LUT UNIVERSITY
LUT School of Energy Systems
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INFLUENCE OF WEATHERING CONDITIONS ON THE PERFORMANCE OF CERAMIC AND POLYMERIC COATINGS ON WOOD

Examiner(s): Professor Timo Kärki
D. Sc. Marko Hyvärinen

ABSTRACT

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Influence of weathering conditions on the performance of ceramic and polymeric coatings on wood

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Nowadays, the application of human-made construction materials leads to a tremendous amount of energy consumption and non-recycled waste generation. The quantity of harmful chemicals and other components used in construction is astonishing and continues to increase constantly. Wood is one of the organic construction materials and the only one considered a renewable one. Therefore, wood becomes a preferable construction material to build safe low-energy structures which do not cause detrimental environmental impact.

However, the building of wooden prefabricated residential units is mainly limited by legislation, standards, and safety requirements. The fact that wood can ‘’breathe’’, absorb, and release moisture makes this material not very durable and, consequently, not always relatively reliable. Therefore, many new different coatings and other technologies developed nowadays to achieve the greater mechanical properties of wood operated under weathering conditions such as moisture, UV irradiation, fungi, et cetera.

The main target of this thesis was to assess and compare the durability of ceramic and polymeric wood coatings, which are developed to enhance wood resistance to ambient conditions and, as a result, prevent wood structure degradation. The artificial accelerated weathering and cycling tests have been carried out to imitate environmental conditions under which the wood should be operated. The tape method was performed to estimate the adhesion properties of the coatings under study. The most favorable conditions for application of ceramic and polymeric coatings have been revealed, and the potential improvements which can be done in this field of study also have been suggested.

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LIST OF ABBREVIATIONS AND SYMBOLS

$DE*$	indicator of color changes
ΔE	total color difference
ΔL	the change of surface lightness
ASTM	American Society for Testing and Materials
AWC	American Wood Council
CAs	Contact angles
CAGR	Compound Annual Growth Rate
CLT	Cross-laminated timber
CuO	Cupric oxide
DTG	Differential thermogravimetry
FRT	Fire Retardant Treated
FT	Freeze-thaw cycles
IBC	International Building Codes
LVL	Laminated veneer lumber
MA	Maleic anhydride
MAPP	Maleic anhydride modified polypropylene
MF	Melamine-formaldehyde
MoE	Modulus of Elasticity
MTMS	Methyltrimethoxysilane
Na_2SiO_3	Sodium metasilicate
NPs	Nanoparticles
PA	Phthalic anhydride
PF	Phenol-formaldehyde
PMHS	Poly(methylhydrogen) siloxane
PU	Polyurethan
SA	Succinic anhydride
SFE	Surface free energy
Si	Silicon

SiO_2	Silicon dioxide
SNPs	Silicon dioxide nanoparticles
SSOCE	Silica/silicone oil complex emulsion
TG	Thermogravimetry
TiO_2	Titanium(IV) oxide
UV	Ultraviolet
ZnO	Zinc oxide

1 INTRODUCTION

Timber and other wooden-based products have been applied as the construction material around the world for millennia. Timber, as a natural organic material, is typically used to construct a significant number of structures, including but not limited to bridges and housings. Figure 1 presents that interior wood products, a great range of wooden furniture, doors and windows, sports equipment, and some art pieces are also considered forest industry products. (Oberhofnerová et al. 2018)

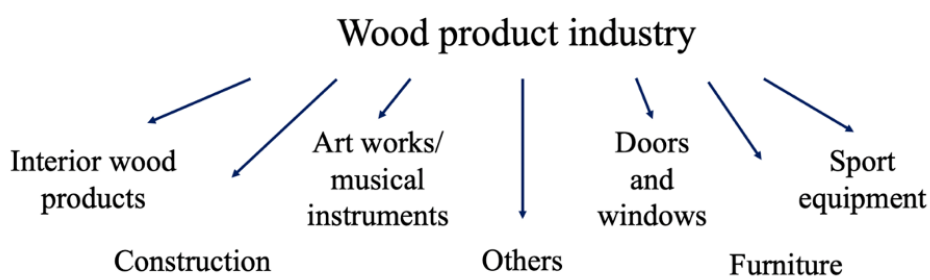


Figure 1. Products of the wood industry (Salim & Johansson 2016).

Although wood is a highly used and competitive material, its usage faces problems associated with constant effect of temperature fluctuations, insects' attacks, moisture absorption, fungi, ultraviolet (UV) irradiation exposure, fire, natural resources scarcity, and et cetera. All these factors can worsen mechanical properties and durability of the wooden structures. Currently, a huge number of research projects are devoted to both the study of wood microstructure changes caused by influence of weathering conditions and the development of preservative treatments for timber such as the application of protective coatings and fire retardants which may help to prevent the adverse impact on the wood by improving its resistance. The timber is likely to be one of the most preferred construction materials in the nearest future in connection with acquired knowledge. (Abimaje & Baba 2014)

1.1 Research questions

Research questions of this thesis are based on the effect of coatings on wood to provide greater resistance of wood products against the influence of weathering conditions. Firstly, there is a need to determine the main fields of wood application to define its basic operating conditions. In addition, to determine the main advantages and disadvantages of this type of construction material. What possible problems can happen during the usage of wood for various construction purposes? Can these problems be solved by using protective coatings? Finally, how long can the coatings under study resist external influences?

When the main drawback of timber application is determined as an occurrence of structural degradation under ambient conditions, the possible solutions which may help to achieve higher resistance of wood products to damaging influence caused by moisture absorption, constant thermal cycles, UV absorption, and the reduction of mechanical properties should be considered thoroughly. The main goal of this thesis is to find out the most suitable and effective types of wood coatings that allows to overcome highly discussed problems and to produce high-quality research work based on detailed literature review and experiments which were conducted in LUT laboratories.

1.2 Research problem

Currently, wood is one of the most widely used natural building materials in the world. Many valuable characteristics such as low heat and electrical conductivity, rather high strength, and others make wood prevalent building material. However, the application of timber for construction purposes can be limited due to structural damage, which is basically caused by environmental conditions. Great level of water ingress results in wood swelling, the impact of UV irradiation leads to wood discoloration, constant temperature cycles are responsible for low mechanical properties of the studied material due to wooden structure degradation. Many other factors make consumers replace wood with other construction materials such as metal or, for example, composites. Thus, the main problem of this research is the influence of weathering conditions, which results in a major effect on the wood structure of construction units.

1.3 Aim and scope of the thesis

In this study, the areas of wood material applications have been investigated. Requirements and standards which should be followed to use wood as a construction material also have been studied. Different treatments and chemical modifications of a wooden structure that allow achieving its greater performance even after weathering conditions exposure have been defined. Performance was evaluated based on changes in durability of the coated samples. The main aim of the master's thesis was to assess the durability of protective wood coatings by estimation of changes in its adhesion characteristics caused by moisture, UV irradiation, and other weathering conditions.

This work does not include experiments of other types of coatings used nowadays. The focus was on the research of ceramic and polymeric coatings characteristics under the influence of environmental conditions.

1.4 Research method and framing

The theoretical framework corresponds to the selected research methods, research questions presented above, and the material provided to answer them.

The real-world practical contribution has not been executed during the current stage of this study. In the paragraphs representing the background and basics, scientific papers and researches were mainly used as sources. Only high-quality peer-reviewed scientific papers were selected as sources. A quick look at the contents and selecting the most suitable scientific paper according to the focus of this work content have been carried out. Most of the sources are widely cited and have been found with the help of the LUT Primo Academic Library's search service.

2 APPLICATION OF WOOD

The modern wood materials market consists of such products as a veneer, plywood, engineered wood and reconstituted wood products produced by entities (companies, traders, organizations, and partnerships). This market is likely to rise from a compound annual growth rate (CAGR) of 8.07 % in 2021 to 315.7 billion dollars in 2023 and 256.9 billion dollars in 2020. The worldwide manufactured wood materials market is also expected to grow till 2030 and can be equal to 525.4 billion dollars. (Ng'andwe et al. 2015)

2.1 Fields of wood application

Nowadays, wood for construction purposes is a rather popular and widely used material around the world. It is usually applied in building both large and small constructions, where the most common ones are houses and bridges. Processed wooden beams and planks are called lumber or timber and basically used for construction needs. The main difference between them is that lumber is smaller in width and thickness compared with timber. (Ramage et al. 2017)

Mostly, tall wood buildings and bridges are produced by "mass timber" material. It is a type of wooden-based composites that includes glue-laminated timber called glulam, structural composite lumber, and cross-laminated timber (CLT) presented in Figure 2. Glulam is a massive beam with the structure of stacked lumber sticked along the grain. Structural composite lumber is basically made from wood veneers or flakes placed in a straight line with the parallel direction in respect to the grain. For example, laminated veneer lumber (LVL) is a composite with a structure composed of veneers. (Jakes et al. 2016)

Figure 2. Mass timber. CLT, LVL, and glulam presented from the left to the right sides (Jakes et al. 2016).

CLT is also a type of wooden blocks, namely, massive panel products created by lumber layers. The orientation of these layers is 90° in relation to the previous layer. The thickness of these massive products can be changed from about 50 mm to 500 mm. Modern manufacturing methods make it possible to produce CLT up to 18 m long. Eventually, ready-made constructions can be delivered to the customers with all holes for doorways and openings for windows. Moreover, the orthogonal, laminar structure and its ability to bear loads in- and out-of-plane make it possible to apply CLT as a full-size wall and floor elements. (Brandner et al. 2016; Jakes et al. 2016; Mbereyaho et al. 2019)

This hard and solid material as wood is an excellent option for furniture production due to its high durability. Furniture can be made by both hardwood such as oak, walnut, cherry and softwood (for example: pine, spruce) material because they can provide products with rather important characteristics - stability and reliability. Endurance also makes wood rather popular and easy in maintenance among consumers. Occasionally, it is required to carry out varnishing, polishing, and coating processes if there is a need to prolong a term use. And it is worth noting that these functions do not take much time and effort (Namichev & Petrovski 2019).

Wood plays a significant role in several recreational activities or athletic pastimes too. Probably in every sport field some sorts of wooden material are used. Both whole pieces of wood and fractional ones are typically applied for sports equipment manufacturing. For instance, baseball bats are made from a variety of woods like maple, ash, hickory, or bamboo, while the most modern skateboards are produced with sugar maple. Therefore, wood material is considered to be the best available on the sports facilities market. In addition, artworks such as the frames for canvases, statues, sculptures, carvings, and other decorative objects can be made by wood as well, for instance, pine, maple, and cherry wood. In addition, wood as a material is required for the production of musical instruments (piano, violin, drums, guitar, and others) due to making a perfect tune. For example, mahogany, maple and ash wood are very popular materials for guitars production. (Ramage et al. 2017)

2.2 Comparison of wood with other construction materials

Construction building is a complicated and multi-disciplinary field of study. The decisions of material selection are affected by different factors and parameters such as economic, type of building, designing, and the impact on ecology. Today, the application of wood in building is supported by strong arguments. In some cases, it is even more preferable than steel, plastics, and others. First of all, wood has excellent mechanical properties. Lightweight characteristic does not prevent the wood from outperforming steel in tensile strength characteristics (or self-support length). Wood also provides with a natural electrical conductivity resistance and a high level of sound absorption. Besides, timber is a sustainable building material. The application of this environmentally friendly, reusable, flexible in usage, and durable material helps to reduce carbon emissions during the manufacturing process. Moreover, the energy loss is considerably less in respect to metal and concrete. The comparison of wood with the most widely applied construction materials is presented in Table 1. (Kuzman & Grošelj 2012; Nässén et al. 2012)

Table 1. Impact of metal and concrete compared to wood on environmental issues (Nässén et al 2012).

