

ARISTOTLE UNIVERSITY OF THESSALONIKI

SCHOOL OF CHEMISTRY



Erasmus Mundus Joint Master in Archaeological Material Science

Hybrid coatings for the protection of cultural heritage materials

Mariana Monteiro Moraes Ramos

Supervisors:

Ioannis Karapanagiotis
24.10.2024 13:17

Dr. Ioannis Karapanagiotis

Konstantinos Triantafyllidis
25.10.2024 08:41

Dr. Konstantinos Triantafyllidis

Panagiotis Spathis
Panagiotis Spathis
25.10.2024 11:39

Dr. Panagiotis Spathis

Vasiliki Kamperidou
24.10.2024 17:24

Dr. Vasiliki Kamperidou

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Mariana Monteiro Moraes Ramos (m53965, 2145840)

Dr. Ioannis Karapanagiotis – Department of Chemistry, Aristotle University of Thessaloniki

Dr. Konstantinos Triantafyllidis – Department of Chemistry, Aristotle University of Thessaloniki

Dr. Panagiotis Spathis – Department of Chemistry, Aristotle University of Thessaloniki

Dr. Vasiliki Kamperidou – Department of Forestry and Natural Environment, Aristotle University of Thessaloniki



Thessaloniki, 2024

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ABSTRACT

Studies aiming to protect and conserve cultural heritage materials have been developed on the last decades and many techniques have been produced. Between the different types of material, the one less researched is wood, due to complexity of its structure, the variability between species, territories and the climate it was exposed, the existence of substances already applied to the surface when it was originally used, and the wood substrate itself with its irregularities. The variability created by those variables make it hard to reproduce the technique around the world and obtain similar results.

The following novel target two different types of wood more used on the Greek territory since ancient times, chestnut and oak, using a commercial coating and nanolignin as an additive. The main goal was to understand the properties that can be enhanced with the use of the nanolignin on the composition.

With the results obtained, it was possible to see a pattern where the additive coating shows better results than the one using the pure commercial coating, and oak kept showing better values than the chestnut. The increase on hydrophobicity existed on a certain degree, and adhesion, UV ageing protection and biocide properties were enhanced. The analysis made were able to complement and confirm the results, giving a good perspective on this research and showing possible next steps that can be made on future researches.

KEY WORDS: Heritage, lignin, coating, SIVO 121, wood

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1- INTRODUCTION

Wood is one of the materials used by humanity since the ancient times. It was used as a building material for houses, temples, castles, boats, structures for agriculture, development of tools, canvases, creation of idols and decoration objects. Since it is an organic material, it is hard to find intact ancient structures in some areas of the globe due to degradation processes.

One of the main factors that can interfere is water. Not only it can create degradation by itself, but it can also carry with it pollutants, microorganisms and salts that, inside the structure, can create different forms of chemical and physical weathering and erosion. Macro and micro biological cultures can create problems on the structures by itself, but also can generate subproducts that enhance the degradation processes.

The study of conservation of ancient wood structures and artifacts is an important topic, not only because cultural heritage is important for us to understand the past and how our ancestors lived, but also because it is an economical source in many places, both inside museums and archaeological sites, being constantly visited by the people of its own country and also by foreigners. Considering the list of World Heritage that exists on the UNESCO website [1], some of the examples that can be given are found on the Northern Europe (Norway, Finland, Sweden), other parts of Europe (Bulgaria, Romania), North America (USA and Canada), Asia (China, South Korea, Japan, Nepal, Laos), Africa (Ghana), to more recent constructions around the 18th century, such as internal structures of churches found in Brazil.

To protect wood from different degradation processes, coatings with different materials have been since ancient civilizations, with the main goal being to work as a mechanical barrier between the substrate and the environment. Nowadays, the idea of coating remains the same, but with specific goals, like reducing humidity, biocidal properties, reducing the change of its original colour, etc. Besides, it is necessary to consider that many times in structures, the wood has a paint coat on it for aesthetic reasons, and this layer also needs to be considered when thinking about a protection method.

Research have been developed on the past decades focusing on different points: protect against flame or acting as a flame retardant, biocide, cleaning properties, hydrophobic and superhydrophobic properties, increase of specific mechanical properties, between other options. The following thesis is a novel development of a hybrid coating, using a commercial inorganic coating with nanolignin, a renewable organic material, as an additive to increase the properties of the original substance. Different experiments were done to create a first scope of the

properties that could be measured, and two different types of wood were used to compare how the same material would act on distinct substrates.

The main parameters used to compare the results will be variation of contact angle and colour variation of the substrate. The experiments chosen can show different aspects that could incur structural and surface damage on wood, such as variation of pH of the solution on the surface, water absorption through capillarity, peeling cycles simulating removal of the coating, UV aging chamber for the direct effect of the UV rays without other interferences. Weathering and burial are the long-term experiments chosen to see how a combination of factors can affect the substrate, and the coating used on the surface.

Gathering all the results can create a first understanding of the behaviour of the coating and additive, showing possible uses and future researches that can be done on this field, using different substrates or new methodologies for the formulation and application of the coating, or other experiments that can be done to understand other properties of the studied material.

2- OBJECTIVES

2.1- General Objective

Novel development of a hybrid of organic and inorganic coating to protect wood species that can be found in cultural heritage. The goal is to determine how nanolignin working as an additive can improve properties of the coating through the use of different types of experiments focusing on different parameters.

2.2- Specific Objectives

- Compare the results between chestnut and oak on the experiments.
- Induce hydrophobicity on the surface of the wood species with the use of the coating technique.
- See the increase of adhesion of the coating using nanolignin as additive while doing the peeling cycle experiment.
- Check the increase of stability on the coating when using nanolignin as additive while doing the UV ageing chamber experiment.
- Compare the mass reduction on the burial experiment between uncoated sample, sample coated with pure SIVO and sample coated with SIVO and nanolignin as additive.
- Observe what can be considered behaviour of the substrate and behaviour of the coating used.

3- LITERATURE REVIEW

3.1- Wood as a Cultural Heritage Material

Wood is a material used by humans in many situations since ancient times. Material for fires, as a construction material (as the examples on image 01), used for tools, between other uses. Since it is an organic material, most of the times it is hard to find structures made of wood in ancient archaeological sites. One exception is waterlogged material, and it is possible to see this type of material being studied in [2], [3], [4] and [5]. On those articles, is noticeable that most of the time the research is more focused on characterization and microbiological activity.



Image 01: Examples of wood cultural heritage in Europe and North America. From left to right - SGang Gwaay mortuary pole in Canada (open source), Urnes Stave Church from the 12th century in Norway (Credit: Petr Šmerkl, Wikipedia), Gammelstad town from the 15th century, Sweden (open source).

It is also quite frequent in constructions around Asia, like temples and castles built in China [6], Japan [7], South Korea [8], Laos, Nepal, as an example on the pictures on image 02. Since wood is a common material in most parts of the world, but with different species that are influenced by climate, temperature, average precipitation, type of soil, it is seen as an interesting but, at the same time, hard to study material. Even though some species have common characteristics between each other, the behaviour might not be the same. Even a same species of wood might be distinct from another one that grew in a different place or a different season.

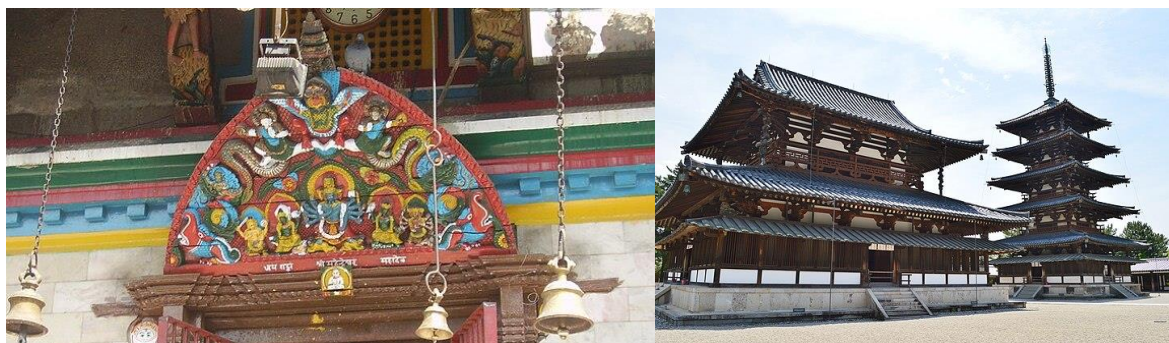




Image XX: Examples of wood cultural heritage in Asia. From top to bottom, left to right – temple entrance in Kathmandu (open source, altered), Horyu-ji Buddhist monuments in Japan (open source) Imperial palace of Ming and Qing dynasty in China (open source), Tripitaka Koreana woodblocks in South Korea (open source), and Himeji-jō Castle in Japan (open source)

Because of that, most of the studies related to wood as a cultural heritage material focus more on the identification of the species and more general techniques of protection and conservation, taking into consideration the more common characteristics in all species. Other type of research that can be made is identification of the type of protection method used on the material on the original application, being common on paintings and the wood used as canvas for example, like it can be seen in the articles on [9], [10] and [11].

The two types of wood used for this novel, chestnut (*Castanea sativa*) and oak (*Quercus frainetto*) were picked as the model because they are found on the Greek region and there are reports and articles of those being materials used since ancient times by the people living on the region ([12], [13] and [14]), making them excellent choices to start this study.

3.1.1- Chestnut

The species of chestnut used on this thesis is the *Castanea sativa*, also commonly known as sweet chestnut. It is the only native species of this genus inside Europe. It can be found in many countries inside the continent and also in Morocco and south-western Asia, as it can be seen on the map below (image 03). Usually reaches between 30-35m and it can live up to 1000 years. The species can also be found in North America and Australia due to European settlers, being younger than some of the individuals that can be found in Europe [15].

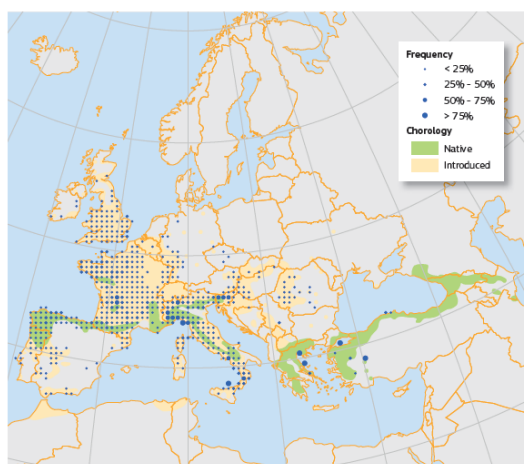


Image 03: Map showing localization and frequency of *Castanea sativa* (source: Conedera, M., Tinner, W., Krebs, P., de Rigo, D., Caudullo, G., 2016. *Castanea sativa* in Europe: distribution, habitat, usage and threats. In: San-Miguel-Ayán, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A. (Eds.), *European Atlas of Forest Tree Species*. Publ. Off. EU, Luxembourg, pp. e0125e0+)

Its original place and ecology is not completely understood since it was introduced by humans in many different places, as it can be also seen on the map, but one of the macro-regions that was probably part of it is the Greek peninsula, including the Peloponnese and Thessaly. Even though there is palynological evidence of cultivation of the species dating back to 2100-2050 BC on the region, it only have a subsidiary value.

As a species, it grows better on places with an average temperature of more than 10°C for at least half of the year, and a minimal rainfall staying between 600-800mm. It does not grow well in situations of draught, and it prefers neutral to acidic soil. It is sensible to frost but well adapted to fire-disturbance. Some examples can be seen on image 04.

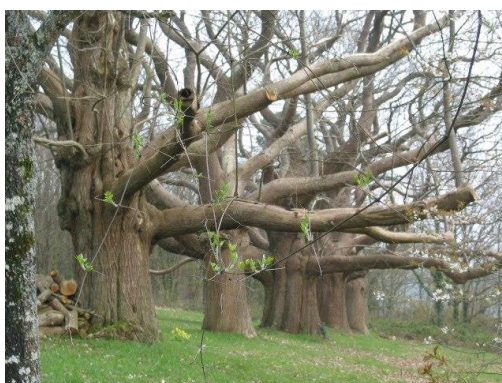


Image 04: Example of *Castanea sativa* (open source)

Their high quantity of tannin helps with the protection against weathering decay, being interesting when considering its use on outside constructions. Since one of its main use was to get poles and wood for smaller objects like barrels, this characteristic influenced on the applications.

3.1.2- Oak

The species chosen for oak is the *Quercus frainetto*. Even though its common name is Hungarian oak, it is actually not common on the area and was probably introduced instead of being original from there. It also reaches more than 30m of height but, unlike the chestnut, it is rare to see individuals living more than 200 years [16].

According to palaeoecological evidence, it could be found on the Peloponnese region since ancient times (6000 years ago) [14]. Its larger distribution is on the Balkan Peninsula, which is comprehensible since it is a species that is better developed on regions with a climate between the Mediterranean and the continental as it can be seen on the map (image 05) below.

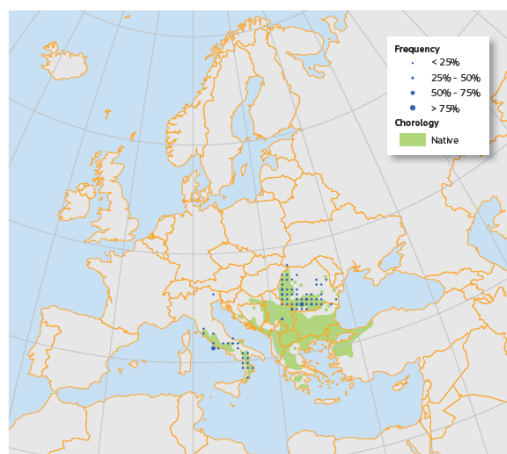


Image 05: Map showing localization and frequency of *Quercus frainetto* (source: Mauri, A., Enescu, C. M., Houston Durrant, T., de Rigo, D., Caudullo, G., 2016. *Quercus frainetto* in Europe: distribution, habitat, usage and threats. In: San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A. (Eds.), European Atlas of Forest Tree Species. Publ. Off. EU, Luxembourg, pp. e01de78+)

Because of it, it can survive both a warm summer and a cold winter. Like chestnut, it also prefers acidic soil, being able to grow even in heavy acidic situations. It can tolerate some level of waterlogging, but it does not thrive well with high levels of shading. Since it possesses a wood of high durability, it was used on civil engineering and mining as a building material. Example of the species can be found on image 06.



Image 06: Example of *Quercus frainetto* (open source)

3.1.3 – Lignin

Lignin is one of the three main components of wood, together with cellulose and hemicellulose. It is responsible to keeping the structure and it also have biocidal properties. Its chemical structure is a macromolecule with alcohols, phenolic rings [17] and other aromatic rings, as it can be seen on the image 07 below.

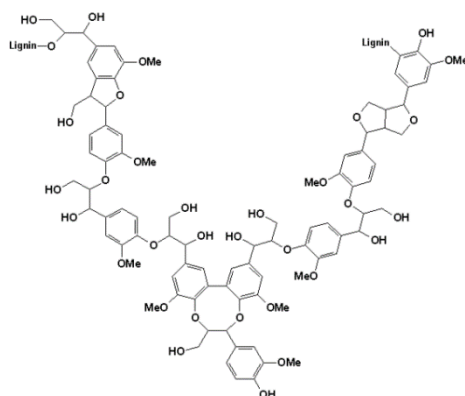


Image 07: Structure of lignin (open source)

Originally, lignin was considered a residue of the paper and cellulose industry, obtained through the Kraft process [18], and it was mostly used as fuel inside the industry itself. Over the past decades more research on applications of this material have been done, considering it is a renewable material with a lot of potential. One of the issues considering its application is colour, since it is hard to eliminate the brown or yellow tone in anything created with this substance. Between the applications we can find research on coatings, foams and adhesives.

Research and patent can be found to reduce the colour, but it is possible changing some parts of its structure, which might be a problem in some applications. As an example, the phenolic rings are responsible for the good adhesive properties of it, but on the patent US4454066A, there is a break of those rings in order to reduce the colour, reducing its property.

There are different methods of obtaining the lignin on its nano form [19]. Currently it can be found commercially as a powder, but it is also possible to be obtained inside the laboratory using a batch reaction. The final product on the organosolv process will be on colloidal form, but it can be filtrated and dried out to have access to the powder.

3.2- Basic concepts of wettability

Wettability is related to the ability of a solid material surface to have contact with a liquid. The interactions are described on molecular level and take into consideration the adhesive and cohesive forces acting between the molecules of both the surface and the liquid.

Three main factors influence on this property: surface energy, roughness, and inhomogeneity [20]. Energy directly affects the type of interaction between the molecules, roughness on the model that best describe the static contact angle and inhomogeneity how replicable the results are along the surface.

The main parameter used to analyse wettability on a surface is its static contact angle, commonly known as SCA [21]. Thermodynamically speaking, it can be described as the equilibrium between the three phases, as it can be seen on the image 08 below. The simplest way to explain the contact angle is to imagine that the solid-vapour interface turned into a solid-liquid one with the addition of the drop of the liquid. Since it is an equilibrium between the three states that determinate the format of the water on the surface, we can also find the SCA being referred as equilibrium contact angle (θ) [22].

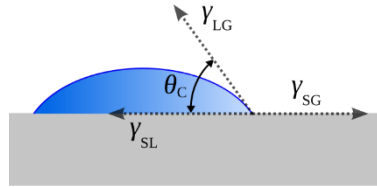


Image 08: Diagram of the three interfaces (open source)

The best way to explain the wettability is showing the Young contact angle equation [20]. Since it is theoretical, it considers an atomically smooth surface, meaning lack of texture on it. This is a reality almost impossible to reach with the use of laboratory materials, and it cannot be found naturally.

$$\gamma_{sv} = \gamma_{lv} \cos \theta_Y + \gamma_{sl} \quad (1)$$

Where:

- γ is the surface tension defined by each of the interfaces (solid-vapour, liquid-vapour, solid-liquid)

- θ_Y is the Young contact angle, defined for drops with less than 10 μ L and being specific to the material being analysed.

3.2.1- Models used in Wettability

Wettability in theory follows two different basic models: Cassie-Baxter and Wenzel. They were created after the Young model, since this one needs a smooth atomic surface that cannot be found naturally. In both cases, they are described in relation to θ_s , the apparent contact angle, taking into consideration how a real surface is found, with porosity and roughness.

For Cassie-Baxter, demonstrated on equation 2, we have the porosity enhancing the hydrophobic behaviour of the material, being originally hydrophilic or hydrophobic not taken into consideration [23]. The equation has f_s as the solid fraction with water, being usually lesser than 1 in most cases. If dealing with an ideally flat surface, its value became exactly 1.

As it can be seen on the image 09, the drop is on top of the surface, with bubbles of air among the irregularities. This type of model shows low hysteresis and a good rolling behaviour for the drop, since it has a lower surface contact, generating a lower adhesion. Self-cleaning surfaces usually will present the behaviour explained by this model, since the liquid can roll out through the surface carrying impurities easier.

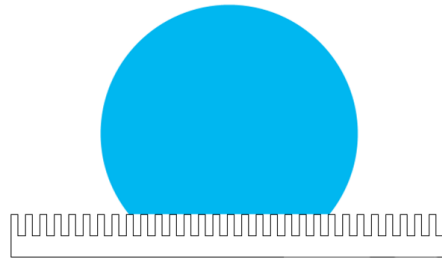


Image 09: Cassie-Baxter model

$$\cos\theta_s = -1 + f_s(\cos\theta_Y + 1) \quad (2)$$

On the other hand, Wenzel [24] suggests roughness enhancing the original behaviour of the material (hydrophobic getting more hydrophobic and hydrophilic getting more hydrophilic). It uses r as the ratio between the value of actual and geometric surface, being usually larger than 1, but exactly 1 in cases of ideally flat surfaces. The equation 3 represents the model.

As it can be seen on Image 10, the surface contact on this model is bigger than the geometric surface, since the liquid will occupy the irregularities of the solid. The roughness is the r described above for the equation. This generate the resting drop, which does not move easily on the surface.

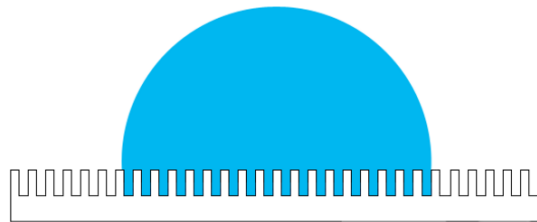


Image 10: Wenzel model (open source)

$$\cos\theta_s = r\cos\theta_Y \quad (3)$$

The main point of both cases being theoretical models is that, in some real-life situations, none of them can actually explain the behaviour of the surface. The most famous case that does not fit in any of these models is the Lotus leaf, which is responsible for the term Lotus effect [25]. Due to this type of situation that further research and studies are still being made, in order to comprehend and explain what doesn't fit the current models.

