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Electro-spinning Derived Cellulose-PVA Composite Nano-fibre Mats

Abstract

A study of the manufacturing and characterisation of poly (vinyl alcohol) (PVA) nano-fibre mats reinforced with microcrystalline cellulose (MCC) is presented. Results obtained from Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectrometry and Scanning Electron Microscopy (SEM) of the products are discussed and interpreted. PVA nano-fibre mats reinforced with MCC nano-whiskers (CNWs) were prepared from aqueous PVA solutions by NanospiderTM high-voltage electro-spinning on NS Lab 200 (Elmarco) equipment with a circular cylinder as the emitting electrode. PVA/CNWs mats of a modal nano-fibre diameter of 300 nm and average diameter within the range from 350 to 294 nm were obtained by the electro-spinning technique. Solution parameters, such as the content of CNWs in the solution and PVA concentration and viscosity were varied in an attempt to produce possibly finer cellulose nano-fibres.

Key words: electro-spinning, cellulose, PVA, nano-fibres.

One of the promising spinning solutions are compounds of cellulose and synthetic polymer because of excellent biocompatibility, good thermal and mechanical properties of cellulose, and the fact that it is [4] an accessible and inexpensive organic compound. However, due to crystallinity and extensive hydrogen bonding, cellulose has very low solubility in conventional organic and aqueous solvents, making the production of fibres by spinning from solution difficult [1]. Nano-fillers such as cellulose nano-whiskers (CNWs) improve the mechanical and thermal properties of the nano-composite [5]. However, despite the use of CNWs as nano-fillers and challenges in application in nano-composites, the number of studies reported is limited [5 - 9].

Polyvinyl alcohol (PVA) has excellent film-forming ability as well as emulsifying and adhesive properties. It is also a biocompatible and non-toxic polymer resistant to oil, grease and solvents. PVA has better fibre-forming properties through electro-spinning and it is a poly (hydroxyl) water soluble polymer [10]. PVA has a high tensile strength and flexibility and is widely used in numerous applications [11]. In recent years much attention has also been devoted to the use of PVA nano-fibres in biomedical applications [12 - 15], such as drug delivery, tissue engineering and many more.

As it is impossible to obtain electro-spun CNWs suspensions from microcrystalline cellulose without adding polymer, it is subject to ultrasound treatment and blended with PVA used as a matrix material. The pre-treatment of microcrystalline cellulose by ultrasound has been

reported to decrease the MCC dimensions [16].

The content of cellulose and polymer in the solution and the size of CNWs are factors affecting a successful outcome. The goal of the present study was to obtain a mat from PVA nano-fibres with microcrystalline cellulose and find the effects of cellulose on the fibrous structure of the electro-spun mat.

Materials and methods

PVA powder of 60,000 g/mol molecular weight and 88% hydrolysis grade, from Kuraray (Japan), was dissolved in distilled water at 80 °C by magnetic stirring for 2 hours. CNWs were prepared from MCC by treatment with a UP 200Ht (200 W, 26 kHz, sonotrode S26d14, d = 14 mm, Germany) (HIUS) ultrasonic processor for 15 min in distilled water. After that the CNWs were added to the PVA solution in amounts to obtain final CNWs contents of 1, 2 & 3% (w/w) while keeping the total PVA concentration constant at 8 wt%, with continuous stirring for 2 hours more. Microcrystalline cellulose powder of 20 µm particle size was purchased from Sigma Aldrich (Ireland).

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR was used to confirm the presence of CNWs inside the PVA webs. All spectra of the samples examined were recorded on a Spectrum One (Perkin Elmer, UK) FTIR spectrometer in the range of 4000 - 450 cm⁻¹ at a resolution of 4 cm⁻¹.

Introduction

Electro-spinning is found to be one of the most efficient, simplest and versatile methods to obtain non-woven nano-size fibre (nano-fibre) webs [1]. Since electro-spun nano-fibres have a large specific surface area, small pores, high porosity and are able to incorporate different additives, they have a variety of potential uses, for example, in tissue engineering, wound healing, drug delivery, medical implants, dental applications, biosensors, military protective clothing, filtration media, and other applied industrial uses. The properties of electro-spun polymer fibres can be modified by spinning polymer blends to create composite nano-fibres that better fit to fulfil specific industrial requirements in terms of their material properties, thereby widening the potential range of applications [2, 3].

