STSM SCIENTIFIC REPORT

Investigation of Clear Wood Coatings Containing Inorganic Nanosized Particles Resistance to UV and Microfungi

Action: COST FP1006
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STSM Scientific Report Contents:

1. Introduction and purpose of the STSM

Is well known, that the clear water-based wood coatings are susceptible to the harmful ultraviolet (UV) rays, since they can easily penetrate through the system of the coating and start to destroy the surface of wood [1]. From the basic chemical composition of wood: cellulose, hemicellulose and lignin, only the latter absorbs the UV rays quite intensively [2]. Intensive sunlight, oxygen, changes of temperature and atmospheric moisture affects the colour of wood surfaces. At first, the colour of wood surfaces varies from the light to yellow and brown, until the surface of wood is grayed out [2-3].

In order to improve the efficiency of the clear water-based wood coatings against the harmful UV rays, a small amount (up to 5 %) of different inorganic and organic nanoparticles additives can be used. Inorganic nanoscale UV absorbers are characterized by their stability and inhibition properties of UV spectra, which reduces the photodegradation processes speed of the wood surface [4]. Also it is known, that some inorganic particles (e.g. TiO_2, etc.) improve the resistance of wood surface against microfungi.

The purpose of this STSM in Poznan University of Life Sciences was to study the properties and behavior of clear wood coatings containing nanosized inorganic particles. STSM work was divided into three topics of interests: resistance to UV exposure of coated wood surfaces and free coating films as well as resistance of coated wood surfaces against the microfungi. This topic of STSM was a good opportunity to start the collaboration between Poznan University of Life Sciences and Kaunas University of Technology.

2. Description of the work carried out during the STSM

All samples were prepared at home institution before STSM. During the stay in Poznan, the researches were divided into 3 topics:

- Investigation of clear wood coatings containing inorganic nanosized particles resistance to UV exposure;
- Investigation of free coating films containing inorganic nanosized particles resistance to UV exposure;
- Investigation of clear wood coatings containing inorganic nanosized particles resistance to common microfungi.

2.1 Materials

For the researches, radial/tangential planed defect free kiln-dried pine (*Pinus sylvestris L.*) and ash (*Fraxinus excelsior L.*) wood samples with dimensions of 45×45×24 mm and 30×20×8 mm were chosen. Five formulations of clear water-based acrylic wood coatings containing inorganic nanoparticles were mixed at home institution laboratory (Table 1). The top of wood samples were coated by brush (2 layers). All of the samples were initially conditioned at temperature 23°C ± 2°C and relative humidity of 50% ± 5% for 20 hours.

Samples of free coating films were formed by 1 layer on the clear glass plates with dimensions of 45×45×5 mm. Wet film thickness did not exceeded 200 µm. Samples of free coating films were cured at the same conditions.

Table 1. Information about the formulations of clear water-based acrylic coatings

Type of nanoparticles	Concentration in mixture, %					
	AK	AKT1	AKT2	AKTZ	AKZ	AKC
TiO_2 (<100 nm)	-	1	0,5	1,25	-	-
ZnO (20 nm)	-	-	-	1,25	5	-
CeO_2 (10 nm)	-	-	-	-	-	5

In total, 156 samples of coated wood in dimensions of 45×45×24 mm and 150 samples in dimensions of 30×20×8 mm were prepared. Also 60 samples of free coating films were prepared.

Some initial measurements at home institution were performed also: the anatomy of wood, number of growth rings per 1 cm and growth rings orientation, density of wood samples, moisture content, wettability and surface roughness (R_a, R_z, R_{max}) in three directions were evaluated. After application of the coatings, the dry film thickness was measured.

2.2. Part 1: Investigation of clear wood coatings containing inorganic nanosized particles resistance to UV exposure

During the first part of the research, 13 samples of the different coating systems and species of wood were chosen: 1 sample as a reference, 6 samples for initial measurements, 6 samples for ageing. The description of performed measurements and equipment used:

- For the initial measurements, adhesion strength of the coating was evaluated carrying out the pull-off test (in accordance with DIN EN ISO 4624). The dollies were glued perpendicular to the coating surface of the dry coating film using two-component monosilane-epoxy adhesive. After 3 days of the conditioning, the adhesion strength was measured using hand-operated PosiTest Pull-off Adhesion Tester. After each test the nature of the fracture was evaluated visually.
- For the accelerated ageing of coated wood samples the SOLARBOX 1500e light exposure chamber was used (Fig. 1). The irradiation light source was a xenon-arc lamps combined together with a filter of outdoor S250/S450. The samples were exposed to 550 W/m^2 radiation intensivity resulting in a wood sample surface temperature of approximately 60°C (black panel temperature). The wavelengths of UV were λ = 280 nm. Due to the short period of STSM, we performed 40 h of accelerated ageing to assess the primary ongoing changes in coated wood surfaces.
- The measurements of the decorative properties (gloss according to DIN 67530, ISO 2813 and colour changes according to CIE-$L^*a^*b^*$ system) of wood samples were performed after 0, 1, 2, 5, 10, 15 and 20 cycles (1 cycle – 2 hours of UV exposure). In each sample, 5 measurements spots (with diameter of 9 mm for colour changes) were selected. Gloss measurements of the coated wood surfaces were performed in three angles (20°, 60° and 85° along the wood grain) using photoelectric gloss meter PICO GLOSS 503 (Fig. 2). The measurements of colour changes were performed using DATACOLOR 600 reflection spectrophotometer (Fig. 3). The colour in CIE-$L^*a^*b^*$ system was characterized by 3 parameters: L^*, a^* and b^*. These L^*, a^*, b^* coordinates in each spot of sample (using special template) were measured after every cycle of accelerate ageing. L^*, a^*, b^* values were used to calculate the total colour change ΔE^* as a function of UV-irradiation duration (Eqs. 1-4).

