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Dipartimento Territorio e Sistemi Agro-forestali
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Corso di laurea magistrale/Second Cycle Degree (MSc)
in Forest Science

Study of the Effects of Tannin Impregnation to Spruce Wood

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Abstract

This thesis explores the influence of tannin concentration and cross-linking agents on the impregnation, leaching resistance, mechanical performance, and color stability of Norway spruce (*Picea abies*). Chestnut tannin solutions at 10%, 20%, and 30% were applied, both alone and in combination with glyoxal, hexamine, or furfural, to assess their effectiveness as sustainable wood treatments. The findings indicate that a 20% tannin solution achieved the most efficient impregnation, balancing uptake and viscosity. Among the hardeners, furfural consistently delivered the strongest results, enhancing fixation, leaching resistance, hardness, and color stability. Glyoxal provided moderate improvements, while hexamine performed poorly under unadjusted pH conditions, though its potential under optimized formulations remains a promising avenue for future research. Across all treatments, tensile strength was preserved, confirming that tannin modification does not compromise structural integrity. Colorimetric analysis further revealed that tannin–furfural treatments resisted uneven darkening and ultraviolet degradation, thereby improving both durability and aesthetic stability. Collectively, these results highlight tannin–furfural systems as particularly promising bio-based alternatives to conventional preservatives, aligning material performance with environmental responsibility.

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Introduction

The construction industry accounts for nearly 40% of global CO_2 emissions and material consumption, making it a critical sector in the transition toward climate neutrality. Wood has emerged as a key material in this shift, offering a renewable, carbon-storing alternative to concrete and steel. With expanding applications in multi-story and tall buildings, ensuring the durability of timber is essential for maximizing its environmental and economic benefits (Järvinen et al., 2022). Yet, wood's hygroscopic and biodegradable nature makes it vulnerable to degradation from abiotic factors such as UV radiation, moisture, and temperature fluctuations, as well as biotic threats including fungi and insects (Peng et al., 2021). Climate change intensifies these pressures, as extreme weather events, droughts, and pest outbreaks increasingly interact to weaken forest resources and wood-based products (Teshome et al., 2020). As a result, effective and sustainable wood preservation methods are becoming ever more important to extend service life and safeguard timber's role in low-carbon construction (Järvinen et al., 2022).

Conventional preservative systems, often based on chromium, copper, or synthetic resins, are effective but environmentally problematic due to leaching and toxicity (Peng et al., 2021). Bio-based alternatives are therefore attracting growing attention, with tannins with polyphenolic compounds abundant in bark and other plant tissues emerging as promising candidates. Tannins can crosslink with hardeners such as hexamine or glyoxal to form stable polymers, reducing formaldehyde emissions and enhancing durability (Ballerini et al., 2005; Thevenon et al., 2008). Research has demonstrated that tannin-boron and tannin-hexamine formulations improve resistance against leaching, fungi, and insects (Tondi et al., 2012a), while also enhancing mechanical strength and fire resistance of wood (Tondi et al., 2012b). However, high water solubility and susceptibility to weathering remain significant challenges that limit outdoor applications (Peng et al., 2021).

With these considerations the present study addresses these gaps by investigating the effects of tannin concentration and hardener type on Norway spruce (*Picea abies*). Chestnut tannin was applied at 10%, 20%, and 30% concentrations, both alone and in combination with glyoxal, hexamine, and furfural. The treated samples will be evaluated for impregnation, leaching, hardness, tensile strength, and color stability. By systematically comparing formulations, this work contributes to understanding how tannins can be optimized as sustainable wood treatments both practically and aesthetically.

Background

2.1 History of Tannins

The history of tannins stretches across millennia, beginning with simple craft practices and eventually developing into a sophisticated global industry. Ancient societies discovered, long before the science was understood, that animal hides could be transformed into durable leather when immersed in baths filled with bark or wood steeped in water. The process was remarkably slow. Skins were shifted between pits over many months, often taking a full year before they were strong enough to be used. This slow pace was accepted because no faster method existed, and the results were essential to daily life (Pizzi, 2008).

The scientific recognition of tannins did not arrive until much later. In the seventeenth century, the Italian chemist Giovannetti began exploring the strange behavior of plant extracts when mixed with iron salts. His observations were some of the first steps in identifying tannins as a distinctive class of natural products. By 1772, Carl Wilhelm Scheele had successfully isolated gallic acid, a key component of many tannins. Over the following decades, chemists such as Deyeux, Bartholdi, and later, Proust, confirmed that these "astringents" represented a unique family of molecules characterized by their gallic acid content (Pizzi, 2019). This scientific recognition provided a foundation that allowed tannins to be studied not merely as mysterious plant compounds but as chemicals with definable properties and potential industrial value.

