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Caffeine and TiO_2 Nanoparticles Treatment of Spruce and Beech Wood for Increasing Transparent Coating Resistance against UV-Radiation and Mould Attacks

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Abstract: The effect of the initial modification of beech and spruce wood using a solution of caffeine and of a commercial product FN-NANO® FN-1 containing a water dispersion of TiO_2 nanoparticles for increasing the service life of a transparent oil and acrylate coatings during 6 weeks of artificial accelerated weathering was tested. Changes in colour, gloss, and the contact angle of water were monitored. Degradation of the coating film was also evaluated visually and microscopically. The resistance of the coatings to mould growth was also subsequently tested. Based on the results, it is possible to recommend the initial treatment of spruce and beech wood with a 2% caffeine solution or 15% solution of FN-NANO® dispersion to increase the overall life of a transparent acrylic coating in exterior applications. No positive effect of the applied treatments was observed with the oil coating. In addition, lower concentrations of FN-NANO® did not have a sufficient effect, and the synergistic effect of using FN-NANO® in a mixture with a 1% caffeine solution was also not confirmed.

Keywords: wood; caffeine; TiO_2 nanoparticles; transparent coatings; UV-resistance; mould attack

1. Introduction

Wood is a material of natural origin which is subject to a relatively rapid loss of its original appearance in exterior applications [1]. This is caused both by abiotic influences [2] and biotic infestation, in particular by moulds and wood-staining fungi [3,4]. The original appearance of wood in an exterior location can be further preserved using coating systems [5]. Transparent coatings can preserve not only the original design but also partly the colour of the base wood; however, their long-term stability is reduced compared to pigmented coatings by deeper and more intense penetration of sunlight into the coating film and base wood [6,7]. Another factor causing faster defoliation of coatings is the growth of fungal hyphae on their surface and in the zone between the coating and the wood surface [8,9]. In practice, penetrating base coatings containing fungicides and photo-stabilising components are most often used to suppress fungal growth, increase the bio-resistance of non-durable wood species, and increase photostability [5,10]. Ultraviolet (UV) stabilisers, hindered amine light stabilisers (HALS), and nanoparticles [1–13] are most often used as additives, and substances based on triazoles, carbamates, and others are most often used as fungicides [14,15].

An interesting possibility for increasing bio-resistance in parallel with photo-stabilisation of wood is the use of TiO_2 nanoparticles in anatase form [2,13,16–18]. The use of various substances of natural origin extractable from renewable sources is a more ecologically acceptable form of wood protection against bio-attack [19]. One of the substances with a proven biocidal effect is caffeine [20–22], but it is also disadvantageous in terms of its washability from wood [23]. However, this disadvantage would be eliminated through use of the top barrier layer of the coating system, which protects the base caffeine-impregnated wood. Nevertheless, it is necessary to determine whether the initial pre-treatment with TiO_2 nanoparticles and caffeine adversely affects the overall service life of the applied top coating, as described in some works [24,25]. Woods of the Norway spruce (*Picea abies* L. Karst) and European beech (*Fagus sylvatica* L.) were selected for research in this work. Spruce wood is widely used in exterior structures without a shelter—class 3 by EN 335 [26]. This is a type of wood with lower resistance to bio-attack [27] and its additional protection against bio-attack is often required. Transparent exterior coatings on this type of wood do not have optimal durability [28,29]. Beech wood is rarely used outdoors due to its low resistance to bio-attacks [27]. Its deep impregnation is necessary, and creosote oils are used, for example, for its use on railway sleepers [5]. Additionally, due to climate change, it is possible to anticipate an increase in its share in the total volume of wood processed—here, in Central Europe in particular [3,30,31]. The use of a suitable coating system and fungicidal components represents one of the simplest and cheapest variants of its possible use in class 3 by EN 335 [26]—outdoors without a shelter and without contact with the ground and water.

The aim of the experiment was to determine how the overall service life of the acrylate and oil coating system is affected by the initial surface modification of the underlying spruce and beech wood using caffeine solutions, dispersion of TiO_2 nanoparticles, and their combinations. The method of artificial accelerated weathering in a UV-chamber and a subsequent test of mould growth on both ageless and weathered surfaces of treated wood were used for testing.

2. Material and Methods

2.1. Wood Samples

Norway spruce (*Picea abies*, L. Karst) wood with an average density of 412 $kg \cdot m^{-3}$ and beech wood (*Fagus sylvatica*, L.) with an average density of 710 $kg \cdot m^{-3}$ were used for the experiments. Test specimens measuring 20 mm × 40 mm × 150 mm with a milled test area of 40 mm × 150 mm were prepared. Prior to treatment, the samples were conditioned in the laboratory at $T = 20$ °C and in air humidity of $\phi = 65\%$ to an equilibrium humidity of 12%, and they were subsequently modified for further testing.

