COST ACTION FP1405 ActInPak

# SHORT TERM SCIENTIFIC MISSION REPORT- URŠKA VRABIČ BRODNJAK

# "OBTAINING OF PAPER SAMPLES, CONTAINING OF BIO-BASED COMPONENTS AND INVESTIGATION ON ITS INFLUENCE OVER THE PROPERTIES OF PAPER"

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## 1 INTRODUCTION AND THE PURPOSE OF THE STSM

The purpose of this visit was to find out if packaging paper, with bio based components (for example chitosan, chitin and rice starch), used as filler or coating, exhibits great barrier properties for packaging materials. If it could be used in packaging and how these properties could be improved. This visit was meant also for a collaboration between the University of Ljubljana, Faculty of Natural Sciences and Engineering in Ljubljana, Slovenia and University of Chemical Technology and Metallurgy, Department of Pulp, Paper and Printing Art in Sofia, Bulgaria. The common interest was to prepare paper samples containing bio-based components which will be included as fillers and not as coatings and to investigate the changes in paper properties. This kind of paper could be used as packaging material with great barrier properties; to be a good and sufficient substitute for non-recyclable materials used in this field of packaging.

## 2 THE WORK CARRIED OUT DURING THE STSM

### 2.1 Materials

For preparation of paper samples we used pulp prepared from softwood (beech) and hardwood (pine and spruce), chitosan (Sigma Aldrich, Austria), rice starch (Farmalabor, Italy), acetic acid (Sigma Aldrich, Austria), retention additive: modified cationic polyacrylamide (Kemira, Finland).
The paper sheets were prepared using 6 different variations and concentrations of pulp, bio polymers (chitosan and rice starch) and additives.

The preparation was followed with mixtures:

1) Only pulp (Sample 1)
2) Pulp and retention additive (Sample 2)
3) Pulp, 5% chitosan, retention additive (Sample 3)
4) Pulp, 5% of rice starch and chitosan, retention additive (Sample 4)
5) Pulp, 7.5% chitosan, retention additive (Sample 5)
6) Pulp, 7.5% of rice starch and chitosan, retention additive (Sample 6)

### 2.2 Preparation of different pulp mixtures

Pulp was prepared with 50% of softwood (pine and spruce) and 50% of hardwood (beech).
Chitosan solution was prepared by dissolving chitosan in acetic acid in order to prepare 5% and 7.5% of the solution. The solution was mixed for 10 min at 85°C and then cooled to room temperature.
Rice starch was also prepared separately by dissolving rice starch in distilled water. It was mixed until it gelatinised (85°C for 10 min) and also cooled to room temperature.
The chitosan-rice starch solution was prepared by mixing the same amount of rice starch and chitosan solution (5% or 7.5%).

The procedure of mixing pulp and other additives was as followed: firstly 2000 ml of pulp was mixed, then the chitosan and rice starch were added. The mixing proceeded and after that the retention additive was added.

### 2.3 Preparation of paper samples

All samples were prepared on paper laboratory machine (Blattbildungsanlage, Germany) as seen on Figure 1 and 2. Samples were dried at 90°C for 7 minutes.