Industrial use began in earnest around the mid-nineteenth century. In Lyon, chestnut tannins were processed to make iron tannate, a black dye used to color silk blouses. This large-scale application brought about a wave of small factories, especially in France and northern Italy, that specialized in extraction. However, the industry was precarious. As fashion moved away from black silk in the 1860s, the demand for tannin-based dyes collapsed. Many factories failed, while others merged in hopes of surviving (Pizzi, 2008). A few resourceful producers pivoted to leather tanning, convincing hide processors that tannin extracts could transform their industry. By dissolving tannins directly into the tanning pits, they reduced the time needed to make leather from the traditional twelve months with oak bark to just twenty-eight days (Pizzi, 2019).

The promise of producing leather more quickly and more consistently ensured the rapid spread of tannin extract use, and the industry entered its second major period of growth. Growth that Europe alone could not provide sufficient raw material to meet. By the early

twentieth century, factories had expanded far beyond their original bases. Mimosa bark from southern and central Africa and quebracho wood from South America became the primary sources of commercial tannins, feeding markets across Europe and North America (Pizzi, 2008). These new supply chains were robust enough to support large-scale production, and vegetable-tanned leather became standard in many industries. (Pizzi, 2008).

The world wars gave the tannin trade an additional boost. Soldiers marched in leather boots, and the need for reliable, heavy-duty footwear meant enormous quantities of tannin were required. To give a sense of scale, South Africa produced about 110,000 tons of tannin extracts in 1946, just after World War II (Pizzi, 2008).

While at that moment, tannins seemed indispensable, the triumph was brief. By the 1950s and 1960s, profound changes undermined the dominance of tannins. Petroleum-derived materials such as synthetic rubber and neoprene began replacing leather in shoe soles. At the same time, mineral tanning processes using chromium salts offered faster, cheaper methods to soften hides, especially for the upper parts of shoes (Ciriminna et al., 2024).

The downturn in demand forced producers to seek new outlets. During the 1960s and 1970s, researchers explored a surprising range of applications. Tannins were tested as metal primers to prevent corrosion, as agents for pollution control in water treatment, and even in cement as superplasticizers (Pizzi, 2008). Some of these uses showed promise, but few could sustain the industry. One exception was wood adhesives. Condensed tannins, especially those from mimosa and quebracho, were found to be reactive enough to partially replace synthetic phenols in resins. By the 1970s, tannin-based adhesives had reached industrial scale, producing thousands of tons of resin for particleboard and plywood (Pizzi, 2008). This marked the third major transformation in tannin history, moving from leather to adhesives.

Even as condensed tannins dominated adhesives, hydrolysable tannins like those from chestnut did not disappear. Research in the 1970s revealed their biological activity, particularly their ability to inhibit enzymes used by pathogens to invade plants. These findings hinted that tannins might have agricultural or medicinal value beyond their industrial roles (Ciriminna et al., 2024).

A breakthrough came in the late 1980s, when studies in Yugoslavia showed that adding small amounts of chestnut tannin to livestock feed improved digestion and reduced ammonia formation. Over the following decades, similar research confirmed benefits ranging from

protecting liver and kidney tissues to improving gut health (Ciriminna et al., 2024). Parallel work in Italy uncovered another unexpected application: chestnut tannins functioned effectively as plant biostimulants and biofertilizers. This discovery, combined with the animal feed findings, opened entirely new agricultural markets for tannins. By the early 2000s, these two uses had grown into significant end markets, giving chestnut tannin a second life after decades of stagnation (Ciriminna et al., 2024).

At the same time, research in medicine began to take tannins seriously. Their astringent and protein-binding properties, long recognized in traditional medicine, were investigated in modern contexts. Studies pointed to antiviral activity, anticancer potential, and roles in managing gastrointestinal disorders (Pizzi, 2019).

The story of tannins is one of cycles of adaptation. What began as an ancient craft practice became a nineteenth-century dye industry, then a cornerstone of leather tanning, then an adhesive material, and now an agricultural and medical resource. At each stage, the industry has faced crises, from the collapse of fashion markets, the rise of synthetic materials, or the environmental concerns linked to chromium tanning. Each time with tannins finding new relevance. Their versatility, rooted in their unique chemistry, has allowed them to remain valuable despite changing times.

2.2 Classifications & Chemistry

Tannins are a class of polyphenolic compounds synthesized by plants as part of their defense strategy. They can be broadly divided into two structural groups: hydrolysable tannins and condensed tannins. Hydrolysable tannins are esters of glucose with gallic acid or hexahydroxydiphenic acid, which upon hydrolysis form gallic or ellagic acid derivatives (Comandini et al., 2014). In contrast, condensed tannins, also known as proanthocyanidins, are polymers of flavonoid units such as catechin and epicatechin (Cesprini et al., 2022a). Chestnut (*Castanea sativa*) is especially rich in hydrolysable tannins, predominantly ellagitannins, with vescalagin and castalagin being characteristic components (Comandini et al., 2014; Viriot, 1994).