Environmental impact compared to wood	Embodied energy	Climate impact	Negative impact on air quality	Negative impact on water	Resources consumed by weight	Waste produced
Metal	+53%	+23%	+74%	+247%	+14%	-21%
Concrete	+120%	+50%	+115%	+114%	+93%	+37%

It can be inferred from Table 1 that the embodied energy indicator of concrete consumed during the building process is twice higher than the same indicator for metal. Wooden buildings use the least embodied energy and have the lowest results of embodied energy. As for climate issues and air quality, the worst figures are shown for concrete material as well. However, the negative impact on water is greater during the usage of metal as a construction material. Besides, waste production during building processes is lower for metal and higher for concrete usage. Finally, it can be concluded that wood is a preferable material compared with concrete and metal due to the less hazardous effect on the environment.

Nowadays, different mathematical models have been created to make a rational selection concerning the most appropriate material. For example, in (Kuzman & Grošelj 2012), the decision tree consists of different criterions such as quality of living, construction costs and time, design, depreciation costs, and embodied energy was built to compare and choose the best material among wood, steel, concrete, and brick. The final results for different types of construction materials are presented in Figure 3.

Figure 3. Priority of different types of materials for construction purposes (Kuzman & Grošelj 2012).

The priority indicator of the wood frame was the greatest and constituted 0.26. The solid wood construction indicator was slightly lower and equalled to 0.22, while concrete and brick construction indicators were probably the same - 0.20 and 0.19, respectively. The steel frame construction showed the poorest result. Its priority indicator was about 0.13. Such results can be explained by the positive trends concerning low-carbon wood construction, low-energy consumption, low-emission building, and rather good safety aspects. The application of timber in the building can decrease the carbon footprint on the global level.

However, the ignitability of wood still set limits to its increased use as a construction material by restrictions provided by practically all countries in the world. These building regulations mainly apply to higher and larger buildings. Many scientific research projects devoted to the fire behaviour of wood structures have recently been performed worldwide to determine the basic principles of reliable timber application.

2.3 Fire protection in wood constructions. Legislation

The main precondition for broad usage of wood as a construction material is adequate fire resistance. Building codes should be followed to ensure the desired flame protection level regardless of the applied materials in terms of fire safety during building. Wood constructions also should meet strict standards to obtain high efficiency, or otherwise, the timber is replaced with other construction materials. All these restrictions and requirements are described in the guidelines, which content can vary slightly in respect to the considered country. For example, “Fire Safety in Timber Buildings – Technical Guidelines for Europe” presents standards that should be followed by European countries when the International Building Code (IBC) refers to the Code Conforming Wood Design Series developed by the American Wood Council (AWC). (Östman, Brandon & Frantzich 2017)

The main idea of building codes implemented for fire safety reasons is the ranging of buildings in terms of their occupancy and type. According to this classification, the building codes limit construction areas and heights. Basically, there are five different types of buildings classified by the selected construction material and demanded level of refractoriness considered in Table 2. The first two are presented as fire-resistant construction (Type I) and noncombustible construction (Type II). Both of them limit the usage of combustible materials as building elements. The selection of wood for building purposes can be permitted only by the Type III (ordinary), Type IV (heavy timber), and Type V (light-frame). The possibility of wood application as a construction material of ordinary products such as interior walls, roofs, and other small wood members, is described in Type III. In Type IV buildings, wood beams, floors, and columns should follow specific dimensions, and all closed spaces are forbidden. In both highly mentioned types, there is a requirement to make exterior walls from noncombustible materials or fire-retardant-treated (FRT) wood. FRT is allowed in Type III assemblies when a rating concerning fire resistance level constitutes 2 hours or less. The last one, Type V, all parts such as walls, floors, roofs, and others can be of any dimension lumber. Moreover, combustible materials may be applied for the exterior walls building. All these types except Type IV are subdivided into two depending on the fire resistance ratings: A (protected part) and B (unprotected part). For instance, in Type V-A, the majority of structural elements obtains 1 hour in fire-resistance rating. However, there are no fire safety needs for Type V-B which corresponds to unprotected light structures. (White & Dietenberger 2010)

Table 2. Requirements of fire-resistance rating for building units - hours (International Code Council. International building code. 2018).

BUILDING ELEMENT	TYPE 1		TYPE II		TYPE III		TYPE IV	TYPE V	
	A	B	A	B	A	B	HT	A	B
Primary structural frame (see Section 202)	3[a,b]	2[a,b]	1[b]	0	1[b]	0	HT	1[b]	0
Bearing walls Exterior	3	2	1	0	2	2	2	1	0
Interior	3[a]	2[a]	1	0	1	0	1/HT	1	0
Nonbearing walls and partitions Exterior	See Section 602.4.6								
Nonbearing walls and partitions Interior	0	0	0	0	0	0	See Section 602.4.6	0	0
Floor construction and associated secondary members (see Section 202)	2	2	1	0	1	0	HT	1	0

Other factors such as the distance of fire separation from the plotline or a centerline of an object also are included in the demanded fire resistance ratings for exterior walls. These requirements are considered to decrease the chance of external fire exposure. In addition, both untreated and fire-retardant-treated wood are regarded as combustible materials in accordance with their performance presented in the American Society for Testing and Materials (ASTM) E 136 test. However, in some specific applications, when there is a need to use noncombustible wood, the FRT wood can be allowed by building codes permission. Specific timber treatment and chemical modification procedures are determined for FRT wood application in such cases. (Buchanan & Frangi 2014)

Finally, there is an assumption that mechanically or chemically modified wooden-based products are likely to hold the main market share in the future. Their ability to withstand the detrimental weathering conditions and to enhance fire resistance properties is likely to be significantly higher than the ability of non-treated timber. Therefore, better durability, mechanical and thermal properties will make treated timber a rather competitive material on the market. (Aseeva, Serkov & Sivenkov 2014)

3 TYPES OF PROTECTIVE COATINGS APPLIED FOR WOOD CONSTRUCTION MATERIALS

As has been described in chapter 2, currently, wooden materials and structures have been widely used for a massive number of purposes due to their unique characteristics, for example, perfect electrical insulation, relatively easy processing, and rather high mechanical specific strength. Unfortunately, the usage of this material can be limited because of moderately low natural durability, especially within outdoor conditions. Therefore, there is a certain growth of mechanically or chemically modified wood-based products due to the possibility to achieve desirable properties for better operation of wood structures. (Xie et al. 2013; Zhang et al. 2020)

3.1 Types of chemicals

Several research papers have been devoted to this field of study with the main focus related to the ability of treated wooden structures to resist aggressive environmental effects (mechanical properties, moisture, ultraviolet radiation, fungi, fire resistance). The most common types of chemicals which can be used in coatings are anhydrides, isocyanates, silicon dioxide, aldehydes, epoxides, and et cetera. (Geradin 2016)

3.1.1 Anhydrides

It was stated in the studied scientific papers that wood properties (such as poor dimensional stability because of the moisture absorption and low durability due to decay caused by fungi) could be improved by chemical modification of wood surface using etherification, esterification and cyanoethylation reactions. (Efanov 2001; Sereshiti & Rovshandeh 2003)

One of the most usable ones is esterification. Esters are often formed by reaction between lignocellulosic materials and carboxylic acids/ acid anhydrides. The significant benefit of many acylations with anhydrides is that there is no need to use catalysts and organic solvents during the reaction, which can be a reason for a bad smell or human diseases. Currently, phthalic (PA), maleic (MA), and succinic (SA) anhydrides are applied to esterify the timber with the primary aim to create thermoformable products. (Hassan & Peppas 2000; Li et al. 2000)

For instance, in Ruxanda, Teacă & Spiridon (2008), the thermogravimetry (TG) and differential thermogravimetry (DTG) curves have been presented for chemically modified sawdust. During the experiment, curves shifted to the zone of higher temperatures. This fact reveals an improvement in thermal stability of the anhydride-modified wood samples compared with non-treated ones. This effect becomes more evident when the reaction time is grown.

To sum up, the esterification modification of anhydrides can improve the technical aspects of wood samples. For example, an acetylated wood (using acetic anhydride) has a rather high dimensional stability and more superior decay resistance. However, the residual acetic acid is retained, and it may later cause the corrosion of the ferrous elements.

3.1.2 Isocyanates

Chemical modification of wood products with hydroxyls with isocyanates consists of a nitrogen-containing ester formation. Exposition of phenyl isocyanate at 100–125 ℃ can lead to the higher dimensional stability of timber and better mechanical strength with a slight change in color compared with non-modified wood products. The chemical reaction between wood and chemicals is presented in Figure 4. (Rowell & Ellis 1984)

$$\text{Wood–OH} + \underset{\text{Isocyanate}}{\text{R–N=C=O}} \rightarrow \text{Wood–O–C(=O)–NH–R}$$

Figure 4. Reaction of wood product with isocyanates (Rowell 1983).