3.2.2- Contact angle

Currently, the terminology can be divided in four different parts that can be used for water (hydro), oils (oleo) and every other liquid (omni): super-phility (less than 5°), phility (between 5 and 90°), phobicity (between 90 and 150°) and super-phobicity (over 150°) as is seen on image 11.

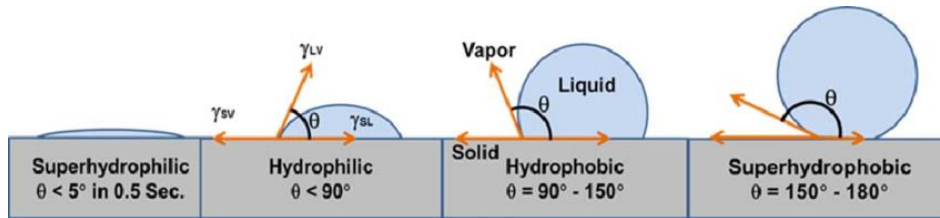


Image 11: Schematic of contact angle and its respective nomenclature for water(open source)

Another important contact angle that is used on wettability is the tilt contact angle (θ_t), referring to how many degrees the surface should incline for the water drop roll down the surface [26]. For the surface be considered repellent, it is necessary to have a tilt angle being lower than 10°. Considering θ_A the advancing contact angle and θ_R receding contact angle, the minimal force that is necessary in order to start the movement of the drop can be described by:

$$F = \gamma_{lv}(\cos\theta_R - \cos\theta_A) \quad (4)$$

The repellence or not on the surface is responsible for two known effects: rose petal and lotus [26]. In both cases, the surface has a contact angle higher than 150° but, while on the lotus effect we see repellence of the drop, on the rose petal we see the drop staying pinned down on the surface, even when the surface is upside down, as it can be seen on the Image 12 below.

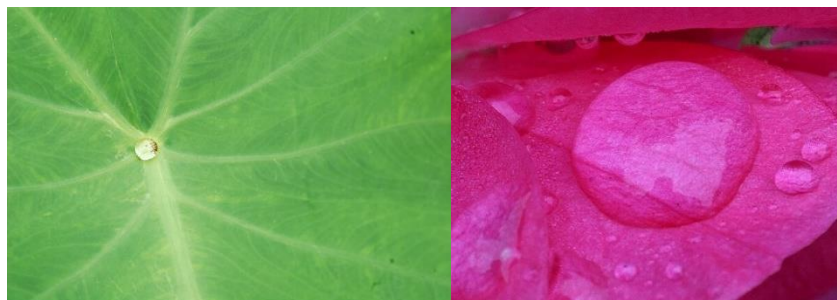


Image 12: Lotus effect (left) and rose petal effect (right) (open source)

3.3-Coating

Coating is a method of protection of materials and their surface against outside action. It can work simply as a barrier between substrate and environment, but it can also have specific properties in order to enhance its use and quality, like hydrophobicity [27], fire retardant [28], biocide [29], self-cleaning [30], enhancement of mechanical properties [31], enhancement of chemical stability [32], UV protection [33], corrosion protection [34], as examples.

Most of the time, a coating is not applied for a single reason, and the components on it can enhance different characteristics. One example can be the use of oxides, that usually enhance biocide properties (specially titanium and zinc oxide), but it also has some anticorrosion [35] and UV barrier properties.

The application of coatings methods as it is seen on image 13 depends on multiple factors: size of the substrate, material it is made of, format, thickness of the coating that can be applied and if it is a fixed structure or it can be moved. From simple methods as paintbrush, paint roller, to aspersion, bath, and even electrolytic coating, to define the method it is necessary to consider a series of variables, and maybe even act some trials (if possible) [36].



Image 13: Some application methods for coatings (source: A review on tribology of polymer composite coatings - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/Schematic-diagram-of-various-methods-for-preparing-polymer-coatings_fig3_347224053 [accessed 22 Sept 2024])

The thickness of the coating [37] influences in many factors: colour variation, curing process, mechanical behaviour for scratches and other impressions. Thickness can be directly influenced by the method of application (usually paintbrush will have a thicker layer than spray paint for example). Not only that, but it also influences on how homogeneous the thickness of the coating is along the surface. Simpler techniques have a tendency of generating more irregular thickness.

That can be a problem because, for example, regions with a thin layer being scratched can have the coating completely removed of the surface while it lasts on the rest of the surface. If we are talking about a metal substrate, this point scratched could start different methods of corrosion that could propagate underneath the coating and turn the entire material frail, but not visible since part of the corrosion would be covered by the coating. For a stone or wood substrate, it could be an area of biological action, which could incur in effects inside the whole structure.

But, at the same time, a thick layer is not always the solution. Coatings using nanomaterials, for example, can have its properties enhanced when applying a thin layer. It is also easier to be studied considering microscope and other surface techniques, since we cannot be sure if the behaviour remains the same during the entire thickness of it. The curing might also not be regular on a thick coating, since solvents can take longer to evaporate.

3.4 – Protective methods for wood

Wood has been protected when used by humans since the ancient times. It is possible to observe that ancient groups chose the wood according to the use it was going to have. Aboriginal people in Australia knew how to use termite and specific species of wood for graves, Maias built a temple using termite-resistant wood, ancient literature in different countries would have topics about durable wood [38] [39].

The basic forms of coating and consolidation for wood were made using mainly biological materials, like natural oil from multiple plants, resins and wax. Tar, pitch and bitumen was also used, just as techniques such as charring the surface or storing it on salty water.

Many of the techniques developed on the ancient times kept being used in during the centuries until the Renaissance. Periods such as the age of exploration and industrial revolution required more complex and efficient methodologies for the protection of wood, since the degradation of the structures could also incur in economic problems for the kingdom using it.

With the time, it became more common the use of chemical treatments instead of the use of natural materials. That opened the possibility of more refined techniques, being created with specific components. One example is the treatments Leonardo da Vinci would do on the wood panels used for his paints [38], using mercury chloride and arsenic oxide. Not only that, but the evolution of the science helped understand the weathering processes happening to the wood and the agents involved in it, being another important step on the development of the current methods used.

Nowadays, methods using products considered environmentally friendly have been an important topic, since many of the techniques used up to this point involve the use of toxic and environmental unfriendly materials, such as cyanides, bromomethane, and some inert gases that contribute for global warming.

Methods of wood conservation can be categorized as protective methods and consolidation methods. Some of the techniques and materials used works for both categories. When the method is being decided, one important factor considered is if the wood is being kept dry or if it is wet/waterlogged, being a big influence on the method that can be used.

The method of preservation is composed of a biocide or a preparation that contains a biocide. It will also have the vehicle (solvent or combination of solvent), plus extra materials to add extra properties to the mixture, such as surfactants, pigments or binders. When the vehicle is water, it can be used on dry or damp wood and is usually a treatment with salt compounds that work as biocides. When organic solvents are being used, it is better suited for dry or semidry wood, and it can be an undercoating, coating (protection or decoration) or impregnation.

Some of the salts used are: sodium chloride (antique form of preservation), copper salts (started to be used on the 18th century), mercury chloride (started to be used on the 16th century), zinc salts, arsenic salts(16th century onwards), fluorides, fluorosilicates, boron compounds, and chromium compounds. Organic biocides used during the centuries: wood tar (ancient form of preservation), coal tar oil, kerosene, chlorinated hydrocarbons, dichlorobenzene, dicophane, lindane, cyclodiene insecticides, organophosphates, carbamates, phenols, and other recent organic materials developed.

When applying the preservative method, the fixation of the material is important. If the biocides can move, the external water or the humidity can transport the particle to the surface, get attached to contaminants or dust and end up being removed of the substrate, reducing the efficiency of the technique.

4- MATERIALS AND METHODOLOGY

4.1 – Materials Used

4.1.1 - Dynasylan® SIVO 121

Commercial product by Evonik Industries, it is a wood surface impregnation agent with hydrophobic and oleophobic properties. The treatment method is said to have influence on the water repellence and possible prevention of adhesion and permeation of oils and greases. It has also a high QUV, giving a good protection for outside materials against weathering and UV ageing [40]. It also maintains the breathing of the surface possible, which is important to not keep vapour of water stuck inside the structure.

Other characteristics described on the leaflet provided by Evonik [41] are: low colour variation on the surface and reduce the growth of microorganisms by keeping the surface dry. It can be applied by roll, paintbrush, and spray. Its density and viscosity are close to water, and it has an acid pH in a mixture 1:1 with water. The recommended dosage that implicates in 1500h of QUV-stability is of 300g/m².

It is a material sensitive to freezing temperatures. A low temperature can possibly generate the formation of flocculate material upon defrost, creating problems on its properties. It should not be applied to surfaces with a humidity higher than 18%.

It is a water-borne silane substance (as it can be seen on image 14) with multiple fluoroalkyl functional groups that are responsible for its UV protection properties. It is said to be environmentally friendly due to the low amount of VOC present. Even though it is resistant to UV irradiation, it has a weak UV absorbing strength. This makes the decomposition of lignin be delayed but not stopped.

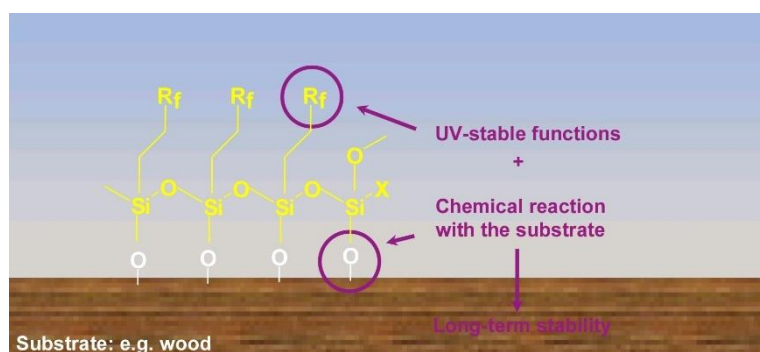


Image 14: SIVO 121 reacting with the substrate to adhere on the surface (source: Evonik Industries. (2008, January). *Dynasylan® SIVO 121 Surface Impregnation of Wood*. Catalogue Evonik Dynasylan SIVO 121. <http://www.finchem.lk/wp-content/uploads/2016/12/Catalogue-2.pdf>)

During the writing of this novel thesis, this product will be commonly called simply as SIVO to simplify the writing.

4.1.2 – Nanolignin

The nanolignin used for this thesis was made inside the Environmental laboratory of the chemistry department of the Aristotle University [42], [43],[44]. It is made following the process below. The final product that was applied to the coatings was a dark brown powder with low density.

Thirty grams of lignocel from birch are mixed with 300mL of a mixture 60% ethanol and 40% water. Then 321 μ L of pure sulfuric acid is added as catalyst. This mixture is put inside a 600mL reactor, heated to 175°C and with rotation of 400rpm. When the temperature reached the working value, the reaction occurs for an hour. After that the reactor is depressurized and let to cool down. The filtration is made with an ice bath, later adding water to the mixture to reduce the lignin solubility, as it is seen on the image 15 below. On the second filtration, the lignin gets retained on the filter, then is let drying on room temperature overnight. To finalize the dry step, the nanolignin is kept inside the oven at 80°C for six hours on the following day.



Image 15: Solution with the lignin going through decantation after the addition of water on the mixture

The final product is denominated organosolv lignin. Even though it is considered nanomolecular, it is on the higher size of this type of particles, possessing approximately 570nm. Due to its high size, it is interesting to not use a large quantity of it on a hydrophobic coating, since it can reach a saturation point relatively easy when compared to smaller molecules. The final product can stay on powder form or as a colloidal solution.

4.1.3 – Solvents

During the step of using a solvent to make the lignin soluble, adding this mixture to the SIVO, four different solvents were tested. All of them were obtained also inside the environmental laboratory, being acetone, ethanol, isopropanol and methanol. Since all the substances are analytical reactants, the purity is higher than 99%.

4.1.4 – Wood samples

The species of chestnut and oak were obtained by and cut on the forestry department. Both species were originally from the Halkidiki region on north Greece, having one trunk of each species harvested for the experiments. When arriving at the laboratory infrastructures of the department, the samples were cut into thick boards and left under the stable conditions of 20°C and 65% of relative humidity to dry naturally with time. The drying process is made this way to avoid natural defects, such as cracks. This process also keeps the quality of the wood.

All the pieces were cut using the same equipment to ensure comparative surface quality characteristics, being used a disc cutting machine first on the preparation of the samples. There was no use of planning process, since the surface after the use of the disc cutting machine presents an acceptable surface quality.

4.2 – Methodology to determinate the coating composition

The first step on the development of the coating was the decision of how to add the nanolignin to the SIVO and how to make the mixing of it to guarantee a uniform solution. Each step of this procedure would be tested comparing the values of the pure wood and pure SIVO on each wood in relation to the mixtures obtained. The variables used for it were the colour variation and the contact angle (in °) obtained. The main goal was to obtain a small increase in colour while reaching the highest contact angle possible.

4.2.1- Variation of sonication time on the mixture

Considering the high percentage of water existing on the SIVO solution [45], the first idea was to add a small percentage of nanolignin directly on it and mix it. Firstly, a mechanical mixing using a stir bar on a magnetic stirrer was used. The results were not satisfactory, which made the use of sonication necessary. With that in consideration, the next step was to decide how long the mixture should be under the sonic waves, using at the start a lower percentage of nanolignin. After deciding the optimal time, the next step was to variate the concentration of the nanoparticle to see the results.

4.2.2- Solubilizing the Lignin on a second solvent and adding to SIVO

Considering previous research [46] [47], it is known that the addition of a second organic solvent can increase the solubility of the nanolignin on a mixture with water as the main solvent. To apply this concept on the research, 4 different solvents (acetone, ethanol, isopropanol, and methanol) were mixed with 0.5% w/w of nanolignin (image 16), and part of this mixture was added to the SIVO and applied to the two types of wood. The condition of the solvent-nanolignin mixture, and the variations of colour and contact angle were taken into consideration when deciding the best solvent to be used on the final mixture.

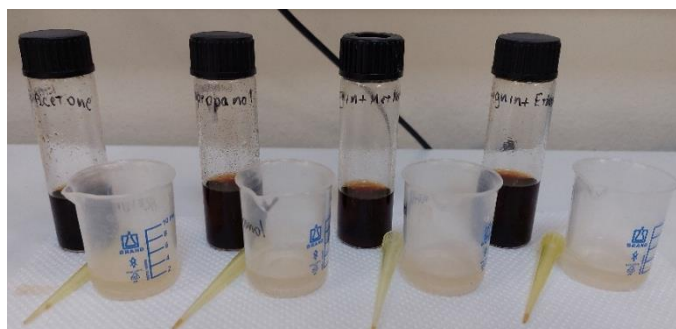


Image 16: Mixture of second solvent and nanolignin added to beakers with SIVO

4.2.3- Variation of lignin concentration

After deciding the second solvent to be added, the next step was to create different solutions using distinct concentrations of the nanoparticle in order to check if the material would suffer a saturation on the surface and decrease the contact angle, or if it was going to reach a plateau and have similar values with different concentrations of the additive. The values used were of 0.5%, 1.0%, 2.0%, 3.0% and 4.0% w/w related to the mass of second solvent, as it is visible on image 17. The value of second solvent with nanolignin added to the SIVO was constant, controlling one of the possible variables on this study case.

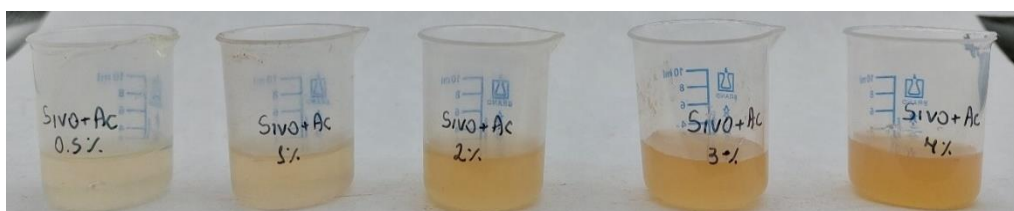


Image 17: Variation of nanolignin concentration on the second solvent

4.3- Contact angle measurements

Most of the contact angles were measured using the software ImageJ, except the intermediary ones made during the process of ageing on the UV chamber and the samples for

weathering, when an automatic MSA was used setting the baseline manually to guarantee the right measurement of the angle. To assure that the contact angle measure with both techniques was the same, the samples that went through the UV ageing chamber were submitted to both techniques at the end of two months, and the values obtained were compared.

For the manual measurements made on the rest of the thesis, the coated sample would be put on the system showed on the image 18, with the syringe filled with water (or the pH solutions for the specific experiment), having a drop with a volume of approximately 3 μ L. The image was captured, opened on the ImageJ software, treated to increase the visibility of the contact angle, then the measurement was taken with the angle tool. Drops would be applied around the central part of the surface, since the irregularities on it would create sometimes a large variation of the results obtained, and an average in the end would be calculated.



Image 18: System created to photograph the drops for contact angle.

4.4- Colorimetry measurements

The colour variation was measured using the Colorimetry PCE Instruments model PCE-CSM1, showed on image 19. The results are given in L^* , a^* , b^* coordinates. Those coordinates represent different aspects, with L^* relating to the lightness observed (on a scale from 0 to 100, lower values are closer to black, while higher values relate to white), a^* relates to the green-red axis (negative values relate to green and positive values to red) while b^* relates to the blue-yellow one (negative values relate to blue while positive relate to yellow).

To calculate the variation, it is necessary to have both measurements made around the same region of the sample, since the colour have different results around the surface. To obtain both measurements, the pure wood samples were first measured, creating the values identified as L_i , a_i , b_i (measured on triplicate). After the coating was applied and cured, a second triplicate would be made, generating L_f , a_f , b_f . The final value then would be calculated with the following equation:

$$\Delta E = \sqrt{(L_f - L_i)^2 + (a_f - a_i)^2 + (b_f - b_i)^2} \quad (5)$$



Image 19: Equipment used for colorimetry

When dealing with experiments that will have colour variation with time, after the values of the base coating was identified for both woods, (4.9 and 4.10), the initial measurement was of the coated sample and the final of the aged/weathered coat after the experiment. An important parameter during this part of the process was to identify the samples with $\Delta E < 5$, since it is important on cultural heritage a low colour variation for the methodology to be accepted.

4.5 – Water absorption through capillarity

Following the methodology used inside the lab, capillarity was measured by weight (g). The samples would be positioned inside a box, with wet paper covering its lower part, making the coated part of the sample being constantly in touch with the wet surface, as it can be seen on image 20. After every ten minutes, the samples would be weighted, firstly removing any water excess existent on the surface. This is made to measure only the water absorbed through the capillarity. This procedure was repeated until 2 hours (120 minutes) were completed, creating a graph of water absorbed (in g) versus time of analysis (in minutes).



Image 20: Water absorption experiment

4.6 – Contact angle with different pH solutions

For this procedure, 5 solutions with different values of pH were used (1, 2.5, 7, 10 and 12.5). Each sample would receive 3 drops of approximately 3 μ L of each solution, with a picture made for each drop. Those pictures would be treated and have their angle measure on the ImageJ software. This analysis was made to understand if changing of the pH of the solution hitting the surface would create different responses.

4.7 – Peeling cycles

On this experiment, a tape would be attached to the surface of the sample with the coating, as it can be seen on image 21. Then, the peeling movement would be applied multiple times on the surface, changing the patch of tape after every five times. After those five times, a drop of approximately 3 μ L would be deposited on the surface to measure the contact angle. This procedure would be repeated until the angle decreased to a value close or lower than 90° or a total of 100 cycles was reached. It is expected a higher value on the samples with lignin on the coating because, as it was previously studied in [48], [49], [50], [51], [52], it is known that the phenolic rings on the lignin structure increase the adhesion of a coating to its surface.

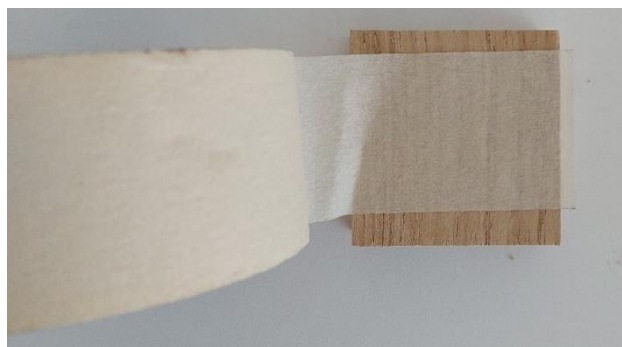


Image 21: Sample in contact with tape for peeling cycles

4.8 – SEM imaging

Images of the pure woods and its counterparts were obtained using the equipment JEOL JSM-6390 OLV from the Physics department of Aristotle University. The images were obtained with 100x amplification, with some specific points being taken with a larger amplification to see the structure of the particles deposited on the top of the coated surface.