These ellagitannins can undergo dimerization and hydrolysis during wood ageing, generating ellagic and gallic acids, which contribute to the durability and antioxidant properties of the wood (Viriot et al., 1994). The dominance of ellagitannins in chestnut distinguishes it from many other tannin sources, such as quebracho or mimosa, which are dominated by condensed

tannins (Cesprini, et al., 2022b). The key chemical difference between hydrolysable and condensed tannins lies in their stability and reactivity. Hydrolysable tannins are generally less stable under acidic or basic conditions, leading to cleavage of ester bonds and release of smaller phenolic acids (Comandini et al., 2014).

Condensed tannins, however, are more resistant to hydrolysis due to their carbon–carbon interflavonoid linkages, and they instead undergo oxidative reactions and polymerizations (Cesprini et al., 2022a). This divergence strongly influences their industrial use: chestnut hydrolysable tannins are widely applied in leather tanning due to their high reactivity with proteins, while condensed tannins are more suited for adhesive formulations (Pizzi, 2016; Pichelin et al., 2006).

Water solubility is a defining property of tannins and is directly connected to their functionality in both natural and applied systems. In chestnut, the majority of extractives are water-soluble ellagitannins, which are easily obtained using aqueous alcohol or acetone extractions (Viriot et al., 1994). Solubility, however, also creates challenges, since tannins can leach out under moist conditions, reducing their long-term effectiveness in wood preservation (Cesprini, et al., 2022b).

It is also important to consider how the pH influences tannin reactivity and formulation stability. For example, the gelation and curing behavior of tannin adhesives are strongly pH-dependent, with optimal performance often occurring under slightly acidic to neutral conditions (Ballerini et al., 2005). In alkaline media, condensed tannins crosslink efficiently with hardeners like hexamine, producing stable, water-resistant networks (Cesprini, et al., 2022b). Hydrolysable tannins such as those from chestnut are more sensitive to pH extremes, where excessive acidity accelerates hydrolysis and excessive alkalinity can cause oxidation (Comandini et al., 2014).

Beyond industrial applications, tannins provide ecological and physiological benefits. In trees, ellagitannins protect chestnut wood against microbial and fungal decay by acting as chemical barriers (Viriot et al., 1994). Additionally their astringent nature and protein-binding ability help contribute to herbivore deterrence (Comandini et al., 2014). Tannins also contribute to abiotic stress tolerance. They can absorb ultraviolet (UV) radiation, thereby protecting plant tissues from photooxidative damage (Comandini et al., 2014)

In chestnut, ellagitannin accumulation during heartwood formation enhances resistance against both UV light and oxidative degradation (Viriot et al., 1994). Furthermore, their antioxidant properties reinforce cellular redox balance, strengthening resilience against environmental fluctuations (Cesprini et al., 2022a).

Recent studies have highlighted tannins as renewable biomaterials for sustainable wood treatment. By impregnating low-durability timber with condensed tannins from quebracho, durability against biotic agents is significantly improved, mimicking natural defense mechanisms (Cesprini, et al., 2022b). Similar strategies may apply to chestnut ellagitannins, which already provide high intrinsic durability. Chestnut tannins are commercially significant, with several thousand tons extracted annually in Europe for leather processing (Viriot et al., 1994). Their reactivity with proteins makes them ideal for tanning hides, while their antioxidant properties have found uses in enology and animal nutrition (Comandini et al., 2014).

From a green chemistry perspective, tannins have attracted attention as sustainable alternatives to petroleum-based adhesives and preservatives. Condensed tannins from quebracho and mimosa are widely studied for adhesive formulations, often crosslinked with bio-based hardeners such as furfural or glyoxal (Cesprini et al., 2022a; Ballerini et al., 2005).

These systems produce panels with good bonding strength and minimal formaldehyde emissions (Pichelin et al., 2006). In preservation, tannin-based treatments offer eco-friendly alternatives to heavy metals and synthetic biocides, although water solubility remains a challenge (Lyon et al., 2007).

2.3 Wood Preservation

Wood has long been valued as a structural material because it is renewable, lightweight, and strong relative to its density. It also stores significant amounts of carbon, making it a key resource for sustainable construction and climate change mitigation. Increasingly, timber is used in buildings not only for traditional applications but also multi-story and tall structures, where it can provide a low-carbon alternative to traditional materials (Järvinen et al., 2022).

However, the very properties that make wood attractive also contribute to its vulnerabilities. Its hygroscopic nature allows it to absorb and release moisture, which causes dimensional changes and creates conditions favorable to decay organisms (Winandy & Morrell, 2017).

This sensitivity means that when wood is exposed outdoors or in contact with soil or water, its service life can be shortened drastically if not protected (Järvinen et al., 2022).

The need for preservation arises because wood is subject to both abiotic and biotic degradation. Abiotic factors include ultraviolet (UV) radiation, temperature fluctuations, and moisture cycling, which together lead to discoloration, cracking, and loss of mechanical strength. Lignin, which binds cellulose fibers in the wood structure, absorbs most of the UV irradiation, and its degradation is the main cause of surface graying (Peng et al., 2021). Repeated wetting and drying cycles can cause warping and surface checking, which reduce performance and open pathways for further deterioration. At the same time, biotic agents such as fungi and insects pose serious risks. Brown-rot fungi, for example, are particularly destructive in softwoods, rapidly consuming cellulose and hemicellulose, which leads to sharp declines in mechanical strength even in the early stages of decay (Peng et al., 2021). Termites and other insects can also feed on structural components, while molds and staining fungi, though less damaging structurally, compromise appearance and marketability (Järvinen et al., 2022).