Treatment of the wood components such as cellulose, hemicellulose, and lignin by reacting hydroxyl groups in wood with isocyanates can enhance wood bio protection properties. As a consequence, a wood-urethane derivative is created. During this procedure, no toxic residues are retained on the wood surface because the chemicals are grafted to the timber matrix. This approach becomes widely used due to the possibility of obtaining the desired changes in wood properties. For example, many chemical impregnation techniques can lead to worse product characteristics due to leaching and weathering. While the permanence of the bonding processes makes chemically modified wood superior to chemical impregnated ones. (Williams & Hale 2003)

However, it is worth mentioning that isocyanates are considered as a toxic group. Therefore, it is vital to define isocyanates' impact on ecology aspects to produce sustainable and environmentally friendly timber treatment processes. First of all, the isocyanates content should be investigated in generated sewage, especially during solvent-based processes. Secondly, the emission of volatiles during modification does not exceed the critical level. Because even at low concentrations, isocyanate-based volatiles can lead to human diseases, especially during the permanent exposition. In order to improve the environmental issue of chemical modification processes, they have to be conducted in a more efficient manner and follow the Principles of Green Chemistry. Long-lasting periodic batch procedures, the necessity of starting and stopping them, and high usage of organic solvents should be continuously replaced by uninterrupted processes. All these factors make isocyanates modification of wood rather complex. (Hejna et al. 2020)

3.1.3 Aldehydes

Research papers focused on the chemical modification of wood samples with melamine-formaldehyde (MF) resins became widely spread in European countries due to satisfactory results concerning dimensional stability and high resistance degree to fungi. A variety of studies have presented that modification with melamine-formaldehyde resin may also enhance compressive strength and hardness characteristics. Besides, wood products which were treated with phenol-formaldehyde (PF) resins may improve the dimensional stability and prolong the operation period of the timber products. For example, modification with PF-resin causes the growth in modulus of elasticity (MoE) and bending strength of plywood. At the same time, the impact bending strength characteristics decline. (Gindl, Zargar-Yaghubi & Wimmer 2003; Kielmann, Militz & Adamopoulos 2012; Bicke, Mai & Militz 2012; Evans et al. 2013; Sint et al. 2013; Kielmann et al. 2014; Bollmus, Beeretz & Militz 2020)

The main disadvantages of chemical modification with aldehydes are the significant costs and the low crack resistance of wood samples during cycling tests. None of the highly described impregnation modification techniques allow to achieve the desired results. (Sandberg, Kutnar & Mantanis 2017)

3.1.4 Epoxides

The reaction of simple epoxides with wood cell wall polymers proceeds rapidly. No by-products are produced during the reaction, especially in dry wood, and the formed chemical bonds are stable. Moreover, there is an evident increase in wood sizes. It can be explained by the fact that the reaction occurs in the cell wall. The volume of treated wood samples is proportional to the quantity of added chemicals. When there is a need to achieve better dimensional stability, high levels of chemical additives are applied. In such cases, the procedure is rather expensive and is likely to see the only limited industrial application. Overtreatment causes a lower dimensional stability because of cell wall damage. (Jebrane et al. 2015)

The chemical modification of wood with epoxides is predicted to be quite popular in the future due to better fire resistance properties of treated final products. For example, fire retardant substance is basically bonded firmly to the wood cell wall by the epoxides. A high enough level of chemical additives can lead to dimensional stability, a satisfactory degree of biological attack resistance, high fire resistance level, and no additional costs are required in such case. To overall, the application of epoxides chemical modification of wood can allow enhancing fire retardancy, color and dimensional stability, resistance to fungi attacks and UV stabilization. (Rowell 2012)

3.1.5 Alkyl chlorides

Hydrochloric acid is the by-product of the reaction which typically occurs between alkyl chlorides and wood structure presented in Figure 5.

$$\text{Wood–OH} + \text{R–Cl} \rightarrow \text{Wood–O–R} + \text{HCl}$$

Alkyl Chloride

Figure 5. Reaction of wood product with alkyl chlorides (Rowell 1983).

As a consequence, the strength properties of the chemical modified wood are poor. The result of better dimensional stability of treated timber is caused by the reaction of allyl chloride in pyridine, but on soaking in water, it is lost. Also, control agent's composition for protecting timber against fungi which causes mildew is typically contained alkyl chlorides as well (Gillis et al. 2015).

3.1.6 Silicon dioxide

With awareness-raising in environmental vulnerability and at the same time need to obtain a long duration of wood products operation, manufacturing technologies and methods have been advanced to enhance wood properties without the addition of toxic chemicals (Rowell 2009, Rowell 2012, Gérardin 2016). Such chemicals can be silicates and silicon compounds classified as non-toxic and initially created as a salt of silicic acid form. Moreover, there is a great diversity of organic and inorganic silicon compounds that may be used as additives for protective coatings of wood. (Temiz et al. 2006)

Impregnation wood with silicon is one of the most effective ways to improve the mechanical characteristics of wood and prolong the operation time of wooden products. During mineralization, the cell wall of wood decomposes, and the silicon dioxide (SiO_2) is deposited subsequently on the wood surface. The structure of the silicon dioxide molecule is presented in Figure 6. The SiO_2 molecule is shown as a three-dimensional network of a silicon ion surrounded by four oxygen atoms. The Si-O bond is approximately 0.162 nm in length, while the basic distance for two oxide bonds is 0.262 nm. (Doubek et al. 2018)

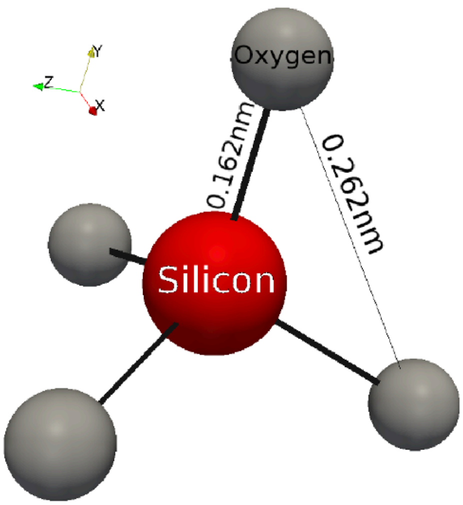


Figure 6. Silicon dioxide molecular model (Astsatryan et al. 2015).

Millions of years are needed to implement natural mineralization procedures. Therefore, artificial mineralization is preferable, and it can be carried out rapidly under extraordinary conditions. Artificial treatment of timber with silicate ceramics causes the same changes in structure as in natural mineralization. The mineral substance or particles enters the wooden-based product structure and then remain in lumens, or also can penetrate into the cell walls to react chemically with components. (Akahane et al. 2004; Hill 2006; Rowell 2006; Kim et al. 2009)

Currently, a great variety of types of organic silicones exist on the market. The widely applied in chemical modification of timber are monomeric and polymeric silicones. Despite the penetration of small silicon dioxide molecules into the wood structure performs well, the appeared connections are not strong and furthermore firstly react with water. During this reaction, silanes are created and then interact with timber products (OH groups). Other experiments were done with water glass, sodium metasilicate - Na_2SiO_3. Water glass (aqueous sodium silicate solution) is basically used substance nowadays in practice. The main component is glass sand which is treated with alkaline fluxing agents at a temperature interval between 1400 and 1600 °C. Commonly water glass is applied for producing a coating on the wood products such as industrial floors and fireplace linings to obtain special fire-resistant characteristics. It also can be coated to save colors and improve resistance against fungi. (Donath, Militz & Mai 2006; Hill 2006; Svoboda et al. 2013)

One of the most modern substances presented on the market, which contains the unique properties of silicon dioxide, is a Lukofob. This silicone-based substance is usually applied when there is a need to protect the wood from moisture. Lukofob, as a kind of ceramic coating, reduces the absorption of rainwater by the wood structure, dirtiness, and decrease the degree of soluble components washing out. Moreover, no acid rain effects occur and the thermal insulation of ceramic-coated products is maintained (Bořůvka, Zeidler & Doubek 2016).

Research papers investigating the chemical treatment of wood structure by silicon dioxide mineral particles which as usual include in the ceramic coating, are mostly concerned with the increasing resistance against moisture and UV absorption, soil microorganisms and termites, fire, fungi, reduction of mechanical properties, constant temperature changes and other environmental factors.

3.2 Influence of weathering conditions on wood coated with ceramic coatings

In this paper, the literature review concerning the influence of the ceramic coating on the wood structure contained a significant number of silicon dioxide particles has been carried out. Application of ceramic coatings to prevent detrimental effects such as swelling, discoloration, combustion, degradation caused by various microorganisms or environmental conditions has been considered.

3.2.1 Water resistance properties

Wood absorption property plays an essential role in the assessment of the life expectancy of wooden constructions. The significant degree of water uptake can lead to deformation, swelling, cracking and rot in accordance with Wang, Chai & Liu (2013). The greater water resistance characteristics of wood can be achieved by creating superhydrophobic coatings on wooden structures (Ma & Hill 2006; Liu et al. 2019). The superhydrophobic surface can be attained by creating a rough surface with low surface energy as has been investigated in Latthe et al. (2019).

For example, the rough superficial layer can be coated on wood by deposition of SiO_2, TiO_2 and ZnO nanoparticles.

In Zhang et al. (2020) research work, SiO_2 nanoparticles and poly(methylhydrogen) siloxane (PMHS) have been used to obtain superhydrophobic SiO_2/PMHS ORMOSIL film on wooden substrates. The water-repellency of wood increased obviously after deposition of this coating. The indicator of water absorption fell considerably from 70.3% to 24.1%. The best hydrophobicity of treated wood was registered when the SiO_2 particles were about 75 nm in size.

The application of a sol-gel technology to improve water resistance properties of wood by generating SiO_2 with tetraethoxysilane and methyl triethoxysilane has been studied in Fu et al. (2016). The moisture content of wooden samples coated by the ceramic film was less compared with non-treated ones. Moreover, it was registered that the moisture uptake also declined when the dipping time rose. The long-lasting dipping time is preferable because it leads to better dimensional stability of the samples. In addition, the water absorption rate of wood after treatment was significantly lower compared with results of the untreated samples.

In the research of Temiz et al. (2006), the water-repellency properties of SiO_2, acetylated wood samples after heat treatment have been investigated by conducting water absorption and anti-swell efficacy tests. The impregnation process of mineral particles consists of 30 minutes vacuum (90%) and 90 minutes pressure (11 bars) procedures. It has been detected that samples with ceramic coating had lower water absorption compared with untreated ones, 46% and 80%, respectively. But still higher than that of acetylated and heat-treated samples. Besides, 30 nm mineral particles provided wood structures with greater water resistance than particles with 15 nm granules. Finally, the wood samples coated by superficial ceramic layer with the 15 nm size of mineral obtained the same moisture resistance as untreated samples.

Wood samples made of Scots pine were impregnated with quaternary ammonium quat-silicone micro-emulsion with particle size below 40 nm, amino-silicone macro-emulsion with particle size approximately 110 nm, and silicone macro-emulsion with alkyl modified side groups which size was about 740 nm. The application of the first studied micro-emulsion with 30% solution of silicone results in the highest indicator of cell wall soaking equaled to 4.8% and anti-swelling properties consisted 21.8%. Finally, the combination of all studied emulsions provided wooden substrates with a hydrophobic surface which was tested by conducting a capillary water uptake test (Ghosh, Militz & Mai 2009).

Inorganic silicon is also widely spread as a compound for wood treatments. Its performance is mostly connected with condensation products of silicic acid. Such products can be colloidal silicic acids, silicate ceramics, ‘‘water glass’’ and others. All of them go through the hydrolysis and then condensation stages to finally generate sols and gels. In the scientific paper Mai & Militz (2002), different wood treatments using organo-silicon and tetraalkoxysilanes have been studied. This combination forms inorganic-organic gel systems at the end. This organo-silicon superficial layer provides the wood with greater water-resistant properties because of the organic methyl groups.