**Figure 1:** Laboratory paper machine

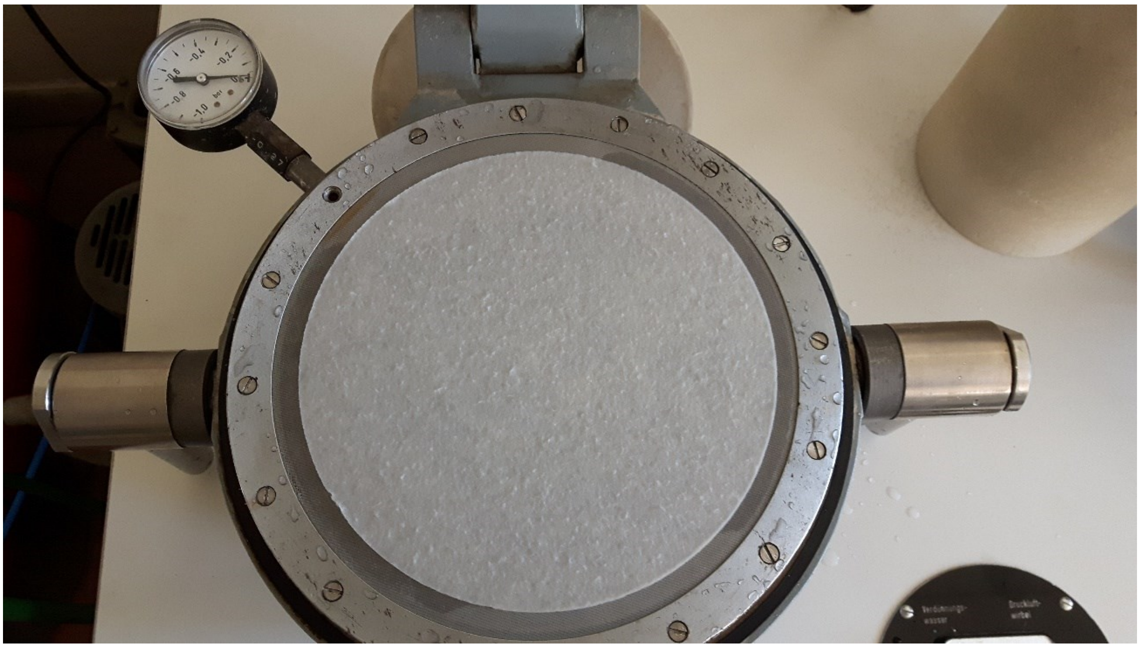


**Figure 2:** Paper sheet (not dried)

### 2.4 Methods

#### 2.4.1 Analysis of pulp

After preparation of each pulp mixture, the turbidity and dewatering time has been measured. For determination of Turbidity, NTU - Nephelometric acc. ISO 7020 (Turb 350 IR), the turbidimeter was used, which was equipped with integrated pH meter and temperature recorder.
The dewatering time was determined on Shopper Riegler apparatus (Germany). The apparatus provides a measure of the rate at which a suspension of pulp could be dewatered. The measured quantity was 700 mm and the time (in seconds) of achieving this amount was determined.

#### 2.4.2 Analysis of paper samples

Firstly, it was necessary to determine grammage, which also had influence on other properties of paper (bending stiffness, air permeability etc.).
Grammage was determined in accordance with ISO 536 standard. The thickness was measured with precision digital micrometre as described in standard ISO 534.
Water absorptiveness was determined with Cobb value as described in standard method ISO 535 where the given amount of water was in contact with paper for 60 seconds. Weight differences were calculated.
Air permeability and smoothness were also determined according to standard TAPPI T460 and ISO 8791-2. Bending resistance is important to provide the paper rigidity, which is required especially at printing and folding. It was determined according to standard TAPPI T511, with specimen preload 1000g, where 175 bending/minute has been proceeded.
The colour of all sample papers was determined with a CIE colorimeter i1Pro2. The CIE Lab scale was used to determine the L*, a* and b* colour values and after that colour difference was calculated. The plate was used as a standard (L*=92.82, a*=–1.24, b*=0.5). For each sample, ten measurements were made at different locations on the surface.
To analyse and determine the differences which was also proven with other analysis, scanning electron micrographs (SEM) on microscope JSM-6060LV, have been made. All micrographs were made at magnification 500x and operating voltage 10kV.

## 3 RESULTS AND COLNCLUSIONS

Usually, the dewatering ability gives us indirect information about the flocculation ability of the paper suspension. Not all of the examined bio-based combinations have positive effect over the accelerate drainage of the paper suspensions (Table 1). Best results are obtained in the presence of 7.5% chitosan, followed by the combination of 5% chitosan and starch. In Sample 3 the presence only of 5% chitosan probably is not enough to compensate the negative charge of the pulp fibers so that the resulting flocks to be uniform and stable. The effectiveness of 7.5% chitosan and starch (Sample 6), over the dewatering of the suspensions is higher than that in Sample 3 (only 5% chitosan), which means that the system is overloaded and the flocculation and dewatering have no homogenous character.

Regarding the turbidity of the white waters the results are similar to those for the dewatering ability, but here all the examined combinations have positive effect compared to the Sample 1 (only pulp). Best results are obtained for Sample 5 (7.5% chitosan), which means that the white waters are clarified and the flocculation has its optimal conditions. Higher turbidity of Sample 2, which is only pulp and retention additive, probably is due to the large molecular weight of the modified polyacrylamide and for this combinations of softwood and hardwood pulp the retention additive should be with lower molecular weight, so that the obtained flocks to be smaller.