Climate change is intensifying these challenges by combining stress factors. Hotter droughts, storms, and shifts in precipitation increase the likelihood that abiotic and biotic stresses act together, making trees and wood products more vulnerable (Teshome et al., 2020). In forestry and construction alike, this combined pressure highlights the importance of protective strategies that can extend service life and ensure reliability. Without preservation, wood risks being seen as less competitive compared to other construction materials (Järvinen et al., 2022).

A wide range of methods has been developed to protect wood against these threats. Conventional preservative treatments rely on pressure impregnation with biocidal chemicals. Copper-based preservatives such as alkaline copper quaternary (ACQ) and copper azole (CA) are widely used today, replacing older formulations like chromated copper arsenate (CCA) that were banned in many regions for both environmental and health concerns. These preservatives penetrate deeply into the wood, making it resistant to fungi and insects. Leaching, however, remains an issue, particularly in outdoor applications, where prolonged water exposure can gradually reduce their effectiveness (Peng et al., 2021).

Surface treatments such as paints, varnishes, or oils are also common, but they require regular maintenance as coatings crack and degrade over time. An alternative approach has been thermal or chemical modification of the wood itself. Thermal modification reduces hygroscopicity and increases dimensional stability by degrading hemicelluloses and altering cell wall polymers. Chemical modifications, such as acetylation, replace hydrophilic hydroxyl groups with more hydrophobic acetyl groups, thereby reducing water uptake and enhancing durability (Järvinen et al., 2022). These methods avoid the use of toxic preservatives, but they could affect mechanical properties and often come with higher costs of upkeep.

Increasing attention has been directed toward natural plant-derived compounds as sustainable alternatives. Tannins, abundant in barks and leaves, are promising because they act as natural antioxidants and antimicrobial agents. Studies show that aqueous tannin solutions increase resistance to both white-rot and brown-rot fungi, as well as termites (Peng et al., 2021). However, tannins are highly water-soluble and prone to leaching, limiting their effectiveness in outdoor exposure unless combined with other treatments. One promising development involves combining tannic acid with tung oil. Tung oil forms a polymerized hydrophobic barrier on the wood surface, while tannic acid provides UV absorption and resistance to fungal colonization. When used together, they significantly improve durability against both photodegradation and biodeterioration (Peng et al., 2021).

Industrial advances have also focused on bio-based adhesives and preservatives derived from tannins. Tannin–glyoxal adhesives, for example, can be used to produce particleboards without formaldehyde emissions, offering both strong bonding and environmental compatibility (Ballerini et al., 2005). Similarly, tannin-bonded particleboard and MDF have already reached industrial production, showing that natural extracts can replace synthetic resins in commercial settings (Valenzuela et al., 2012). Such approaches illustrate how preservation and material performance can be combined with the principles of green chemistry (Pizzi, 2016).

Extending the service life through preservation reduces the need for premature replacement, lowering both costs and environmental burdens (Winandy et al., 2017). Additionally, good construction practices, the use of naturally durable species, and treatments that alter or protect the wood surface all contribute to durability (Järvinen et al., 2022). In practice, no single method is universally sufficient, and combining strategies tailored to climate and exposure

conditions achieves the most reliable outcomes (Teshome et al., 2020). The long-standing reliance on chemical preservatives is now being complemented by plant-derived alternatives and modification technologies, reflecting a growing demand for environmentally safer solutions (Peng et al., 202; Pizzi, 2016). In the context of climate change and the growing reliance on renewable materials, effective preservation therefore remains central to securing wood's competitiveness as a sustainable construction material (Järvinen et al., 2022).

Ultimately, wood preservation is about ensuring that a natural, renewable material fulfills its potential in modern construction. As wood increasingly substitutes carbon-intensive materials like steel and concrete, protecting it from abiotic and biotic deterioration is crucial not only for performance but also for sustainability objectives (Järvinen et al., 2022).

2.4 Industry Approaches

The wood industry has evolved significantly in its preservation and processing methods, driven by both the need to extend service life and the pressure to meet environmental goals. Historically, the construction sector has relied heavily on carbon-intensive materials, but in recent decades wood has been promoted as a sustainable alternative because it stores carbon and reduces embodied energy in buildings (Järvinen et al., 2022). For timber to fulfill this role, however, industry approaches must address its vulnerabilities and adapt production to the changing requirements of durability, fire safety, and recyclability (Hidlebrandt et al., 2017).