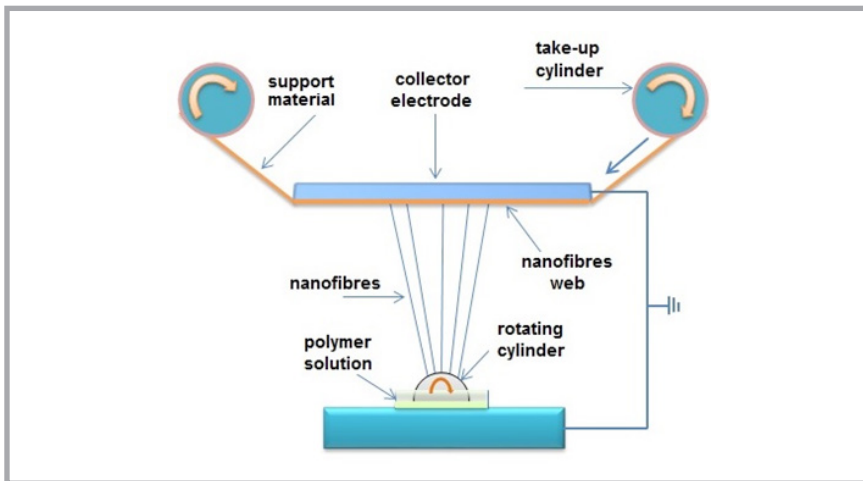


Figure 1. Scheme of the “Nanospider”™ electro-spinning setup [8].

Scanning Electron Microscopy (SEM)

The morphology of the PVA and electro-spun PVA/CNWs blend fibres were studied using Field Emission Gun (Tescan Mira/Lmu, Czech Republic) equipment. Prior to SEM evaluation, the samples were coated with gold plasma sputtering. CorelDRAW Graphics Suite X6 software was used to measure the diameter of electro-spun fibres from two-dimensional micrographs.

Viscosity measurements

Spinning solutions of different concentrations were prepared by mixing for 4 to 6 hours with a magnetic stir bar. The viscosity of the PVA/CNWs solutions was measured by a HAAKE Viscotester 6 plus (Germany) at a temperature of 20 ± 0.5 °C.

Electro-spinning

Non-woven webs of PVA and PVA/CNWs were obtained by means of Nanospider™ NS Lab 200 (Elmarco, Czech Republic) electro-spinning equipment.

While rotating, the cylindrical electrode is covered by a film of the polymer solution (**Figure 1**). As the electrostatic force exceeds the surface tension of the polymer solution, liquid jets launch from the surface of the rotating cylindrical drum in the form of Taylor cones with natural self-optimised distances between them. The jets move towards the upper electrode and set down on the spun-bonded polypropylene substrate (surface density $Q = 21.5 \pm 3$ g/m²). Meanwhile the nano-fibre becomes thinner and, as the solvent evaporates, solidifies [17]. A scheme of the electro-spinning setup of the “Nanospider”™ is shown in **Figure 1**.

Adjusted spinning parameters of the equipment during the experiment: distance between spinning and collector electrodes - 13 cm, applied voltage to ensure spinning - 70 kV, speed of substrate - 0.25 m/min, speed of the spinning solution feeding the roll - 4 r.p.m, the temperature of the environment 20 ± 2 °C, and the humidity $\gamma = 45 \pm 2\%$. All compositions of the solution were

spun under the same spinning conditions since the PVA concentration (8 wt%), being the main reason for necessary adjustments of the electro-spinning parameters, was constant.

Results and discussion

Figure 2 shows the ultrasonic impact on the dimensions of the fibres. As found by SEM (**Figure 2**) studies, the CNWs of the microcrystalline cellulose (MCC) average diameter below 100 nm is obtained after treatment by HIUS (**Figure 2.C**). However, it is also seen that some MCC fibre sizes are not decreased down to a nanometre scale (**Figure 2.B**), possibly because of uneven ultrasonic treatment.

The viscosity of the PVA polymer solution increases when adding MCC (**Table 1**), as was found in our previous study in the case of the cellulose of hemp fibres and shives [18]. The viscosity of the solutions affects the threshold of the applied voltage [19]. It was found that a higher applied voltage is necessary for solution of a higher polymer concentration.