$$\Delta L^* = L_1^* - L_0^* \quad (1)$$

$$\Delta a^* = a_1^* - a_0^* \quad (2)$$

$$\Delta b^* = b_1^* - b_0^* \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

where, ΔL^*, Δa^* and Δb^* are the changes between initial (0) and final (1) values.

Fig. 1 Light exposure chamber SOLARBOX 1500 e

Fig. 2 Three-angle gloss meter PICO GLOSS 503

Fig. 3 Spectrophotometer DATACOLOR 600

2.3. Part 2: Investigation of free coating films containing inorganic nanosized particles resistance to UV exposure

In the second part of the research, 10 samples of the different free film coating systems were chosen: 1 sample as a reference, 5 samples for intensive UV+IR ageing and 4 samples for UV accelerated ageing. The description of performed measurements and equipment:

- For the intensive UV+IR ageing of coated glass samples, a special quartz lamp (Fig. 4) was used (accordingly to Polish Standart PN-88/F-06100/07). The radiation energy of quartz lamp (type VT-4) was 740W. The distance between samples and quartz lamp did not exceeded 400 mm. In total, 30h of intensive UV+IR ageing was performed. The ageing was divided into 6 cycles. The measurements of decorative properties, transparency and hardness were performed after 0, 1, 3, 6, 10, 20 and 30 h of ageing.
- Accelerated UV ageing of coated glass samples was performed using SOLARBOX 1500e light exposure chamber under the same conditions analogous to Part 1 of the investigation.
- During the ageing, the measurements of colour (according to CIE-*L*a*b** system) and gloss changes (according to DIN 67530, ISO 2813) were observed (analogous to Part 1). In this case of the research, the white background for coated glass samples was used. Without decorative properties of coated glass samples, the transparency and the hardness were evaluated also. For the transparency measurements a special stand with the light source and apparat of LUKSOMIERZ type L-02 were used. For the evaluation of transparency, 5 measurements points were selected. The hardness of the coated glass surface was evaluated in 2 measurement points in each sample, using a Persoz pendulum hardness tester (Fig. 6). The hardness of the coated glass surface was measured taking account of oscillation time.

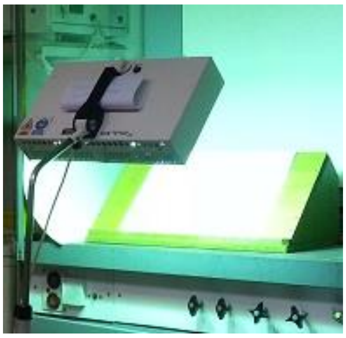

Fig. 4 UV+IR quartz lamp

Fig. 5 Stand for transparency measurements

Fig. 6 Persoz pendulum hardness tester

2.4. Part 3: Investigation of clear wood coatings containing inorganic nanosized particles resistance to common microfungi

In the last part of the investigation, 5 coated and 5 uncoated samples of one species of wood were chosen to evaluate the resistance against one type of microfungi. In this part, whole types of coatings were investigated, except coating, containing CeO_2 nanoparticles. The spore suspension for the microfungi species was the following: *Aspergillus niger* (*An*), *Trichoderma viride* (*TV*), and mixture of *An*, *TV* and *Chaetomium globosum* (*Chg*). The evaluation of the efficacy was made by the visual assessment of fungal growth on the wood surface in accordance to the scale set out in Table 2 (accordingly to ASTM D 5590-94). Storage time of samples exposed to microfungi at the temperature 29°C and relative humidity 80% was 21 days. The visual evaluation of microfungi growth was performed after 4, 7, 14, 18 and 21 days. A good fungicidal protection was given when there was no growth of fungi on the specimen (index 0). Before the investigations and after overgrowth of microfungi, the chemical analyses were performed using ALPHA FT-IR spectrometer.

Table 2. Rating system for fungal growth

Index	Rating system
0H	no growth of fungi on the specimen, inhibition zone on the nutrient
0	no growth of fungi on the specimen
1	less than 10 % of the specimen area covered by fungi
2	less than 30 % of the specimen area covered by fungi
3	less than 60 % of the specimen area covered by fungi
4	specimen totally overgrown by fungi

3. Description of the main results obtained

A short discussion and conclusions of the main results obtained are divided according to the parts of the investigation.