One of the most established approaches has been the use of chemical preservatives. Boron-based formulations are a prime example: they are inexpensive, effective against fungi and insects, and relatively safe for humans (Lyon et al., 2007). Although it is important to note that preservative development must always be a balance between efficacy, environmental persistence, and regulatory acceptance (Trosa & Pizzi, 2001). Their major limitation is high solubility, which leads to leaching under weather exposure. This prompted research into ways of fixing boron within the wood structure. Ammonium borate oleate (ABO), a compound combining oleic acid's hydrophobicity with boric acid's biocidal effect, has demonstrated both water repellency and termite resistance when used as a preservative. Tests on Japanese cedar and beech showed a toxicity threshold of around 2.0 kg/m³, indicating strong protective potential (Lyon et al., 2007). By integrating repellence and biocidal function, ABO exemplifies how the industry has sought multifunctional preservatives that can withstand outdoor conditions.

In addition to preservative based formulations, industries have invested in modification technologies. Thermal treatments degrade hemicelluloses and alter wood polymers, making timber less hygroscopic and more dimensionally stable, while acetylation replaces hydroxyl groups with hydrophobic acetyl groups, lowering moisture uptake (Järvinen et al., 2022). These approaches are gaining ground because they avoid the toxicity concerns associated with earlier preservative chemicals. However, they can also bring trade-offs, such as higher production costs and potential impacts on mechanical strength, forcing industries to balance durability with performance.

Another industry trend has been to integrate tannins into wood products. Tannins, abundant natural polyphenols, have been developed into adhesives, preservatives, and flame retardants. Industrial production of tannin-bonded particleboard and medium-density fiberboard (MDF) demonstrates the viability of using renewable extracts at scale. Factories have shown that pine tannin adhesives can replace formaldehyde-based resins, reducing emissions while maintaining product quality (Valenzuela et al., 2012). Similarly, structural beams made from thick wood panels bonded with formaldehyde-free tannin adhesives have been produced industrially, proving that these bio-based alternatives can perform in demanding applications (Pichelin et al., 2006)

Preservation systems combining tannins with other compounds have also attracted industrial interest. Tannin–boron complexes are notable because they fix boron into less leachable forms while enhancing mechanical and fire properties. Studies show that these systems can provide durable protection against decay while contributing fire resistance, addressing two major industry concerns simultaneously (Tondi, et al., 2012b). This multifunctionality is important because industrial uptake depends not only on ecological advantages but also on cost-effectiveness and compliance with stringent safety standards, a concern also addressed in the development of wood products in Järvinen et al. (2022).

The broader history of tannin use underscores its adaptability. Originally central to leather tanning, tannins became critical in the dye industry and later were adopted in adhesives and coatings. The modern period has seen tannins emerge in bio-based composites, foams, and even medical applications. Industrial adoption follows cycles of availability, cost, and technological adaptation. The leather boom of the nineteenth century gave way to adhesive development in the twentieth, and today the focus is on advanced bio-based materials that

align with sustainability agendas (Pizzi, 2019). This trajectory shows how industries continuously reshape tannin applications to meet changing demands.

Policy and market drivers are also shaping industry approaches. The European Union's climate targets emphasize reducing carbon emissions by substituting renewable materials in construction. Engineered wood products like cross-laminated timber (CLT), laminated veneer lumber (LVL), and glulam are increasingly recognized for their potential to lower emissions compared to steel or concrete. Scenario modeling suggests that widespread adoption of engineered wood products could achieve carbon storage equivalent to tens of millions of tonnes of CO_2 per year in Europe by 2030 (Hildebrandt et al., 2017). To realize this potential, industries must ensure that these products are durable, safe, and competitive in cost and performance. Preservation technologies, adhesives, and coatings thus become not only technical solutions but also enablers of climate policy goals.

In practice, industry approaches involve a combination of methods. Pressure impregnation with modern preservatives, surface coatings with high-performance finishes, thermal or chemical modification, and integration of bio-based additives like tannins all contribute to ensuring longevity. The choice depends on the target market: high-value architectural projects often prioritize environmentally friendly solutions, while commodity products may still rely on conventional treatments for cost reasons. At the same time, global markets impose their own pressures. Exported timber must account for risks like termite exposure in warmer climates, driving the development of preservatives that perform reliably under diverse conditions (Järvinen et al., 2022).

The wood industry's current trajectory suggests that innovation and sustainability are no longer optional but essential. Conventional preservatives will remain important, but their role is shifting as natural-based formulations and modification technologies gain traction. Tannin-based systems demonstrate that industrial-scale adoption of bio-based chemistry is possible, from adhesives to preservatives. Engineered wood products show how structural innovation can align with climate policy. Altogether, these approaches reflect an industry adapting to both ecological pressures and market opportunities. By combining functionality, environmental responsibility, and scalability, the wood sector is positioning itself to play a central role in low-carbon construction and in advancing the circular economy.