The superhydrophobic surface layer intended for wood substrates has been developed and investigated by impregnation of poplar samples with a silica/silicone oil complex emulsion (SSOCE). This emulsion was mostly contained hydroxy and hydrogen silicone oils and micron/nano-scaled silica particles. During this study, concentrations of emulsion (5%, 10%, 20%, 30% and 40%) were prepared to determine the difference in the impact on surface free energy (SFE) and static contact angles (CAs) of substrates. The concentration of 5% showed dramatic growth in the water contact angle up to 150 degrees and a decrease in the SFE results to an extremely low level. It can be explained by the fact that a new superficial silicon-based layer coated on the wood samples formed a strong covalent bond Si-O-C. Also, the rough coating surface obtained by dual-sized silica particles enhanced the water repellence characteristics. Finally, it was stated that silicone complex emulsion formed a very durable and uniformly attached layer on the wood surface. (Liu & Cao 2018)

To conclude, ceramic coatings contained predominantly silicon dioxide particles cause a noteworthy influence on wood absorption characteristics. Moreover, the larger the mineral particle size, the rougher the coated surface, and as a result, the greater the water contact angle is formed, which results in worse wetting properties.

3.2.2 Mechanical properties. Adhesion of ceramic coatings

The abrasion resistance property of wood is of importance, especially when this material is selected for exterior applications due to a great variety of outdoor exposures, which can cause the occurrence of cracks or high mechanical stresses. Basically, high abrasion resistance can be achieved from a well-established balance between hardness and processibility of the coating, which is then applied to wood samples. A ceramic coating with a silicon-based matrix of a coating can ensure the wood substrate with a rather high processibility, while the incorporation of nanoparticles (NPs) such as SiO_2, TiO_2 (titanium (IV) oxide) and others can increase the hardness values. Silicon dioxide is one of the most widely used NPs for achieving high mechanical properties and a great level of water-repellence. (Han et al. 2007)

In the study of Kanokwijitsilp et al. (2016), coating with 20 nm colloidal silicon dioxide nanoparticles (SNPs) is used to provide great strength and hardness properties to the wooden material. Methyltrimethoxysilane (MTMS) was added to enhance the processibility and to guarantee good adhesion characteristics between coating and wood samples. It was found that the coating with the composition of 40:60 (SNPs: MTMS) prevent abrasion better compared to the control samples. Abrasion resistance property can be described not only by the well-selected ratio between MTMS and SNPs. The physical and chemical bonds between the coating and wood substrates also play a major role (sol-gel method has been performed).

Improved mechanical properties of wood also may be attained by mineralization based on the chemical modification. It has been studied in the research work of Doubek et al. (2018), how wood modification with SiO_2 impacts on mechanical properties of constructions. Ceramic film on beech and silver fir samples has been coated. Thus, only a minor influence on the tested mechanical characteristics of the artificially treated samples has been registered. It can be described by poor SiO_2 penetration into the lumens of cells and weak covalent bonds due to insufficient time for tight formation.

In the dissertation of Lahtela (2016), it also has been mentioned that the hardness of the ceramic coated wooden samples is similar to untreated ones. It should be highlighted that the standard deviations of the hardness values are surprisingly high after impregnation modification. Such feature can be described by the heterogeneous nature of wood material.

Ceramic coatings have also become widely used due to the presence of environmentally friendly inorganic-based products. However, its acceptance in civil engineering, especially in the wood sector, can be limited by requirements in complex surface preparation and precise adjustments in formulations to generate a durable coating. In the work of Cheumani et al. (2021), the adhesion characteristics of different silicate-based mixtures to the wood substrate (Fagus sylvatica L.) have been investigated for potential future improvements. The main parameter (adhesion strength) has been defined by carrying out pull-off tests. It was discussed that in most cases, adhesion mechanism is greatly dependent on the substrate surface quality. For example, the penetration depth of the ceramic coatings into the wood can be influenced significantly by the surface roughness. Moreover, the formulation of coatings affects adhesive strength considerably. Thus, the poorest indicator of strength equaled to (<2 MPa). Satisfactory values also have been obtained (2.5 – 2.70 MPa), while the only difference was concerned with the chemical composition of a coating. Great growth in the adhesion properties up to 3.8 MPa was achieved by wood pretreatment with a double impregnation of potassium silicate and boric acid. In contrast, such additives as polyols (glycerol, sucrose or D-xylose) were less effective in enhancing the mechanical properties of coatings. In addition, the scratch and impact resistance of coatings have been assessed as satisfactory, but the water resistance properties still do not acceptable for the wide application of such coatings on the market.

The main aim of the study was to define the influence of the wood samples impregnation with silicon dioxide on the bending strength and MoE. Oriental beech and sessile oak have been selected as substrates. Impregnation was performed with the 1% and 3% concentration of silicon dioxide based on the ASTM-D 1413-76 (1976) standard. As a result, when the concentration of the solution increased, the total and percentage retention grew as well in all wood samples. However, the bending strength and MoE values declined. The maximum average result of mechanical properties discussed above was during testing of oriental beech samples. The minimum result was noticed after testing of samples with sessile oak substrate with a 3% solution. Such values can be explained by the fact that oriental beech wood provides a higher density of (0.630 - 0.685 g/cm^3) compared with sessile oak wood. Mechanical characteristics such as bending strength and MoE decreased to 3 - 5% and 0.6 - 9%, respectively, in all wood samples which have been treated with SiO_2 (Karaman, Yildirim & Yaşar 2019).

To sum up, the application of ceramic coatings can provide materials with high corrosion and oxidation stability, great hardness, wear, and temperature resistance. While the main disadvantage is the significant brittleness of ceramics compared with polymeric and metallic coatings. Thus, the degree of improvement in mechanical properties largely depends on treatment method, formulation of ceramic coating, and type of the wood substrate. (Barroso et al. 2019)

3.2.3 UV resistance

Currently, superficial layers based on ceramics for exterior wood applications have become more available and popular among consumers. It can be explained by great resistance to UV radiation which they provide over a wide range of temperatures. Moreover, the application of ceramic coating also can help to avoid the occurrence of poor gloss properties and the appearance of 'chalking', which can be caused by loose pigment particles.

The silicon intermediates mentioned in the scientific paper of Easton & Poultney (2007), have alkoxy (Si–OR) or silanol (Si–OH) reactive groups. Commonly, these silicon intermediates can be added to waterborne acrylic and alkyd resins in order to enhance the weather resistance properties of color coatings. The gloss characteristics grew up, while the chalking degree of coatings decreased significantly.

In the study of Fu et al. (2016), the combination of SiO_2 with tetraethoxysilane and methyl triethoxysilane by a sol-gel method on the wood surface allows to safe the color of the tested samples after aging treatment. Occurred changes were not so significant compared with control wooden samples. Thus, SiO_2 had a strong ability for UV absorption. Moreover, the impact of exposed times of UV radiation on the properties of wooden samples has been investigated in (Han et al. 2007). With the increase in exposure period, the change of surface lightness (ΔL) was not so great, and the indicator of total color difference (ΔE) had a tendency to decrease as well.

In Temiz (2006) research work, the weathering tests, contained cycles of 2 hours of UV radiation and water spray for 18 min, were performed for studying the wood samples' behavior with a ceramic film. Samples also have been acetylated and heat-treated. According to the obtained results, the treated samples presented not so considerable color changes than wood samples without any treatment. Finally, it was founded that color changes (DE^*) of coated and untreated wooden samples were similar to each other after 400 and 800 h.

The effect of chemical modification of the wood to decrease the sensitivity to UV radiation has also been investigated in several scientific papers. The wood modification was carried out by the usage of silanes to decline the rate of material degradation and discoloration. It was demonstrated that silylation of wood is an effective approach to obtain great photostability characteristics of the surface applying α- and γ-methacryloxysilanes and γ-epoxysilane. Free radicals were formed practically 35% less in comparison with controlled samples. Moreover, insignificant color changes were determined. Thus, the main purpose of silylation was to provide wood samples with weathering protection and avoid photodegradation which can be caused by the detrimental effect of UV radiation. (Jebrane et al. 2009; Baur & Easteal 2013; Petrič 2013)

In addition, ceramic coatings have become widely known due to their environmentally friendly composition. Such a coating has been prepared in the research by hydrolyzing silane compounds. It was provided with a three-dimensional net structure which allows to enhance both optical and thermal stability. The ceramic coating also had good adhesion strength due to strong Si–O bonds and demonstrated great resistance to ultraviolet aging. The results showed outstanding durability of the coating under UV light (340 nm) radiation exposure which was lasted 480 hours. Moreover, the generation of the Si–O network structure improved the rigidity of the ligand and, at the same time, decreased the energy loss. Furthermore, UV light started to convert into red light more effectively due to higher symmetry in the rare earth ions arrangement. Such coordination environment resulted in great energy transfer between the ligand and rare earth ions. Due to these changes, less UV radiation damage and better fluorescence stability were noticed. To conclude, highly discussed ceramic coatings also was considered to be a very effective and environmentally sustainable approach to obtain outstanding protection of wood against radiation. (Li et al. 2020)

3.2.4 Cycling tests of wood material

One of the concerns regarding the usage of glulam and other wood-based materials is the adverse effect of water, cold weather, and freeze–thaw (FT) cycles on the products during service. This circumstance led to a great body of research focusing on the performance of timber operation and the creation and development of standardized test methods. (ASTM D7031-04)

Previous studies have presented that fluctuations in ambient temperature and humidity have adverse impact on the mechanical and physical properties of wood-based material (Sombatsompop & Chaochanchaikul, 2004).

In Pilarski et al. (2006) scientific research, it has been shown that the natural durability of pinewood after 15 cycles of accelerated freeze-thaw cycling was lowered. Also, it was reported that the wood-based products' density did not change under the testing. While the moisture absorption has been increased, and flexural properties have been decreased.

The influence of temperature fluctuations and moisture on the discoloration of coated spruce was studied. The experiments were carried out on test samples provided by six producers. The artificial weathering tests and 30 temperature cycles were performed. The obtained results showed that the producer of ceramic coatings with SiO_2 and methyl-siloxane additives had the greatest performance among other types of coatings. Moreover, its color difference after temperature cycling could not be noticed by the naked eye ($\Delta E^* < 3$). (Oberhofnerová et al. 2018)

In the research work of Ghosh et al. (2009), scots pine has been treated by three different types of emulsion: a quat-silicone emulsion with 40 nm particles, an amino-silicone emulsion with 110 nm particles, and an alkyl modified silicone emulsion with 740 nm particles. Coated and untreated wooden boards were prepared to perform weathering tests. Finally, it was concluded that silicone emulsions treatment did not improve the color stability, while quat- and amino-silicone emulsions were less affected by fungi and showed better surface properties even under significant temperature fluctuations compared with control and alkyl-modified silicone samples.

To sum up, constant temperature cycles caused by changes of seasons affect wood product properties badly. Thus, a great variety of research papers are devoted to the application of ceramic coatings, which provide the wood with great technical characteristics. This can prolong the operation period of constructions studied constantly.

Based on the presented literature review, it can be stated that the authors are mostly dedicated their papers to develop a ceramic coating formulation that can improve the wood structure’s performance considerably. This type of coatings provides wood products with great resistance characteristics against the biotic and abiotic factors. However, it is worth noting that the structure of chemical modified or coated wood is also changed. It can lead to a significant variation in physical and mechanical properties. Thus, there is a need to investigate both all detrimental operation conditions of wood constructions and concomitant changes in the structure and properties of the material thoroughly.