2.2. Treatments of Samples

In the first step, the test specimens were soaked in more concentrations of impregnation solutions containing an aqueous dispersion of commercial product FN-NANO© (FN-1) (FN-NANO® s.r.o., Prague, Czech Republic). FN-NANO® dispersion containing about 7.5% TiO_2 nanoparticles in anatase form with the addition of 2.4% $ZnSO_4$ fulfilling the function of binder. Other sets were impregnated in 2% caffeine solution (Sigma-Aldrich, Prague, Czech Republic) and sets with different concentrations of FN-NANO® in solution combined with 1% of caffeine were also prepared (see Table 1). The intake of the solution and the soaking time were adjusted and controlled by continuous weighing of the samples so that the intake of impregnating substance into the wood was about 120 ± 20 $kg \cdot m^{-3}$ for both types of wood (beech is significantly more permeable compared to spruce). Subsequently, the samples were dried again in the laboratory at $T = 20$ °C and in air humidity of $\phi = 65\%$ to an equilibrium humidity of 12%. After drying, in the second step, top coatings were applied by brush to the samples. Acrylic (AC) transparent exterior glaze (Impranal profi with UV-filter, Stachema a.s., Kolín, Czech Republic) and transparent coating based on vegetable oils (OL) for exterior OSMO UV 420 (Osmo, Münster, Germany). Both were applied in two layers by the producers' recommendations with a deposit of approximately 100 $g \cdot m^{-2}$. A total of 4 test specimens were prepared for each type of treatment (see Table 1) and testing. After drying the coating systems, tests of artificial accelerated weathering were performed.

Table 1. Tested sets of specimens and their specification.

Types of Samples	Solution of FN-NANO® Dispersion (Concentration)	Caffeine Solution (Concentration)	Acrylic Coating (AC)	Oil-Based Coating (OL)
R-R	–	–	–	–
R-A	–	–	2 layers	–
1-A	10%	–	2 layers	–
2-A	15%	–	2 layers	–
3-A	10%	1%	2 layers	–
4-A	15%	1%	2 layers	–
5-A	–	2%	2 layers	–
R-O	–	–	–	2 layers
1-O	10%	–	–	2 layers
2-O	15%	–	–	2 layers
3-O	10%	1%	–	2 layers
4-O	15%	1%	–	2 layers
5-O	–	2%	–	2 layers

Note: The spruce samples were marked (S) and the beech samples (B). Solutions of FN-NANO® dispersion with concentrations 3.5% and 5%, as well as their combinations with a total 1% concentration of caffeine were also prepared, but the achieved results after artificial weathering were unsatisfactory, and they have therefore not been further evaluated in this article.

2.3. *Artificial Accelerated Weathering*

Artificial accelerated weathering (AW) was performed on the basis of EN 927-6 [32] in a UV chamber (Q-Lab, Cleveland, OH, USA) (radiation parameters 1.10 Wm^{-2}; T on black panel = 65 °C were modified) as standard with 2.5 h radiation phases and 0.5 h spraying with distilled water in the dark, and air conditioning at 45 °C once a week for 24 h. In addition, once a week, 3 temperature cycles (1 h at 80 °C and one hour at −25 °C) were inserted in the Discovery My DM340 air conditioning chamber (ACS, Massa Martana, Italy). The tests lasted for 6 weeks and the selected properties of the tested samples were evaluated at the beginning and after the 3rd and 6th week of AW.

2.4. *Tested Properties—Colour, Gloss, Surface Wetting, and Visual Evaluation*

The evaluated properties were colour changes measured by a spectrophotometer (CM-600d, Konica Minolta, Osaka, Japan) with an observation angle of 10°, $d/8$ geometry, D65 light source, and the SCI setting was used. The colour changes of the parameters L^* (brightness), a^* (+red; −green), b^* (+yellow, −blue), and the total colour change ΔE^* according to the known relationship $\Delta E^* = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{\frac{1}{2}}$ were evaluated [33]. Twelve measurements were made for each group of test samples and AW time.

The gloss was measured with an MG268-F2 glossmeter (KSJ, Quanzhou, China) at an angle of 60° according to EN ISO 2813 [34]. Twelve measurements were performed for each group of tested samples and AW time.

