SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: Cost Action FP 1405
STSM title: 3D Printing of nanocellulose materials for food packaging
STSM start and end date: 02/07/2018 to 20/07/2018
Grantee name: Eduardo Espinosa Víctor

PURPOSE OF THE STSM/

The main objective of the Action is to develop knowledge on sustainable, active and intelligent fibre-base packaging. This STSM advances towards this objective by increasing the valorization of a residue (wheat straw) as a component in biocomposite products for packaging. These products have shown huge potential to optimize the supply chain, and increase the self-life of foodstuff and enhance consumer consciousness of food utilization. Increase of the barrier properties of biocomposite films is one of the ways to maintain food in optimum conditions, as well as developing products that interact with the environment or product in the desired way.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

((L)CNF film production

Unbleached and bleached wheat straw pulp were used to obtain cellulose nanofibers by different techniques. For unbleached samples a mechanical pretreatment (PFI beating) followed by 3 different treatments (Ultrafine friction grinder supermasscolloider "Masuko", High Pressure Homogenizer "GEA" and Twin Screw Extruder). In addition, an enzymatic pretreatment was tested in order to increase the effectiveness in the Twin Screw Extrusion treatment. However, for bleached samples a mechanical pretreatment and the 3 different treatments were used.

Mechanical properties

A LCNF nanopaper (2g of dry weight) was prepared for measuring the mechanical properties. The mechanical properties of LCNF nanopapers were measured using an Instron 5965 machine equipped with a load cell of 5 kN capacity. Tests were done on rectangular samples (100 mm x 15 mm) at a cross-head speed of 5 mm/min. The samples were conditioned in a weather room at 25 ºC and 50% humidity for 48 h according to ISO standard 5269-2.

Laser profilometry

The films were sputtered with a thin layer of gold (Agar Auto Sputter Coater). Ten Laser profilometry (LP) topography images were acquired from each film sample using a LP (Lehmann, Lehman Mess-Systeme AG Baden-Dättwil, Germany). The lateral and z-resolution of the LP system was 1 µm and 10 nm, respectively. The size of the local areas was 1 mm x 1 mm. The root-mean-square (Sq) was quantified on the LP images.

Oxygen transmission rate (OTR)

The OTR was measured with a Mocon OX-TRAN® 1/50 test system (Mocon, Minneapolis, MN, USA) at 50% relative humidity and 23 ºC.

The wheat straw CNF were tested for 3D printing. Unfortunately, this CNF were not suitable for 3D printing. In order to demonstrate the concept, a nanocellulose prepared by RISE PFI from kraft fibre was used (1% consistency). Foams with a controlled pore geometry were formed by 3D printing nanocellulose and freeze-drying.

3D printing

The 3D printing was performed with a Regemat3D bioprinter (version 1.0), equipped with the Regemat3D Designer (version 1.8, Regemat3D, Granada, Spain). Scaffolds with length of 40 mm, with of 20 mm and height of 2 mm were printed directly on microscopy slides for exemplification purposes. The track of the printed tracks was targeted in 0.41 mm. The space between the tracks was 2 mm. The flow speed was 3 mm/sec, using a 0.58 mm conical nozzle. The inks were kept at room temperature (25 ºC) for 24 h before printing.

Moisture absorption capacity

Samples were place in a climate chamber at 90% relative humidity and 23 ºC and were periodically weighted. The moisture content was calculated as the difference of mass measurements in different time periods and the initial dry state weight.

Water absorption capacity

The water sorption capacity was measured by immersing a pre-weighted dry sample in distilled water. The excess surface water was blotted out with filter paper before weighting at different time periods. The water sorption capacity was calculated using the following equation:

$$Water\ sorption\ capacity = \frac{W_t - W_0}{W_0} * 100$$

where W_t is the weight of the sample at a specific time and W_0 is the weight of dry sample.

The printed materials may have potential as oxygen scavengers and the moisture absorption was assessed during 24 hours.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed with a Hitachi SU3500 microscope, in secondary electron imaging (SEI) mode. Images were acquired with 100x magnification, using 5 kV acceleration voltage.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Mechanical properties

The mechanical properties of the films were measured (Fig. 1). From the data obtained it is concluded that the use of ultrafine friction grinder supermasscolloider and high pressure homogenization produces films with higher mechanical strength compared to those obtained with Extruder. However, there are no significant variations in mechanical properties taking into account the lignin content. In addition, the use of enzymatic pre-treatment reduces the mechanical properties of the films, mainly due to the hydrolysis and shortening of the fibers produced with this pre-treatment.

