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STSM SCIENTIFIC REPORT

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STSM Research Theme: “Modification of nano cellulose and characterization of its composites”

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1. Purpose of the STSM

The main objective of this STSM was to start the work with nanocellulose as reinforcing filler in outdoor wood coatings based on expertise of group of Prof. Dr. Wolfgang Gindl-Altmutter. His group has several years of experience and significant achievements with nano cellulose in wood adhesives and coatings.

High surface area of nano fillers causes difficulties in dispersion into the polymer and tendency towards agglomeration. Also hydrophilic nature of cellulose is very different compared to most polymers used as binders in coatings and this difference can lead to low interaction between them in formed composites. These issues can lead to premature failure of coatings. Both of these problems can be tackled with grafting of specific functional groups onto the nano cellulose so focus of this STSM was on modification of nano cellulose.

Additional objectives of this STSM was to gain experience and knowledge about work in different scientific environment and strengthen the collaboration between research group I am part of at University of Copenhagen with the research groups at BOKU, University of Natural Resources and Life Sciences, Austria.

2. Description of the work carried out during the STSM

Nano cellulose in raw form was slurry of cellulose nanofibrils (CNFs) and of acid hydrolyzed cellulose nanocrystals (CNCs). Outdoor wood coating was based on an alkyd emulsion.

Nano cellulose was incorporated into the alkyd emulsion with high speed Ultra-Turrax laboratory homogenizer. After homogenization, defoaming was accelerated in a sonic bath. Coating was applied with Byk-Gardner casting knife on Teflon plates and on Leneta drawdown test charts.

Free films of coating were removed from Teflon plates after 10 days of curing at room temperature. Free films were used for dynamic mechanical analysis (DMA) of coatings which was done on Netzsch DMA 242C in tension mode (Figure 1a and 1b). Sample dimensions were about 25mm (length) x 5.5mm (width) x 0.05mm (thickness). Samples were heated from -40°C to 60°C at a heating rate of 2°C /min, a frequency of 1Hz and amplitude of 50µm. Storage modulus and tan δ were taken as a function of temperature. Free films were also exposed to Q-Sun Xenon Test Chamber for accelerated UV exposure at irradiation strength of 0.51 W/m² with a maximum at 340nm wavelength for 72h at 65°C.

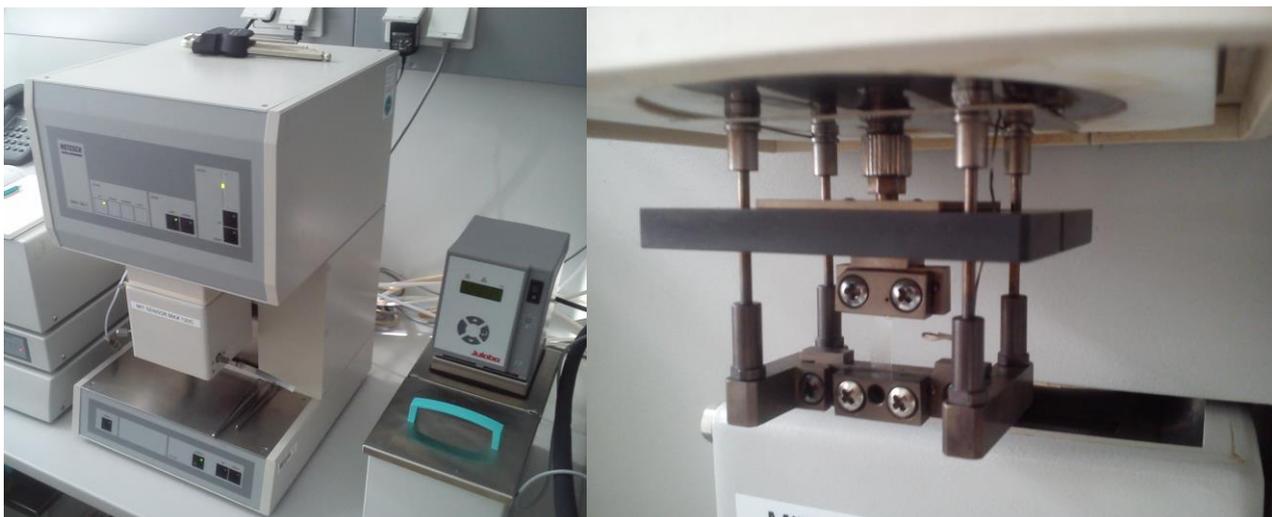


Figure 1. a) Netzsch DMA 242 C and b) Coating free film positioned in tension mode clamp

Before chemical modification pH of CNCs was adjusted to around 7 to allow re-dispersion from dry state and afterwards CNCs were frozen and sublimated in a freeze drying procedure to eliminate the water.

Chemical modification:

Esterification of CNCs was attempted with long molecules in gas state and in liquid state.

Gas state esterification:

Modification was attempted first on CNCs in powder form and then also on CNCs in sheet form. Reagent used to perform this modification was dodecen-1-yl succinic anhydride (DSA) and no catalyst was used. DSA was placed at the bottom of a laboratory desiccator while CNCs were placed on a mesh above. Desiccator was connected to a vacuum pump and heated and kept at 190°C in an oil bath and kept for different amount of time (0.5h-4h) (Figure 2). After this procedure CNCs were rinsed with solvents to remove non-reacted DSA, hydrolyzed DSA etc.



