Cost Action - FP1405 ActInPak - STSM report

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Potential applications of electrohydrodynamic processes in paper and board-
Use of cellulosic nanofibers for high performance papermaking products

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I. Introduction

The global packaging market is witnessing a fast growth because of an increasing population, technological advancements and rising consumer demands related to product packaging

The goal of this project is to investigate different materials and methods to produce cellulosic nanofibers using electrohydrodynamic technologies which can be used as active intelligent packaging in the paper and board industry.

This topic becomes more and more important, as electrodynamic processes, like electrospinning and electrospraying, are cost effective, facile and flexible methods.

Advantages of electrospun fibers are e.g. their submicron to nanoscale diameter, large area to volume ratio or high sensitivity to changes in surrounding atmosphere. Active packaging systems can include oxygen scavenger, antimicrobial agents, moisture absorbing, antioxidant releasing or flavor or odor absorbing systems. In addition, food contact packaging materials are acceptable by customers if they are natural and non-toxic like bioactive plant extracts or natural compounds (GRAS status).

Most solvents which are used to produce cellulose solutions are toxic and are not allowed to be used for food processing applications; in addition the low throughput restricts the commercial exploitation at a large scale.

To get rid of this major drawback many efforts are made in paper research. So does the proposed project.

To reach this aim, cellulose, the most abundant biopolymer on earth which offers an attractive alternative to synthetic polymers because of its renewability, sustainability and biodegradability, will be used to produce polyvinyl alcohol (PVOH) nanofibers containing cellulose nanocrystals (CNCs).

Therefore several aqueous solutions of PVOH and CNCs having different wt%-concentrations will be created. Afterwards the CNCs will be prepared in the electrospinning apparatus. The machines parameters will be varied means change of flowrate, spinning time and voltage to achieve a wide range of conditions. The

characterization of the experiments, meaning orientation and morphology will be performed via TEM, SEM and Raman spectroscopy.

II. Work plan carried out during the STSM

For the experiments two different types of PVOH had been used.
The concentration of PVOH in water (distilled) was 12w/w%. It has been dissolved using a magnetic stirrer at 75°C for 24h.
In addition, the viscosity, the surface tension and the conductivity had been measured of all the samples.
Afterwards, freeze dried cellulosic nanocrystals (CNCs) were subsequently added to the PVOH solutions.
As an additional layer PHB was coated on the top.

III. The main results obtained during the STSM

About 24 different samples have been produced during the STSM.
The experiments had been performed on the FLUIDNATEK LE-10 electrospinning machine which is characterized as a proof-of-concept machine.

Figure 1: LE- 10

a) Adjustment of the parameters for the electrospinning process

To adjust the parameters of the Electrospinning machine, the first samples were only made of PVOH solutions.
The following parameters had been established:

Parameters LE-10 PVOH	
$\dot{V}$ [ml/h]	**Results will be published in scientific papers (first quarter 2017) before being accessible to the public**
$d_{Syringe}$ [mm]	
V [kV]	
$rpm_{collector}$	

Table 1: Adjustment of Electrospinning parameters

The results ended up in creating a smooth homogeneous electrospun PVOH film as it can be seen in Figure 2: PVOH film.