SEM is an imaging technique that can obtain high resolution photos. It is a microscope that uses a beam of electrons directed to the surface. When generating the image, we can use the data obtained by the electrons that reach the surface of the specimen and interact with it on an

inelastic (secondary electrons) or elastic (backscattered) way. The high-resolution imaging and the depth observed (topographical image) is obtained through the secondary electrons [53] [54].

In order to be able to use this technique, it is necessary to have a conductive surface. The method used to obtain that on this case, since wood is not conductive, is through carbon coating. The samples are put inside a chamber that has two fragments of carbon touching each other. Vacuum is applied inside the chamber and then a current pass through the carbon fragments, making them release a thin layer of coating on the top of the sample. If not completely coated, the method can be repeated and, if necessary, special conductive tapes can also be added to the surface to enhance its conductivity, generating better images.

The main reason of this analysis was to conclude if it was possible to see or not the changes on the surface with the variation of the coating formulation, and possible a saturation of the additive used. The images obtained on the SEM are also interesting to show how irregular is the surface of the types of wood used without coating, and how this can influence on the behaviour of the coated samples.

4.8.1 – SEM-EDS

The EDS spectra was obtained with the intent of understand the composition of the coating due to the results on contact angle obtained for 4.9 and 4.10. The stability of the contact angle after long period experiments is not always common, so it became necessary understand what could be causing such stability. Only two samples were used on this case, one coated with pure SIVO and one with the mixture of SIVO and lignin, both applied to the oak substrate.

The oak substrate was chosen simply because it was the species showing better values of contact angle, and keeping the same substrate would avoid a possible interference caused by the wood composition, if the thickness of the coating is low enough for the technique to reach under it. The expectation was to see a reduction of the contact angle with time of exposure.

EDS is a spectroscopical technique that can be used while using the SEM to obtain data related to chemical composition using the atomic number and the backscattering electrons. The areas with heavier (higher atomic number) elements will appear lighter on the image, since more electrons are being deflected, while darker areas correspond to low atomic number [55] [56]. The equipment has a software that is able to convert this type of information into a spectrum, identifying the elements present on the designated area and its percentage in %w/w.

Two points are important while doing this analysis for this specific situation. The first one is that it is hard to know for sure if the depth the electrons reach on the coated substrate refer only to the coating or the pure wood as well, as it was mentioned before. The second point is that, if low concentrations of a specific element appear only on a single point around the entire substrate, it is probably the case of a contaminate being found on the surface instead of being part of the formulation of the coating.

4.9 – UV aging chamber

The UV aging chamber used is located on the Hydraulics building of the Civil Engineering department. The samples were left inside the chamber for a total of 60 days (1440 hours), being checked twice every week, having the contact angle measured with the MSA like it is seen on image 22. On each check, the position of the samples would be changed inside the chamber to make the exposition of the UV lamp as uniform as it could be.



Image 22: MSA used on the sample

The values of the MSA would be recorded on a table and, at the end of the analysis, the samples also had the contact angle measured with photo and the ImageJ software. Colour variation was also measured to see if the direct exposition of UV light would interfere with the colour of the coating.

4.10- Natural weathering

The samples for natural weathering had their colour measured after the application and curing of the coating. After that, it was measured again during the procedure each month and the calculations were made. Contact angle was measured monthly to compare with previous values. To be exposed to a natural environment for the weathering, the samples stayed settled

as it can be seen on image 23, located on the terrace of the School of Forestry and Natural environment of the Aristotle University, located outside the main campus. For this specific experiment, the idea is not to calculate the variation of colour before and after the analysis, since it would show that all the samples surpassed the limit established for the protection of a cultural heritage material. It will be a comparison to understand how different factors can affect the variation of colour, considering not only ΔE but each variable (L^* , a^* and b^*).



Image 23: Samples positioned for natural weathering

4.10.1- Roughness Measurement

The Roughness was another parameter used to identify the effect of the weathering on the samples. Its use is also interesting because it is able to demonstrate the roughness created by the coating, comparing the formulations used with the non-protected wood. The parameters used are R_a , R_z and R_q , and they follow what is described at [57] and [58]. The equipment is put on top of the sample, as shown on image 24, and a distance of 4 mm going and coming back is covered by a sensible stylus, with the values being shown on the equipment. The three parameters are recorded and showed on a table but, for comparison of results, only **R_a** will be used, since it is the usual parameter used in articles having this type of analysis.

The equipment has some limitations, one of them being how much can the reading deviate from the average value. If, while doing the reading, the stylus finds a place deeper or higher than a certain distance from the average, the equipment stops the reading and shows the message of error. It is also a really sensible to disturbance equipment, so it is recommended that no pressure points or equipment creating vibrations on the table should exist, or the results can be affected.



Image 24: Equipment on top of the sample measuring the roughness

4.11- Burial experiment

This analysis focus on the mass variation with time the sample was kept buried. The samples were measured and weighted. After that they were put inside the oven for 24h at 75°C to remove the moisture inside of them, this whole process being shown on image 25. On the following day, the dry mass was measured and then the moisture content and dry density were calculated.



Image 25: Cutting, measuring, and drying the samples

After that, they were buried with a dept of 10cm on the outside area of the School of Forestry and Natural Environment, as it can be seen on image 26. When they were removed from its burial ground, the dirt attached to the surface would be cleaned and the sample would be dried at the same temperature and measured again on the analytical scale for the comparison.



Image 26: Samples on the burial area and demarcation of the burial site

Since a reduction on the mass is expected with time, the relative density of the samples would also reduce accordingly. The volume of the volume was kept the same, but the mass would be lower. Another expected idea is that, with time, the degradation process became faster. This would happen because, if the sample is less dense, it means that it is less compact. This affect directly with the substrate having more internal space for water and microorganisms to be transported, increasing the surface area for them to make the weathering process.

5- RESULTS AND DISCUSSION

5.1- Formulation of the coating

The formulation and definition of the best formulation for the coating went through multiple phases:

- Analysis of the pure SIVO to have its parameters as a blank to compare.
- Definition of the mixing and resting time.
- Variation of concentration of nanolignin.
- Test to determine the second solvent that would be added to in order to improve the solubility of the nanolignin on SIVO.
- Variation of the concentration of nanolignin on this new formulation.

Following next, it will be explained how each of those phases were realized and values that were used. The values of contact angle and colorimetry will follow each step of the formulation because there were some differences with the improvement of the measurement methods during the whole process.

a) Analysis of the pure SIVO

Half of two blocks with 5x5cm of surface was coated with pure SIVO, one of chestnut and one of oak, as it can be seen on image 27. The samples were left to cure for 24h before the measurements were taken. 0.15 ± 0.02 g of coating was applied. Important to mark, for this step and all the other ones taken later, the weight of the wood block is measured, the coating is applied and right after is measured again, this value being the one noted as mass of the coating. This was defined because the weight of wood will vary during the day due to the water content of the block, values that were observed on the next steps with the use of a 4 decimal digit scale. Also, after the coating is applied, the solvent starts to evaporate, being another variable for the weight values. The best way found to reduce those errors was to measure the difference with the shortest time gap possible. The values of contact angle (°) and colorimetry are on table 01.



Image 27: Samples coated with pure SIVO (top part). On the left Chestnut, Oak on the right.

	Colorimetry Values				Contact Angle (°)
	Average L*	Average a*	Average b*	ΔE	
Chestnut	2.80±0.25	1.86±0.37	2.60±0.65	4.25±0.12	103.3±0.8
Oak	1.54±0.94	0.63±0.27	1.87±0.68	2.50±0.19	111.6±1.4

Table 01: Pure SIVO values of Colorimetry and Contact Angle

Since each value (L*, a*, and b*) would have its own standard deviation, when calculating the deviation of ΔE, it became necessary to calculate propagation of error. This was possible using the two following equations:

$$\sigma_w = \frac{\sigma_x * w}{2 * x} \quad (6)$$

$$\sigma_{\Delta}^2 = \sigma_L^2 + \sigma_a^2 + \sigma_b^2 \quad (7)$$

Considering the general equation to find ΔE (5), first is necessary to apply equation (6) on each variable (L*, a*, and b*). After that, the individual errors from those variables are added using (7). To find the final value, (6) is applied again, this time using σ_{Δ} in place of σ_x , and w as the value of ΔE without errors.

Following, on image 28, we see examples of the drops photographed for this part of the experiment that have their values shown together with the value of ΔE on the table 01 above:

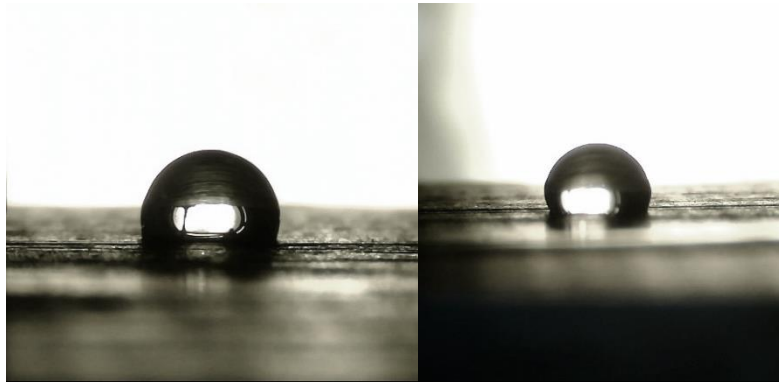


Image 28: Drop on chestnut (left) and on oak (right) with pure SIVO

This first step determines the hydrophobic values of the pure SIVO, and served as a base to compare with all the other values during the stage of determination of the formulation with lignin. The comparison always considered what would be the best parameters considering ΔE and contact angle combined. As an example, a good result on contact angle but with a high variation of ΔE is not interesting for this study, since the colour variation based solely on the coating should be low. Important to notice that both woods, without any coating, are hydrophilic and the drop would be absorbed too fast to be measured.

b) Definition of time of mixing and time of resting

The original idea was to mix directly the nanolignin (obtained on the Environmental lab of the Chemistry department of Aristotle University) in powder form to the SIVO, using 0.5% w/w of total weight. The first step was to try to mix it using the normal stirrer with magnetic bar, but, as it can be seen on image 29, the result was not effective.



Image 29: Side and top vision of beaker after magnetic bar mixture

The solution for this problem was the use of sonication. The sample would be inside a beaker, inside an ice bath to keep the temperature lower, since the sonication process generates heat, which is not recommended for the stability of the nanolignin. The schematic for it can be seen on image 30. It was decided to let the sample stay on sonication for 15 minutes total, then 30 min total.



Image 30: Ice bath and sonication on the sample for mixing

On the surface, it was applied 4 different situations: right after the sonication in each total time, and after letting the sample rest for a similar period, using the colloidal created. The final schematic of this step can be seen on the image 31.

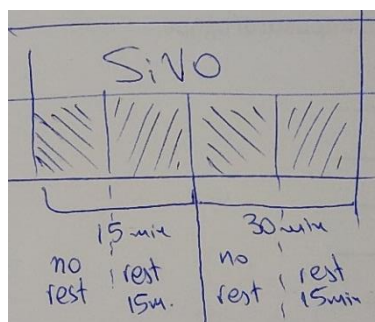


Image 31: Schematic of the distribution of the coatings on the wood substrate

It was visible that the colour would have a larger variation when the mixture was fresh out of the sonication instead of using the colloidal, as it can be seen on the image 32 below. With that in mind, a new experiment was thought, now with a variation of the nanolignin concentration using also 1% and 2%, analysing the difference between freshly sonicated and after the colloidal formation.



Image 32: Chestnut (on the left) and oak (on the right) after the applications

The values found during this step of the formulation can be found on the table 02 below, and some examples of the water drops for contact angle are on the images 33, and 34 right after. The measurement of nanolignin is in w/w.

		Colorimetry Values				Contact Angle (°)
		Average L*	Average a*	Average b*	ΔE	
Chestnut	No rest 15 min	7.56±1.37	3.43±0.36	3.74±0.59	9.11±0.29	125.5±1.1
	Rest 15 min	4.68±2.60	2.63±3.53	3.46±0.96	6.39±0.61	120.7±0.9
	No rest 30 min	2.39±1.79	1.98±0.45	2.80±0.93	4.18±0.30	124.2±0.9
	Rest 30 min	2.86±0.46	1.92±0.42	2.12±0.23	4.04±0.10	123.5±0.9
Oak	No rest 15 min	7.06±2.52	4.20±1.69	3.89±1.66	9.09±0.56	135.5±0.6
	Rest 15 min	3.58±1.18	2.56±0.29	2.91±0.84	5.28±0.23	118.4±0.8
	No rest 30 min	1.80±1.35	2.27±0.45	2.63±0.79	3.91±0.21	126.2±0.6
	Rest 30 min	0.99±0.98	1.73±0.21	2.40±0.64	3.12±0.15	125.2±0.5

Table 02: Values using 0.5% w/w nanolignin

Chestnut drops: from left to right representing in order the samples of table 02

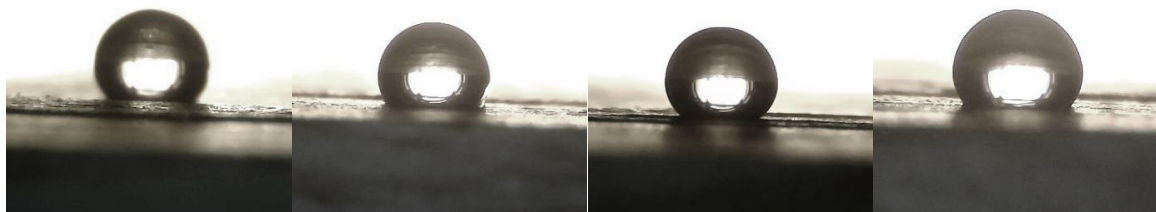


Image 33: Drops on chestnut changing sonication and rest time

Oak drops: from left to right representing in order the samples of table 02



Image 34: Drops on oak changing sonication and rest time

So far, the conclusion would be that a larger sonication time for the mixture would be associated to a lower colour variation on the sample without a heavy interference on the contact angle measured. Also, leaving the sample to rest, which forms the colloidal, reduces even more the ΔE . This happens because some of the heavier particles that will go to the bottom of the becker are responsible of part of the visible particulate that can be seen on the coating applied freshly out of the sonication.

On the other hand, the use of the colloidal create a side problem. Since phases are being separated, the concentration %w/w originally described is not equal to the one used, considering that an unknown percentage of the lignin ended up at the bottom of the flask. This can also interfere with the results obtained, and what is being seen do not correspond to the real values with the expected concentration.

c) Variation of nanolignin concentration on pure SIVO

The next blocks of wood were divided according to the following scheme on image 35. The idea of having one eight of surface without any coating and one eight with pure SIVO was to make the process of doing the colour and contact angle measurements more practical, since the laboratory where both analyses were made is outside of the University campus. However, after this part of the process it was observed the necessity of measuring the system blank (pure

wood) around the same spot of the surface where the measurement of coated surface would be taken. Sonication is without resting, and colloidal is after resting time.

1	2	3	4
Blank	Pure SIVO	0.5% sonication	0.5% colloidal
5	6	7	8
1.0% sonication	1.0% colloidal	2.0% sonication	2.0% colloidal

Image 35: Scheme of coatings distribution

This was observed as a necessity after realizing that the results obtained for this parameter were not faithful to the reality, and the main reason for it is the variation of the colour along the surface of all the blocks. Wood is a very irregular surface, both in means of its texture and colour. To reduce this error, this new methodology for measuring colour variation was applied for all the future steps of the thesis.

During the mixing and resting of the mixtures to form the colloidal, it became evident the next problem that would need to be solved. As it can be seen on the image 36, when the phases separated, most of the nanolignin would end on the bottom and walls of the beaker, leaving only more light particles on top with the rest of the solution. The biggest first issue with this was that it became impossible to determinate the real concentration of nanolignin on the solution applied.



Image 36: Side and top view of the beakers with the mixture of 1% and 2% nanolignin

In later steps, it was also possible to notice that the coating with higher concentration of nanolignin had a decrease on the contact angle and even lost its hydrophobic behaviour, possibly suggesting a saturation of nanoparticles on the surface. The colorimetry results for this step were also not satisfactory, since in multiple moments the value was bigger than 5, that it can be already considered an extrapolation of the value accepted on cultural heritage considering only the coating and not the substrate.

Following, the image 37 of the wood substrates, the tables 03 and 04 with values and images 38 and 39 with some of the drops with the contact angles for each case. Like it was said before, on the first table it will be possible to notice that only one of the results in colorimetry was lower than 5, indicating the necessity of a change on the formulation. Also, on the naked eye, it was possible to notice conglomerates of the nanoparticle, proving that the mixture was not being homogeneous.



Image 37: Chestnut (on the left) and Oak (on the right), right after the application of the formulation 8

		0.5%		1.0%		2.0%	
		ΔE	Contact Angle(°)	ΔE	Contact Angle(°)	ΔE	Contact Angle(°)
Chestnut	Sonication	6.58±0.16	132.5±0.6	5.24±0.10	140.5±0.6	7.70±0.18	146.8±0.7
	colloidal	5.69±0.15	129.5±0.4	5.93±0.12	139.4±0.4	5.72±0.16	147.7±0.5
Oak	Sonication	6.15±0.15	138.8±0.6	6.34±0.15	143.7±0.5	6.56±0.16	146.9±0.3
	colloidal	4.39±0.14	137.4±0.5	5.02±0.08	143.2±0.8	6.39±0.11	146.9±0.5

Table 03: Values of contact angle and ΔE for spaces 3 to 8 on the substrate

Space on Substrate	Chestnut			Oak		
	Average L*	Average a*	Average b*	Average L*	Average a*	Average b*
3	4.65±0.78	2.87±0.45	3.66±0.39	4.46±0.75	2.50±0.17	3.41±0.43
4	3.53±0.93	1.28±0.34	4.27±0.21	3.40±0.66	1.56±0.33	2.29±0.47
5	1.23±0.76	2.41±0.58	4.49±0.28	4.55±0.67	3.01±0.53	3.23±0.45
6	3.00±0.85	1.83±0.27	4.78±0.28	4.19±0.36	1.87±0.22	2.03±0.31
7	5.62±0.91	3.48±0.54	3.94±0.27	4.81±0.81	2.74±0.39	3.52±0.41
8	3.02±0.66	1.24±0.64	4.70±0.62	5.43±0.27	2.13±0.47	2.62±0.79

Table 04: Values of L*, a* and b* to determinate the ΔE of table 03

Chestnut drops

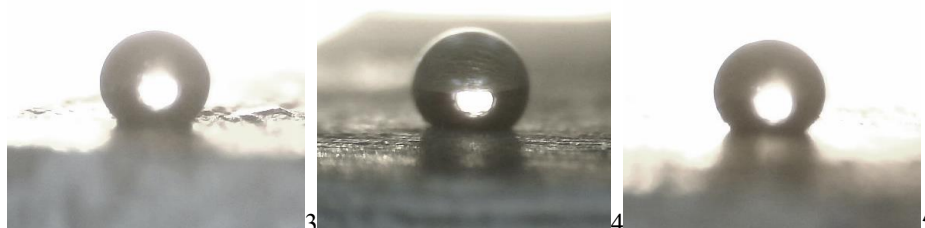




Image 38: Drops on chestnut for formulations between 3 to 8

Oak drops

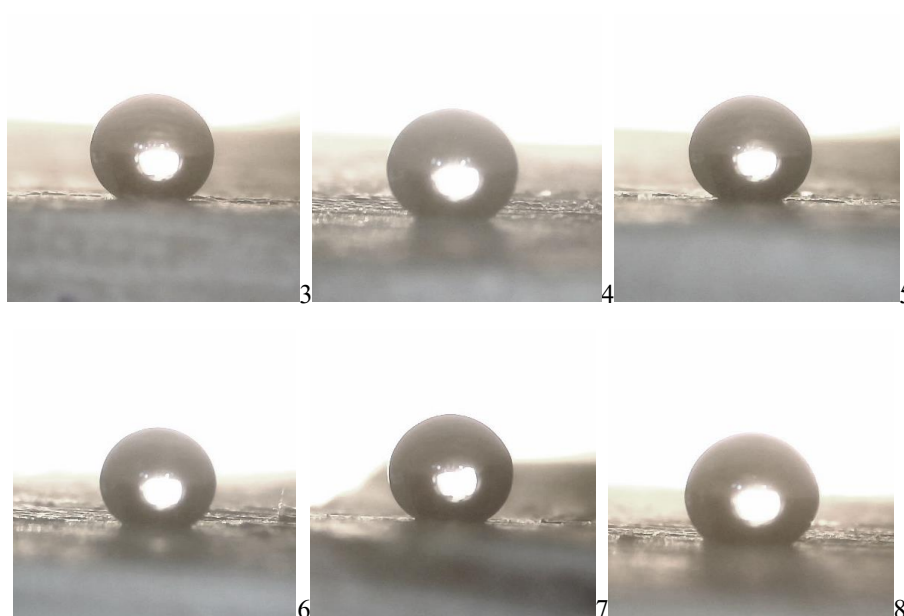


Image 39: Drops on oak for formulations between 3 to 8

Considering all of those details, the next step determined was the test of a second solvent added in small concentration to the SIVO. To make this procedure, the idea was to add the nanolignin to the second solvent, and then take a sample of this mixture and add to the SIVO.