4 MATERIALS AND METHODS

This chapter provides information according to materials and methods chosen to study the central issue of this thesis. The source of materials and their parameters are pointed out thoroughly. The selected methods, standards, processes, and testing machines are also presented.

4.1 Wood samples

After investigation of numerous analogues and prototypes of different wood coatings to increase their durability and fire protection characteristics, it has been found that one of the most promising option is to combine magnesium and polymineral fire-retardant impregnation of wood with an aqueous solution of sulfonated graphene. The most two effective combinations of hydrated magnesium compounds with other hydrated mineral compositions have been selected by the volumetric experimental selection to produce ceramic coatings #1 and #2 presented in Figure 7. The polymeric coating #3 also has been created for more extensive research work.

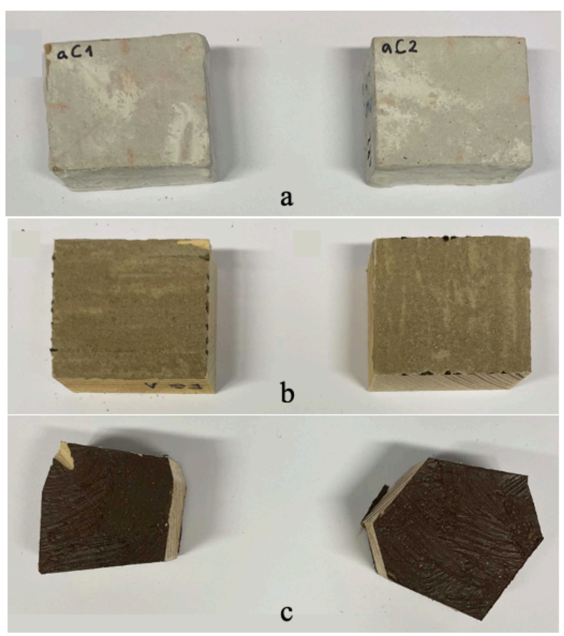


Figure 7. Image of two selected effective combinations of the studied ceramic coating (a - coating #1, b - coating #2) and the polymeric coating (c - coating #3).

Initially, 36 wood samples made of Scots pine (Pinus sylvestris) were coated by three different types of coatings in advance. There were 12 samples of each type of highly described coatings. Cleaned non-coated cross ends of these samples were treated with epoxy before experiments to avoid disturbance of test results caused by more rapid interaction of the naked wood surface with ambient conditions such as moisture presence. The samples were dried within three days after the treatment.

4.2 Tape method. Estimation of adhesive strength of the studied coatings

Before starting the experiments, commercial flexible transparent adhesive tapes of 40 mm have been prepared. Ceramic- and polymeric-coated samples, black and white matt finish backgrounds have also been arranged for this experiment in advance.

The experiment began when the adhesive tape was placed on the samples' upper surface with the coating. After that, the firm pressure was applied, and the whole area of connection was rubbered. Then, this tape was removed perpendicularly to the upper surface and put on the selected background to provide the more notable contrast of the tape with coating residues. The black background has been chosen to test the coating #1 and coating #2, while the white matt one has been selected for experiments with samples coated by the coating #3. Next, the degree of the flaking and chalking was determined by estimation of coatings' residues on the adhesive tape following ISO 4628. Finally, when the tape method was carried out, and the durability of the coating was assessed, the first six samples of each type of coatings were selected to conduct accelerated weathering tests, and another six samples were applied to perform cycling tests. When highly mentioned tests had been completed, the intact surfaces of samples were exposed to the tape method one more time to define the changes in adhesion properties of the coatings for further assessment of their durability characteristics.

4.3 Accelerated weathering tests

The accelerated weathering test has been carried out to meet all the requirements and, finally, to determine the degradation of different types of coatings under UV irradiation, heat and moisture exposures, and corresponding changes in the physical, chemical, and optical properties of the studied coatings.

Based on SFS-EN ISO 4892-2, the test chamber with xenon-arc lamps Q-SUN XE-3, showed in Figure 8 (Q-Lab Corporation, USA), has been programmed with selected experimental conditions. The whole experiment lasted 500 hours. It contained several alternating UV-light exposure and water spray periods, which continued 102 min and 18 min, respectively. The verification of apparatus operation has also been done according to these conditions. Only after that six samples have been placed in the test chamber and attached by sample holders by the intact side to the top to avoid any applied stresses that may occur during an experiment.

Figure 8. Xenon test chamber Q-SUN XE-3 (Q-SUN, 2020).

All samples have been marked by a permanent marker. The radiometer (UV light metre UV-340A (LT, Lutron)) has also been mounted and calibrated to measure the irradiance of the tested samples. The black-standard and white-standard thermometer have been mounted at such plane and orientation as the samples to estimate the whole range of absorbed radiation and temperature of the wood samples in the exposure chamber during the experiments. A water spray device has been applied to simulate the moisture effects during an experiment. Sprayed water contained a maximum of 1 μg/g of solids and 0,2 μg/g of silica to exclude the possibility of spots or stains occurrence, which is not typical for exterior exposures. Wetting and humidity-control equipment has also been used to check the moisture condition in the test chamber. Finally, only the upper side of the samples has been investigated and assessed.

4.4 Cycling tests

In accordance with EN 321, cycling tests of coated wood samples have been performed to determine the impact of temperature changes and moisture on the durability of ceramic and polymeric coatings.

Six samples of each coating have been cut based on EN 326-1 standard beforehand. The test pieces have also been conditioned to a constant mass under the relative humidity of (65 ± 5) % and temperature of (20 ± 2) °C. Two successive weight measurements have been performed with the interval of 24 hours, and the difference between results did not exceed more than 0,1% of the mass of every sample. Only after that, the dimension of their sizes was done in accordance with EN 325. Cycling treatment began with the first cycle and immersion of the samples in the water bath standing on one edge and with the distance between them equaled to at least 15 mm, their positions illustrated in Figure 9. The upper edge was covered by water more than (25 ± 5) mm during the whole immersion period. Fresh water in this bath had pH = (7 ± 1), and its temperature was approximately (20 ± 1) °C. The immersion period constituted 28 days.

a b c

Figure 9. The coated samples immersion into the water bath (a - coating #1, b - coating #2 and c - coating #3).

Then, the samples have been removed from the water bath, drained off several times, and placed in the freezing cabinet standing on the same edge as when immersed, Figure 10. The distance of 15 mm between samples also was kept. The temperature in the freezing machine varied from - 12 °C to - 25 °C. The whole period of freezing lasted (24 ± 1) h.

Figure 10. The location of coated samples during the cycling testing in the freezing cabinet.

After the freezing cabinet, samples immediately were placed into the drying cabinet with the temperature of (70 ± 2) °C, Figure 11. The position of them in the drying cabinet was identical to the position in the water bath and freezing cabinet. The drying period was selected (72 ± 1) h.

Figure 11. The position of coated samples into the drying cabinet.

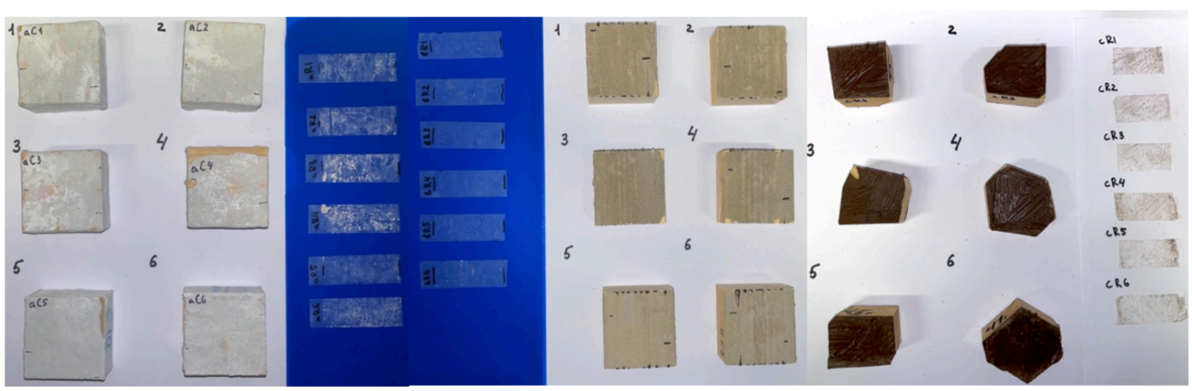
After the drying period, cooling of samples under the temperature of (20 ± 5) °C was done during (4 ± 0,5) h. The procedures of the second and third cycles were identical to the first one. There were only two differences: the immersion period in the water bath under the temperature (20 ± 1) °C lasted (72 ± 1) h, and the imposition of samples was alike during these cycles. In the second cycle, the samples were inverted to stand on their opposite edge compared with the first cycle, while during the third cycle, samples stood on the same edge as in the first immersion period. Finally, reconditioning of samples was carried out by measuring the constant mass of exposed samples.

5 RESULTS AND DISCUSSION

The results of coating durability characteristics before and after both cycling and accelerated weathering tests have been obtained, analysed, and further discussed in Chapter 5. Main features concerning the degradation of coating structure due to ambient conditions exposure have also been noted and described.

5.1 Referenced samples

The flaking determination of the samples coated by three different coatings was carried out by a tape method. The illustration of the samples after the experiments is shown below in Figure 12. The term "flaking" usually means the coating separation from the substrate caused mostly by low adhesion properties.



a b c

Figure 12. The results of tape method implementation using referenced samples with coating #1 (a), coating #2 (b) and coating #3 (c).

The code was implemented in Python Programming Language to calculate the number of coating residues on the tapes after experiments. For the code as input, the black/white images of tapes were used. The code assigned the fraction for each pixel of the picture. In Figure 13, coating residues are illustrated as yellow spots on the dark blue background (clear tape). The threshold for determining the spots of coatings was also established and varied from 0.8 to 0.85 depending on the obtained image.

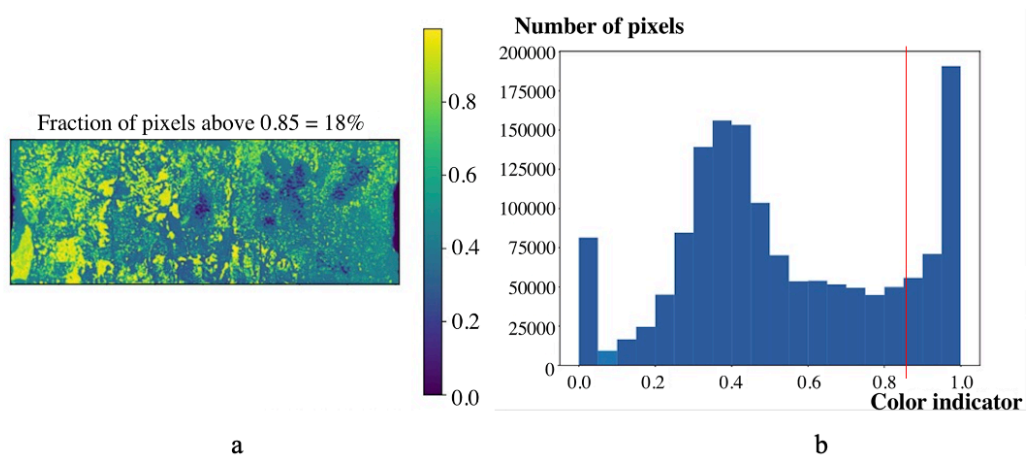


Figure 13. Estimation of coating residues proportion remained on the tape (a - an image used in the code to define the quantity of coating residues and b - the graph presenting the number of pixels related to the specific colour).