3.1. Part 1: Colour and gloss changes of the coated wood samples after UV exposure

- In comparison of the wood species, the discoloration of coated wood samples performance was different. After 40 h of UV exposure, the higher retention of colour and better gloss performance of coated wood surface were observed in group of ash wood samples.
- Estimating the samples of ash wood, the lowest value of ΔE^* after 40h of UV ageing, was observed in group of AKC samples (ΔE^*=1,76). The good performance of the ΔE^* was established in group of AKT1 samples also (ΔE^*=3,37). Meanwhile, the colour retention of AKT2, AKZ and AKTZ groups of samples were almost pararel to AK group (coating with no nanosize additives). The different performance of coatings, containing inorganic nanoparticles, was observed in group of pine wood samples. Here the lowest ΔE^* values were established in AKTZ group (ΔE^*=2,45) and AKZ group (ΔE^*=3,03). It is worth to mention, that the ΔE^* parameter of AKZ coating (containing 5% of ZnO nanoparticles), after 30h of accelerated ageing in both groups of wood species, started to decrease.

- During the UV ageing, the inorganic nano additives also influenced the gloss performance of coated wood surfaces. Increasing the time of UV ageing, the gloss started to decrease. The most stable gloss parameter (in the angle of 60º) after 40 h of UV ageing, was observed in the group of AKZ coating.
- For preferably understanding the resistance of coated wood samples to UV exposure, the chemical analysis should be performed also the ageing process should be continued.

3.2. Part 2: Colour and gloss changes of the free coating films after UV+IR and UV exposure

- In this case, the changes of colour were more stable in comparison to the Part 1 of the investigation. The significant influence of IR rays was observed. After 20 h of ageing, the value of ΔE^* was 1,20 – 2,02 times higher using intensive UV+IR ageing method than accelerated UV ageing.
- After 30 h of intensive UV+IR ageing, the lowest colour changes were established in group of AKZ coating films (ΔE^*=3,07). Moderate ΔE^* performance was observed in groups of AKC (ΔE^*=6,20) and AKTZ (ΔE^*=7,68) samples. During the ageing, the gloss of coating films, containing TiO_2 nano particles decreased significantly. The higher ratio of TiO_2 nanoparticles in coating mixture caused the higher loss of coating film surface gloss. Meanwhile, the other coating films (containing CeO_2 or ZnO nanoparticles) have not shown the considerable differences in the surface gloss.
- During the UV ageing, the lower values of ΔE^* were observed in all groups of coating films containing inorganic nanoparticles compared with the film of clear acrylic coating (AK). Here the lowest colour changes were observed in AKZ group (ΔE^*=1,84) while the coating films, containing TiO_2 nanoparticles were more sensitive. The gloss of free coating films during the UV ageing started to decrease. The most stable gloss parameter (in the angle of 60º) after 40 h of UV ageing, was observed in group of AKZ coating also.

3.3. Part 2: Transparency and hardness changes of the free coating films after UV+IR and UV exposure

- The intensive UV+IR ageing influenced the transparency of the free coating films. After 20h of UV+IR ageing, transparency decreased 1,16 times, while after the same time of UV ageing only, the difference of transparency was only 1,04 times. The type, amount and size of used inorganic nanoparticles also influenced the transparency of the coating films. The high transparency, accordingly to the film of clear acrylic coating (AK) had the films with AKC and AKZ formulations of coatings, meanwhile the films, containing TiO_2 nanoparticles were less transparency.
- Different ageing type also caused different hardness performance of coating films. During the UV+IR ageing, the hardness of the free coating films in all cases increased 1,29 – 1,38 times, meanwhile, during the UV ageing only, the difference of the hardness was 1,05 times.

3.4. Part 3: Wood coatings resistance to common microfungi

- In comparison of wood species, the higher resistance against microfungi were observed in groups of ash wood samples. Also the coatings, containing inorganic TiO_2 nanoparticles, performed higher resistance also.
- After 21 day of microfungi overgrowth, the resistance of coatings, containing inorganic nanosized particles, against *Aspergillus niger* was less (index 1 – 2), compared with other types of microfungi (index 0 – 1).

4. Future collaboration with host institution (if applicable)

Durring my stay in Poznan University of Life Sciences, the possibilities of collaborations were discussed. We deciced to continue the collaboration in this frame of researches also the possibility to perform the different researches was discussed also.

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

As a result of this STSM, we decided to prepare two joint publications with citation index, also we will present results in two international conferences in the near future.

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

The document is in a separate file.

7. Other comments (if any)

I would like to thank the COST action FP1006 committee for supporting this research. Also I would like to thank Prof. Dr. Hab. Bartlomiej Mazela for a possibility to perform researches in the Faculty of Wood Technology and Dr. Tomasz Krystofiak, my supervisor during the STSM, for a full assistance. Also I am very grateful to Dr. Barbara Lis, Dr. Hab. Magdalena Zborowska for a constant help and support. Many thanks to PhD Candidate Waldemar Perdoch for sharing the experience of microfungi and helping me to perform this part of the research. During the STSM, I have gained a lot of knowledge and research experience. The atmosphere was very warm and comfortable. STSM was a fantastic experience for me and very useful for my PhD researches.

8. References

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