SEM micrographs of the electro-spun nano-fibres obtained from pure PVA (A) and from PVA with 3 wt% of CNWs are shown in **Figure 3**. The morphology of the mat of nano-fibres, for example, the concentration of defects, distribution and shapes of fibres, is not affected by the composition of the spinning solution. The fibre morphology depends on the processing parameters, processing and ambient conditions [20].

The electro-spun nano-fibre web consists of a variety of nano-fibres of a specific distribution of the size of diameters, as analysed by Malašauskiene & Milašius

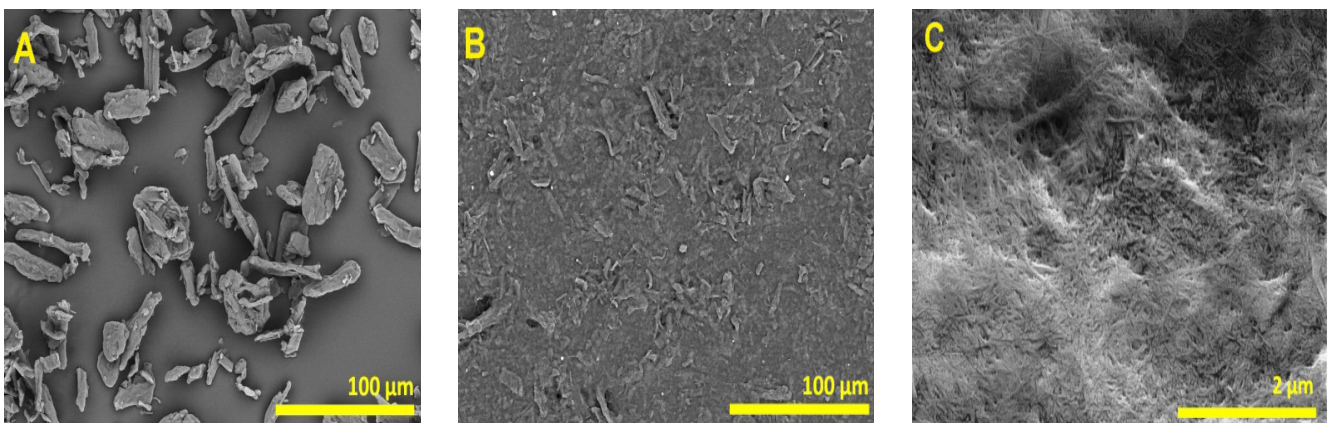


Figure 2. SEM micrographs of the MCC before (A) and after (B); C) HIUS.

[21, 22]. As seen from **Table 2** and the graphs of **Figure 4**, the modal diameter of neat PVA nano-fibres formed by electro-spinning is equal to 300 nm, the average fibre diameter being 350 nm, while the diameter of 11% of fibres is less than 200 nm. The addition of 2 wt % of CNWs increases the modal diameter (200 nm and less) of nanofibres from 11% to 20%, while the addition of 3 wt % of CNWs – to 34% (**Table 2**). The average fibre diameter decreases from 338 nm to 294 nm (by 13%) with an increase in the content of CNWs in the blend from 2 wt% to 3 wt%. A decrease in the average diameter of electro-spun fibres can be a result of the negatively charged cellulose changing the ionic strength and conductivity of the spinning solution [6].

To confirm the presence of microcrystalline cellulose, ATR-FTIR spectra of the electro-spun nano-fibre mats obtained were recorded (**Figure 5**, see page 46). As seen from the FTIR results, increasing the concentration of CNWs changes the chemical bonding. Absorption in the 1732 - 1713 cm^{-1} frequency range assigned to the stretching of the C-O and C=O of residual acetate groups in the PVA matrix [12] is of equal intensity in all samples. The absorption band between 1087 and 1026 cm^{-1} of the C-O of the alcohol groups of cellulose is clearly present in the electro-spun PVA/CNWs