**Table 1: D**ewatering time ($T_{700,s}$) and turbidity ($T_{NTU}$) of all pulp mixtures

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|
| $T_{700,s}$ | 6.37 | 11.16 | 7.51 | 6.09 | 5.56 | 6.60 |
| $T_{NTU}$ | 18.50 | 21.60 | 16.20 | 15.60 | 13.90 | 16.10 |

**Table 2:** Results of grammage, thickness, specific surface, density and water absorptiveness (Cobb value) of all samples

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|
| Grammage [g/m$^2$] | 80 | 80 | 80 | 80 | 80 | 80 |
| Thickness [mm] | 0.084 | 0.095 | 0.091 | 0.090 | 0.095 | 0.096 |
| Specific surface [m$^3$/g] | 0.0011 | 0.0012 | 0.0011 | 0.0011 | 0.0012 | 0.0012 |
| Density [g/m$^3$] | 952.38 | 842.11 | 879.12 | 888.89 | 842.11 | 833.33 |
| Cobb value [g/m$^2$] | 20.24 | 20.27 | 24.21 | 27.63 | 28.82 | 30.04 |

As expected, the thickness of the samples had mostly the same values (Table 2). The changes were at specific surface and density, where sample 1, with only pulp and no additives, had the highest density, compared to other tested papers.
Ability of fluids to penetrate the structure of paper is highly significant property to the use of packaging paper. Resistance towards the penetration of water was measured by Cobb values, as explained in ISO 535. From the obtained results, the addition of chitosan-rice starch decreased water absorptiveness i.e. Cobb value, as seen in Table 2. The higher, the concentration of solution was, higher resistance towards water penetration has been detected.

Paper is highly porous material, composed of a felted layer of fibres and the additives could cause the variation of many properties. One of the affected properties are for sure smoothness and air permeability. Chitosan and rice starch included in the paper sheets, filled the pores and holes. The open surface of paper sheets decreased with increasing amount of mentioned polymers.

Smoothness was better at samples with chitosan and rice starch. When the amount of bio polymers increased, the smoothness improved as well. As expected and seen in Figure 3, the air permeability was the worse at paper, where only pulp was included. With addition of bio polymers and retention additive, the structure of the paper became more even and filled, therefore the properties improved.

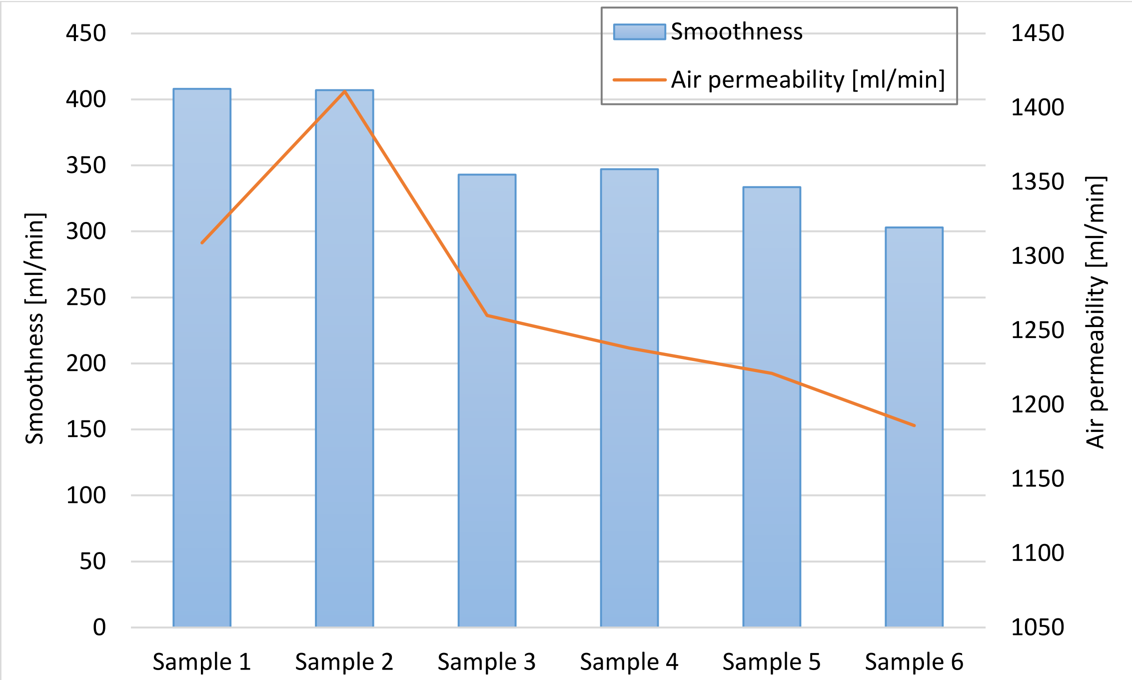



**Figure 3:** Smoothness and air permeability of all samples

Resistance to bending is important for packaging papers. At samples where we added different additives, the resistance improved significantly (Figure 4). In the case of suspension with increasing chitosan or combination of chitosan and rice starch, the bending resistance increased. The best results were at sample where 7.5% of chitosan-rice starch solution was added (5489).