The high colour variation with this method is a barrier on the development of the coating using this type of formulation. On a scenario that ΔE was not important as a variable, it could be a line of research but, as far as it is concerned for this thesis, it has turned into a problem that could not be ignored.

d) Second solvent analysis

Four organic solvents were used on this step: acetone, ethanol, isopropanol, and methanol. The stability of nanolignin on those solvents was also taken into consideration. As you can see on the image 40 **a** (acetone), **e** (ethanol), **i** (isopropanol) and **m** (methanol), the

material is not completely soluble in all the cases, creating a sort of particulate at the end of the flask that it was deposited.

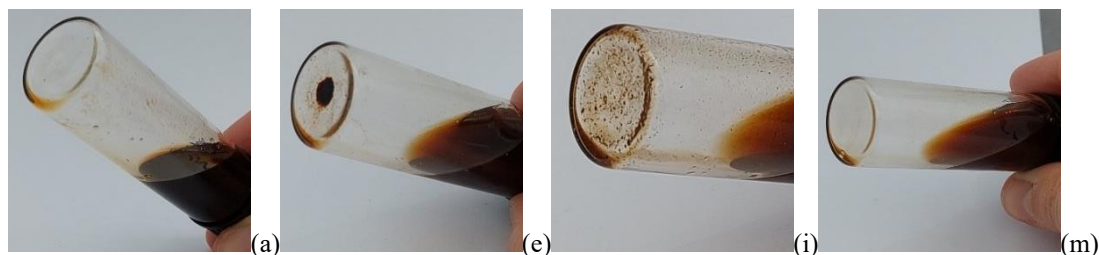


Image 40: Bottom part of the flasks containing the solvents with nanolignin

To keep the parameters, 5ml of each solvent was mixture with 0.05g of nanolignin. Then, 1% in weight of this mixture would be added to SIVO and this mixture would be applied. The values obtained were compared with the values of the 0.5% colloidal. Just by observing the behaviour of the solvents with the nanomaterial, it was visible that ethanol and isopropanol were not good options considering the particulates found on the bottom of the flasks. Comparing the results that can be seen on tables 05 and 06 and images 41 and 42, and also observing the behaviour of the lignin with the second solvent, it was decided that the best formulation to follow would have the addition of acetone to the mixture.

		0.5% Lignin	Acetone	Isopropanol	Methanol	Ethanol
Chestnut	ΔE	5.69±0.15	3.68±0.09	4.42±0.11	4.85±0.10	5.06±0.10
	Contact Angle (°)	129.5±0.4	132.1±0.5	136.6±0.6	131.2±0.4	136.2±0.5
Oak	ΔE	4.39±0.14	2.44±0.16	2.79±0.12	3.76±0.15	1.93±0.12
	Contact Angle (°)	137.4±0.5	131.9±0.6	136.7±0.5	133.1±0.5	136.8±0.4

Table 05: Comparative values of contact angle and ΔE between pure colloidal and second solvents

Second Solvent	Chestnut			Oak		
	Average L*	Average a*	Average b*	Average L*	Average a*	Average b*
Acetone	0.64±0.70	0.91±0.27	3.51±0.33	1.57±0.88	0.88±0.19	1.65±0.48
Isopropanol	1.79±0.70	1.47±0.52	3.76±0.31	2.11±0.93	0.83±0.13	1.62±0.32
Methanol	0.63±0.88	1.47±0.30	4.58±0.38	3.07±0.61	0.78±0.14	2.03±0.57
Ethanol	1.12±0.63	2.17±0.23	4.43±0.41	0.92±0.84	0.52±0.10	1.62±0.34

Table 06: Values of L*, a* and b* for the formulations with second solvent

Chestnut drops

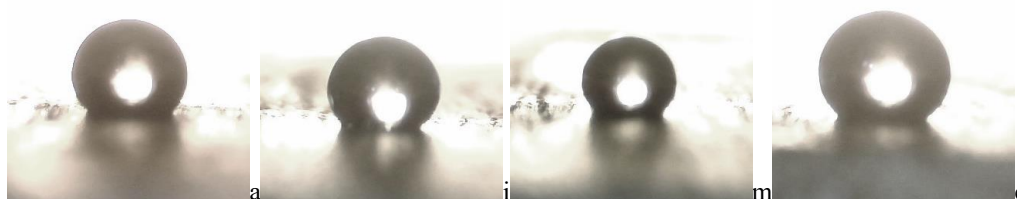


Image 41: Drops on chestnut with mixed coating (order: acetone, isopropanol, methanol, and ethanol)

Oak drops

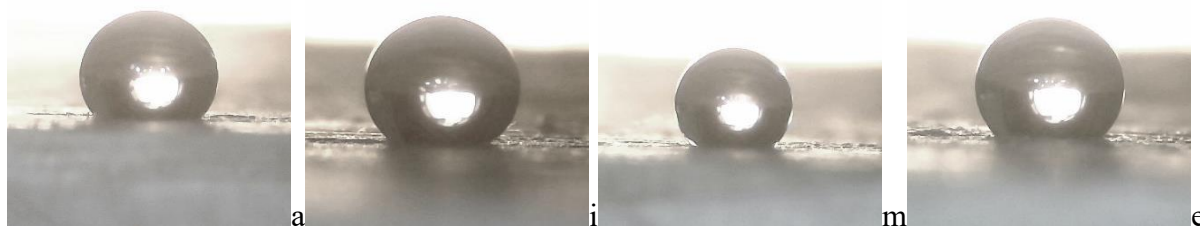


Image 42: Drops on oak with mixed coating (order: acetone, isopropanol, methanol, and ethanol)

The choice of the acetone was due to all the results taking into consideration. After checking the bottom of the flask where it was mixed with lignin, only the acetone and the methanol did not show particulate stuck to the surface of the flask, indicating complete miscibility. After that, comparing the values of contact angle and ΔE , the first has a similar result compared to the methanol, but the colour variation is lower. In total, this would be the optimal solvent to be added to the mixture.

e) Variation of nanolignin concentration added to acetone

To prove that the addition of a second solvent would incur better results, for this final step two blocks of each type of wood were divided in 6 parts. Both would have the nanolignin varying its concentration between 0 and 4%, but, while one would still use the colloidal path, the other one used the nanolignin on acetone. To variate the concentration on the acetone path, the amount of nanolignin added to the acetone would have the variation of mass, while the SIVO would always receive 1% w/w of the mixture.

On the following images 43 and 44, it is possible to see the schematic of how the coatings were distributed around the square substrate and their appearance during the cure process. Each part of the schematic has two numbers because between 1 to 6 is related to colloidal solutions, while 7 to 12 are the ones with nanolignin on acetone.

Pure SIVO (1 and 7)	Nanolignin 0.5% (2 and 8)	Nanolignin 1.0% (3 and 9)
Nanolignin 2.0% (4 and 10)	Nanolignin 3.0% (5 and 11)	Nanolignin 4.0% (6 and 12)

Image 43: Schematic of the substrates with coating



Image 44: Substrates during cure process after the application of coatings with acetone and nanolignin

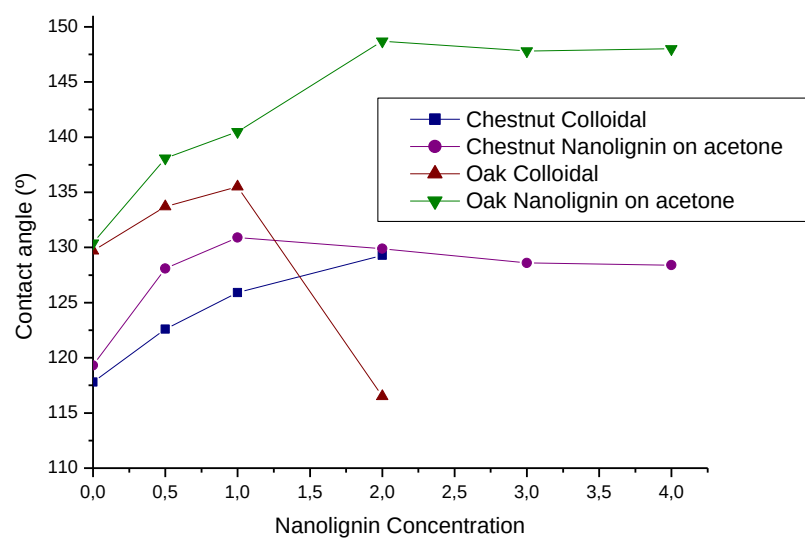
This was the moment that it was possible to observe the saturation of nanoparticles on the surface, turning impossible for the drops of water to keep shape on top of it, as it can be seen on tables 07 and 08, drop photos on images 45 and 46, and its respective graph 01 below. On the other hand, this problem was not visible on the blocks of wood using the mixture with acetone. This proves the necessity of a second solvent on the case studied, since it decreased the colour variation, made it possible to increase the contact angle to a point of almost superhydrophobicity, and it also avoided the problem of saturation.

		Chestnut			Oak		
		Average L*	Average a*	Average b*	Average L*	Average a*	Average b*
Colloidal	1	4.08±0.20	2.05±0.19	3.03±0.17	1.59±0.10	0.25±0.05	2.37±0.02
	2	4.25±0.06	2.52±0.05	3.34±0.14	0.61±0.10	0.21±0.08	2.11±0.17
	3	4.29±0.08	2.32±0.09	3.45±0.05	0.67±0.27	0.19±0.08	1.77±0.18
	4	4.80±0.42	2.20±0.27	2.23±0.04	0.43±0.14	0.21±0.09	1.08±0.04
	5	4.33±0.17	1.40±0.14	1.92±0.16	0.38±0.02	0.48±0.07	1.75±0.15
	6	4.90±0.26	2.49±0.15	2.94±0.06	1.22±0.05	0.30±0.06	0.33±0.11
Nanolignin on acetone	7	3.86±0.36	2.09±0.36	1.66±0.66	1.03±0.14	0.43±0.09	2.39±0.07
	8	3.21±0.49	2.68±0.26	3.72±0.08	0.93±0.10	0.50±0.07	2.30±0.04
	9	3.94±0.60	2.17±0.12	3.57±0.22	1.73±0.04	0.29±0.06	2.41±0.15
	10	3.78±0.24	2.52±0.44	3.20±0.12	1.70±0.21	0.73±0.09	2.28±0.10
	11	3.90±0.08	2.20±0.07	3.99±0.15	1.62±0.21	0.61±0.05	2.45±0.16
	12	3.93±0.48	2.01±0.12	3.87±0.10	1.34±0.16	0.93±0.17	2.42±0.05

Table 07: Values of L*, a* and b* for ΔE values of table 08

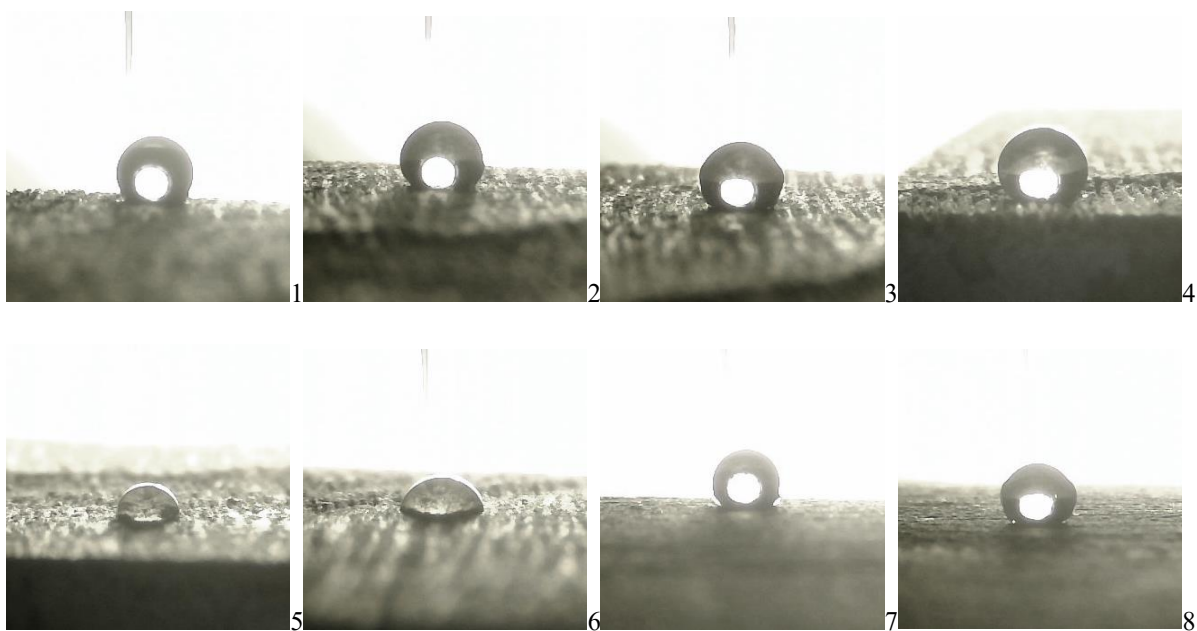
Chestnut		Pure SIVO	0.5%	1.0%	2.0%	3.0%	4.0%
SIVO+ Lignin	ΔE	4.08 $\pm$ 0.20	4.25 $\pm$ 0.06	4.29 $\pm$ 0.08	4.80 $\pm$ 0.42	4.33 $\pm$ 0.17	4.90 $\pm$ 0.26
	Contact Angle ($^{\circ}$)	117.8 $\pm$ 0.7	122.6 $\pm$ 0.5	125.9 $\pm$ 0.4	129.3 $\pm$ 0.7	-	-
SIVO+ Lignin on Acetone	ΔE	3.86 $\pm$ 0.36	3.21 $\pm$ 0.49	3.94 $\pm$ 0.60	3.78 $\pm$ 0.24	3.90 $\pm$ 0.08	3.93 $\pm$ 0.48
	Contact Angle ($^{\circ}$)	119.3 $\pm$ 0.9	128.1 $\pm$ 0.9	130.9 $\pm$ 0.6	129.9 $\pm$ 0.5	128.6 $\pm$ 0.5	128.4 $\pm$ 0.5
Oak		Pure SIVO	0.5%	1.0%	2.0%	3.0%	4.0%
SIVO+ Lignin	ΔE	1.59 $\pm$ 0.10	0.61 $\pm$ 0.10	0.67 $\pm$ 0.27	0.43 $\pm$ 0.14	0.38 $\pm$ 0.02	1.22 $\pm$ 0.05
	Contact Angle ($^{\circ}$)	129.7 $\pm$ 0.8	133.7 $\pm$ 0.6	135.5 $\pm$ 0.8	116.5 $\pm$ 0.7	-	-
SIVO+ Lignin on Acetone	ΔE	1.03 $\pm$ 0.14	0.93 $\pm$ 0.10	1.73 $\pm$ 0.04	1.70 $\pm$ 0.21	1.62 $\pm$ 0.21	1.34 $\pm$ 0.16
	Contact Angle ($^{\circ}$)	130.4 $\pm$ 0.9	138.1 $\pm$ 0.7	140.5 $\pm$ 0.8	148.7 $\pm$ 0.5	147.8 $\pm$ 0.6	148.0 $\pm$ 0.4

Table 08: Values of ΔE and contact angle comparing colloidal and SIVO with nanolignin on acetone



Graph 01: Variation of Contact Angle ($^{\circ}$) in relation to nanolignin concentration (%)

Chestnut drops:



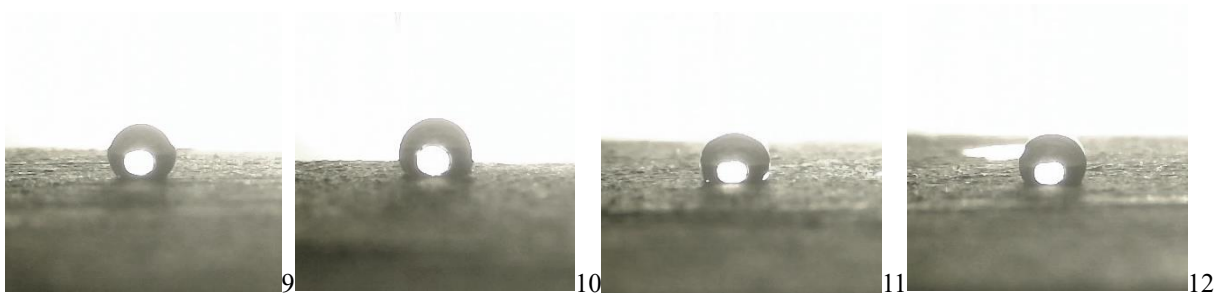


Image 45: Drops in chestnut for all the 12 positions of the table 08

Oak drops:

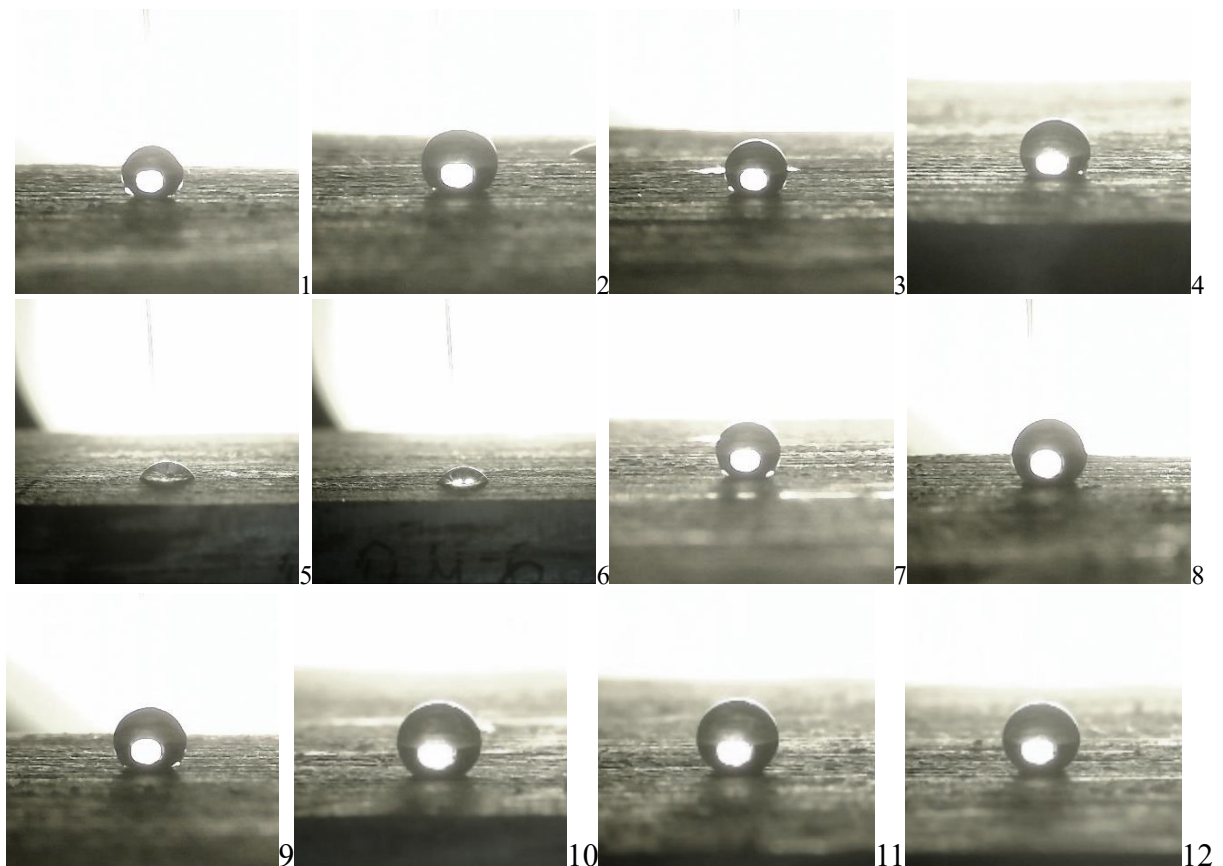


Image 46: Drops in oak for all the 12 positions of the table 08

The other important aspect to notice at this point, being later confirmed by results on the other experiments, is the fact that oak behaves better with this coating formulation. Even though in both cases it is possible to see an increase of contact angle, oak is able to reach some points of superhydrophobicity on its surface, and in other points the contact angle gets really close to the lower limit of hydrophobicity, 150° . Not only that, but the colour variation is lower, probably because the colour matrix of the oak is more similar with the one from the coating than the chestnut, which has visibly a lighter shade.