Surface wetting was evaluated using Goniometer DSA 30E (Krüss, Hamburg, Germany) and Krüss software (Krüss, Hamburg, Germany). The sessile drop method was used. The dosing volume of the distilled water drop was 5 μL and measurement time of the water contact angle on the surface after deposition was 5 s. A total of 20 measurements for each type of treatment and AW time were performed.

Visual evaluation was performed using 10× folder magnification and scans of samples (using a desktop scanner at a resolution of 300 dots per inch (DPI) (Canon 2520 MFP, Canon, Tokyo, Japan) before and during AW. Microscopic analyses of surfaces used a confocal laser scanning microscope (Lext Ols 4100, Olympus, Tokyo, Japan) with 108-fold magnification.

2.5. *Mould Resistance Test*

The test samples without weathering and after 6 weeks of artificial accelerated weathering were tested for the resistance of the surfaces to moulds. Petri dishes with Czapek–Dox agar were left in the open for 24 h to free up mould spores. This method provides more variable results compared to the laboratory methods using pure mould cultures, but it corresponds better to the real conditions of the exposed wood. The samples were then sealed and left at 30 °C and 90% relative humidity. After checking the growth of mould in the dish, moist test specimens measuring 15 mm × 40 mm × 10 mm were placed in the dishes with growing moulds, where their upper side measuring 40 mm × 15 mm was manipulated from the surfaces of the exposed test specimens, and not exposed to artificial accelerated weathering. The samples were placed on a low plastic pad to prevent the agar from seeping into the wood. Two test specimens were placed in each dish so that one dish did not contain samples from the same set of the tested types of treatments. Mould growth was evaluated after 7, 14, 21, and 28 days of the mould test based on the ČSN 490604 [35] standard, where degree 0 corresponds to samples without growth, 0%–10% is evaluated by degree 1, 10%–30% by degree 2, 30%–50% by degree 3, and above 50% of the stand at degree 4.

2.6. Statistical Evaluation

The results of the obtained measurements were evaluated using Statistica software (version 13.4) (StatSoft, Palo Alto, CA, USA) and using mean values, standard deviations (SD), and whisker plots using means and 2 ± SD.

3. Results and Discussion

3.1. Visual and Microscopic Evaluation

Based on visual evaluation supplemented by a microscopic analysis of the surfaces of the tested samples after artificial accelerated aging, positive effect of certain types of pre-treatments improving the durability of the acrylate coating (Figure 1) were evident. Compared to untreated wood and two layers of acrylic coating (Figure 1b), these were mainly 2% caffeine solution treatments (Figure 1c), the surface treated with 15% FN-NANO® dispersion (Figure 1e), in beech wood also 10% FN-NANO® dispersions (Figure 1d), and in spruce, the combination of 1% caffeine solution and 10% FN-NANO® dispersion (Figure 1f) also had a relatively good effect. For other types of treatment, the result was better compared to the initially untreated surface, but the positive effect was not as expressive. As with other types of bio-treatments [36], the effect of caffeine treatment on wetting can be explained by waterborne acrylate coating by reducing the contact angle of water wetting and increasing surface free energy, which positively affect the adhesion of coatings to wood [37,38]. Based on our further research, it was found that the contact angle of water wetting in beech decreased after adjustment from the original 63.7° to 52.6° and from 105.6° to 83.4° in spruce, whilst surface free energy increased from 49.15 to 53.70 $mN{\cdot}m^{-2}$ in beech and from 30.5 to 43.9 $mN{\cdot}m^{-2}$ in spruce [39,40]. Regarding the positive effect of FN-NANO® containing TiO_2 nanoparticles, it was documented that at certain concentrations—in particular, if TiO_2 nanoparticles penetrate deeper into the wood—the effect on the service life of the top-coating system may not be negative, as evidenced by certain works [24,25]. In fact, they can even reduce the degradation of the under-laying wood surfaces by capturing part of the incident UV and visible radiation spectra. The potential synergistic effect of a mixture of TiO_2 nanoparticles and caffeine on improving the service life of coating systems due to weathering was not demonstrated in this work. Only in the case of spruce was the overall appearance of the coatings slightly better after the combined treatment, whereas for beech it worsened (Figure 1d,e versus Figure 1f,g). Figure 1a shows the fully degraded surface of untreated native wood with a preserved layer of non-photodegradable cellulose [41], causing significant lightening of the test specimens during artificial accelerated weathering (Figure 1a).

