītis J., Kukle S., Belkova L., Veveris A., Tupciauskas R., Putniņa A., Stikute A. Technical Hemp Fibres Treatment by Steam Explosion// *Proceedings of conference „From Forest and Agricultural Biomasses to High Added Value Products: Processes and Materials”* – 2011. – 173.-176. lpp. ISBN 9788895688657.

26. Гравитис Я. А. Теоретические и прикладные аспекты метода взрывного автогидролиза растительной биомассы// *Абзор Химия древесины* – 1987. – Nr. 5. – 3.-21. lpp.
27. Gandolfi S., Ottolina G., Riva S., Pedrocchi Fantoni G., Patel I. Complete chemical analysis of carmagnola hemp hurds and structural features of its components// *Bioresources* – 2013. – Nr. 8. – 2641.-2656. lpp.
28. Wang B, Sain M., Oksman K. Study of structural morphology of hemp fiber from the micro to the nanoscale// *Appl Compos Mater* – 2007. – Nr. 14. – 2. – 89.-103. lpp.
29. Qua E.H., Hornsby P.R., Sharma H.S.S. Preparation and characterisation of cellulose nanofibres// *J Mater Sci* – 2011. – Nr. 46. – 18. - 6029.-6045. lpp.
30. Paranhos C.M., Soares B.G., Oliveira R.N., Pessan L.A. Poly(vinyl alcohol)/clay-based nanocomposite hydrogels: swelling behavior and characterization// *Macromol Mater Eng* – 2007. – Nr. 292. – 620.-626. lpp.
31. Technical Association of the Pulp and Paper Industry, Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021. Internets – http://www.tappinano.org/12FALL_div06.asp
32. Sriupayo J., Supaphol P., Blackwell J., Rujiravanit R. Preparation and characterization of α -chitin whisker-reinforced poly(vinyl alcohol) nanocomposite films with or without heat treatment// *Polymer* – 2005. – Nr. 46. – 5637.-5644. lpp.
33. Nelson M.L., O'Connor R.T. Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part II. A new infrared ratio for estimation of crystallinity in celluloses I and II// *J Appl Polym Sci* – 1964. – Nr. 81. – 1325.-1341. lpp.
34. Strawhecker K.E., Manias E. Structure and properties of poly(vinyl alcohol)/ Na_þ montmorillonite nanocomposites// *Chem Mater* – 2000. – Nr. 12. – 2943.-2949. lpp.
35. Kongkhlang T., Tashiro K., Kotaki M., Chirachanchai S. Electrospinning as a new technique to control the crystal morphology and molecular orientation of polyoxymethylene nanofibers// *J Am Chem Soc*–2008.–Nr.130. – 15460.-15466. lpp.
36. Gaume J., Taviot-Gueho Ch., Cros S., Rivaton A., Thérias S., Gardette J.L. Optimization of PVA clay nanocomposite for ultra-barrier multilayer encapsulation of organic solar cells// *Solar Energy Mater Sol Cel* – 2012. – Nr. 99. – 240.-249. lpp.
37. Pyda M. The Advanced THERmal Analysis System (ATHAS) Data Bank. Internets – <http://athas.prz.rzeszow.pl/Default.aspx?op=db>.
38. Medeiros E.S., Mattoso L.H., Ito E.N., Gregorski K.S., Robertson G.H., Offeman R.D., Wood D.F., Orts W.J. Electrospun nanofibers of poly (vinyl alcohol) reinforced with cellulose nanofibrils// *Polym Eng Sci* – 2008. – Nr. 2. – 3. – 231.-242. lpp.