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ELECTROSPINNING AND CHARACTERIZATION OF CELLULOSE/POLYMER NANOCOMPOSITE FIBER MATS

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ABSTRACT

In this study, cellulose nanowishkers (CNW) and poly (vinyl alcohol) (PVA) composite fibers were prepared via needle-free high voltage, free liquid surface electrospinning with cylindrical electrode. CNW were obtained from hemp shives as a result of various treatments including steam explosion pretreatment, ball milling and ultrasonication technologies. The electrospinning of PVA /CNW composite solution has been successfully used to produce nano- and micro fibers. The goals of this paper are to determine the morphology of electrospun mats and study the mechanical and optical properties of nanofibre composites.

I. INTRODUCTION

Electrospinning is one of the fast growing nanofibre producing technologies and at the present only a single method for industrial scale nanofibres production. Although a wide range of application possibilities have already been proven, nevertheless scientists are trying to find more and more opportunities to produce nanofibres from biodegradable and non-toxic materials with eco-friendly technologies. Cellulose is the most widely used biomass material in nature. Major studies have shown that cellulose nanosized particles could be used as fillers to improve mechanical properties of biocomposites [1-4]. Recently, the production of submicron-scale cellulose fibers via direct dissolution has been proposed, but this issue remains demanding due to the difficulty of cellulose dissolution into common solvents [5].

II. EXPERIMENTAL

Hemp shives used in experiments represent the woody parts of stems of plant - Cannabis sativa that is free from plant fibers. Hemp variety Bialobrzeskie grown on the experimental fields of the Latgalian Agriculture Research Center LLZC (Latvia, district Vilani). Cellulose nanowhiskers were prepared from hemp shives using steam explosion (SE) pretreatment, ball milling and ultrasonication as described in our previous research [6].

The PVA powder of molecular weight 145 000 g/mol and hydrolysis grade ~99.0 – 99.8 mol% purchased from Sigma Aldrich Europe GmbH, Germany.

X-ray XRD patterns were determined on a Bruker D8 Discover diffractometer using copper radiation (CuKα) at a wavelength of 1.54180 Å. The tube voltage and amperage were set to 40 kV and 40 mA. The divergence slit was set at 0.6 mm, and the anti-scattering slit was set at 8.0 mm. The diffraction pattern was recorded using a scanspeed 0.5s/0.02° from 5–45° in 2θ scale and LynxEye position sensitive detector.

The crystallinity index (CI), which is a measurement of the amount of crystalline cellulose with respect to the global amount of amorphous materials, was evaluated using Segal empirical method. The Segal method is used for empirical measurements to allow rapid comparison of cellulose samples. The CI has frequently been determined by means of the empirical Segal equation [7];

$$C,\% = \frac{I_{crystalline} - I_{amorphous}}{I_{crystalline}} x100$$

The PVA solutions in the concentration 9 and 10 wt% were prepared by dissolving the PVA powder in distilled water at 90°C for 2 hours with a magnetic stir bar. Distilled water was used as a solvent in all compositions. After that the CNW were added to the PVA solution in amounts to obtain final nanocomposite concentration 10 wt% relative to mass ratio to PVA, the stirring continued for 2 more hours.

Viscosity of the PVA/CNWs solutions was measured by a HAAKE Viscotester 6 plus (Germany) at the temperature of 22 ± 0.5°C. The conductivity of the solutions was measured using a conductivity meter (Win-Lab® DataLine Conductivity Meter) at 22± 0.5°C.

Electrospinning of the solutions was carried out using Nanospider^{TM} NS Lab 200 (Elmarco, Czech Republic) electro-spinning equipment on the spun-bonded polypropylene substrate (surface density Q = 21.5 ± 3 g/m^2). Electrospinning parameters were fallowing: distance between spinning and collector electrodes - 12 cm, applied voltage to ensure spinning 65 kV, speed of substrate 0,2 m/min, speed of the spinning solution feeding roll 4 rpm. The temperature of the environment 22 ± 1 °C and the humidity γ = 35 ± 2%.

Morphology of the PVA and the electro-spun PVA/CNWs blend fibres were studied by Scanning Electron Microscopy (SEM), Field Emission Gun (Tescan Mira/Lmu, Czech Republic) equipment. A CorelDRAW Graphics Suite X6 software was used to measure the diameter of electro-spun fibres from micrographs.