The comparison between samples with sonication as mixing method and the ones using acetone to mix the lignin to the SIVO were interesting for many reasons. Firstly, because it showed that the amount of lignin that can be added is higher when considering the contact angle when using the solvent. Second, it showed a second problem for the study of the direct mixture of the SIVO with lignin, turning this method impossible considering both of the parameters used to control the results. Lastly, it is important to mark that the methodology using acetone is also faster to formulate than the one without it, since it is necessary only a couple of minutes on the vortex to generate a homogeneous solution with known concentration.

5.1.1- Tilt angle and Rose petal effect

It is known that hydrophobic surfaces, especially the ones with a contact angle reaching the superhydrophobic standard, usually are also repellent surfaces for the water. However, this was not observed for our studied case. It was the opposite case, with the drop remaining attached to the surface even after flipping the same upside down, as it can be seen on image 47. With that in mind, a side small test was made.



Image 47: Rose petal effect on the sample

Using a micropipette, different volumes of water were deposited as drops on the surface in order to determine the point that it wouldn't remain stuck to the surface. After surpassing 40 μ L, the drop would leave the surface after tilting it. However, it wasn't a case of repellence, but the action of gravity on a drop far heavier than the ones used for hydrophobicity experiments, as it can be seen on image 48.

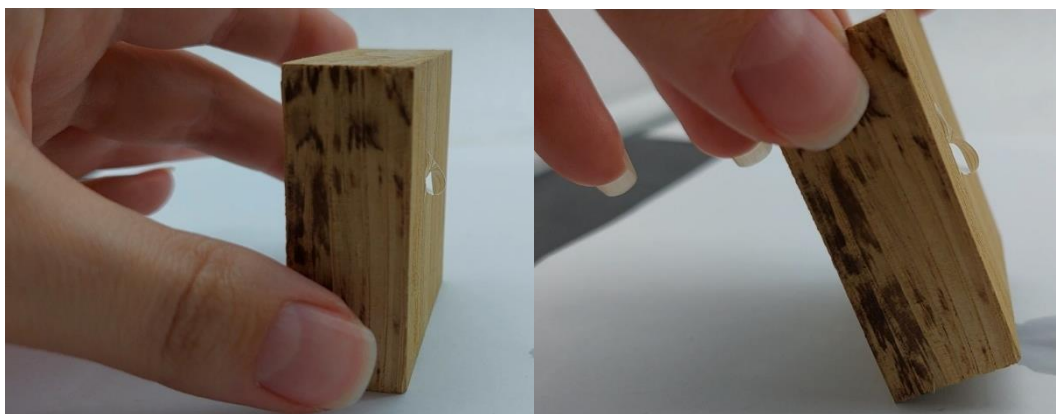


Image 48: Drop with 40 μ L not moving (on the left) versus drop with 50 μ L sliding (on the right)

Trying to still reach a repulsion behaviour, the next idea was to increase the kinetic energy of the drops (this time keeping the size below 5 μ L) by horizontally shaking the block. Even though it is impossible to know the exact amount of energy that was added doing this, with a slow-motion video recording it was possible to see the drops rolling out of the surface, indicating repulsion. Some images taken from the video to prove the movement can be seen below on the image 49, taken special attention to the drop on the lower part of the wood.

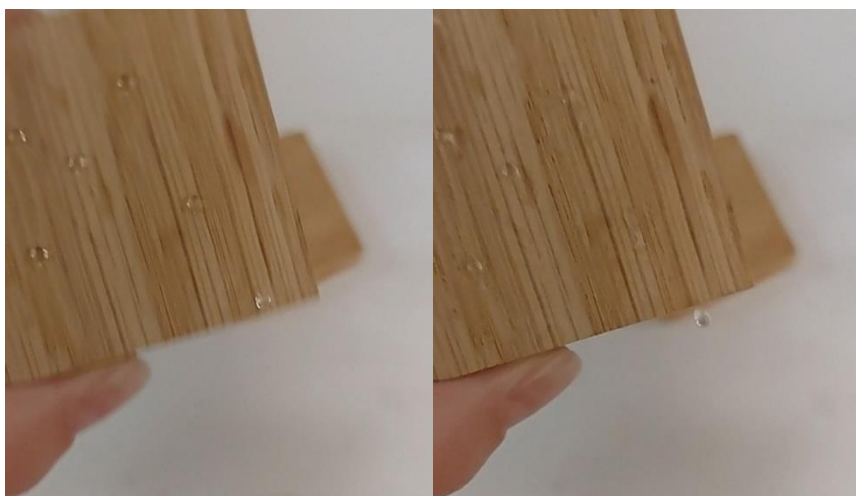


Image 49: Drops rolling with kinetic energy

This behaviour showed can be described as a rose petal effect, and the surface with this coating can be called rose petal like. As explained before, the rose petal effect follows the Wenzel model, having the drop entering the irregularities of the surface, generating a surface contact bigger than the one described by Young. This generates a higher resistance of the drop to move and be repelled to leave the surface.

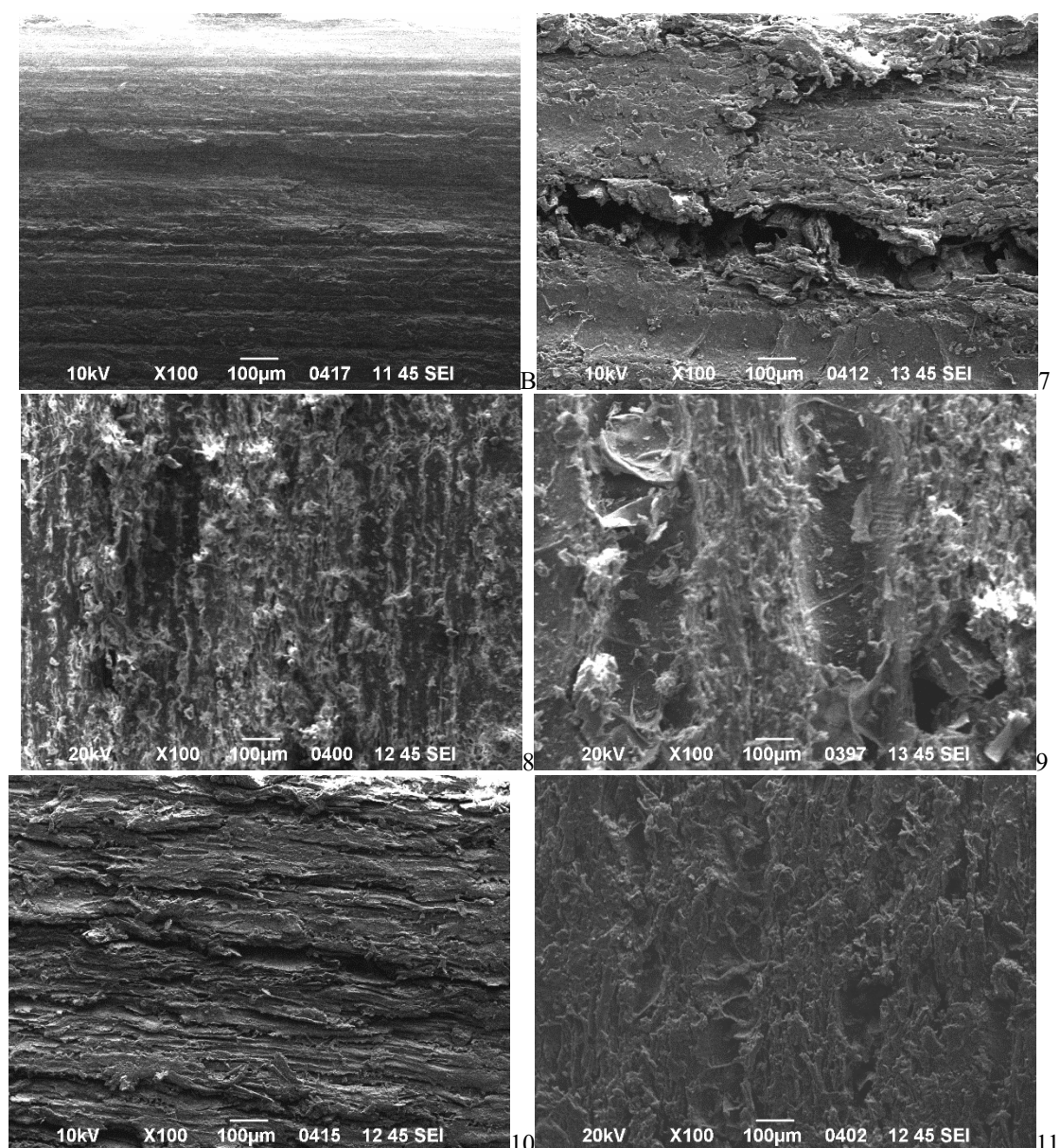
This is why, without the addition of a kinetic force (created by the shaking movement), the energy of the drop alone is not enough to make it move. An interesting study would be to add spin movement to the substrate, controlling the velocity in order to be able to determinate

the minimal energy necessary to make the drop move. Although a hydrophobic surface without repellence is not the best result considering other properties, such as biocidal or cleaning, it would be necessary further research to understand which properties are being affected by it.

5.2 – SEM Surface analysis

Even though images with 200x amplification were also taken, it was decided to keep only the ones with 100x on the thesis, since the necessary information could already be found on this amplification. There is also two images with a large amplification to show structures found on the coating for a better visibility of how the nanoparticles can appear, corroborating with the theory that the used nanolignin possesses molecules of different sizes and shapes.

Chestnut



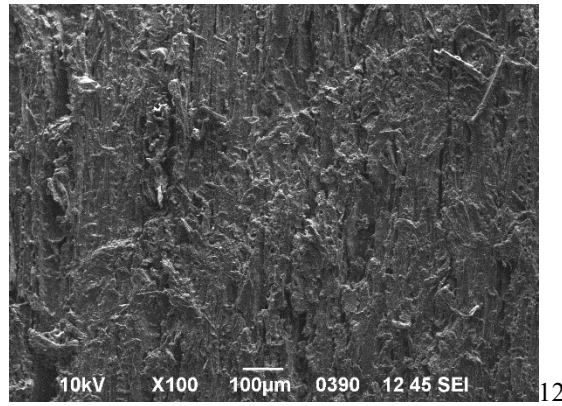
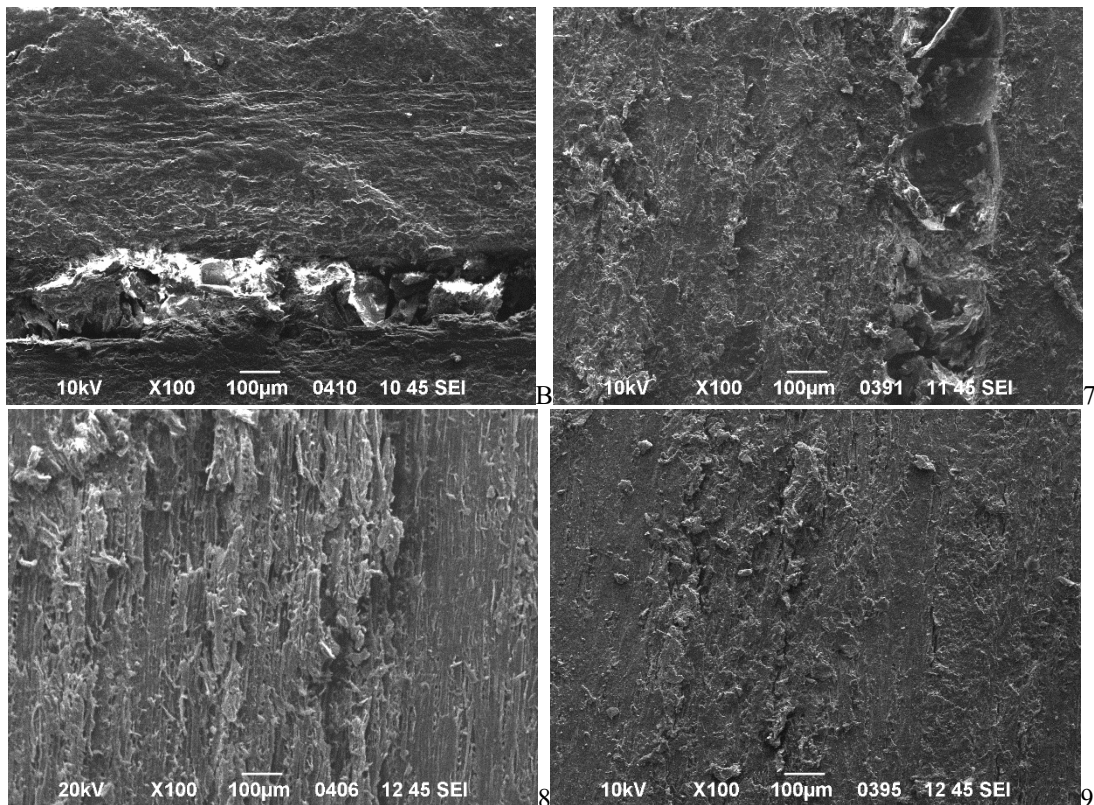


Image 50: SEM imaging of Chestnut with and without coating

It is possible to notice on image 50 the difference between B (sample without any coating) and 7 (sample with pure SIVO) with the increase if irregularities on the surface. From 8 to 12 we have also the increase of lignin particles (0.5%, 1%, 2%, 3% and 4%) that can be seen with the shapes spread on top of the surface. One last key point is that, as it can be seen, the surfaces are similar since they are from the same type of wood (same block between 7 to 12) but with distinct irregularities. This is one of the reasons of why the contact angle varies on the surface even though the coating applied is the same.

Oak



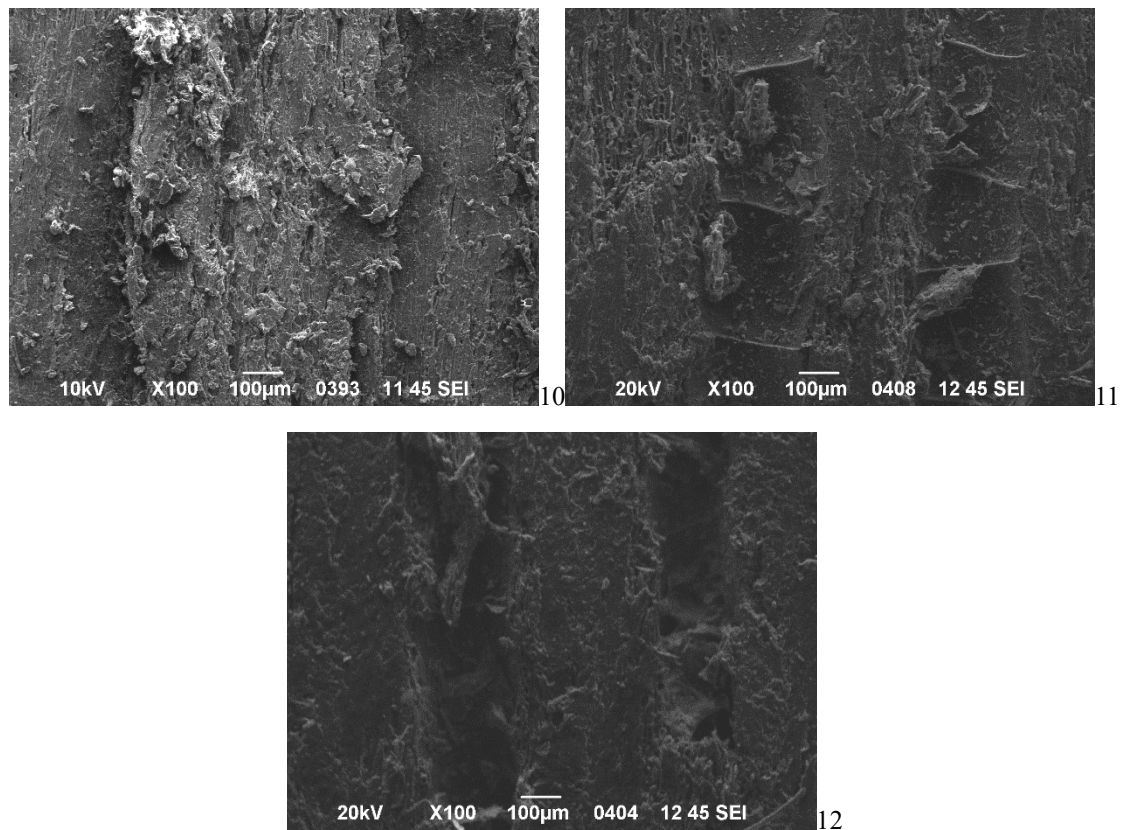


Image 51: SEM imaging of Oak with and without coating

As it is visible on image 51, the pure surface of the wood (B) already presents more irregularities than the chestnut wood, corroborating with the contact angles in oak being larger. It is also possible to observe the increase of irregularities and small and medium particles on top of the surface between (B) and the numbered samples. This represents the addition of the coating and the variation of lignin particles in percentage. As it was talked before, the irregular surface with the particles spread on top of it explain why the contact angle around the samples being different, even with the same coating being applied to.

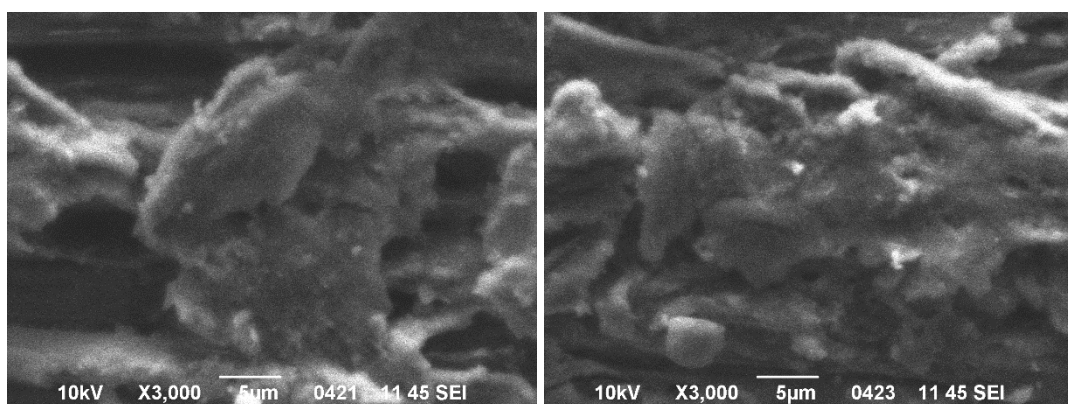


Image 52: Particles on the surface amplified.

The particles on the surface, as it can be seen above on image 52 don't have regular shapes, sizes, or forms. This is also something expected considering that a macromolecule as lignin don't have a specific format, just common characteristics, and organic functions. Besides, when trying to decide the formulation of the coating it was already seen that the lighter particles would remain on the solution while the rest would decant while not using a second solvent.

With that in consideration, it is possible to imagine that the different particles that are visible between 8-12 are related to lignin. In some cases, it could be a case of dust or other contaminate but, considering that the particles start to be more visible after the adding of the lignin on the mixture, the logic is to assume their correlation.

5.3 – Water absorption

Before starting all the next analysis, the moisture content of the wood substrates used was measured. Six samples of each wood had their length and weight values measured to determinate volume and density. After that, the twelve samples were put inside the oven for 24h at 75°C to dry. When they were removed from the oven, the dry mass was measured and, with that, the moisture content was determined. The data for this is on the following table 09:

Sample		Mass (g)	Dry mass (g)	Vol (cm ³)	Moisture (g)	%	
Chestnut	CB-01	27.1030	25.2470	44.7568	1.8560	7.35	moisture percentage average for chestnut: 7.57%
	CB-02	26.5983	24.7280	45.0689	1.8703	7.56	
	C-PS-01	25.9294	23.9758	43.9604	1.9536	8.15	
	C-PS-02	26.1993	24.3957	44.0106	1.8036	7.39	
	C-SL-01	26.7342	24.8149	44.5940	1.9193	7.73	
	C-SL-02	26.5064	24.7177	44.2828	1.7887	7.24	
Oak	OB-01	32.1693	30.0890	47.9898	2.0803	6.91	moisture percentage average for oak: 7.47%
	OB-02	32.6704	30.4936	48.6550	2.1768	7.14	
	O-PS-01	33.1598	30.7496	48.1301	2.4102	7.84	
	O-PS-02	33.3742	31.0788	48.9629	2.2954	7.39	
	O-SL-01	32.6264	30.3193	48.4819	2.3071	7.61	
	O-SL-02	32.8159	30.4023	49.0550	2.4136	7.94	

Table 09: Values for determination of moisture content

Considering only mass values, oak retains more water then chestnut. But, since its volume is also bigger, in the end the percentage became similar between both types of wood. This could be expected since both substrates were left on the same environment. Another expected result is that having only one of the six surfaces of the sample coated would not influence on the moisture content of the substrate, and that can be confirmed comparing the results between samples.