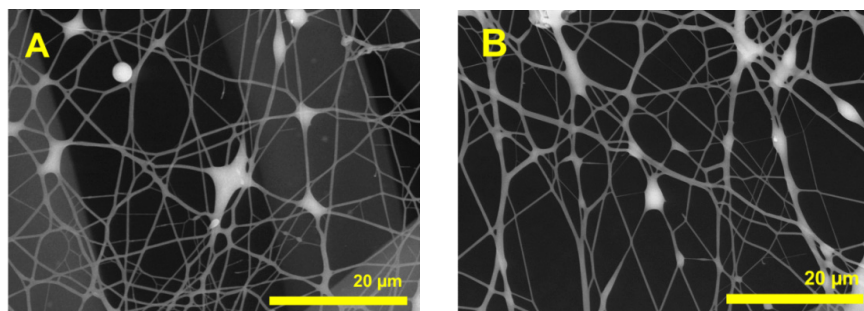


Figure 3. SEM micrographs of pure PVA nano-fibres (A) and PVA/CNWs 3 wt.% nano-fibres (B).

Table 1. Viscosity of polymer solutions.

Composition of polymer solution	Polymer concentration, wt%	CNWs concentration, wt %	Viscosity, $\text{mPa}\cdot\text{s}\cdot 10^{-3}$
PVA	8	0	0.46
PVA/ CNWs		1	0.54
		2	0.58
		3	0.59

Table 2. Fibre diameters.

Fibre diameters, nm	Content of fibres		
	PVA 8 wt%	PVA/CNWs 2 wt %	PVA/CNWs 3 wt%
200 nm and less	11%	20%	34%
Mode, 300 nm	44%	38%	45%
300 nm and less	55%	58%	79%

composites (**Figure 5**). The intensity of the absorption bands in the frequency range of 1051 - 1026 cm^{-1} substantially increases with an increase in CNWs content in the PVA/CNWs solution.

Conclusions

Two-component nano-fibre electro-spun mats were obtained from aqueous solutions containing different proportions