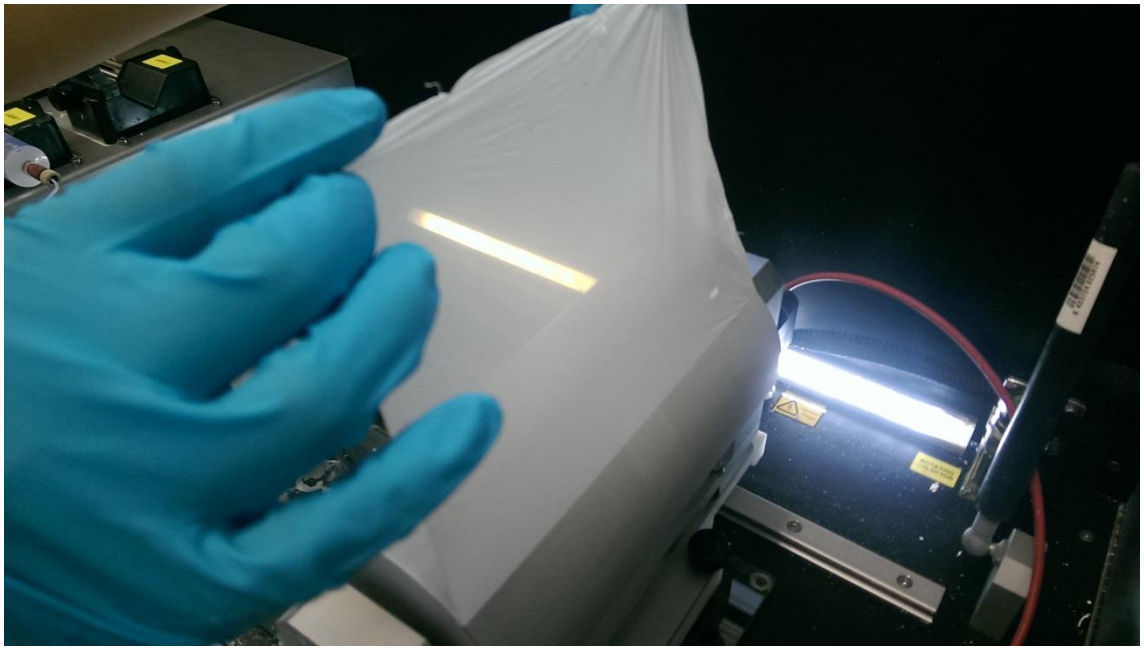

Figure 2: PVOH film

b) Adjustment of the parameters of the Post thermal treatmet (PTT)

Post thermal treatment of the electrospun films has been done to improve several properties of electrospun membrane. Advantages of heat treatment are,

1. Improve membrane compactness (eliminate 'fluffiness' or stray fibers)
2. Improve mechanical property
3. Improve chemical stability
4. Reduce intra-membrane layer delamination

The conditions had been the following:

Parameters post thermal treatment of PVOH electrospun fibers	
Treatment method	**Results will be published in scientific papers (first quarter 2017) before being accessible to the public**
T [°C]	
t [s]	

Table 2: Adjustment of PTT parameters

c) SEM analysis of PVOH films

SEM has been used to analyse the structure and the morphology of the electerospun PVOH fibers.