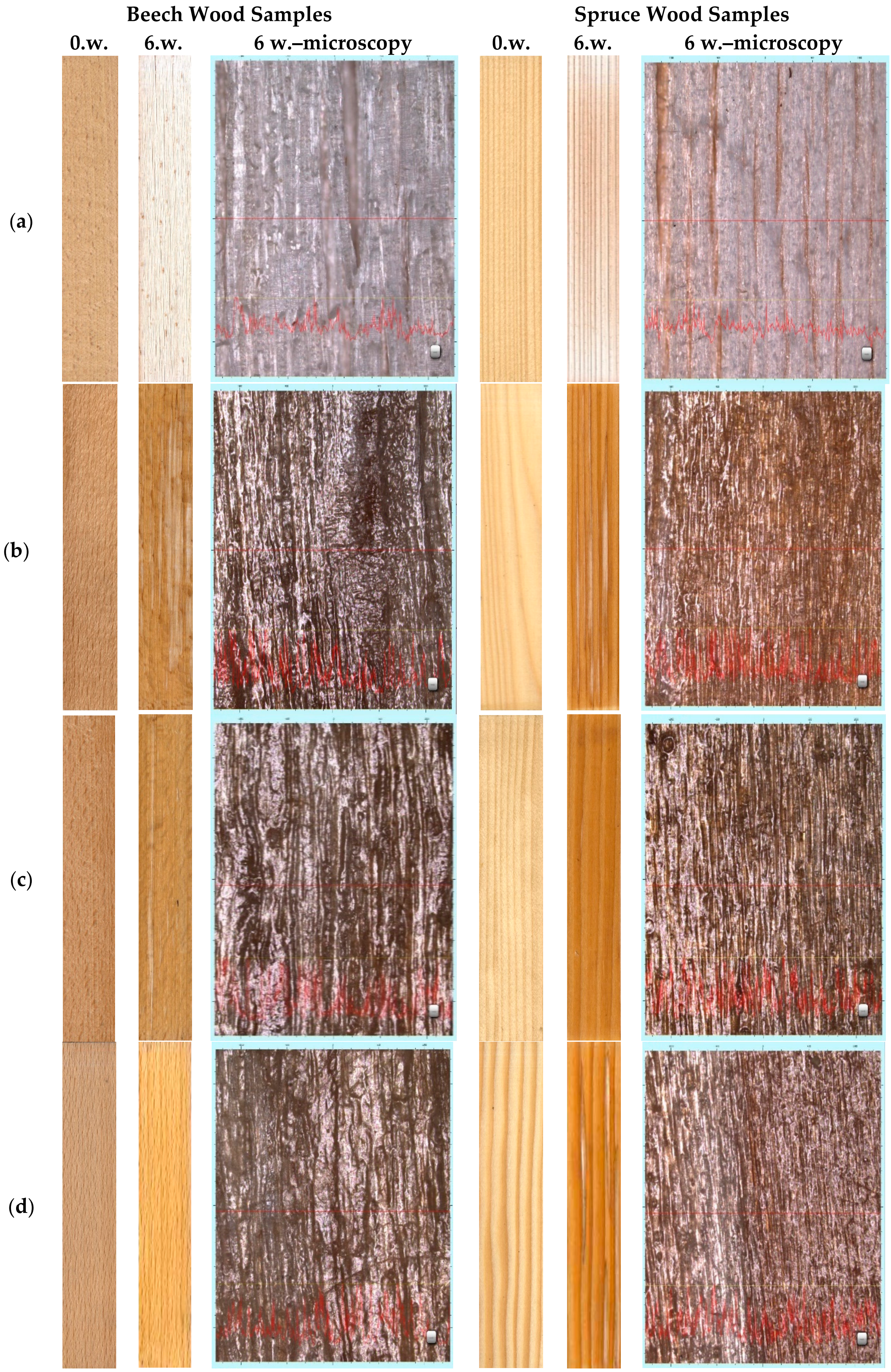


Figure 1. *Cont.*

(e)

(f)

(g)

Figure 1. Beech (left) and spruce (right) wood samples before (0.w.) and after accelerated weathering (AW) (6.w.). (**a**) Reference native wood (R-R); (**b**) acrylic coating on untreated wood (R-A); (**c**) acrylic coating on caffeine treated wood (5-A); (**d**) acrylic coating on wood treated with 10% FN-NANO® (1-A); (**e**) acrylic coating on wood treated with 15% FN-NANO® (2-A); (**f**) acrylic coating on wood treated with a mixture of 10% FN-NANO® and 1% of caffeine (3-A); (**g**) acrylic coating on wood treated with a mixture of 15% FN-NANO® and 1% of caffeine (4-A). Note: The real observed area of microscopic picture was 2500 μm × 2500 μm using 108-folder magnification.