Based on the results of flaking determination presented in Table 3, it can be stated that the coating #2 provides the best adhesion characteristic with the substrate.

Table 3. The percentage of coating residues remained on the tape estimated for all coatings understudy.

Sample number	Coating #1, [%]	Coating #2, [%]	Coating #3, [%]
1	2	0	1
2	4	1	1
3	18	0	0
4	21	0	2
5	1	1	1
6	3	3	1
average	8,17	0,83	1,00

The amount of coating residues of coating #2 remained in the tape in respect to the whole tested area varied between 0 and 3%. Coating #3 also showed satisfactory results. The average value of flaking equalled to 1,17%, which is slightly higher compared with the same indicator of coating #2 - 0,86%. Coating #1 showed the worst effect. Its adhesive properties were considerably lower, and the considered proportion fluctuated from 1 to 21%, with an average value of 8,17%.

Previously, Kanokwijitsilp et al. (2016) have studied in their work the influence of the coating technique on the durability characteristics of the films. It was stated that the physical and chemical bonds between the wood substrate and the studied coating depends greatly on the coating techniques.

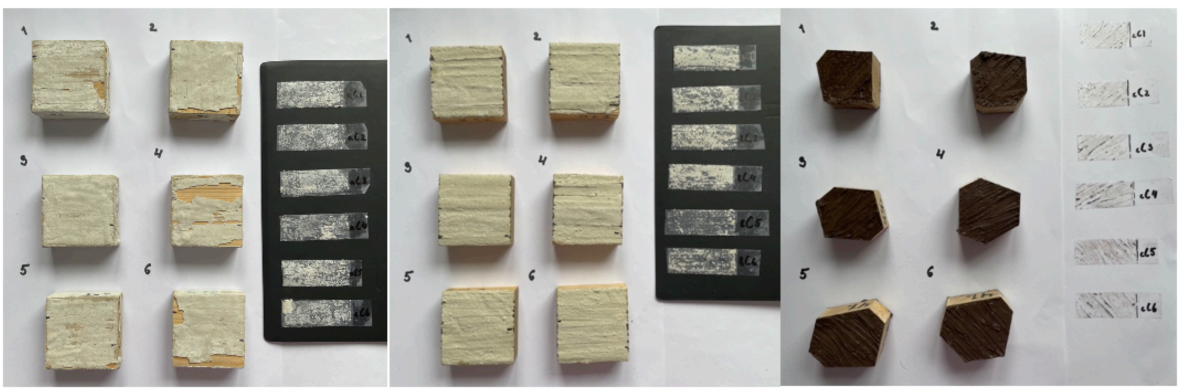
Abrasion resistance can be described not only by the well-selected method of the coating which results in tight bonds formation in the system “coating - substrate”, the ratio between added nanoparticles also plays a very important role. Moreover, the impact of the coating chemical composition and the ratio/sizes of dipped nanoparticles on the adhesion characteristics has been investigated in the paper of Karaman et al. (2019). Therefore, the considerable difference in the results obtained after the tape method can be explained by the varied combination of hydrated magnesium compounds with other hydrated mineral compositions in the ceramic coatings. Namely, the varied chemical composition of coatings under study can provide the greatest influence on the internal connections between the wood surface and applied coatings.

Another suggestion was made in Cheumani et al. (2021) work, where the fact that subtract surface quality can lead to the poor adhesion mechanism of the coatings was discussed. Thus, the high surface roughness can worsen the penetration depth of the coatings into the wood samples and be a reason for the high flaking degree.

Last but not least, in the paper of Doubek et al. (2018), it was discussed that ceramic coating with a large content of SiO_2 provided only a minor influence on the mechanical characteristics of the samples. The main reason was that silicon dioxide particles have poor penetration into the lumen of cells and, due to this, create weak covalent bonds with the substrate. The lack of time also can be a key issue that does not allow to perform a tight formation.

5.2 Samples after cycling tests

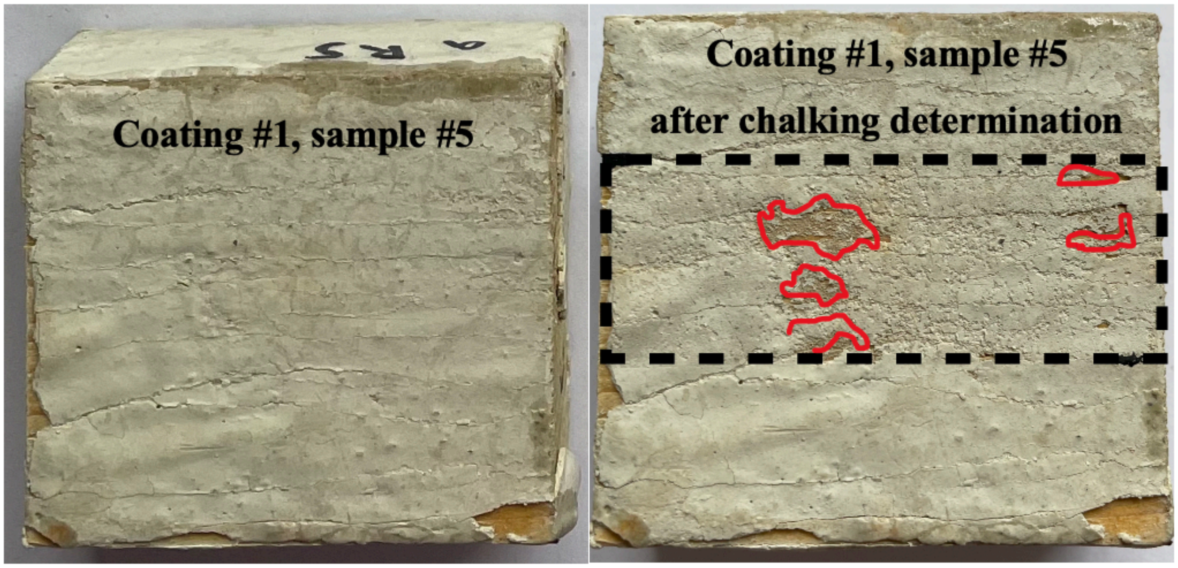
Figure 14 presents coated samples that have been tested under cyclic conditions in accordance with EN 321 standard to further determination of flaking degree. It is evident that the quality of the coatings got worse after these experiments. The number of coating residues remained on the tapes considerably increased for all studied coatings. Coating #1 even had some naked zones on the surface before the implementation of the tape method because the adhesion characteristic was significantly worsened. Even the slightest impact on the samples led to residues crumbling. As for coating #2, its appearance did not change significantly, but a great number of cracks formed. Coating #3 was the least susceptible to external changes. However, after cyclic tests, the stickiness on the surface was noticed.



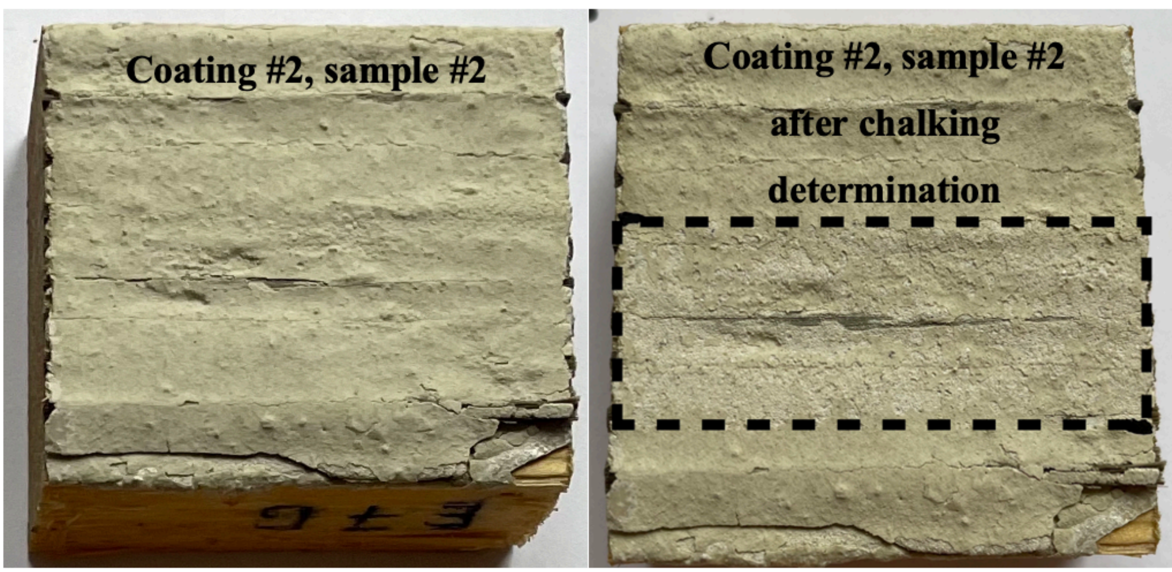
a b c

Figure 14. The illustration of tapes and samples with coating #1 (a), coating #2 (b) and coating #3 (c) after cyclic tests.

After the tape method, the surfaces of coatings #1 and #2 have been investigated in detail due to the considerable flaking degree. It can be seen from Figure 15 that, in most cases, the superficial layer of the coatings was destroyed. As was mentioned earlier, coating #1 had the most imperfect adhesion properties, and it can be proved by the presence of naked wooden spots (marked by red color on Figure 15) after removing tapes with a considerable number of coating residues on them. When the same tests were performed for coating #2, only residues from the top layer were removed. No visible changes were noticed during the chalking degree determination of coating #3.



a



b

Figure 15. The nature of coating degradation obtained after cycling tests by the tape method.

The results of flaking determination of coatings after cycling tests are presented in the Table 4. From the given data it can be noticed that the durability of all three coatings decreased significantly.

Table 4. The percentage of coating residues on the tape estimated for all coatings under study after cycling tests.

Sample number	Coating #1, [%]	Coating #2, [%]	Coating #3, [%]
1	48	67	5
2	43	56	5
3	52	57	8
4	39	65	10
5	59	17	5
6	57	37	8
average	49,67	49,83	6,83

The highest deterioration in properties was defined when coating #2 had been tested. Its average indicator of coating residues remained on the tape was increased from 0,83% to 49,83%. Moreover, coating #2 provided the widest range of the obtained results from 17% up to 67%. As for coating #1, it also had poorer adhesion and surface quality compared with referenced samples. The flaking degree of coating #1 grew considerably after cycling tests from 8,17% to 49,67%, but this result was still less than the degree of coating #2. The least degradation of properties referred to coating #3. The average value of flaking was increased by only 5,66 % in comparison with referenced samples. This result made coating #3 the best option among all studied coatings.