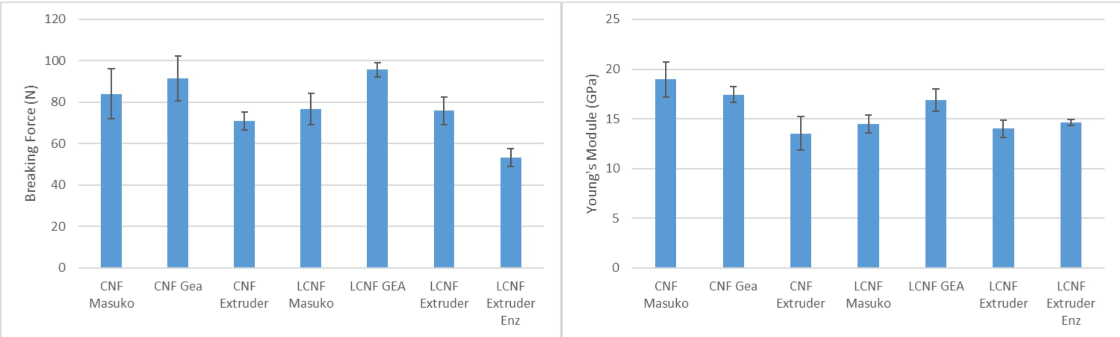

Fig. 1. Mechanical properties of CNF and LCNF films.

Laser profilometry of the films

The surface roughness of the films was measured with laser profilometry (LP, Fig. 2 and Fig. 3). The lower value the smoother and the more fibrillated the material is. The Fig. 2 shows the LP-roughness values of the different films and it can be concluded that Ultrafine friction grinder supermasscolloider (Masuko) is the treatment which presents the lowest values in both cases, cellulose nanofibers and lignocellulose nanofibers. There is a significant linear correlation between the fraction of the residual fibers in the films and the LP-roughness. The ultrafine friction grinder supermasscolloider treatment has been used successfully to obtain cellulose nanofibers with high nanofibrillation yields, as well as the use of high pressure homogenization treatment. However, the use of extruders to obtain cellulose nanofibers with low energy requirements and high consistency, does not reach the nanofibrillation yields of the others treatments. It is also concluded that enzymatic pre-treatment does not improve the nanofibrillation of the fibers. Differences have been found between CNF differing in lignin content, being the roughness values lower when they have low levels of lignin.