Overall, the observed degradations of oil-based coating (Figure 2) were significantly higher compared to the degradations of acrylic coating (Figure 1). They were comparable for both beech and spruce wood without pre-treatment (Figure 2a,c), and the different types of treatments did not have a significant positive impact (Figure 2b,d). For this reason, colour changes, gloss changes, surface wetting, and mould growth were only subsequently evaluated for the acrylic coating system (Figures 3–5 and Table 2).

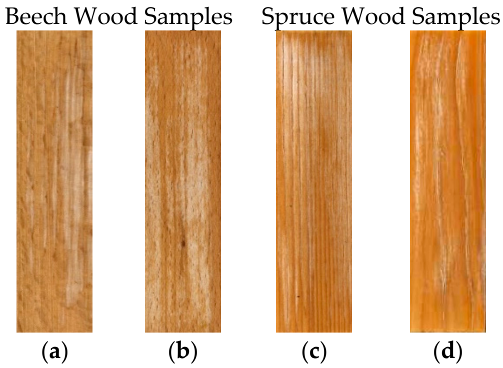


Figure 2. Oil-based coating after 6 weeks of AW. (**a**) Beech wood without pre-treatment (B-R-O); (**b**) beech wood with caffeine pre-treatment (B-5-O) achieved the best results from the tested oil-coated variants; (**c**) spruce wood without pre-treatment (S-R-O); (**d**) spruce wood with 10% FN-NANO® treatment achieved the best results from the tested oil-coated variants (S-1-O).

3.2. Colour, Gloss, and Water Contact Angle Changes during AW

During artificial accelerated weathering, there were significant colour changes in all of the tested surfaces (Figure 3). The changes were smaller for darker beech wood in cases where the coating film was preserved and there was no leaching of darker photodegraded lignin [42], and thus the overall colour change was lower than in comparable cases of overall lighter spruce wood (Figure 1). In contrast, for untreated wood, the ΔE^* was greater for beech, as only light-coloured cellulose remained in the surface zones [4]. Overall, the coated surfaces of the primary treated wood often had a higher overall colour change compared to the untreated surfaces. However, this was due to the disruption of the coating film of the untreated surfaces (R-A) (see also Figure 1) and the leaching of darker photodegraded lignins [43] and subsequent lightening, thus returning the colour to the original lighter shade of wood that had not been weathered. Of the pre-treatments that increased the overall service life of the coating film, they also had a partial effect on reducing the colour changes of 2-A for spruce and 1-A and less 2-A for beech. This confirms the positive effect of TiO_2 on the absorption and reflection of UV radiation, and thus reduces its impact on wood [13,44]. However, it was demonstrated that its effect and suitable concentrations vary for different types of wood (Figure 3). The decrease in gloss of the coatings sensitively predicts the degradation of its surface layers [45,46]. In terms of the tested treatments, a positive effect on the preservation of the original gloss was observed in caffeine-treated spruce wood (Figure 4) with an overall increased service life (Figure 1). The same was observed in beech treated with a higher concentration of TiO_2 nanoparticles B-2-A (Figure 4) with an observed positive effect on colour fastness (Figure 3), as well as the overall service life of the top acrylate coating system (Figure 1). The contact angle of wetting and the reduction of hydrophobicity of the surfaces was observed mainly in untreated photodegraded wood, particularly in beech (Figure 5). Compared to other pre-treatments, a slight decrease in coated samples was only observed for S-1-A, which also confirmed the observed effect on reducing the overall life of the coating film (Figure 1). The hydrophobic effect was otherwise preserved in the samples where the top layer of the coating film was already disturbed (Figure 1), and there were only slight differences in the variability of the observed values (Figure 5). This also corresponds to the results of the work [46], where the preservation of hydrophobicity also did not correspond to the disruption of the overall appearance of the tested oak wood samples. Overall, a relatively high variability of the achieved values was observed (Figures 3–5). This is caused by several factors. The first factor is the variability of the measured values of individual samples in the set due to the inhomogeneity of wood as a material of natural origin. The second reason is the increase in inhomogeneity of some tested surfaces due to weathering, as was documented in Figure 1. It was confirmed that the quality of the coating after aging can be evaluated overall only by a complex of evaluated characteristics, where the overall visual evaluation of the coating film must not be neglected [7].