For all the following analysis, 3 types of samples were used in each type of wood: pure wood, wood with a coating of pure SIVO, and wood with a coating of SIVO and 4% nanolignin on acetone mixing. To better identify the samples for the other cases, the following code was used to name them:

- O or C: identify the type of wood substrate
- WA, PH, PE, UV, NW, B: relates to the analysis being made on the samples (water absorption, pH variation, peeling cycles, UV ageing, natural weathering, and burial)
- PS or SL: identify if the sample is using pure SIVO or the mixture of SIVO and nanolignin
- On the cases a blank sample was also used, weathering and burial, the code for it would be B instead of PS or SL
- Number of the sample

As an example, the samples for water absorption then would have codes such as C-WA-PS-01 or O-WA-PS-03 for samples with pure SIVO and C-WA-SL-02 or O-WA-SL-01 for a coating with SIVO with nanolignin. Burial samples were called CB and OB.

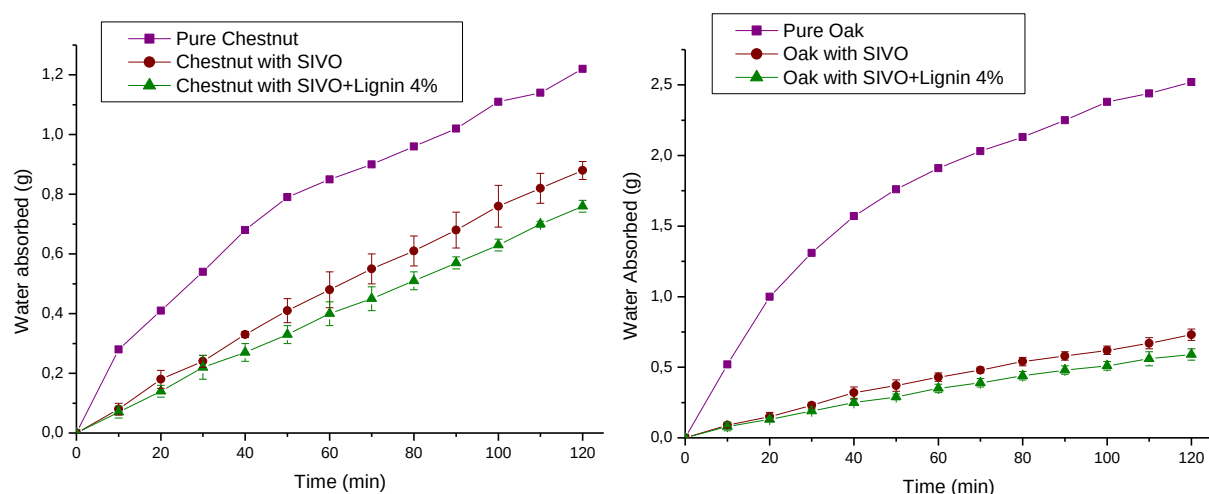
Other important detail is that all the substrates had the amount of coating applied measured right after it, and the average for each analysis was made on a separate table. Still, it is possible to determinate that the average value for all the analysis is 0.01g/cm^2 of coating by substrate surface ($0.2506 \pm 0.0104\text{g}$ of coating per 25cm^2 of surface applied). And one last detail is that articles like [59], [60], [61], [62] and [63] are used as background knowledge for possible results and analysis used.

Not all the analysis were made using a sample without any coating for comparison, since it is impossible to measure the contact angle on those samples (the drop loses its form too fast to measure). For water absorption, one sample of each wood was used without any coating in order to provide a blank value and calculate the reduction of water absorbed through capillarity. The weight was measured on a two digits scale, as it can be seen on the following table 10.

	Chestnut						Oak								
	Pure	SIVO 01	SIVO 02	SIVO 03	SIVO+Lig 01	SIVO+Lig 02	SIVO+Lig 03	Pure	SIVO 01	SIVO 02	SIVO 03	SIVO+Lig 01	SIVO+Lig 02	SIVO+Lig 03	
Measured values	0	27.10	18.63	25.70	26.59	18.50	26.64	25.95	30.05	33.17	32.50	31.18	33.18	32.41	33.03
	10	27.38	18.73	25.77	26.66	18.55	26.72	26.04	30.57	33.27	32.59	31.25	33.26	32.46	33.13
	20	27.51	18.83	25.88	26.74	18.62	26.79	26.10	31.05	33.35	32.65	31.31	33.32	32.53	33.16
	30	27.64	18.89	25.94	26.82	18.68	26.86	26.20	31.36	33.42	32.73	31.39	33.38	32.61	33.21
	40	27.78	18.97	26.02	26.91	18.74	26.90	26.25	31.62	33.49	32.85	31.46	33.44	32.67	33.25
	50	27.89	19.07	26.07	27.02	18.80	26.97	26.31	31.81	33.54	32.90	31.51	33.49	32.69	33.32
	60	27.95	19.15	26.11	27.10	18.86	27.04	26.38	31.96	33.60	32.96	31.59	33.53	32.79	33.36
	70	28.00	19.20	26.19	27.18	18.92	27.09	26.44	32.08	33.64	33.00	31.65	33.57	32.83	33.40
	80	28.06	19.24	26.26	27.24	18.98	27.16	26.49	32.18	33.68	33.06	31.72	33.62	32.88	33.45
	90	28.12	19.33	26.31	27.32	19.05	27.21	26.54	32.30	33.72	33.10	31.76	33.65	32.92	33.49
	100	28.21	19.42	26.38	27.39	19.12	27.27	26.60	32.43	33.76	33.15	31.81	33.68	32.95	33.52
	110	28.24	19.45	26.48	27.46	19.19	27.33	26.66	32.49	33.80	33.20	31.86	33.72	33.02	33.55
120	28.32	19.50	26.56	27.50	19.24	27.40	26.73	32.57	33.85	33.26	31.92	33.76	33.04	33.58	
Difference values for the graph	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10	0.28	0.10	0.07	0.07	0.05	0.08	0.09	0.52	0.10	0.09	0.07	0.08	0.05	0.10
	20	0.41	0.20	0.18	0.15	0.12	0.15	0.15	1.00	0.18	0.15	0.13	0.14	0.12	0.13
	30	0.54	0.26	0.24	0.23	0.18	0.22	0.25	1.31	0.25	0.23	0.21	0.20	0.20	0.18
	40	0.68	0.34	0.32	0.32	0.24	0.26	0.30	1.57	0.32	0.35	0.28	0.26	0.26	0.22
	50	0.79	0.44	0.37	0.43	0.30	0.33	0.36	1.76	0.37	0.40	0.33	0.31	0.28	0.29
	60	0.85	0.52	0.41	0.51	0.36	0.40	0.43	1.91	0.43	0.46	0.41	0.35	0.38	0.33
	70	0.90	0.57	0.49	0.59	0.42	0.45	0.49	2.03	0.47	0.50	0.47	0.39	0.42	0.37
	80	0.96	0.61	0.56	0.65	0.48	0.52	0.54	2.13	0.51	0.56	0.54	0.44	0.47	0.42
	90	1.02	0.70	0.61	0.73	0.55	0.57	0.59	2.25	0.55	0.60	0.58	0.47	0.51	0.46
	100	1.11	0.79	0.68	0.80	0.62	0.63	0.65	2.38	0.59	0.65	0.63	0.50	0.54	0.49
	110	1.14	0.82	0.78	0.87	0.69	0.69	0.71	2.44	0.63	0.70	0.68	0.54	0.61	0.52
120	1.22	0.87	0.86	0.91	0.74	0.76	0.78	2.52	0.68	0.76	0.74	0.58	0.63	0.55	

Table 10: Values for water absorption

Considering the values obtained, it was possible to obtain the following graph 02 of amount of water absorbed (in g) versus time (in minutes).



Graph 02: Water absorbed (g) per time (min)

Considering the value obtained on the wood without coating as the original value, and the values obtained after as the reduced values, with simple mathematics we can say that both species have a decrease in water absorption, with oak (71,03% pure SIVO and 76,59% SIVO with nanolignin) reducing a lot more than chestnut (27,87% pure versus 37,70% with nanolignin). It is also visible that the addition of nanolignin interfere on the results, since in both cases made the reduction of water absorbed was higher. The influence on oak be almost half of what is found on chestnut is probably due to the fact that the reduction with pure SIVO is already higher than 70%, while the second case it was lower than 30% without putting the additive.

5.4 – pH solution variation

For this experiment, it was used six samples of each wood, with three samples of each coating were used. All the drops of different pH were deposited around the same place to try to avoid interference of the substrate on the coating. On the table 11, the values of contact angle of each drop related to the pH of the solution and the average per substrate on each interval.

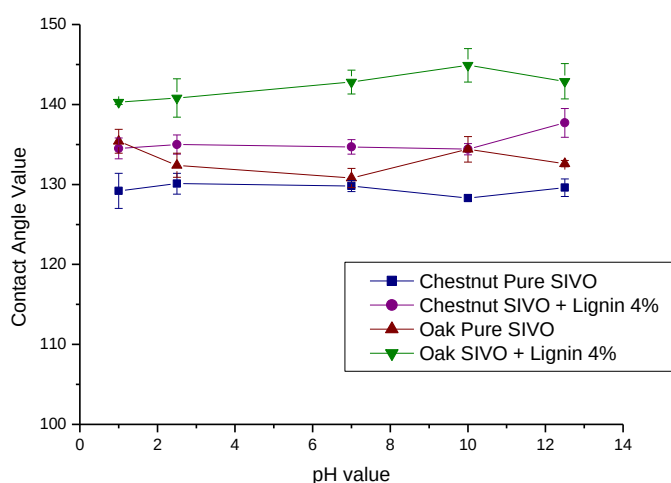
	1				2.5				7				10.5				12				
	Value 01	Value 02	Value 03	Avg	Value 01	Value 02	Value 03	Avg	Value 01	Value 02	Value 03	Avg	Value 01	Value 02	Value 03	Avg	Value 01	Value 02	Value 03	Avg	
Chestnut	C-PH-PS-01	134.6	128.5	130.6	129.6	127.2	131.6	129.8	129.5	130.6	127.3	129.5	129.1	128.8	127.9	127.4	128.0	126.1	130.1	128.9	128.4
	C-PH-PS-02	133.1	126.0	129.8	129.6	130.5	133.5	130.7	131.6	131.0	129.4	128.8	129.7	127.4	129.7	128.9	128.7	131.6	129.4	129.8	130.3
	C-PH-PS-03	128.3	124.9	127.5	126.9	126.9	129.5	130.9	129.1	132.5	132.5	126.5	130.5	129.4	127.6	127.2	128.1	131.0	129.5	130.2	130.2
	C-PH-SL-01	134.6	135.9	134.1	134.9	133.6	138.3	136.6	136.2	132.7	136.7	135.9	135.1	134.5	136.1	133.3	134.6	139.9	137.8	139.9	139.2
Oak	C-PH-SL-02	133.8	136.3	136.6	135.6	131.8	133.7	136.3	133.9	134.2	134.4	132.6	133.7	134.7	135.6	130.8	133.7	139.6	138.8	135.9	138.1
	C-PH-SL-03	129.0	137.5	132.8	133.1	132.4	136.2	136.0	134.9	135.2	135.8	135.0	135.3	135.8	132.5	136.6	135.0	134.3	134.5	138.4	135.7
	O-PH-PS-01	133.9	134.2	133.2	133.8	136.6	134.1	131.5	134.1	129.2	131.6	133.8	131.5	131.5	135.8	133.4	133.6	133.2	132.6	133.1	133.0
	O-PH-PS-02	135.8	137.9	136.5	136.7	131.3	132.1	131.3	131.6	131.6	132.7	129.8	131.4	136.3	138.2	134.1	136.2	131.1	133.1	132.7	132.3
Oak	O-PH-PS-03	134.0	137.7	135.7	135.8	128.6	133.5	132.3	131.5	129.7	129.5	128.9	129.4	135.9	130.9	133.3	133.4	132.3	133.2	132.4	132.6
	O-PH-SL-01	140.7	140.5	138.8	140.0	139.0	138.4	141.8	139.7	142.2	140.3	142.1	141.5	143.3	141.4	142.8	142.5	140.7	139.4	142.7	140.9
	O-PH-SL-02	140.1	141.3	139.5	140.3	138.6	138.4	140.7	139.2	141.3	140.3	145.7	142.4	145.6	148.4	145.1	146.4	139.7	142.3	145.5	142.5
	O-PH-SL-03	140.6	140.8	140.5	140.6	139.6	146.3	144.5	143.5	143.6	143.4	146.3	144.4	144.2	147.5	145.4	145.7	145.1	146.8	143.7	145.2

Table 11: Drops with different pH solutions

On the table 12, is the average with deviation of each type of wood/coating. The graph 03 is used to visualize the behaviour of those values. Considering the irregularity of the wood surfaces, it is possible to assume that pH variation don't happen due to variations of the coating, but due to where the drop is being deposited. The solution drop being deposited on a slightly different point can change the value obtained, and this behaviour was seen in multiple experiments.

Sample type	1		2.5		7		10.5		12.5	
C-PS	129.2	2.2	130.1	1.3	129.8	0.7	128.3	0.4	129.6	1.1
C-SL	134.5	1.3	135.0	1.2	134.7	0.9	134.4	0.7	137.7	1.8
O-PS	135.4	1.5	132.4	1.5	130.8	1.2	134.4	1.6	132.6	0.4
O-SL	140.3	0.3	140.8	2.4	142.8	1.5	144.9	2.1	142.9	2.2

Table 12: average value and deviation for each pH



Graph 03: Contact angle (°) with pH variation

Those results are important especially considering the acid values. Considering pollutants on the environment, the tendency is for the rain to contain an acidic pH. Even when talking about a region with low emissions of pollutants such as SO_x , NO_x , PO_x , the carbon dioxide on the environment can still react with water creating carboxylic acid, a weak compound that breaks easily into CO_2 and H_2O but still reduces the pH of the rain on the area.

If the coating keeps its behaviour, no matter the pH, at least on first moment we can assume that this won't create long term problems if the coating is applied. To have a better understanding, different experiments would be necessary, like exposure to the environment with different pH for a longer period. Following, we can see images 53, 54, 55 and 56 of the water drops used on this stage. The number from 1 to 5 refer to each of the pH used (1, 2.5, 7, 10, and 12.5).

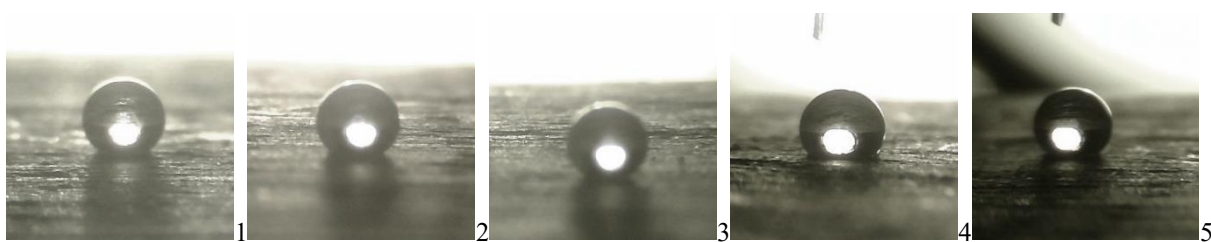


Image 53: Examples of drops on Chestnut with pure SIVO



Image 54: Examples of drops on Chestnut with SIVO and nanolignin



Image 55: Examples of drops on Oak with pure SIVO

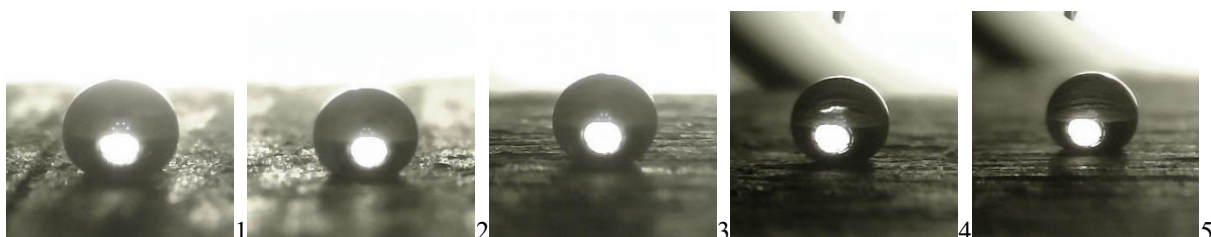


Image 56: Examples of drops on Oak with SIVO and nanolignin

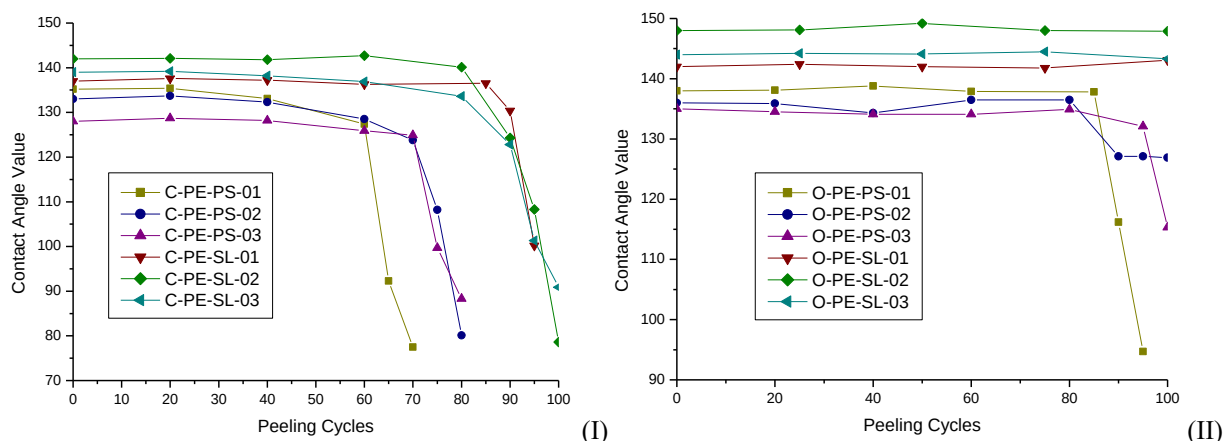
5.5 – Peeling cycles

The peeling cycles proved a behaviour already expected. As said before, phenolic rings improve adhesion when added to a material, and both lignin and its counterpart are known for the existence of those rings. As it can be seen on the table 13, both substrates with the mixed coating have better results than the ones with pure SIVO.

	0	20	25	40	50	60	65	70	75	80	85	90	95	100
Chestnut	C-PE-PS-01	135.5	135.4		133.1	127.4	92.3	77.5	108.2	80.1				
	C-PE-PS-02	133.5	133.7		132.3	128.5		123.8	99.7	88.3				
	C-PE-PS-03	129.0	128.7		128.2	125.9		124.9						
	C-PE-SL-01	137.5	137.6		137.2	136.3					136.5	130.4	100.2	
	C-PE-SL-02	142.0	142.1		141.8	142.7				140.1		124.3	108.3	78.6
	C-PE-SL-03	139.0	139.2		138.2	136.9				133.6		122.8	101.3	90.9
Oak	O-PE-PS-01	138.0	138.1		138.8	137.9					137.8	116.2	94.7	
	O-PE-PS-02	136.0	135.9		134.3	136.5						127.1	127.1	126.9
	O-PE-PS-03	134.5	134.5		134.1	134.1				134.9			132.1	115.3
	O-PE-SL-01	142.5		142.4					141.8					143.1
	O-PE-SL-02	148.0		148.1					148.0					147.9
	O-PE-SL-03	144.0		144.2					144.5					143.3

Table 13: Contact angle (°) values for peeling cycles

This time, the graph 4 (I) and (II) seen below, the values were split between wood type to show better the behaviour. Also, for this section it was more logic to show the curve of each sample instead of doing the average because sometimes the peeling cycle that would start reducing the contact angle was different on the same type of sample. Also, as it can be seen on the previous table, when changing the sample to another one that on theory would have better adhesion, the gap between measures would increase.



Graph 04: (I) Peeling cycles for chestnut; (II) Peeling cycles for oak

That happened because, after doing the first round for the first type of sample (chestnut with pure SIVO), that overall had the lower results compared to the rest, when doing the measurement after every five peelings, it was noticed that it would take multiple cycles to get noticeable variation. With that into consideration, the first forty to fifty first peelings would have less measurements, while every five peelings would have a measurement the closer it would get to the point where the contact angle started decreasing. Considering that many results of oak with pure SIVO and chestnut with the mixed coating would have similar results, the measurement between both was taken on a similar way.

For the SIVO+ nanolignin coating on oak, less points were measured because the simple coating only started to reduce the contact angle after 90 cycles, and the limit stipulated on this experiment was 100 cycles. Proving the theory, the contact angle remained similar for this coating until the one hundred cycle was reached, showing that the addition of the nanolignin and its phenolic rings improved the adhesion of the coating on the surface. On the following images 57, 58, 59 and 60, we can see the contact angle decrease on the coatings.