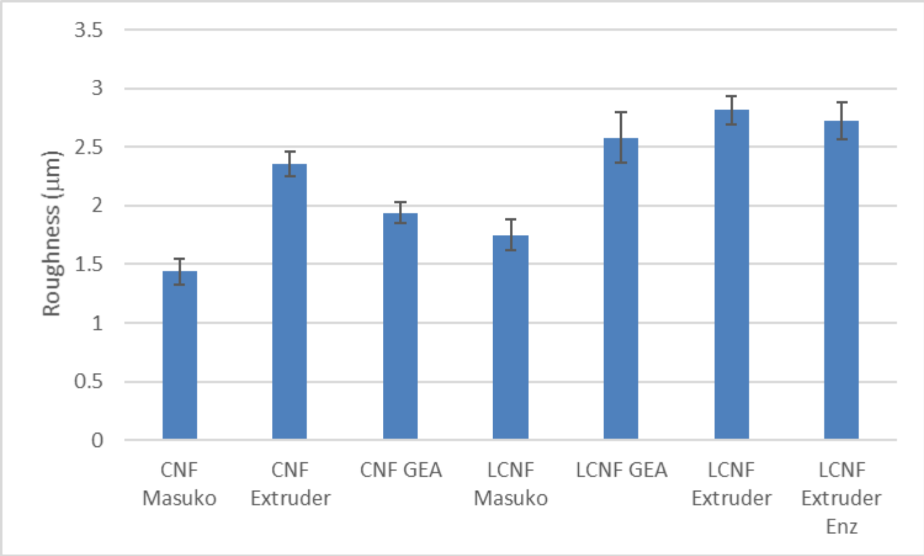

Fig. 2. Surface roughness measured with laser profilometry

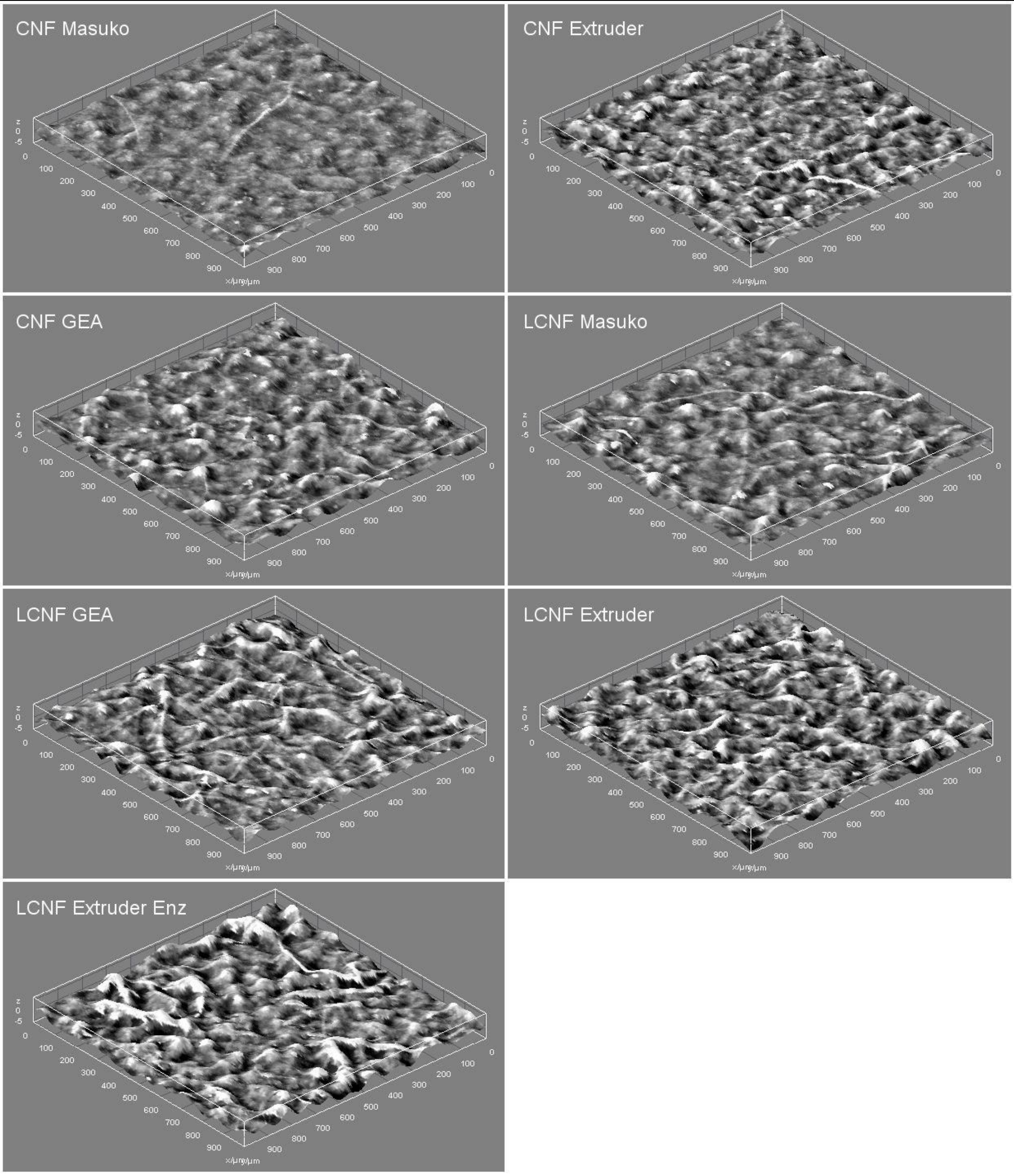

Fig. 3. Laser profilometry 3D representation of the surface structure

Oxygen transmission rate (OTR)

Fig. 4 shows the OTR values for the different films. Low values between 3 and 4 cc/m^2/day were obtained for all the samples. The graph shows that there are no significant differences between the different treatments, but nevertheless, there are slight differences if the presence of lining is take into account. The oxygen permeability of the films is lower if they contain lignin, which correlates with the structural assessment.