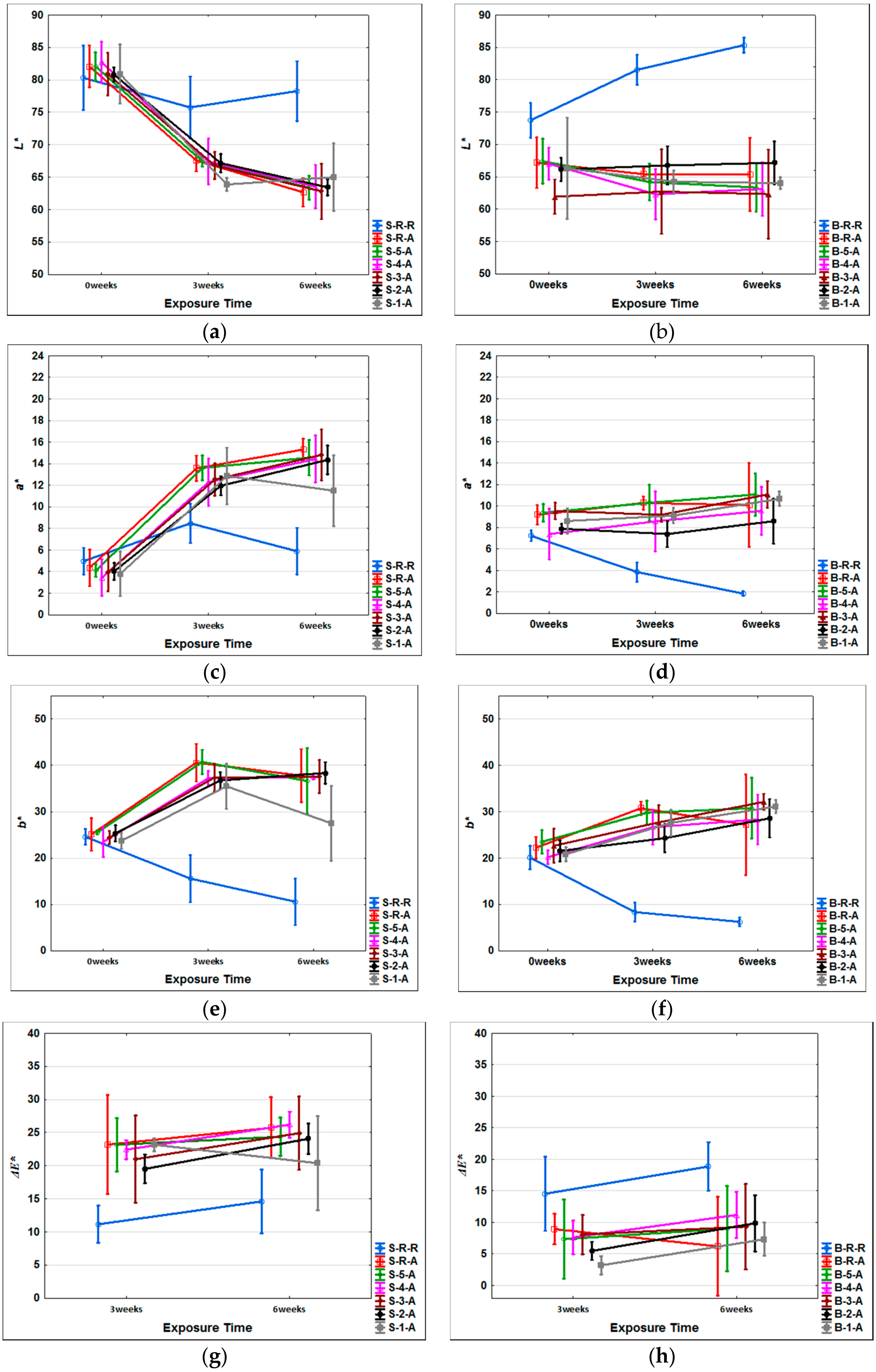
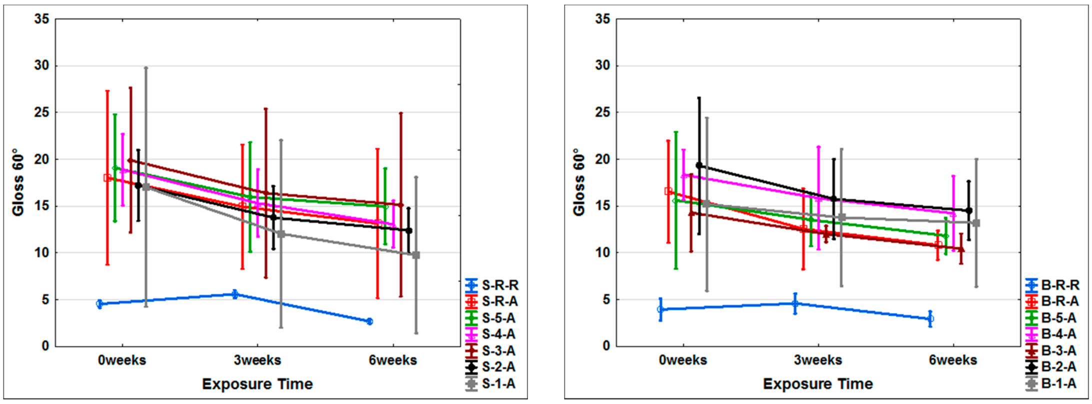
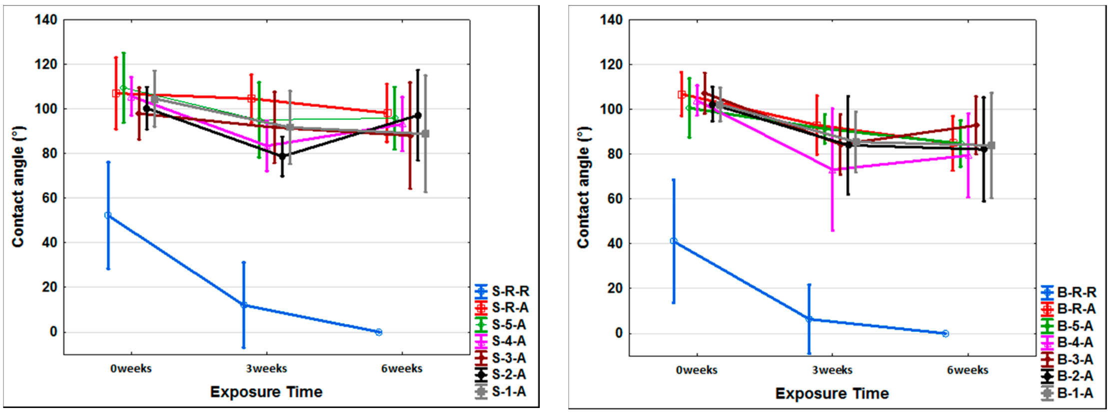