To measure light absorbance of PVA and CNW reinforced PVA nanofiber mats, the instrument UV-Visible spectrophotometer Shimadzu, UV-3700 (Shimadzu Scientific Instruments Kyoto, Japan) with barium sulfate-coated integrating sphere ISR-240A (wavelength range from 400 to 700 nm) was used.

Mechanical properties of the electrospun composite nanomats were measured by Instron Universal Tester (Model 2519-107) with Bluehill software applying deformation speed 1 mm/min and load 1N. Samples 20 mm in length and 10 mm

III. RESULTS AND DISCUSSION

X-ray method was used for identification of changes in the amount of crystalline cellulose in SE treated hemp shives in comparison to untreated shives. From X-ray diffraction patterns in Figure 1(A) can be concluded that SE hemp shives with following water and alkaline after-treatment crystallinity index increased to 72%, comparing to 48% of untreated shives associated with removing of amorphous regions, where lignin and polyose layer such as hemicellulose surrounding the hemp fibres. Figure 1 (B) shows nanowhisker size after following pretreatments. It is visible from Figure 1 (B) that after several treatments of shives the nanosized particles and nanowhiskers can be obtained

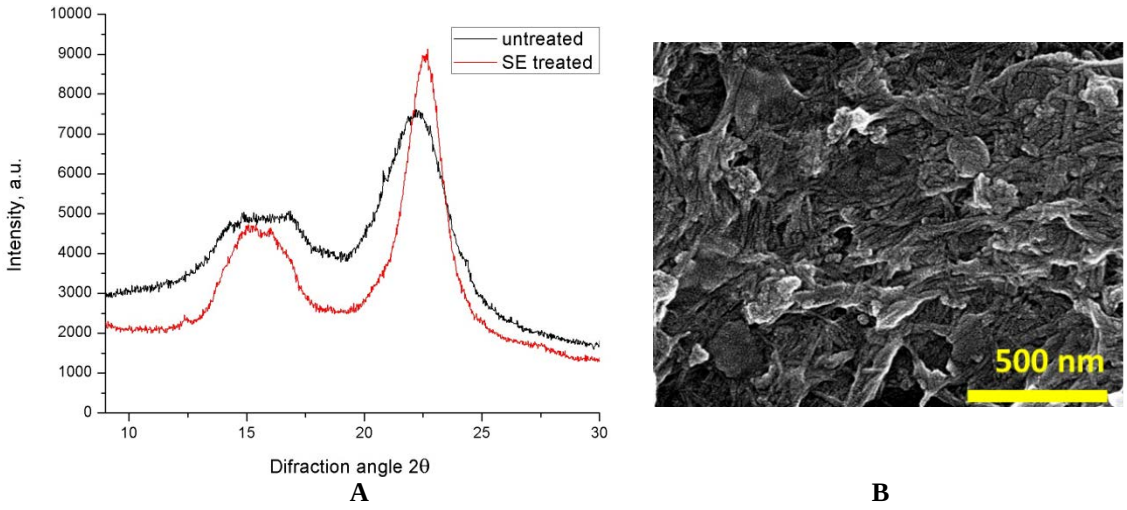

Figure 1. X-ray diffraction patterns for untreated and SE treated hemp shives (A); SEM micrograph of CNW from hemp shives after various treatments (B)

Solution properties have been found to affect the morphology of the fibers. One of the major parameter influencing the fiber diameter is the solution viscosity. The viscosity of the solution is related to the extent of polymer molecule chains entanglement within the solution. A higher viscosity results in a large fiber diameter. The solution viscosity decrease from 856 to 952 mPa.s in result of PVA replacement into spinning mixture with CNW.

The morphology of pure PVA (A) and PVA/CNWs (B) composite mats produced by electrospinning shown in Figure 2. No cellulose nanowhiskers appears to be protruding from the outer surface of the PVA fibres, indicating that they are embedded in PVA matrix and also they may be aligned along the fibre axis during electrospinning process under the electrical field. Addition of CNW to the PVA solution led decrease nanofiber diameter from 500 to 300 nm, because CNWs increase electrical conductivity of pure PVA solution from 383µS to 420 µS. The conductivity of the fiber solution is important to initiate the electrospinning process.