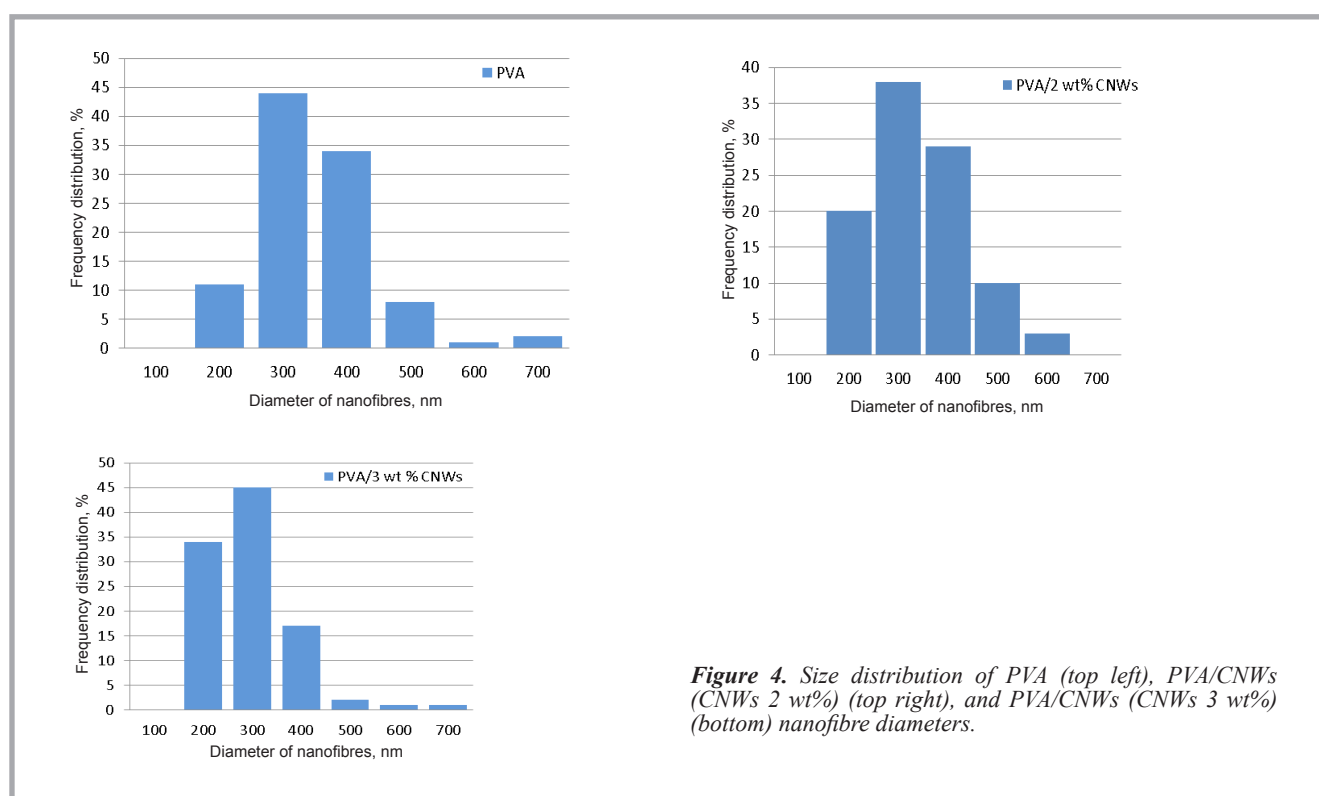


Figure 4. Size distribution of PVA (top left), PVA/CNWs (CNWs 2 wt%) (top right), and PVA/CNWs (CNWs 3 wt%) (bottom) nanofibre diameters.

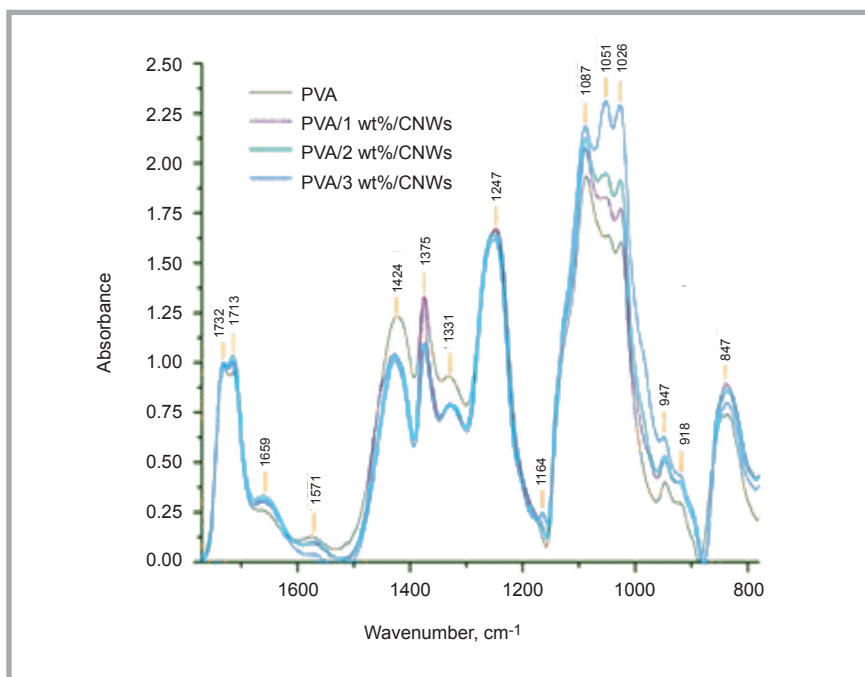


Figure 5. FTIR spectra of PVA and PVA/ CNWs electro-spun fibres.

of the PVA and CNWs components to study the fibrous structure of samples. The average diameter of fibres of the PVA/CNWs composite mats was found to be 338 nm in samples containing 2 wt% CNWs and 294 nm – in samples containing 3 wt% CNWs. The proportion of 200 nm thick and thinner fibres increases up to 34% with an increase in the concentration of CNWs in the spinning solution, while the proportion of 300 nm thick and thinner fibres goes up to 79%. The modal size of the fibre diameter of the electro-spun product is not changed by the amount of CNWs added. The presence of the cellulose component in the composite samples obtained is confirmed by ATR-FTIR spectra. Further experiments are necessary to study the structural stability of cellulose-PVA nano-fibre mats and to provide an even and smoother surface structure of the composite.

Further experiments are desired to assess appropriate properties required for specific potential use of cellulose-PVA-nanofibre composites in industry, medicine, and other particular fields.

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