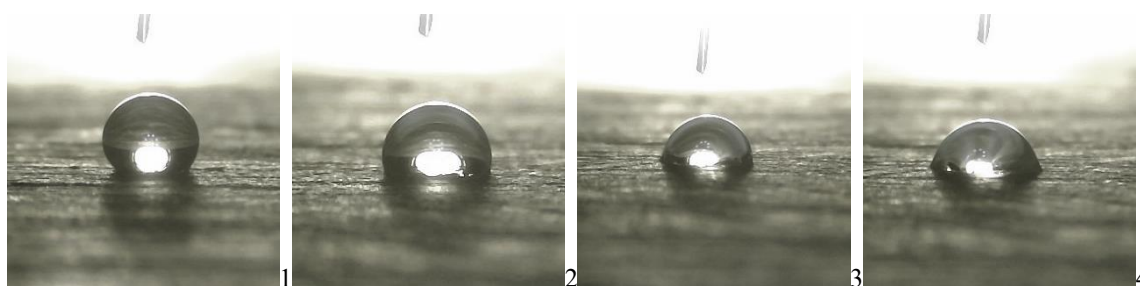


Image 57: Contact angle (°) of chestnut with pure SIVO for 65, 70, 75 and 80 cycles

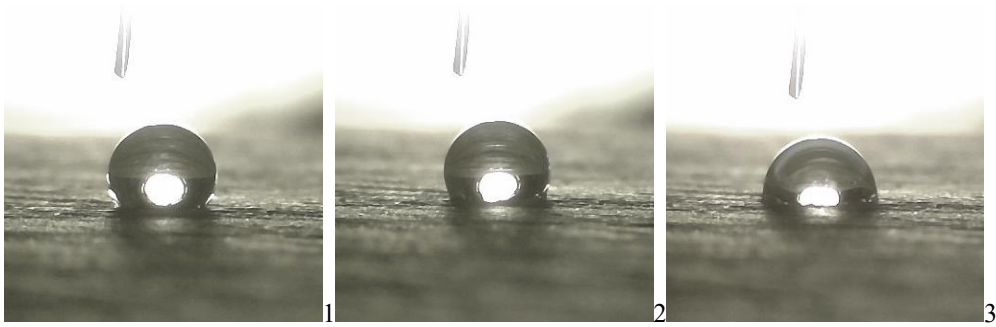


Image 58: Contact angle (°) of chestnut with SIVO and nanolignin for 90, 95 and 100 cycles

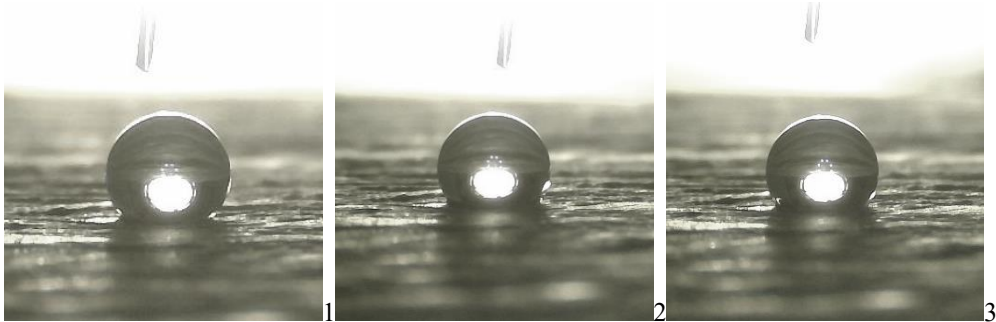


Image 59: Contact angle (°) of oak with pure SIVO for 90, 95 and 100 cycles

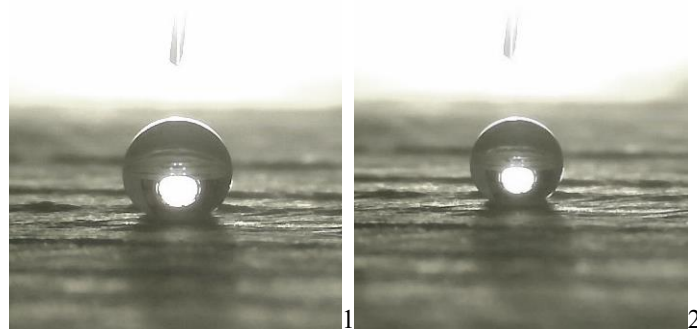


Image 60: Contact angle (°) of oak with SIVO and nanolignin for 75 and 100 cycles

Overall, since all the values found were over 60 cycles, it is safe to say that both versions of the coating have a good adhesion on the substrate, no matter the type of wood used. For optimization of use in this parameter, the coating with additive is the best choice in both cases, showing values around 90 cycles to decrease the contact angle for chestnut and past 100 for oak, which is an outstanding result.

5.6- UV aging chamber

The samples were distributed inside the chamber. Twice a week the samples would be placed in different positions on top of the plate to guarantee a more uniform exposition of the light, starting on 09/07/2024. Between 01/08/2024 to 20/08/2024 the samples were kept inside the chamber closed but with the lamp off for security reasons, since the university was close for the holidays, and nobody was entering the laboratory where it is located. Between 20/08/2024

to 04/09/2024, the samples were exposed to the UV lamp, but the contact angle was not measured by the MSA since the equipment was located inside another laboratory that was kept closed for longer. Finally, the samples were removed on 24/09/2024.

Considering a variation of contact angle that can be considered normal for a surface as irregular as wood, we can assume that the values of contact angle measured by the MSA are inside a gap of what would be accepted on a case of non-variation of the contact angle with ageing process by the use of UV lamp. Even though it is more normal to see a certain decrease of the angle, it is also possible to observe cases where the variation was really low to non-existent, like it happened on this situation. Stable drops would look like the one on image 61.



Image 61: Drop of water measured by the MSA

This situation was expected because of the description of the SIVO found on its Production Information file that can be obtained on the Evonik material [41], since it describes a QUV-stability of up to 900h regarding hydro and oleophobic properties on the surface for non-transparent surfaces. Trying to understand this stability presented, the EDS was made to observe the composition on the surface with the pure SIVO and the SIVO with nanolignin. The results were expected to be the same, but that was necessary to be certain of it.

5.6.1- Contact angle with equipment

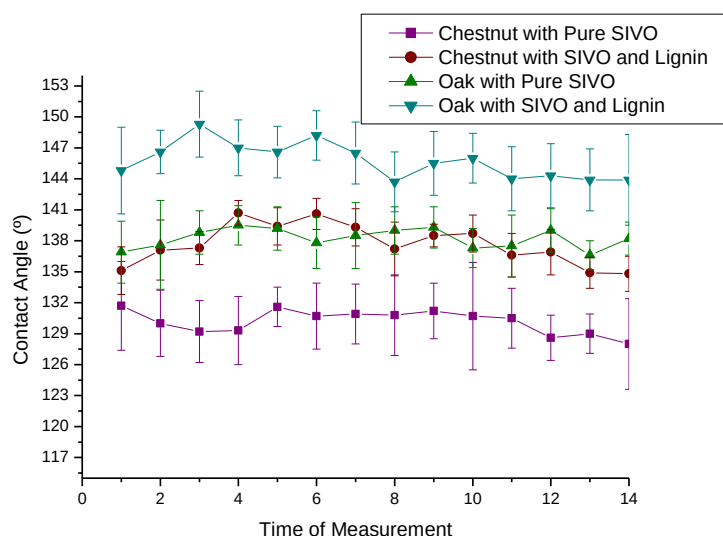
Since the contact angle was measured later with ImageJ, this parameter was only used to compare the variation during the time the sample was inside the chamber, observing if any outlier variation would occur at some point. The average value and deviation for each sample measured was taken, and the graph was created.

The table 14 consists of the average with deviation of multiple contact angles measured around the surfaces in relation to the date of measurement it was obtained. Since it was a fast analysis to be done, and the values worked as a control parameter, it was decided at the start to

take seven measurements in order to cover multiple points around the surface. Graph 05 is the visual representation of the table.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
C-UV-PS	131.7±4.3	130.0±3.2	129.2±3.0	129.3±3.3	131.6±1.9	130.7±3.2	130.9±2.9	130.8±3.9	131.2±2.7	130.7±5.2	130.5±2.9	128.6±2.2	129.0±1.9	128.0±4.4
C-UV-SL	135.1±2.3	137.1±2.9	137.3±1.6	140.7±1.2	139.4±1.8	140.6±1.5	139.3±1.8	137.2±2.6	138.5±1.1	138.7±1.8	136.6±2.1	136.9±2.2	134.9±1.5	134.8±1.7
O-UV-PS	136.9±3.0	137.6±4.3	138.8±2.1	139.5±1.9	139.2±2.1	137.8±2.5	138.5±3.2	139.0±2.3	139.3±2.0	137.3±1.9	137.5±3.0	139.0±2.1	136.6±1.4	138.2±1.6
O-UV-SL	144.8±4.2	146.6±2.1	149.3±3.2	147.0±2.7	146.6±2.5	148.2±2.4	146.5±3.0	143.7±2.9	145.5±3.1	146.0±2.4	144.0±3.1	144.3±3.1	143.9±3.0	143.9±4.4

Table 14: Values of contact angle (°) during the experiment



Graph 05: Contact angle (°) x time it was measured

On the day 10/09/2024, completing 44 days or 1056 hours of exposition, some points on the border of the chestnut samples started showing instability for the water drop, meaning that the coat have probably reached its QUV limit for this kind of sample. It is a result inside the expected hours wise since the values described by Evonik [35] were between 900 to 1400h of protection. An interesting detail is that the unstable borders were mostly the ones close to the tangential cut border. This might have been avoided if the samples were not only changed position inside the chamber, but also rotated 90° each time the movement was made, but it is impossible to make any conclusion on this specific point with the current data.

A simple test made on the final day of this analysis was the following: all the twelve samples were marked with a pencil, dividing the sample into 25 squares of 1x1cm. after that, a drop of 10µL was dropped inside each square to decide with areas had instability or not, as it can be seen on the image 62 below.



Image 62: Chestnut (on the left) and oak samples (on the right) with drops for surface stability

Comparatively, the samples of chestnut with pure SIVO were the ones that presented a larger number of unstable drops, showing with another analysis the fact mentioned before that the lignin and its phenolic rings indeed increased the UV aging protective properties of the surface, as it can be seen on the comparative table 15 below. Oak keeps better results, which could be a sign that this formulation of coating has a better compatibility with this type of wood, possibly because of its surface irregularity.

	Unstable drops out of 25		
	01	02	03
C-UV-PS	15	14	9
C-UV-SL	3	8	4
O-UV-PS	2	1	0
O-UV-SL	1	0	0

Table 15: Number of unstable drops per sample of substrate/formulation

5.6.2- Contact angle with ImageJ

As usual, each substrate received three drops and had their contact angle measured. The average value between those drops and its deviation can be found on the table 16 below. After that, image 63 represent the drops on each type of wood with the different coating formulation.

		Contact Angle (°)			
		Drop 01	Drop 02	Drop 03	Average
Chestnut	C-UV-PS-01	129.0	131.0	128.2	129.4±1.4
	C-UV-PS-02	123.4	128.9	125.6	126.0±2.8
	C-UV-PS-03	125.8	124.6	123.8	124.7±1.0
	C-UV-SV-01	134.2	131.2	132.0	132.5±1.6
	C-UV-SV-02	138.2	133.5	131.7	134.5±3.4
	C-UV-SV-03	135.1	132.1	139.7	135.6±3.8
Oak	O-UV-PS-01	134.9	132.8	140.0	135.9±3.7
	O-UV-PS-02	134.0	134.1	139.8	136.0±3.3
	O-UV-PS-03	136.9	133.8	137.6	136.1±2.0
	O-UV-SV-01	141.1	141.6	148.5	143.7±4.1
	O-UV-SV-02	143.4	140.2	143.8	142.5±2.0
	O-UV-SV-03	147.1	147.5	144.3	146.3±1.7

Table 16: Contact angle values measured

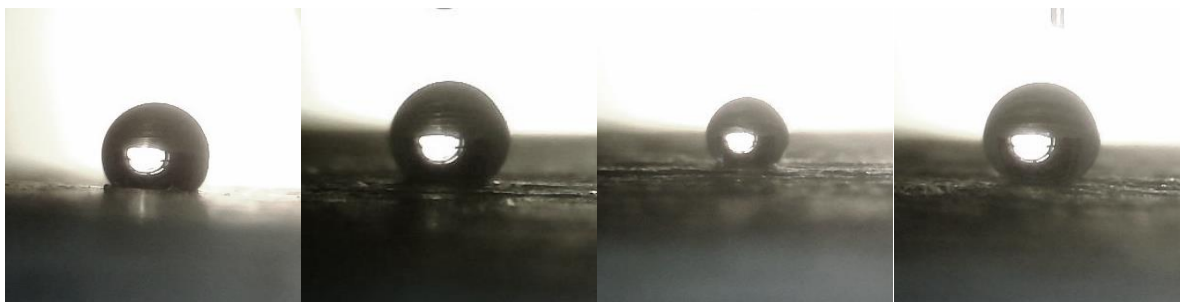


Image 63: Examples of drops of each situation

A last interesting topic for comparison is the values of contact angle obtained using the MSA versus the ones measured with the ImageJ software. As is visible on the table 17 below, we can conclude that the values are close enough to assume that the reading with manual baseline on the equipment and the use of the software are creating similar results. This is important specially for the weathering analysis, since the samples cannot be removed from the schematic, making it impossible to use the ImageJ method for it.

	MSA Value	ImageJ Value
C-UV-PS-02	128.0±4.4	126.0±2.8
C-UV-SL-02	134.8±1.7	134.5±3.4
O-UV-PS-03	138.2±1.6	136.1±2.0
O-UV-SL-03	143.9±4.4	146.3±1.7

Table 17: Comparing values of the two forms to determinate the contact angle

One last point that should be marked for this part of the analysis is the fact that the contact angle values of both techniques are considering the central part of the substrate. This became even more important after the stability of the drops started to drop on the borders. Also, the values used for the comparison on the table above consider the average of the last measurements using the MSA versus the average of the same sample using the ImageJ.

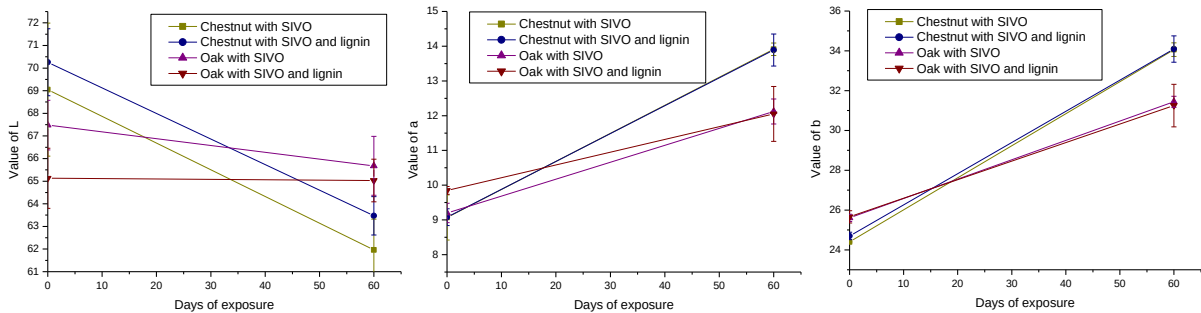
5.6.3 Colorimetry Measurements

As it is possible to see on the table 18 below, the values of ΔE surpassed a lot for chestnut. On oak, even though it is also more than the stipulated value, it is closer to the maximum value of 5, even getting one of the samples with a value lower than it. Looking at the surface of the substrate that never got in contact with the UV rays, it is possible to see the difference.

	ΔE
C-UV-PS-01	11.67±0.24
C-UV-PS-02	12.68±0.33
C-UV-PS-03	14.53±0.25
C-UV-SV-01	13.72±0.27
C-UV-SV-02	11.96±0.36
C-UV-SV-03	11.98±0.44
O-UV-PS-01	7.02±0.20
O-UV-PS-02	6.92±0.22
O-UV-PS-03	6.36±0.22
O-UV-SV-01	6.45±0.15
O-UV-SV-02	4.82±0.23
O-UV-SV-03	7.26±0.18

Table 18: Values of ΔE for this analysis

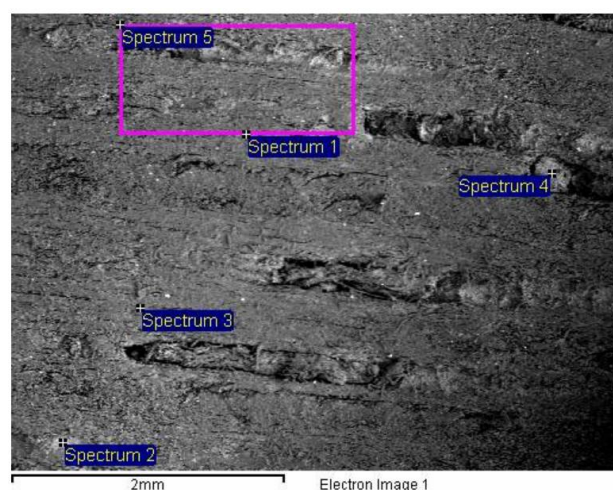
An interesting discussion is the variation of each variable of the equation to determine ΔE , as it is shown on the graph 06 below. The behaviour is related to the type of wood use as it can be seen. Chestnut has a larger decrease of L compared to oak, which has a minimal variation. Chestnut has also a larger increase of a and b compared to oak. Those variations can be an indicative that chestnut is more susceptible to UV altering than oak, complementing the values found for ΔE .



Graph 06: Variations of L*, a* and b* for UV chamber

5.6.4- SEM-EDS

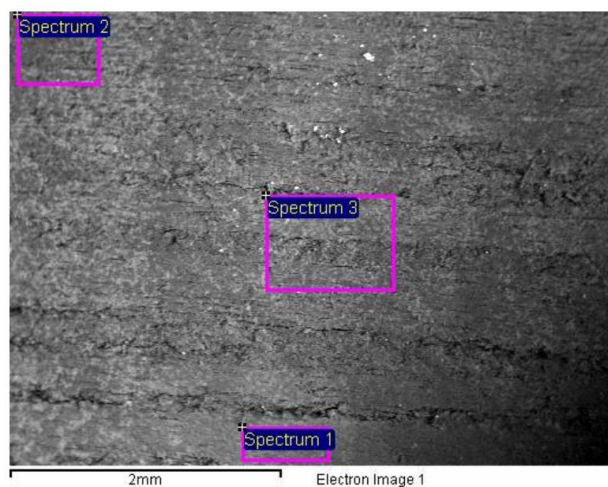
Different spots along the image (spectrum) had the composition analysis, as it can be seen on image 64. The composition of each one can be found on the table that is visible under each image. On the case of the spectrum that presents silver (Ag), the composition can be ignored because it represents the substance added to some points to increase the conductivity of the surface, increasing the quality of the images obtained by the equipment. As it is visible, even though the SIVO is considered and distributed as a silane, a high percentage in weight of fluorine is found compared to the weight of silicon.



1

Spectrum	In stats.	C	O	F	Si	Cl	K	Ca	Ti	Ag	Total
Spectrum 1	Yes	60.70	31.45	7.03	0.44		0.30	0.08			100.00
Spectrum 2	Yes	50.11	24.74	24.29	0.86						100.00
Spectrum 3	Yes	31.82	12.53			6.21				49.44	100.00
Spectrum 4	Yes	42.62	31.99	20.58	1.12			2.51	1.19		100.00
Spectrum 5	Yes	47.46	31.89	20.01	0.64						100.00
Max.		60.70	31.99	24.29	1.12	6.21	0.30	2.51	1.19	49.44	
Min.		31.82	12.53	7.03	0.44	6.21	0.30	0.08	1.19	49.44	

All results in weight%



2

Spectrum	In stats.	C	O	F	Si	Ti	Ni	Total
Spectrum 1	Yes	35.47	23.54	39.23	1.76			100.00
Spectrum 2	Yes	43.33	27.36	28.18	1.11	0.03		100.00
Spectrum 3	Yes	41.40	26.03	31.04	1.12		0.40	100.00
Max.		43.33	27.36	39.23	1.76	0.03	0.40	
Min.		35.47	23.54	28.18	1.11	0.03	0.40	

All results in weight%

Image 64: SEM-EDS of pure SIVO (1) and SIVO with nanolignin (2)

Considering research like [64] and [65], it can be discussed that the fluorine compound or compounds on the coating are the responsible for the results found on the contact angle, since the studies demonstrate that different types of fluorine compounds present a high UV ageing stability. A stable coating will take longer to suffer any degradation form, which would be responsible to a decrease on the contact angle.