Trying to understand the reasons of the flaking degree growth, the cycling conditions accompanied by the changes in the coating structures should be considered. Samples swelling due to moisture absorption is primarily responsible for the lower durability after cycling tests (Wang et al. 2013). The difference between the weight of samples because of water uptake and thickness swelling is shown in Table 5.

Table 5. Weight of samples before cycling tests

Samples number	Weight of samples after and before cycling tests, [g]					
	Coating #1		Coating #2		Coating #3	
	before	after	before	after	before	after
1	20,46	24,17	26,74	30,44	11,95	12,58
2	20,81	23,84	26,33	30,40	12,77	13,35
3	20,67	23,94	25,98	30,42	14,65	15,10
4	21,10	24,52	25,34	30,09	16,63	17,12
5	21,01	24,67	23,27	25,66	17,84	18,76
6	20,64	23,59	22,90	25,20	18,91	19,42
$\frac{\Sigma(\text{after} - \text{before})}{6}$	3,34		3,6		0,60	

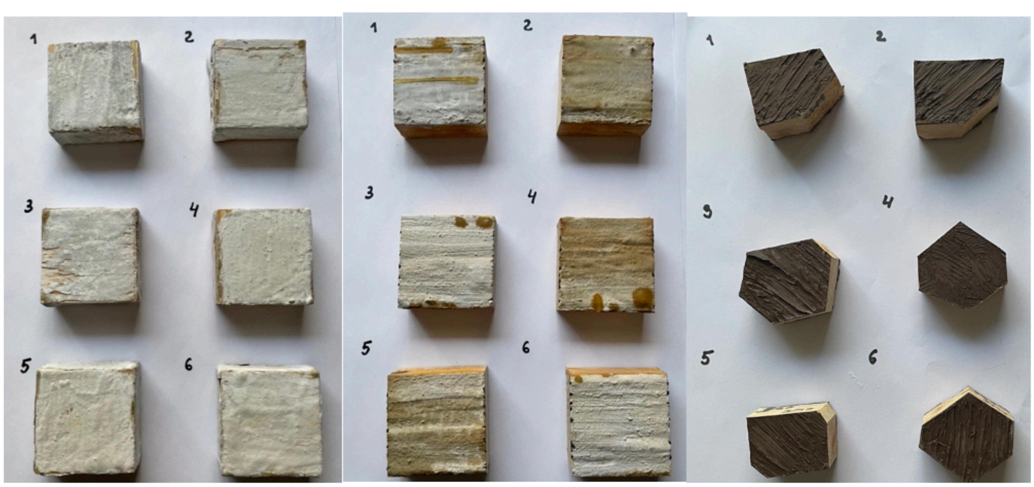
It can be inferred from the given data that the weight of all samples increased after the cycling test. The water absorption of coating #1 and #2 was considerably higher compared with results obtained for coating #3. It is difficult to establish the coating with the poorest water-repellent properties based on weight results due to the high level of flaking of coating #1. However, it remains clear that moisture absorption can lead to worsening of samples adhesion characteristics.

The quality surface of the coatings affects the moisture absorption property considerably. In the paper of Liu & Cao (2018), it has been determined that a rough superficial layer of the coating can contribute to the excellent water repellency. To obtain such a type of surface and limit the water ingress into the samples, the size of nanoparticles added to the coating should be as large as possible. For instance, in X. Zhang et al. (2019), the highest indicator of hydrophobicity has been attained when the particle size of SiO_2 equaled to 75 nm in the ceramic coating. In addition, in the research of Temiz et al. (2006), it was proved that 30 nm mineral particles added in the coating ensure the samples with higher water absorption resistance compared with the usage of 15 nm particles. Besides, 15 nm mineral particles showed the same results of moisture resistance as untreated wooden samples. The advantage of larger mineral particles presenting in the coating composition can be explained by the fact that they provide the surface of the investigated material with high roughness. As a result, the contact angle of such surface becomes higher than 90°, and the reduction in the wettability of solid surfaces occurred. Also, in the Fu et al. (2016), the influence of dipping time duration on moisture uptake has been investigated. During the research, a longer dipping time into the water is preferable because it helps to obtain better dimensional stability of the samples under study.

Finally, poor adhesion which have been demonstrated on the referenced samples for the coating #1 also can cause significant moisture absorption due to the presence of places with weak bonds between the coating and wooden substrates. Naked wooden surface uptake water significantly and leads to even more rapid degradation in the system "coating - substrate".

5.3 Samples after accelerated weathering tests

The samples subjected to accelerated weathering tests are presented in Figure 16. The number of cracks on the sample's surface with coating #1 increased after accelerated weathering tests, as was after cycling tests. It can prove the assumption that the coating # 1 had rather poor moisture resistance.



a b c

Figure 16. The illustration of samples after accelerated weathering test with coating #1 (a), coating #2 (b) and coating #3 (c).

Moreover, the color of several samples covered by coating #2 changed after the experiment, while the color of other coatings remained the same. Such behavior can be explained by the influence of UV light exposure on the coating chemical composition. Ultraviolet irradiation usually contributes to wood structure degradation and to generation of free radicals. This phenomenon is associated with the presence of lignin in the wood structure and its high sensitivity to the reaction with oxygen under outdoor conditions. To increase the durability and strengthen anti-ultraviolet aging properties, in the paper of Han et al. (2020), rare-earth ions were dipped in the coating to react with the UV light and to prevent the deterioration process. This reaction also was accompanied by the coating color changing. The standard host media of such types of ions is silica. Thus, rare-earth ions can enter the crystalline phase of the ceramic coating and react with UV irradiation. In addition, the performance of coating #2 was improved after the reaction with UV rays and this fact can be initially proved by the absence of visible cracks on the surface.

After accelerated weathering test, all samples were used to carry out the tape method test for further estimation of changes in the adhesion characteristics of the coatings. The corresponding results have been presented in Table 6.

Table 6. The percentage of coating residues remained on the tapes assessed for all coatings under study after the accelerated weathering test.

Sample number	Coating #1, [%]	Coating #2, [%]	Coating #3, [%]
1	16	8	20
2	28	4	30
3	38	9	17
4	42	1	38
5	40	2	25
6	53	15	21
average	36,17	6,67	25,17

It can be noted that the adhesion of the ceramic coatings worsened compared with referenced samples and improved in respect to the samples which have been subjected to cycling tests. Furthermore, it should be mentioned that samples covered by coating #2, which have changed the colour notably (samples #2, #4 and #5), showed better results compared with other samples of this type which colour becomes slightly darker (samples #1, #3, #6). This fact confirms that the previous assumption about the reaction between the coating and the UV lights, which leads to significant improvements in anti-ultraviolet aging and mechanical properties, can be the truth. Besides, a significant decline in the adhesion of the coating #3 was observed as well. As can be seen from Table 7, these samples did not absorb much water during the tests because the indicator of the average weight gain consisted only 0,35 g. It means that the main reason for adhesion degradation of coating #3 can be the UV light exposure.

Table 7. Weight of samples before artificial weathering tests

Samples number	Weight of samples after and before artificial weathering tests, [g]					
	Coating #1		Coating #2		Coating #3	
	before	after	before	after	before	after
1	25,05	26,01	26,61	26,69	14,67	15,49
2	25,81	26,28	25,52	25,90	15,60	15,93
3	25,26	25,95	25,67	25,74	18,32	18,58
4	25,53	26,47	25,04	25,38	14,41	14,59
5	25,85	26,71	25,15	25,50	12,81	12,95
6	25,28	26,18	25,10	25,22	16,62	16,96
$\frac{\Sigma(\text{after} - \text{before})}{6}$	0,8		0,22		0,35	

The highly discussed assumption concerning behavior of the coating #3 and the substrate can be confirmed based on the research of Turkulin (2004). After microscopic analysis of the adhesion-tested samples it has been revealed that after UV exposure, the failures in the system "coating - substrate" often happens either in the coating base layer, or in the weak places of the substrate. The coating becomes porous and brittle because of the reaction between the large pigment concentration of the coating and UV irradiation. Therefore, the ingress of water inside the micro-voids and other weak places leads to the loss of adhesion strength of the coatings. Moreover, the considerable protrusions on the coating #3 also can influence on the obtained results. As has been noticed, the poor adhesion was primarily determined on the top layer of the coating at the places where the surface protrusion is great, Figure 17. Surface protrusions are subjected to more significant impact of UV irradiation due to the less distance between the UV source and the coating.

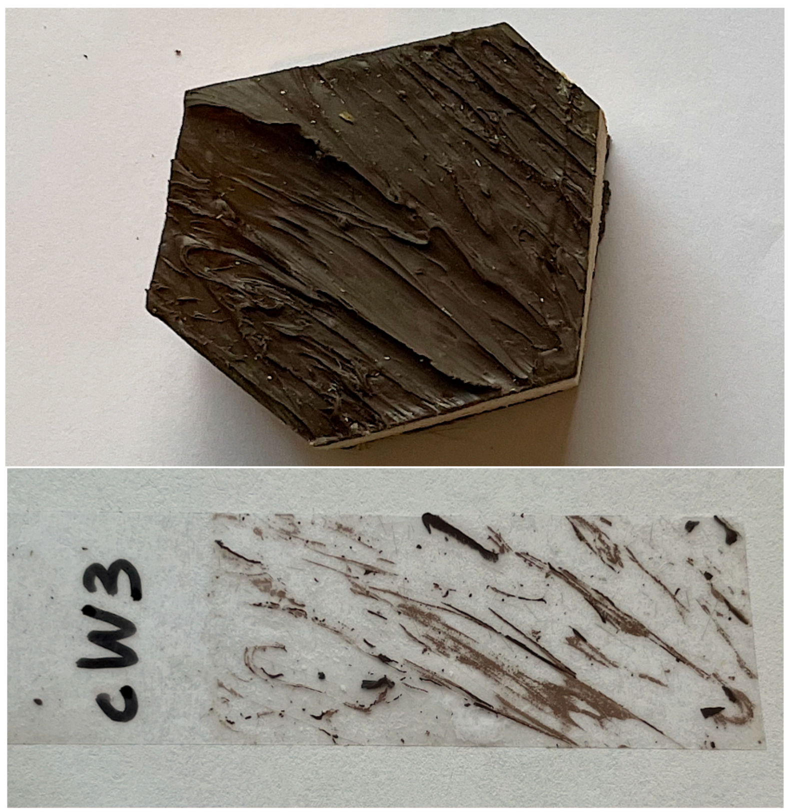


Figure 17. The destruction nature of coating #3

UV irradiation is detrimental to polymeric materials. In the dissertation of Hyvärinen (2014), the influence of weathering conditions on the polymeric coating characteristics has been investigated. As a result, the number of cracks in the polypropylene matrix appeared, and the protrusion of wood particles became notable. Both factors, such as photodegradation of polymer matrix and wood swelling may result in the formation of coatings cracks and, as a consequence, low adhesion.