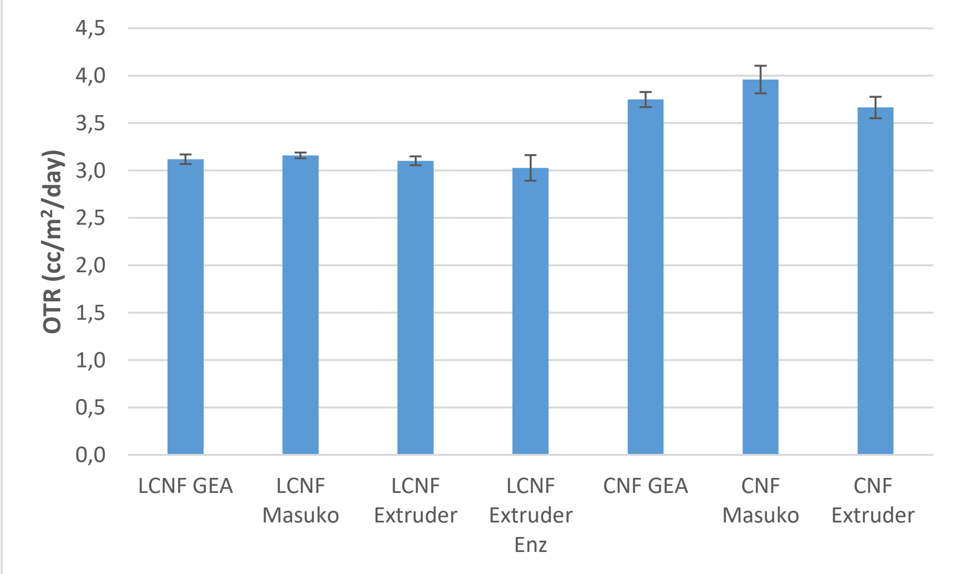

Fig. 4. OTR values for the different (L)CNF films

Moisture and water absorption

Structures with 4 layers (2mm) and a size of 40 x 20 mm were printed using a 3D printer. The corresponding aerogels were prepared using freeze-drying technique from the ink hydrogel after the printing, obtaining a porous structure and used as moisture and water scavenger. Fig. 5 shows a SEM image of a freeze-dried CNF aerogel and Fig. 6 shows the isotherms curves for water and moisture absorption for the CNF aerogels. Its showss that CNF have a great water holding capacity (1800% of weight gain), however, regarding to the moisture absorption, low values (7% of weight gain) were reached. Other polymers or compounds should be used to increase the moisture absorption capacity of the CNF and make it viable for use in food packaging.

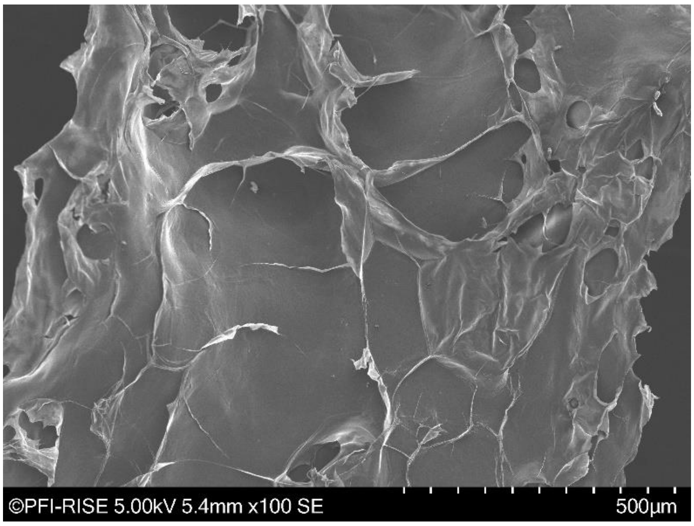

Fig. 5. SEM image of a freeze-dried CNF.

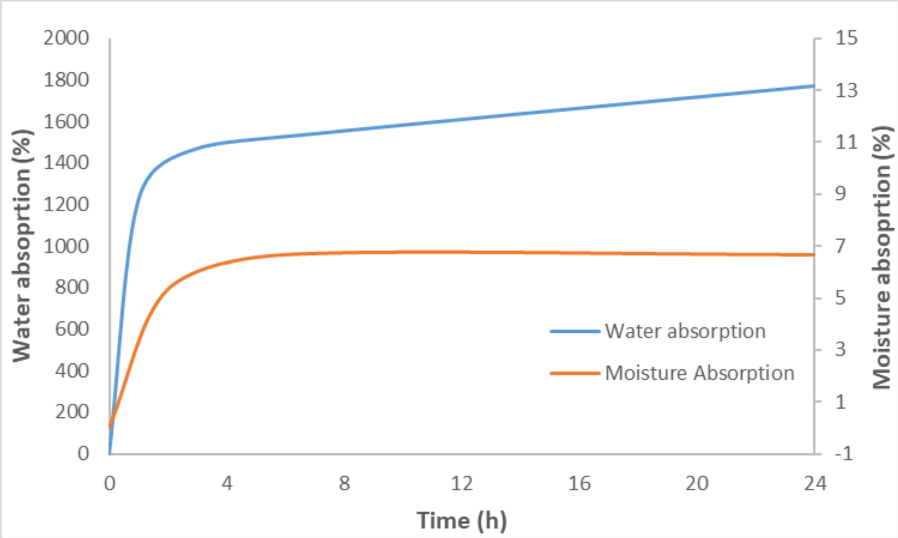

Fig. 6. Water and moisture absorption values for CNF aerogels

FUTURE COLLABORATIONS (if applicable)

This STSM opens the possibility to establish a continuous collaboration between the University of Córdoba (Spain) and RISE PFI (Norway) in the use of cellulose nanofibers (CNF) in the field of active and intelligent packaging (AIP).

The data obtained in this STSM is expected to be valorized in a publication about the use of CNF as moisture scavenger using 3D bioprinting technology.