2.5 The Future of Tannins

Future work on tannins should target the practical interfaces between chemistry, performance, and acceptance in real products. One obvious frontier is adhesive technology. Industrial use already covers multiple wood products, and research has produced routes to very low or zero formaldehyde release via alternative hardeners, aldehyde substitutes, and even autocondensation systems; what remains is head-to-head validation in larger production lines and durability testing under varied climates. Extending resource supply with hybrid copolymers that blend tannin with lignin, proteins, or furfuryl alcohol also merits scale-up studies to resolve consistency and cost (Pizzi, 2019).

A second priority is the photochemistry of ellagitannins at wood surfaces. Controlled UV exposure of European oak shows that ellagitannin transformations correlate with color change, pointing to specific chromophores and degradation pathways that coatings should target (Zahri et al., 2007). Linking this chemistry to protective formulations and service-life models would directly connect molecular behavior to field performance, especially for high-visibility applications where appearance matters. (Zahri et al., 2007).

Chestnut tannin's rapid expansion beyond leather into animal nutrition and agriculture invites systematic efficacy and process studies (Ciriminna et al., 2024). As well as health-related applications remain promising but preliminary. Broad experimental evidence for antimicrobial, antiviral, and antitumor activity suggests pharmacological potential. The translation depends on bioavailability, toxicity margins, and clear structure–activity rules in defined tannin fractions; targeted preclinical programs can close these gaps (Pizzi, 2019). Functional hydrogels built from chestnut hydrolysable tannins are another active vein, with rapid growth in publications that warrants property–processing maps for medical and agricultural uses (Ciriminna et al., 2024).

Finally, adoption depends not only on performance but also on how materials look and are perceived in built environments. Work in ecological economics argues that sustainability evaluations should explicitly include aesthetic dimensions, which affects public acceptance and design choices in forestry and wood use (Panagopoulos, 2009). Embedding aesthetic outcomes alongside durability and emissions in assessment frameworks would align tannin-based finishes and coatings with real decision criteria. (Panagopoulos, 2009).

Taken together, adhesive scale-ups, UV-guided protection strategies, standardized bioactivity in agriculture and feed, translational pharmacology, tannin-based hydrogel engineering, and aesthetics-aware evaluation form a coherent agenda that extends the chemistry and market momentum documented in recent reviews and industry analyses.

Methods and Materials

3.1 Impregnation

Eight treatment groups and one untreated control group were prepared from *Pinus abies*, commonly known as Norway spruce, and cut into two standardized dimensions. Each treatment group contained ten replicates measuring 2 × 2 × 2 cm for mass-based analyses and two larger specimens measuring 8 × 8 × 2 cm for UV exposure testing. Wood samples were lightly sanded when received to reduce frayed edges, dried at 103 °C for at least 24 hours, and then weighed directly prior to impregnation.

Tannin solutions were prepared from commercial-grade chestnut tannins at concentrations of 10%, 20%, and 30%, by dissolving the required mass of tannin in deionized water. For example, a 10% solution was prepared by mixing 10 g of tannin with 90 mL of water, assuming a water density of 1.00 g/mL at room temperature. This procedure was repeated for all concentrations. When hardeners were included, tannin concentration was fixed at 20%. Glyoxal, hexamine, and furfural were evaluated, with glyoxal and furfural tested at 1% and 10%, and hexamine at 10% only. All solutions were mechanically stirred for at least 20 minutes to ensure homogeneity before use. Stirring speeds were low enough to minimize foams or many bubbles from arising in the solution.

Samples were impregnated under identical conditions. Specimens were arranged vertically in a 2L beaker and separated by plastic mesh net to prevent surface contact. The prepared solution was poured until samples were fully submerged– attempting to minimize air bubbles and air pockets– then weighted to ensure complete submersion during the impregnation process. Each beaker was placed in a vacuum desiccator (30 cm diameter × 23 cm height) and subjected to 0.2 mbar for 30 minutes to evacuate internal air. Samples remained submerged for an additional 24 hours under ambient pressure to allow passive infusion via capillary action.

After impregnation, surfaces were blotted with laboratory paper to remove excess liquid, and samples were dried in a convection oven at 103 °C for 24 hours to remove unbound moisture

and stabilize mass. Only the 2 × 2 × 2 cm specimens were weighed at three stages: initial oven-dry weight (W_0), wet weight after impregnation (W_w), and final oven-dry weight after treatment (W_f). The total tannin uptaken in grams was calculated using Microsoft Excel using the following expression:

$$(W_f - W_0) = \text{Uptake in grams}$$

These values were used for the further development of the data.

The larger 8 × 8 × 2 cm samples underwent the same impregnation and drying procedure to ensure consistency but were reserved for later UV and colorimetric analysis.

3.2 Leaching

A subset of samples from each treatment group underwent a leaching protocol to evaluate tannin retention/leaching after repeated water exposure. Five 2 × 2 × 2 cm specimens were selected at random from each treatment type and weighed in their room temperature dry state to establish a baseline mass.

Each sample was placed in a 250 mL beaker in an even layer, then covered with containing 100 mL of deionized water. Some contact between samples was present. A small weight was positioned on top of the wood blocks to maintain full submersion. Specimens were immersed for one hour, removed, blotted with laboratory paper to remove surface moisture, and dried in a convection oven at 103 °C for a minimum of 12 hours. After the drying cycle samples were removed from the oven, left to return to room temperature, and weighed.