I. NON Post thermal treatment

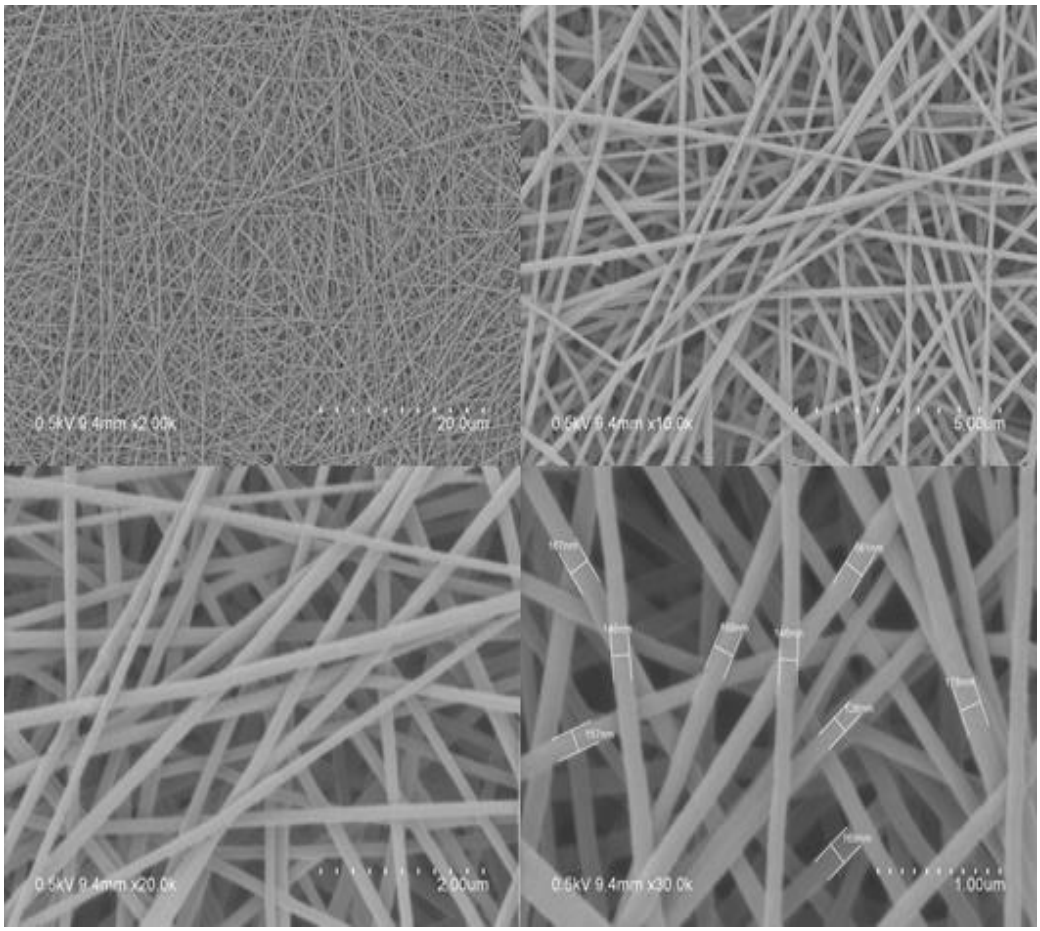

Figure 3: PVOH 28 SEM

Figure 3 shows SEM images of PVOH 28 electrospun fibers with a magnification between 2k and 30k. The nanofiber diameter is between 145 -190 nm.

d) Electrospinning of PVOH fibers including 1w/w% CNC on paper

After settings the parameters PVOH solutions including 1w/w% CNC had been created to spun them directly on paper.
The paper itself has a grammage of 120g/m² having an A4 format.
At first PVOH including CNCs had been coated on paper.
The conditions had been the following:

Parameters LE-10 PVOH on paper	
$\dot{V}$ [ml/h]	**Results will be published in scientific papers (first quarter 2017) before being accessible to the public**
$d_{Syringe}$ [mm]	
V [kV]	
$rpm_{collector}$	
$t_{Spinning}$ [h]	

Table 3: Electrospinning parameters of PVOH-1w/w% CNC solution on paper

Results will be published in scientific papers (first quarter 2017) before being accessible to the public