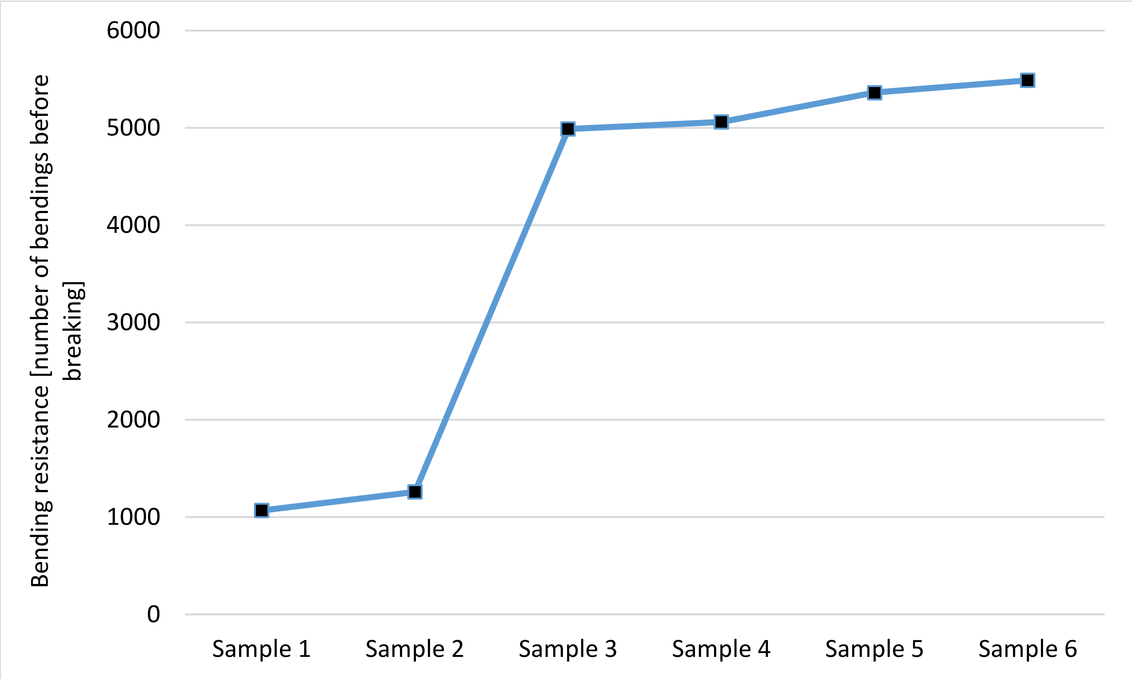


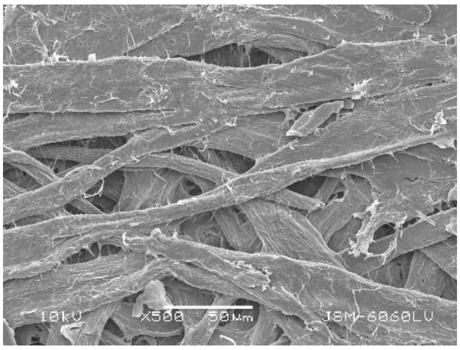

**Figure 4:** Bending resistance of all samples

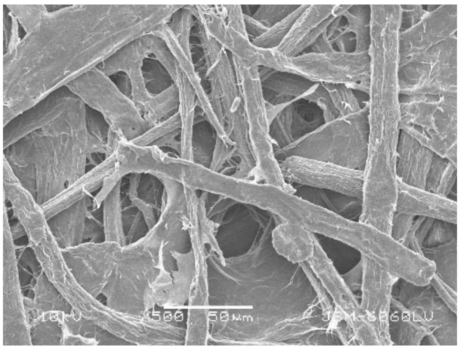
**Table 3:** Colour difference of samples 2-6 in comparison to sample 1 (Pulp only)

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|
| ΔE | / | 0.39 | 1.86 | 1.27 | 1.89 | 1.55 |