This leaching–drying cycle was repeated on three consecutive days, resulting in a total immersion time of three hours per sample. After the final drying phase, specimens were weighed to determine the stabilized post-leaching mass.

Tannin loss was calculated in Excel by first calculating the grams of tannin lost:

$$W_0 - W_f = T_L$$

Total tannin retained was determined by subtracting the tannin lost in grams from the grams uptaken calculated from the impregnation data development. The standard deviations were then calculated.

3.3 Hardness

Hardness testing was conducted on the five non-leached specimens from each treatment group to assess the effect of modification on surface mechanical resistance. Testing was performed using a Universal Testing Machine (Galdabini) equipped with a rounded steel indenter tip, designed to apply a controlled, consistent load to the surface. Each $2 \times 2 \times 2$ cm specimen was tested on all four vertical faces to account for potential variation in density and structural features within the wood.

The load applied by the press produced a circular indentation on each face. Immediately after indentation, the diameter of each mark was measured to the nearest 0.01 mm using calipers. All measurements were entered into the analysis software, Labtest- Galdabini, which calculated the Brinell Hardness (HB) value for each indentation based on standardized calibration procedures. Each specimen yielded four HB values—one for each tested face—which were averaged to produce a specimen mean. The sample means were then averaged within each treatment group to obtain a group mean HB with outliers removed, with standard deviations calculated in Microsoft Excel.

3.4 Compression

Following hardness testing, the same five non-leached samples from each treatment group were used to assess compressive strength. Compression tests were conducted using the same Universal Testing Machine (Galdabini) employed for the hardness measurements, but with the use of two spherical seating style compression plates.

Each $2 \times 2 \times 2$ cm cube was positioned in a parallel orientation, meaning that the wood fibers were aligned longitudinally with the direction of applied force. This configuration allowed for measurement of compressive strength along the grain, representing the natural load-bearing direction of the material.

During testing, the force was gradually applied until failure or maximum compression was reached. The press was linked to the same proprietary software system used previously, which recorded and processed the data in real time.

The Rm (tensile strength) values for all five replicates within each treatment group were exported into Microsoft Excel. Group averages and standard deviations were then calculated to enable comparison across treatment types with outliers removed.

3.5 Color Analysis

The 8 × 8 × 2 cm specimens reserved for colorimetric analysis were prepared for outdoor weathering following the impregnation and drying process. Each sample was fitted with a screw-in hook post-treatment, allowing it to be fixed on an outdoor exposure frame. This frame remained exposed to natural sunlight under ambient environmental conditions for the duration of the study.

Image 1. Samples placed randomly for exposure.

To enable consistent and repeatable color measurements, each sample was labeled at three distinct positions on the exposed face. These marked locations served as fixed reference points for all subsequent color readings. A portable spectrophotometer was used to measure surface color in accordance with the CIE L*a*b* color space, capturing values for lightness (L), red-green axis (a*), and yellow-blue axis (b*).

Color data was collected at the listed intervals over a 125-day period, with measurements taken on the following days of exposure: 0, 3, 7, 10, 15, 22, 30, 49, 69, 90, and 125. In instances where samples showed visible signs of moisture accumulation (e.g., rain exposure), they were temporarily removed from the exposure frame and placed in a convection oven at 40 °C for a minimum of 8 hours to ensure surface dryness before color readings were taken. In these cases the time considered exposed was stopped until they were placed back on the exposure frame. This step was performed only when moisture was present to minimize variability caused by water interference.

All color data was exported and organized in Microsoft Excel. For each sample, the three readings per location, per timepoint, were averaged to produce a single L*, a*, and b* value

per specimen. These values were further averaged across replicates within each treatment group to generate a treatment-level average at each timepoint. The resulting dataset was used to track color changes based on UV and environmental impacts over time to allow for graphical comparison between trends in treatment groups.

Results

4.1 Impregnation

Actual tannin uptake was measured across eight treatment groups and one untreated control. Among the concentration-only treatments, uptake increased from tannin 10% (A) ~0.28 g to tannin 20% (B) ~0.46 g, which recorded the highest value in this comparison. Tannin 30% (C) showed a slight decrease to about 0.45 g, suggesting that further increasing concentration may limit penetration, possibly due to higher viscosity. (Figure 1)
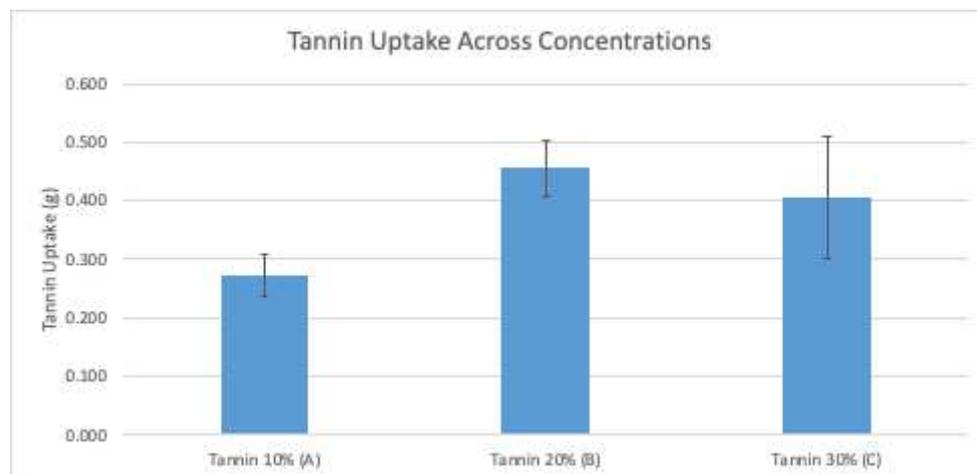