Figure 4: PTT of PVOH- 1w/w% CNC solution

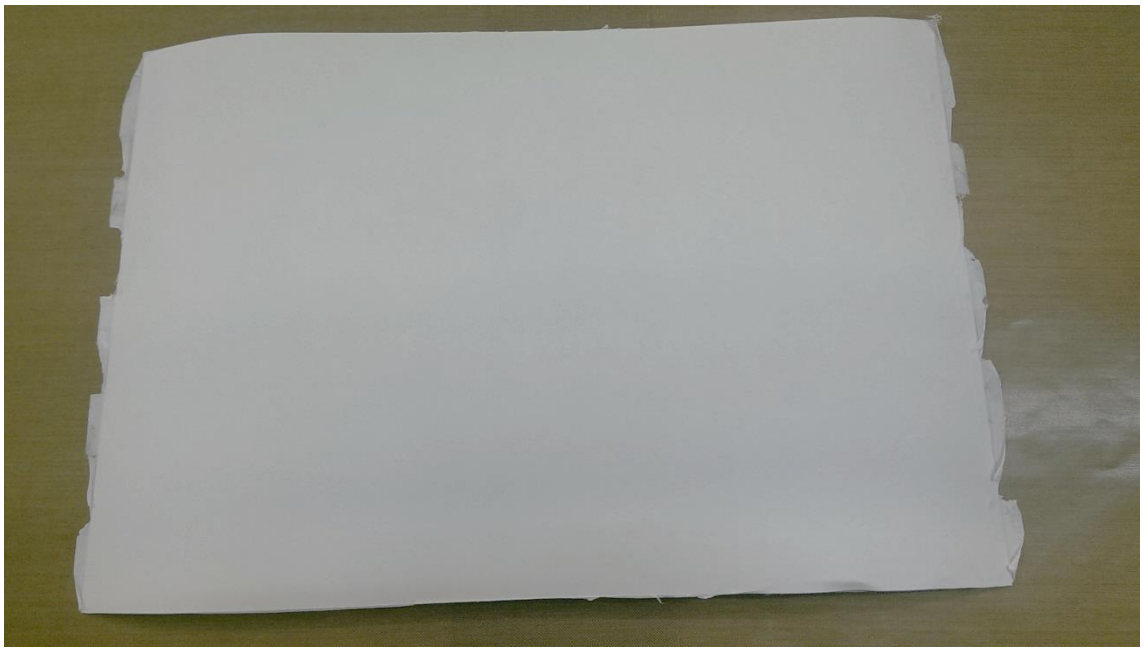

Figure 5: PVOH- 1w/w/ CNC fibers coated on paper

In the next samples PHB as additional hydrophobic layer had been coated on the paper.
The conditions had been the following:

Parameters LE-10 PHB	
$\dot{V}$ [ml/h]	**Results will be published in scientific papers (first quarter 2017) before being accessible to the public**
$d_{Syringe}$ [mm]	
V [kV]	
$rpm_{collector}$	
$t_{Spinning}$ [h]	

IV. Conclusion

To achieve good results the machine parameters ($\dot{V}$, V, rpm, $t_{spinning}$) as well as material parameters (viscosity, conductivity, surface tension) have to be perfectly coordinated with each other. The results have been proven that the use of cellulose, respectively cellulosic nanocrystals, as a biopolymer in combination with PVOH shows great potential to produce bio-based nanofibers for paper based applications.
By using SEM analysis techniques, the orientation of the nanofibers as well as the fiber diameter can be determined and shows the dependency of the machine – and process parameters. Further the influence of the post thermal treatment process has a significant influence on the results. It could be shown, that the adjustment of process time and – temperature is highly important to create smooth, homogenous films on paper. The dependency has been verified by using SEM technique.
Regarding my personal experience during the STSM, I had a very interesting time at IATA-CSIC institute located in Valencia, Spain. During my stay, I had the possibility to work in a very positive and productive atmosphere. The members of the working group showed great effort to share their knowledge of electrohydrodynamic techniques which had been previously unknown for me bevor taking the chance to make the STSM.
During the STSM I gained lots of new experiences, ideas and possibilities to use electrospinning in the paper based industry.
All in all I would totally recommend the opportunity to participate in a Short Term Scientific Mission, because I see great potential to foster collaboration between institutes as well as sharing new techniques which can result in long-term collaborations to open up new market segments.

V. Follow up

Both institutes, IATA-CISIC as well as PTS, see great consensus to combine their expertise. Therefore a long-term collaboration is intended.
The obtained results form a good basis for further analysis of the materials. Therefore IATA-CSIC institute is performing TEM, FTIR, DSC, WVTR, Limonene and O_2 permeability, while PTS is making grease test, surface tension, contact angle and polarity as well as roughness, homogeneity of the film, scoring characteristics and water absorptiveness analysis of the coated paper.
At the end the results will be published as scientific papers.