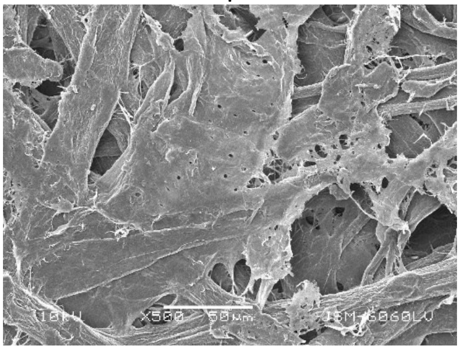
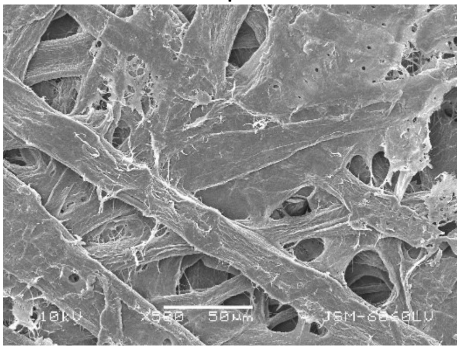
The chitosan and rice starch contribution was however in accordance with differences in colour values of prepared papers.
As expected the colour difference has shown that sample 2, where only pulp and retention additive has been in the paper, the lower difference between the samples is detected. For chitosan it is known that has yellowish appearance and therefore it has an effect on colour of the paper. This it can be observed form Table 1. At samples, where rice starch was added, the colour difference was lower. Rice starch is a white powder and has an effect on final paper appearance. Chitosan is naturally yellow colour, which can cause difficulties at printing properties. With the right amount and ratio of the rice starch, we could avoid these problem, but should be careful, because with addition of the rice starch, microbial properties can decrease.

With scanning electron micrographs we have proven the differences between samples (Figure 5). Results proved that chitosan and rice starch have great impact on paper properties. The surface of these samples is more even, there are big areas of filled chitosan and rice starch mixture. Higher amount of the solution (only chitosan or in combination with rice starch) gave the paper better appearance in more even surface. Which will also have an effect to printing properties.

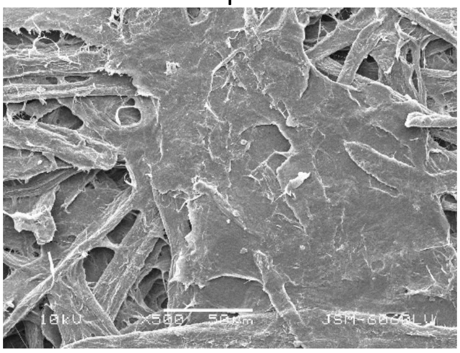
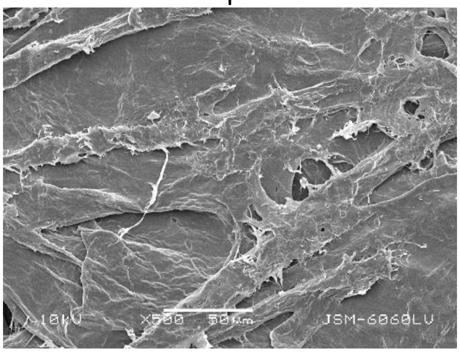





Sample 1 Sample 2

Sample 3 Sample 4


Sample 5 Sample 6

**Figure 5:** SEM micrographs of paper samples (500x magnification)

The incorporation of chitosan and rice starch to the pulp slurry exhibited paper sheets with improved properties. There were still holes and pores in the paper sheets detected, but this was reduced by increased concentration of used polymers.

## 4 PERSPECTIVE AND FUTURE COLLABORATION

Results expected at our scientific mission were, that prepared paper samples with bio based polymers will be sufficient and will be appropriate at certain packaging industry. Till now, the results have shown improved properties, which are going in the right direction for packaging material. More analysis on these samples will be carried out in order to have broad information about the influence of these polymers to the paper properties. Additional research will be done and analysis such as FTIR, DMA, water absorptiveness, tensile properties, grease, moisture and microbial barrier properties, which are very important for materials used in packaging field. In the medium to long term, future collaboration with the

host University of Chemical Technology and Metallurgy, Department of Pulp, Paper and Printing Art in Sofia will be done.
The final results will also help to produce new materials, developed at this visit and to research further within ActInPak action.
The results will be disseminated through publication in scientific journal, presentation at COST meeting and presentations at international scientific conferences.