Figure 3. Colour changes in tested wooden surfaces during AW: (**a**) L^* changes on spruce; (**b**) L^* changes on beech; (**c**) a^* changes on spruce; (**d**) a^* changes on beech; (**e**) b^* changes on spruce; (**f**) b^* changes on beech; (**g**) ΔE^* changes on spruce; (**h**) ΔE^* changes on beech.



(**a**) (**b**)

Figure 4. Gloss changes in tested wooden surfaces during AW: (**a**) Gloss changes on tested spruce samples; (**b**) Gloss changes on tested beech samples.



(**a**) (**b**)

Figure 5. Water contact angle changes in tested wooden surfaces during AW: (**a**) Water contact angle (°) on tested spruce samples; (**b**) Water contact angle (°) on tested beech samples.

3.3. Mould Growth Tests

Moulds pose a significant risk of damage to surface-treated wood products outdoors, and moulds have a significant impact on their appearance [5]. There are various methods for testing mould growth on wood and treated wood [3,4,47]. The results can vary depending on the method used [3]. One of the possibilities is to use a free fall of mould spores into a prepared nutrient medium and subsequent insertion of test specimens [48]. This method provides more variable results similar to tests in natural conditions [4]. In this work, the highest rate of observed mould growth from the tested test samples of each series was evaluated (Table 2). This increases the likelihood that the level of risk will be more accurately verified in real exposures, where different species of mould may begin to grow under appropriate conditions [47], or a combination thereof.

In general, compared to spruce, higher mould growth was observed on the surface of the tested coated beech samples (Table 2). This can be explained by the higher natural bio-resistance of spruce wood [27] and also by the better durability of the coating system after AW on spruce wood (Figure 1). Before and after AW, treatment with a 2% caffeine solution (5-A) with a biocidal effect, which was also confirmed in other works, had a positive effect on beech and spruce wood [2,23]. In comparison with the work of Kwaśniewska-Sip et al. [49], a better biocidal effect was achieved due to barrier protection of treated wood with a coating that effectively prevented caffeine leaching during 6 weeks of artificial accelerated weathering. In several cases, a positive effect of treatment with TiO_2 nanoparticles was visible [8]—in particular, at a concentration of 15% FN-NANO® (2-A and 4-A), more so in samples after AW (Table 2). This may be related to the greater exposure of the TiO_2-treated layer connected with the degradation of the acrylate coating, which in itself did not show a significant anti-mould effect. A similar result was observed for spruce wood, but the growth of mould was generally lower than for beech wood. The result confirms that only higher concentrations of TiO_2 nanoparticles have sufficient fungicidal activity, even if the specific amount required is affected by the co-modifying agent [18,50].