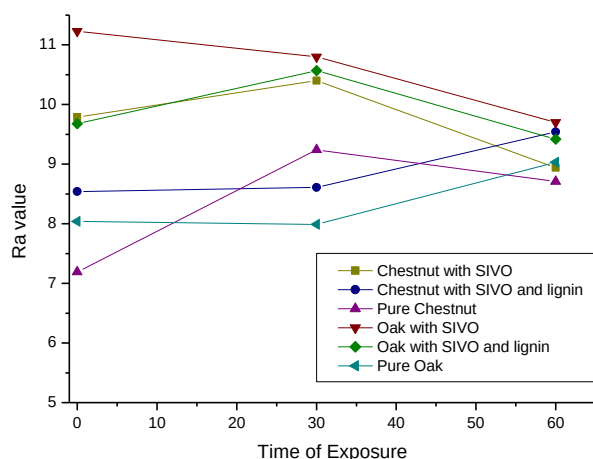
5.7- Natural weathering

5.7.1 – Roughness

The roughness experiment demonstrated by the table 19 below show mixed results that can be the effect of different variables. Starting with the weather of the past two months, August was a month with high temperatures and harsh sun, while September had more rains and temperatures below 30°C.

Between the variables presented, **Ra** is the average roughness and is usually used as a parameter to provide the surface texture on a more general context. **Rq** has a closer value to Ra but is more sensitive to variations and deviations considering how it is calculated. Finally, **Rz** is related to the highest peak and lowest point during the profile reading. It shows the worst-case scenario of the roughness. When using the equipment, is possible to see when the variation became larger than accepted, since the equipment stops the recording pointing error.

Considering just Ra, visible on the graph 07 below, the value of the uncoated samples is slightly lower than the coated ones. The increase and decrease between each measurement does not follow any behaviour that can divide the samples, and the variation is not big enough, creating the assumption that the roughness is not being dependent on the coating used. Might be due to the thickness of the coating or the technique used for the measurement.



Graph 07: Variation of Ra with time of exposure

		Average Ra (μm)				Average Rz (μm)				Average Rq (μm)			
Chestnut	Average C-PS	9.79	10.40	8.94	10.03	53.64	57.72	53.66	57.58	12.48	13.45	11.79	12.98
	Average C-SL	8.54	8.61	9.54	9.12	49.17	49.25	50.30	53.94	10.85	10.99	11.61	11.81
	Average C-B	7.19	9.24	8.71	9.42	43.04	48.98	52.65	54.87	9.64	11.88	11.53	12.36
Oak	Average O-PS	11.23	10.80	9.70	10.11	61.93	58.89	56.34	59.52	14.29	13.68	12.43	13.20
	Average O-SL	9.68	10.57	9.42	8.47	51.02	57.19	52.39	49.46	12.23	13.46	12.12	10.90
	Average O-B	8.04	7.99	9.03	9.46	41.28	45.09	53.11	54.88	10.20	10.65	11.77	12.17

Table 19: Values for roughness

The lack of roughness pattern can also be shown when looking at the table 19. If an average were made between all the values of chestnut or oak during the three months, the deviation would be low. This also helps with the idea that the variations found are related to the substrate and not the coating applied. Some punctual differences can be explained with the fact that not all the samples are suffering the effects of the weathering on the same way. As it can be seen on the image 65 below, some wood blocks have suffered cracks, and some shows dents or another defects, but is not a generalized behaviour.



Image 65: Some of the visible defects after weathering for 3 months

5.7.2 – Colorimetry

The colour variation also had an interesting result for the chestnut. From one measurement to the second, the values of ΔE decreased instead of increase, with the additive coating having a lower average variation. This might have happened because this wood generally gets a darker colour after contact with water. If on the first month, the harsh sunlight decreased the colour, maybe on the second month the opposite happened because of the rain.

Comparing the coated with non-treated surfaces, for chestnut the lack of coating makes the colour variation be more intense. For the oak, change is not that visible as it can be seen on table 20. Most of the results surpasses the limit value of $\Delta E=5$ but is still interesting to notice the behavior between the different situations. Still, to have a more complete image of the situation, this analysis needs more time to determinate better the behaviour of each type of wood. One last interesting point to observe is that the behaviour of the first month is similar to the total colour variation inside the UV aging chamber, showing that this is probably the behaviour expected on a weather with low humidity.

Comparing the samples on the image 66 below, we see that the samples on the UV had their colour getting darker, while the samples on weathering seems to have lost colour, especially the oak sample. A possible explanation for that is that the UV rays by itself react with the surface in a way that produces a darker colour. Meanwhile, all the other variables that exist on a weathering analysis combine with the UV rays from the sun acting on a different way.

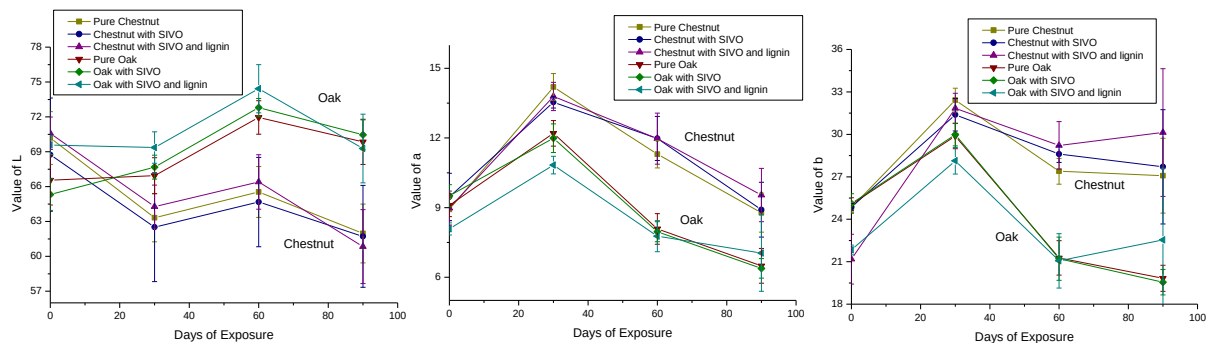
		ΔE_1	ΔE_2	ΔE_3
Chestnut	C-NW-PS-01	11.21±0.22	5.76±0.32	10.32±0.55
	C-NW-PS-02	10.79±0.29	6.17±0.45	10.68±0.47
	C-NW-PS-03	11.00±0.18	5.85±0.30	5.25±0.43
	C-NW-PS-04	10.97±0.21	5.80±0.31	7.09±0.83
	C-NW-PS-05	13.68±0.24	6.99±0.17	10.28±0.25
	C-NW-SL-01	7.79±0.65	4.59±0.36	7.43±0.76
	C-NW-SL-02	10.34±0.28	6.82±0.31	10.10±0.34
	C-NW-SL-03	9.14±0.12	4.62±0.12	3.60±0.27
	C-NW-SL-04	11.81±0.19	7.65±0.17	14.24±0.35
	C-NW-SL-05	11.27±0.10	6.57±0.11	7.83±0.24
	C-NW-B-01	16.09±0.15	9.57±0.14	11.92±0.19
	C-NW-B-02	11.42±0.50	9.00±0.52	16.92±0.54
	C-NW-B-03	12.62±0.27	7.17±0.25	6.26±0.51
	C-NW-B-04	14.62±0.36	12.14±0.43	19.30±0.55
	C-NW-B-05	12.52±0.39	9.81±0.40	12.16±0.46
Oak	O-NW-PS-01	6.06±0.18	7.38±0.24	6.47±0.13
	O-NW-PS-02	5.14±0.23	7.80±0.49	6.74±0.32
	O-NW-PS-03	7.82±0.16	6.44±0.12	5.75±0.22
	O-NW-PS-04	5.92±0.08	7.47±0.14	4.83±0.17
	O-NW-PS-05	7.27±0.28	11.53±0.40	11.50±0.29
	O-NW-SL-01	6.08±0.32	9.96±0.30	10.29±0.25
	O-NW-SL-02	6.69±0.25	8.50±0.36	7.77±0.33
	O-NW-SL-03	5.85±0.18	8.50±0.33	7.23±0.28
	O-NW-SL-04	6.19±0.20	11.95±0.26	9.12±0.29
	O-NW-SL-05	5.45±0.13	8.51±0.24	7.36±0.17
	O-NW-B-01	7.33±0.18	7.85±0.19	4.90±0.18
	O-NW-B-02	7.28±0.09	3.68±0.17	2.52±0.23
	O-NW-B-03			
	O-NW-B-04	7.46±0.16	5.25±0.30	2.54±0.19
	O-NW-B-05	5.58±0.11	7.56±0.36	10.27±0.32

Table 20: Values of ΔE



Image 66: (on the left) UV chamber versus (on the right) weathering samples

To understand the colour variation, it is more interesting to see the behaviour of each variable as it is shown on the graph 08 below instead of looking only to the value of ΔE , just like it was made on the UV chamber experiment before.



Graph 08: Variations of L*, a* and b* for weathering

We can see that the two types of wood present different behaviours between each other, but similar behaviour between the coated and uncoated species. This can be interpreted as a tendency of the wood substrate then, not having a relation with the coating applied. For this behaviour we have: Chestnut decreased then had a small increase, then another decrease in L, increased and then decrease of a and b, except the samples with lignin that had an increase of b between 60 and 90 days; oak have a small followed by a larger increase and then a decrease in L, with the sample with lignin decreasing more abruptly, increase and a large decrease of a and b except the samples with lignin that also have an increase of b between 60 and 90 days.

The increase in b for both samples with lignin after 60 days shows an increase on the yellow colour of the substrate. Considering that materials containing lignin after a process of ageing or oxidation have a tendency of obtaining a yellow tone, this result makes sense with the samples that end up having this variation.

Comparing the results of the variables on the UV chamber with the ones in weathering, we see that the behaviour of the first month of the analysis here is the same on the other experiment. This might be an indicative that UV rays had the larger impact on the first month of the weathering experiment, which makes sense considering that it was a month with strong sunlight, high temperatures and no rain. The values for the third month are probably a result of a combination of values: components of the substrate that were already removed, different temperature and humidity compared to the previous months, oxidation and decomposition of some of the components of the wood.

Those changes depend on the original wood, the mobility of its substrates inside the material and all the factors that can be considered on a weathering analysis, such as wind, UV

exposure, moisture variation, microorganisms that can be carried through air. Since it is a process that depend on many variables and it can show differences also with different samples of the same wood, the only conclusions that are safe to take is that the behaviour that varies the colour depends on the wood used, and that the coating is able to reduce the ΔE variation when compared to untreated samples.

5.7.3 – Contact Angle

As said before, the contact angle was measured also using the MSA, since the equipment is mobile, while the system used to obtain images to use the ImageJ software has a specific space that would be hard to put the samples, since they can't be removed from the net that is supporting it. The values found also present the same behaviour of all the other analysis before, as it is visible on the table 21 below. The variation of the average between months is low enough to suggest that there is no variation on the contact angle to be considered, a similar result with the one found on the UV chamber.

	30 days	60 days	90 days
C-NW-PS	131.0±4.5	130.1±4.6	129.5±3.1
C-NW-SL	135.8±3.1	136.5±3.1	135.2±2.1
O-NW-PS	136.2±3.5	136.2±4.1	136.6±4.6
O-NW-SL	144.9±3.9	143.5±4.1	143.7±4.3

Table 21: Average of the contact angle (°) between months

All the values of contact angle measured among the different analysis is a good indicator that the coating has a good stability even with multiple factors acting simultaneously on it. This is an important detail when considering research, especially because it can be used as a parameter to compare other analysis that can be done on the future.

5.8- Burial

Before any measurement was made, the samples removed from the soil would be separated by type of wood and its three groups (no coating, pure SIVO, SIVO with lignin), as it is shown on the image 67 below. The samples would have the soil removed by brush, so this mass was not considered on the measurement of the scale. After the measurement, the sample stayed for 24h inside the oven to dry and then measured again before being buried on the same place again until the next time it would be checked. If necessary, new soil was added to the burial site to keep the values of humidity.



Image 67: Samples after being removed from the soil

Two parameters were measured, moisture and mass loss, and visual appearance was also considered. The first important result to be looked at is that, even with only 15 days, the samples already showed signals of deterioration and had some level of mass reduction. Between the three types of sample, in both wood substrates, we have the same behaviour when observing, that pure wood lost more mass than the samples coated with pure SIVO, which had a slightly larger loss of mass than the ones covered with SIVO with nanolignin. Considering that one of the roles of lignin on the wood structure is to act as a biocide to protect against microorganisms, that result was expected to be seen. Below we can see on the table 22 the values and deviation of the mass reduction for each type of sample.

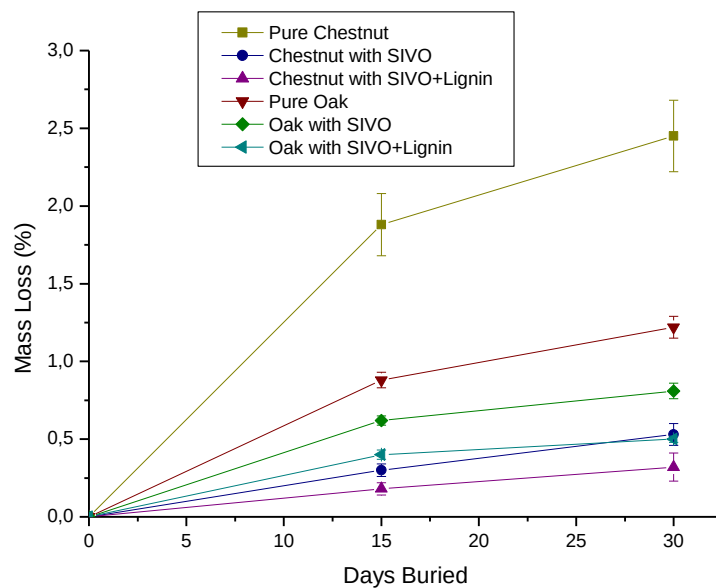
	Average mass reduction (%)					
	15 days			30 days		
	Pure Wood	SIVO	SIVO+Lignin	Pure Wood	SIVO	SIVO+Lignin
Chestnut	1.88±0.20	0.30±0.04	0.18±0.04	2.45±0.23	0.53±0.07	0.32±0.09
Oak	0.88±0.05	0.62±0.03	0.40±0.03	1.22±0.07	0.81±0.05	0.50±0.02

Table 22: Values of mass reduction on the samples

Moisture content was related to the amount of rain received on the soil during the period the samples were buried. Because of this, the first 15 days showed a higher moisture content (more than 50% on the first 15 days and around 25% on the second measurement). This reduction of moisture affected the degradation of the samples as we can see on the graph, since the growth between first and second measurement has a lower angle, indicating a less strong process.

The graph 09 below shows the variation of mass loss considering the number of days the sample was buried. The chestnut samples had a large variation between each other than the oak samples. It is not possible to know all the variables that might have influenced on this result, but one possible factor that is directly involved with it is the density of each type of wood.

Chestnut is less dense than oak, making it easier for the water absorbed to be carried around on the entire substrate.



Graph 09: Mass loss per number of days buried

If the water can move more freely inside the substrate, it became easier for the microorganisms to also move inside of it. This has become even more visible in one of the chestnut samples, where you can see a swelling on a part of the sample by naked eye, provided by the image 68 below. The sample in question is one of the samples that didn't receive any type of coating treatment, which is probably one of the reasons of why it has this type of decaying compared to the treated ones.



Image 68: Sample with swelling

The level of degradation through erosion is visible in all the surfaces of the samples, as it can be seen below on the image 69. The first 15 are chestnut and the other 15 are oak, being first the pure SIVO samples, then the SIVO with lignin samples and finally the pure wood samples. It is visible to the naked eye that the samples without any coating were more affected by the weathering.



Image 69: Eroded samples

After 30 days of burial, it became more visible the erosion signals, including visible dents on the substrate. Below we can see image 70 indicating this defects on the samples. If the samples are left inside the burial site for a longer period, the destructive action of the erosion elements will be more intense, since the microorganisms will have more time to dislocate inside them, consuming and breaking components of the wood substrate.

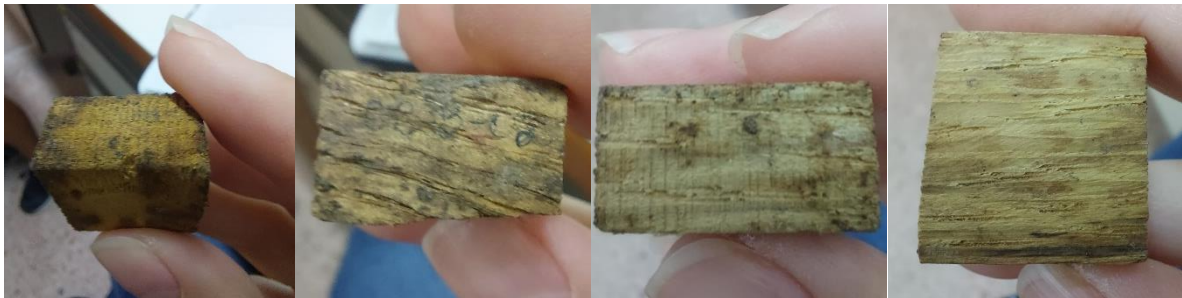


Image 70: Buried samples and its defects

The first two images are of chestnut and the last two of oak. Even on naked eye is possible to realize that the samples of chestnut are suffering more with the erosion caused by the burial experiment, having more darker marks and white areas indicating the microbiological attack to it, and also the dents and swelling that was already visible with 15 days of the experiment. The oak samples, even though they are also losing mass with time, have a less destructed appearance.

6- CONCLUSION

The use of the lignin as an additive has presented interesting results. Superhydrophobicity was not reached, but there is an increase on the contact angle when using this material in combination with the SIVO. Besides, after the formulation of the coating being decided, the values found for contact angle kept similar results between the experiments operated (peeling cycles, pH solution variation, weathering, UV aging chamber).

Considering the colour, we see that the wood substrate has a large variation on its tones when exposed to UV rays and other methods of weathering. It was also possible to realize that a month with harsh sun and lower humidity has the UV as the main factor altering the colour variation, while when it has more raining or with more wind, we see that other factors have a larger role on the variation. Degradation and oxidation will affect only as long as the components that can suffer those reactions still exist. After that, their values will not influence on the colour anymore. The tendency of dry wood substrates is to obtain a light and slightly yellowish tone the longer it stays exposed.

For the benefits of the use of nanolignin, we see that this organic molecule increased the adhesion of the coating, considering the results of the peeling cycle, and increases the stability of the coating under UV action, since the surfaces with additive coating showed a smaller appearance of unstable surfaces having the same time of exposure of the UV lamp. Also, with the burial experiment, we saw that it creates a higher protection of substrates of the microbiological attack, making the samples have a slower reduction of the mass compared to the other samples.

Finally, doing the comparison of those two types of wood, the oak had better results than the chestnut. It is a more dense and rough wood on its surface, and this second factor was the main responsible for the larger contact angle and the behaviour of the coating. Being stiffer on the other hand caused some issues during the thesis, creating cracks on samples and even the loss of a sample on the weathering analysis due to fracture.

Overall, this is an important step on this field of research, and should be considered for future works, for a creation of a larger database of wood species using those formulations, or an upgrade on the formulation, generating a possible superhydrophobic repellent surface with high adhesion, stability and biocide properties.

7- SUGGESTIONS FOR FUTURE WORK

This work was the first step on a research that still have a lot to be developed. The first point would be to try more variables in order to improve even further the formulation using the nanolignin on acetone. For that, larger amounts should be tried on the solvent. Different concentrations of the mixture should be added to the SIVO in order to see the optimal, then a variation of the amount of the mixture should be looked at.

Other detail that would be interesting to study is the application method. Since this novel was a first step on the study, applying the coating by just spreading around the mixture using the same pipette that extracted it from its becker created an acceptable result. But in the future, it can be interesting to try more forms of application and maybe even study the effect of the thickness of the layer with changes on the properties of the coating.

On the analysis, both weathering and burial analysis are long term techniques that should last for longer, and this is why the values presented can be considered a partial result. Other than these two analysis for the durability of the coating, experiments using fungi or bacteria could be done to observe the biological activity behaviour with specific know species. Lignin is the structural part of wood that protects against this kind of attack, so it can be interesting to see how its biocidal properties would be shown.

Another topic would be an increasing on the amount of wood types that could be applied. This novel alone showed that two types of wood presented different properties and behaviour, even though they followed the same pattern considering contact angle. Trying to apply the coating on other species and seeing the parameters would provide what can be a first step to develop a database on the area. Besides, different types of the world used different wood as substrate since ancient time. If it became possible to use more species on this type of research, we would be closer to a formulation that could be considered universal for use.

Lastly, a topic that was already mentioned before would be a study of the rose petal effect on this coating. Discovering how much kinetic energy needs to be added to reach the repellence could be interesting. Other characterization methods, such as FTIR could also show interesting details of this research and a base for its further development.

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