Figure 2. Gas state esterification setup

Esterification was checked with contact angle measurements of CNCs and also with titration after saponification (CNCs in powder form) or simple change in weight (CNCs in sheet form).

Liquid state modification:

First, solvent exchange was performed on CNCs to remove water but with available equipment sedimentation was very incomplete so this route was abandoned and CNCs were freeze dried and re-dispersed in a solvent. This time oleoyl chloride was used as a reactant, pyridine as solvent and auxiliary base and piperidine as a catalyst. Reaction was performed at two different temperatures (40°C and 80°C) for different amounts of time (between 0.5h and 6h). Reaction was stopped by addition of solvent and CNCs were separated by filtration.

3. Description of the main results obtained

It was not planned before the visit, but availability of Q-SUN Xenon test chamber was used for developing a method to quantify changes of polymer properties due to outdoor conditions. Hardening and cracking of outdoor wood coatings due to increase and speed of increase of resins glass transition temperature (T_g) is a very important parameter. Combination of accelerated weathering tests with DMA measurements can allow us significant discoveries in the future with new fillers that are being introduced. Weathering tests can be done on free films or on Teflon plates (with removal of films after the tests) but tests on free films would be recommended to remove the influence of Teflon surface that is very different compared to wood (Figure 3). Very fast increase in storage modulus and T_g (only after 72h) is because in this basic method no pigments or UV stabilizers were used and thickness of free films was also low (Table 1). The same method can be applied in both Xenon and QUV test chambers for accelerated weathering.

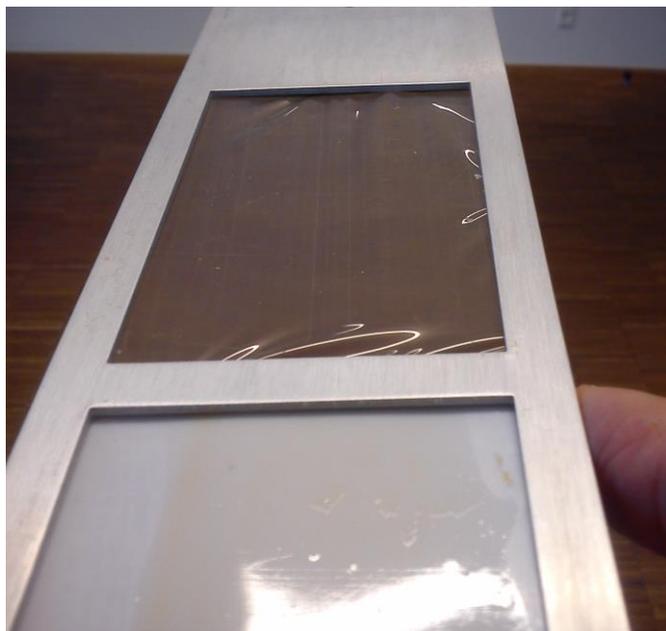


Figure 3. Coating placed in a sample holder for accelerated weathering test on Teflon plate (lower part) and as a free film (upper part)

Table 1: Viscoelastic properties of alkyd coating before and after exposure to Q-SUN Xenon test chamber

	Storage modulus, MPa	$\tan \delta$, °C
Alkyd coating before weathering	47.3	19.1
Alkyd coating after weathering	342.0	36.7

After incorporation of CNFs and CNCs in coatings and application very poor optical properties of coatings with CNFs were noticed. This was probably because of high length of CNFs and further work was done only with CNCs.

Gas state esterification with a cyclic anhydride like DSA is very interesting method as it is a completely environmentally benign. This was the first time it was tried in both our labs but unfortunately it was unsuccessful in this setup. Contact angle measurements showed no difference between native CNCs and after attempted modification. Titration also showed no difference between blanks and actual samples and when eventually it was tried on CNCs sheets there was no weight increase after rinsing. Reason is probably because of high temperature gradient in the desiccator. As the heating was only from below, even though DSA was evaporating, the temperature of CNCs was not high enough for the esterification to happen. After these results in the remaining time liquid state esterification was performed. Change of CNCs properties was now evident as modified cellulose was no longer stable in water. Degree of modification will be tested in the future.

Among the main results is definitely acquired knowledge and hands-on experience that was gained as practically all the things I have tried and performed (besides DMA measurements) were for me completely new.

4. Future collaboration with host institution (if applicable)

I believe that the ground base for personal and institutional cooperation has been established during this STSM. We have opened several possible topics for the future with joint experiments, student exchange and other STSMs.

5. Foreseen publications/articles to result from the STSM (if applicable)

Work that we started during this STSM will hopefully lead to a joint publication by the end of this year.

6. Confirmation by the host institution of the successful execution of the STSM

Confirmation is sent as a separate file.

7. Other comments (if any)

I am happy to say that impressions from my first STSM are very positive. I am grateful to COST Action FP 1006 for supporting this STSM and I believe that these opportunities are especially important for Early Stage Researchers to expand their horizons.

I would also like to thank Prof. Dr. Wolfgang Gindl-Altmutter and Dr. Stefan Viegel for their full support during this stay. The work atmosphere at BOKU, University of Natural Resources and Life Sciences, Austria was excellent and they helped me feel like a full member of their group.