Table 2. Maximum mould growth on tested samples before (R) and after weathering (W).

Beech	Degree of Moulds Growth (% of Surface Covered by Moulds in Parenthesis)				Spruce	Degree of Moulds Growth (% of Surface Covered by Moulds in Parenthesis)			
	Time of Moulds Exposure					Time of Moulds Exposure			
	1 week	2 weeks	3 weeks	4 weeks		1 week	2 weeks	3 weeks	4 weeks
B-R-R-R	0 (0)	4 (80)	4 (90)	4 (90)	S-R-R-R	0 (0)	3 (50)	4 (65)	4 (60)
B-R-R-W	0 (0)	3 (50)	4 (60)	4 (75)	S-R-R-W	0 (0)	3 (50)	4 (60)	4 (90)
B-R-A-R	0 (0)	3 (50)	3 (50)	4 (75)	S-R-A-R	0 (0)	3 (40)	4 (55)	4 (65)
B-R-A-W	0 (0)	4 (75)	4 (75)	4 (75)	S-R-A-W	0 (0)	4 (75)	4 (80)	4 (95)
B-5-A-R	0 (0)	1 (5)	1 (5)	2 (10)	S-5-A-R	0 (0)	0 (0)	0 (0)	1 (5)
B-5-A-W	0 (0)	0 (0)	0 (0)	2 (25)	S-5-A-W	0 (0)	0 (0)	0 (0)	0 (0)
B-4-A-R	0 (0)	0 (0)	0 (0)	2 (25)	S-4-A-R	0 (0)	0 (0)	0 (0)	2 (10)
B-4-A-W	0 (0)	0 (0)	0 (0)	1 (5)	S-4-A-W	0 (0)	0 (0)	0 (0)	1 (1)
B-3-A-R	0 (0)	4 (75)	4 (85)	4 (100)	S-3-A-R	0 (0)	0 (0)	0 (0)	2 (10)
B-3-A-W	0 (0)	0 (0)	0 (0)	2 (25)	S-3-A-W	0 (0)	0 (0)	0 (0)	1 (1)
B-2-A-R	0 (0)	4 (75)	4 (75)	4 (100)	S-2-A-R	0 (0)	0 (0)	0 (0)	3 (35)
B-2-A-W	0 (0)	0 (0)	0 (0)	1 (5)	S-2-A-W	0 (0)	0 (0)	0 (0)	1 (1)
B-1-A-R	0 (0)	4 (75)	4 (75)	4 (100)	S-1-A-R	0 (0)	0 (0)	0 (0)	1 (5)
B-1-A-W	0 (0)	0 (0)	0 (0)	2 (25)	S-1-A-W	0 (0)	1 (5)	1 (5)	1 (5)

Note: degree 0 represents the best results; degree 4 represents the worst results.

Research also confirms that the protection of beech wood against bio-attacks by moulds outdoors using coatings is more difficult. In addition to its lower bio-resistance, its greater permeability may also have an effect [51], and thereby increased demands on the amount of applied protective substance, which does not provide sufficient film-forming protection on the wood surface. However, it is encouraging that higher concentrations of the active ingredient TiO_2 used in this research (sets 2-A and 4-A) represented a relatively effective alternative against mould growth (Table 2).

4. Conclusions

Transparent coatings on wood outdoors do not have sufficient service life and colourfastness due to more significant penetration of sunlight into the coating film and the base wood. Another significant factor causing degradation of coatings in humid environments are moulds. The possibility of increasing the durability and resistance to mould attacks in acrylic and oil coating on beech and spruce wood was investigated. Initial treatments of wood by dipping in a 2% solution of caffeine and various concentrations of commercial FN-NANO® containing TiO_2 nanoparticles and their mixtures were used. A significant positive effect of caffeine treatment on the service life of the acrylate coating system during accelerated artificial weathering was observed in both types of tested woods. The 15% FN-NANO® dispersions treatment also showed good efficiency. The combined effect of a mixture of caffeine and FN-NANO® had no significant positive effect. No improved quality of the oil coating was observed using the initial wood treatments. Degradation by moulds was significantly reduced when the wood was initially treated with a 2% caffeine solution. Higher concentrations of FN-NANO® dispersion had a positive impact—in particular, on samples degraded for 6 weeks in a UV chamber. Based on the results, it is possible to recommend the initial treatment of spruce and beech wood with a 2% caffeine solution or 15% solution of FN-NANO® dispersion containing TiO_2 nanoparticles in order to increase the overall service life of transparent acrylic coating in exterior applications.

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