The insufficient coating thickness on the porous material such as wood also can lead to great chalking after UV irradiation exposure. The term “chalking” defines the formation of a powdery layer on the superficial surface of a coating. This phenomenon is typically occurred after exposure to ultraviolet rays and other types of radiation. (Veleva 2012)

Coating #3 can operate not so effectively due to the leaching of elements from the coating surface. Thereby, further reduction in the coating thickness occurs. Low level of protection left at the wooden surface, which results in decreasing of adhesion between the remaining coating layers and the substrate. (Saha et al. 2011)

The chalking results of coating #1 were still the highest compared with other coatings subjected to accelerated weathering tests. However, the loss in durability was less than after cycling tests. This fact shows that namely moisture causes significant degradation of the coating, while the UV light exposure cannot be the main reason for poor durability characteristics. In addition, such behavior may be explained by the fact that ceramic coating with a predominant content of silicon dioxide nanoparticles does not contribute to enhancing coating properties due to the hypothesis made in Doubek et al. (2018). Thus, weak covalent bonds created between the SiO_2 and the OH- groups of lignin or cellulose, which are the essential part of the wooden structure, facilitate water uptake and result in poor adhesion.

5.4 Possible solutions to improve performance of the studied ceramic and polymeric coatings

It has been investigated that ceramic coatings under study had very low adhesion properties with the wooden substrate especially under influence of moisture presence. Both ceramic coatings after cycling tests degraded significantly and showed the great degree of flaking. After investigation of scientific papers devoted to this field of study, several decisions of this problem have been found.

Impregnating primer or binder layer can be used to enhance durability of coatings for wooden-based materials. Several studies have demonstrated that presence of the specific primer can enhance adhesion in the system "coating - substrate". The explanation of such behavior might be based on low stress formation in the studied system because of the application of an intermediate layer. For instance, in the work of Dawson, Kroese & Hong (2002), no cracks were determined in the “coating - substrate” system due to usage of a hybrid primer. In this study, the primer which possessed characteristics of water- and solvent-based paints has been chosen. In the research of Yona et al. (2021), referenced and pre-treated wood samples were covered by the ceramic coating, and then all samples were subjected to cycling tests. It was investigated that adhesion strength of the pre-mineralized wooden substrates was improved considerably by formation of very tight chemical bonds. Wood samples impregnated with boric acid substance and potassium silicate obtained high degree of adhesion strength as well. However, polyols additives such as glycerol or sucrose did not cause any improvements in the coatings’ durability characteristics. Additionally, in the paper of Milano (1984), the author decided to pre-treat wood samples with chromated copper arsenate (CCA) before application of the superficial coating and this process also led to the reduction in the crack’s formation and resulted in lower flaking degree.

Furthermore, satisfactory adhesion can be noticed when the coating obtains low viscosity because in such case it ensures the great wetting degree which finally results in deeper penetration of the coating into the selected substrate. This fact means that the coating with low viscosity forms rather tight chemical bonds with the wooden substrate. Besides, the slight difference in the coating and timber dimensional changes under influence of moisture can be noticed. Finally, all these facts basically lead to reduction in stresses occurred in the “coating - substrate” system. This assumption was proved in Ozdemir, Bozdoğan & Mengeloglu (2013), where low-viscosity coating showed a great enhancement in the adhesion characteristics while the thickness of coating played a minor role.

Another way to improve surface wettability is the application of plasma treatment for the wooden substrates. Such a process was implemented in the work of Peng & Zhang (2019), to etch the wood surface for better adhesion with the superficial coating and, as a result, for the enhancement of its durability characteristics. Thus, the authors obtained more noticeable surface roughness and affected the adhesion mechanism of the top coating layer with timber significantly. Moreover, plasma treatment can be used to attain the desired level of water repellency of wood. In such case the process should be performed at atmospheric pressure with usage of a dielectric barrier discharge. (Avramidis et al. 2009)

The main problem which has been formulated after the investigation of the results concerned the polymer coating operation under artificial ambient conditions was dedicated to the adverse impact of UV irradiation on the coating structure. One of the widely applied decisions consists in using of specific additives in polymer composition which allow to block or absorb UV rays.

In the research paper of Auclair et al. (2011), the addition of 2% zinc oxide (ZnO) nanoparticles in polymer coating contributed to excellent timber protection from photodegradation. Moreover, zinc oxide particles showed greater results compared with cupric oxide (CuO) nanoparticles. Also, it was concluded that a mix of inorganic and organic UV absorbers led to excellent gloss properties of the coatings. Thus, ZnO additives allow to reduce the color and structure degradation in maleic anhydride modified polypropylene (MAPP) and polyurethan (PU) coatings. (Salla et al. 2012)

Nanoflakes of graphene were dipped into formulation of polymer coating in the work of Nurxat et al. (2013) to improve UV stabilization properties. After accelerated weathering tests, the surface structure and chemical composition of the studied coating have been determined. Obtained results presented that graphene nanoflakes cause beneficial effect and enhance the UV light resistance of the polymer coating considerably. The assumption concerning the wide spread usage of this process in a great variety of industries where there is a need to apply polymer coatings for wood under influence of environmental factors was made.

Finally, the following stabilizing systems can be implemented in accordance with desired process of UV stabilization to achieve higher resistance of polymer coatings against environmental factors, namely UV irradiation. Nowadays light screeners and excited-state quenchers are widely applied, while the most efficient ones are ultraviolet absorbers, free radical scavengers and peroxide decomposers. A deep understanding of degradation processes which occurred in polymer matrix is required to find the best suitable solution of the existing problem. (Yousif & Haddad, 2013)

6 CONCLUSION

The aim of this thesis was dedicated to studying the effects of weathering conditions on the performance of ceramic and polymeric coatings on wood, which are usually applied to enhance the durability of the construction material. The main studied property was the adhesion mechanism of coatings to wooden substrates under moisture, temperature cycles and UV irradiation exposure. The impact of weathering conditions was performed by the cycling tests (EN 321) and accelerated weathering tests (ISO 4892-2). At the same time, the estimation of the adhesion was done by the implementation of the tape method (ISO 4628). The study revealed that both ceramic coatings degraded considerably under cycling tests when the adhesion of polymeric coating decreased notably after accelerated weathering tests.

Currently, wood or timber is considered one of the most widely applied construction materials in the world. It can be used to produce some interior wood products (for example, furniture), exterior wood products (for example, doors and windows), sports equipment, art/ musical instruments and et cetera. However, the most popular application of this material is found in construction (for example, buildings and bridges). To follow all the standards, regulations and safety rules, the wood should be treated or chemically modified. Such processes also contribute to its long operation life and the high degree of reliability under ambient conditions. The wood material is usually mechanically or chemically modified. The most general way to enhance wood properties is to use coatings with additives of mineral particles and/or some types of chemicals such as anhydrides, isocyanates, silicon dioxide, aldehydes, epoxides, and et cetera. Due to the satisfactory resistance of ceramic and polymeric coatings, three coatings of these types were investigated.

In this research, the first two ceramic coatings were created by the most effective combinations of magnesium and polymineral fire-retardant impregnation of wood with an aqueous solution of sulfonated graphene, while the third coating was polymeric one. It was investigated that the flaking degree of referenced samples varied significantly. Coating #1 had the highest indicator equaled to about 8%, while other coatings showed very low results below 1%. Main reasons for such behavior of the coatings can be described by the influence of:

1) applied coating techniques;
   - the applied coating technique causes significant impact on the physical and chemical bonds between the substrate and the coating. If the internal bond strength is low, the durability characteristics of the coatings will be poor.
2) initial surface quality;
   - the high surface roughness of the untreated wood substrate leads to the decrease in penetration depth of the ceramic coating into the wood structure, which also worse the adhesion characteristics and increase the chalking degree.
3) the ratio/size of dipped nanoparticles;
   - the different ratios of added nanoparticles to coating #1 and coating #2, which were created with the same chemical composition, can be one of the reasons for the studied difference in chalking degree. Moreover, the size of nanoparticles also can play a major role because the larger the size of the dipped nanoparticles, the rougher the surface of the applied coating.
4) peculiarity of the mineral particles' interaction with wood structure.
   - silicon dioxide particles which are basically one of the main components in the ceramic films, have poor penetration depth into the lumen of wood cells. Thus, this fact can be a reason for weak covalent bonds of coating with the substrate and, finally, low adhesion results.

Cycling tests were performed based on the procedure described in the EN 321 to determine the impact of temperature changes and moisture on the durability of the studied coatings. As a result, both ceramic coatings showed a dramatic decrease in adhesion. Nearly half of the total tested surface area of the ceramic coatings remained on the tape, while polymeric coating #3 had only 6,83% of coating residues on the tape. First of all, these changes in flaking degree can be primarily connected with higher moisture absorption of coatings #1 and coating #2. Secondly, the rough surface of coating #3 leads to a rather high contact angle which prevents significant wettability compared with the smooth surface of ceramic-based coatings.

Accelerated weathering tests were carried out to examine the weathering properties of the studied coatings. The whole experiment lasted 500 hours and contained several alternating UV-light exposure and water spray periods which continued 102 min and 18 min, respectively. It was noticed that coating #3 degrade considerably. The percentage of coating residues on the tape which left after the experiment increased to 25,17% because UV irradiation is destructive for polymeric materials. Under UV light, the surface cracks usually occur, and wood begin to interact with artificially created ambient conditions. Moreover, UV irradiation also can cause insufficient coating thickness. During the tests, leaching of elements happened, and the coating became thinner. This fact can be a reason for the poor durability of coating #3. In addition, the studied coating may obtain porous and brittle structure after the experiment because of the reaction between large pigment concentration of the coating and UV irradiation.

Furthermore, both the satisfactory level of adhesion of coating #2 was noticed and its color changes were detected after accelerated weathering tests. There is an assumption that the chemical composition of coating #2 contained a high level of rare-earth ions, which can react with the UV light and, by that, improve anti-ultraviolet aging and mechanical properties of the coating. Whereas the results of another ceramic coating, coating #1, were the worst again compared with other studied coatings.

It can be concluded that the durability of all coatings under study worsened due to the influence of weathering conditions. The ceramic coatings showed poor water repellency due to weak covalent bonds which, finally, result in low adhesion. While the study of the polymeric coating revealed the adverse impact of UV irradiation on the polymer matrix due to specific chemical reactions. Currently, coating #2 should be selected for wood products that will not undergo significant temperature changes in combination with high humidity conditions. And coating #3 will operate well if the coated product will not be significantly affected by the sun or other sources of UV light. It was concluded that improving the properties of ceramic coatings can be achieved by application of impregnating primer or binder layer, by making the viscosity of the coating lower and by implementation of plasma treatment for the wood substrates. The performance of the polymer coating can be enhanced by increasing the proportion of UV stabilizers into the coating formulation.

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