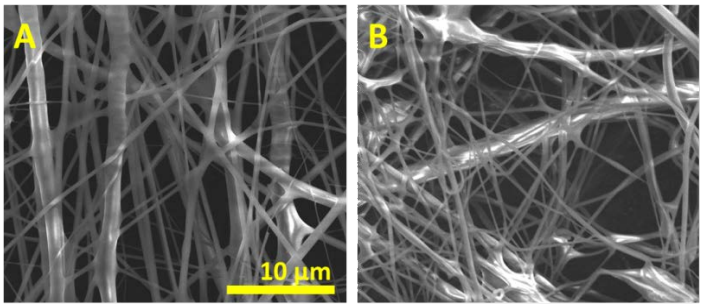

Figure 2. SEM micrographs of electrospun nanofibre mats (a) PVA and (b)10 wt% CNWs

Figure 3 shows the visible light absorption spectra (Kubelka-Munk) of PVA and PVA/CNW nanomats in the wavelength range from 400 to 700 nm. The absorption in wavelength range from 400 to 700 nm increases for PVA/CNW nanomat vindicating the presence of CNW in the electrospun nanomat. It may be attributed to the presence of small amount of lignin in CNW because of it dark brown color therefore absorbing more light.

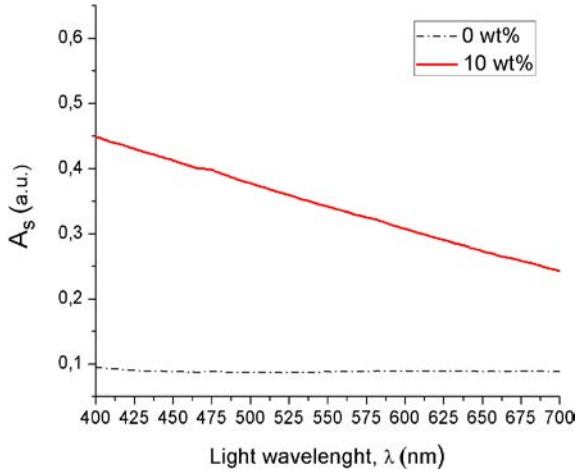

Figure 3. Visible light absorbance (Kubelka-Munk) of PVA nanofibre mat and of PVA/CNW nanofibre composite mat

The tensile strength of PVA and PVA/CNWs nanocomposite mats are shown in Figure 4. Each datum is obtained by averaging the test results of ten samples. The addition of CNW (10%) results in an increase in tensile strength from to 1.4 to 8.5 MPa and the Young's modulus from 0.07 to 0.5 GPa.

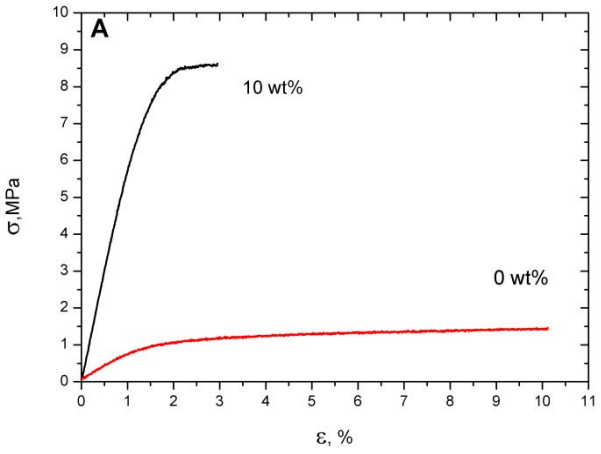

Figure 4. Tensile strength (δ, MPa) of pure PVA and PVA/CNWs electrospun fibers (10 wt %)

IV. CONCLUSIONS

Nanofibre mats were produced from electrospinning dispersions of compositions containing poly (vinyl alcohol) (PVA) and cellulose nanowhiskers (CNW) obtained from hemp shives. The morphology of bicomponent fibers

depending on composition was examined by SEM. The presence of the cellulose component in the obtained composite samples is confirmed by visible light absorbance spectra. The intermolecular interactions between the polymer matrix and the dispersed CNW (10 wt %) played an important role proving mechanical properties of electrospun composite mats. Electrospun PVA nanofibre composites reinforced with CNW can be used effectively as reinforcing material in electrospinning. Nanocomposite mats are expected to have potential use in many particular fields as new functional materials.

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