Figure 1. Shows the tannin uptake from tannin only samples.

When 20% tannin was combined with hardeners, uptake varied by type and concentration (Figure 2). Tannin 20% + 1% furfural (D) and tannin 20% + 1% glyoxal (E) produced similar values of approximately 0.40 g, slightly below the tannin-only group. In contrast, tannin 20% + 10% hexamine (F) showed a pronounced reduction to around 0.33 g, indicating that hexamine may hinder tannin penetration at higher concentrations without accounting for pH changes. Uptake increased with higher levels of furfural and glyoxal: Tannin 20% + 10% furfural (G) reached approximately 0.48 g, and tannin 20% + 10% glyoxal (H) reached approximately 0.45 g.

Using 20% tannin (B) as a baseline (~0.46 g), the results show that higher concentrations of furfural and glyoxal can slightly enhance uptake, while hexamine reduces it. Overall, both

tannin concentration and hardener selection influenced impregnation performance, with 20% tannin and the addition of high-level furfural (10%) producing the highest uptake in this study.
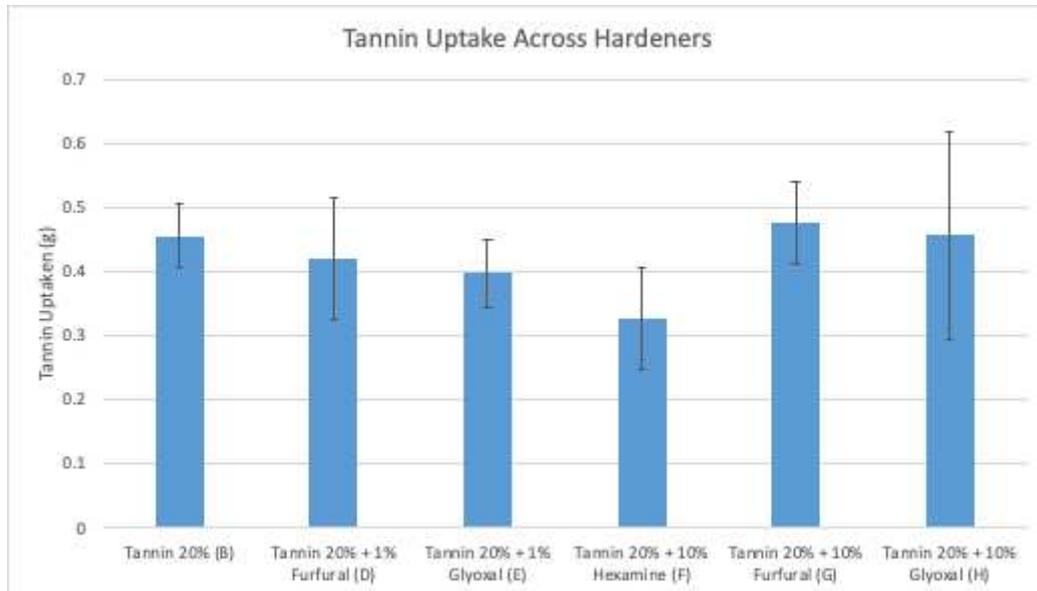

Figure 2. Shows the amount of tannins taken into the wood samples across all samples treated with hardeners.

4.2 Leaching

Figure 3 compares tannin uptake with tannin lost during leaching. The control group showed negligible uptake and only minor apparent mass changes. Samples impregnated with 10% tannin (A) had modest uptake with low levels of loss. Increasing the concentration to 20% (B) and 30% (C) raised the uptake substantially, though higher uptake also coincided with higher loss, significantly with regards to 30% (C). Treatments combining 20% tannin with additives produced variable outcomes. Furfural (D) and glyoxal (E), both at 1%, maintained uptake values close to the 30% tannin group but with reduced losses. Hexamine (F) displayed lower uptake on average with larger variability in loss as shown from the standard deviation. The addition of 10% furfural (G) resulted in uptake comparable to tannin alone but with slightly elevated loss, while 10% glyoxal (H) yielded strong uptake with consistent loss values across replicates.
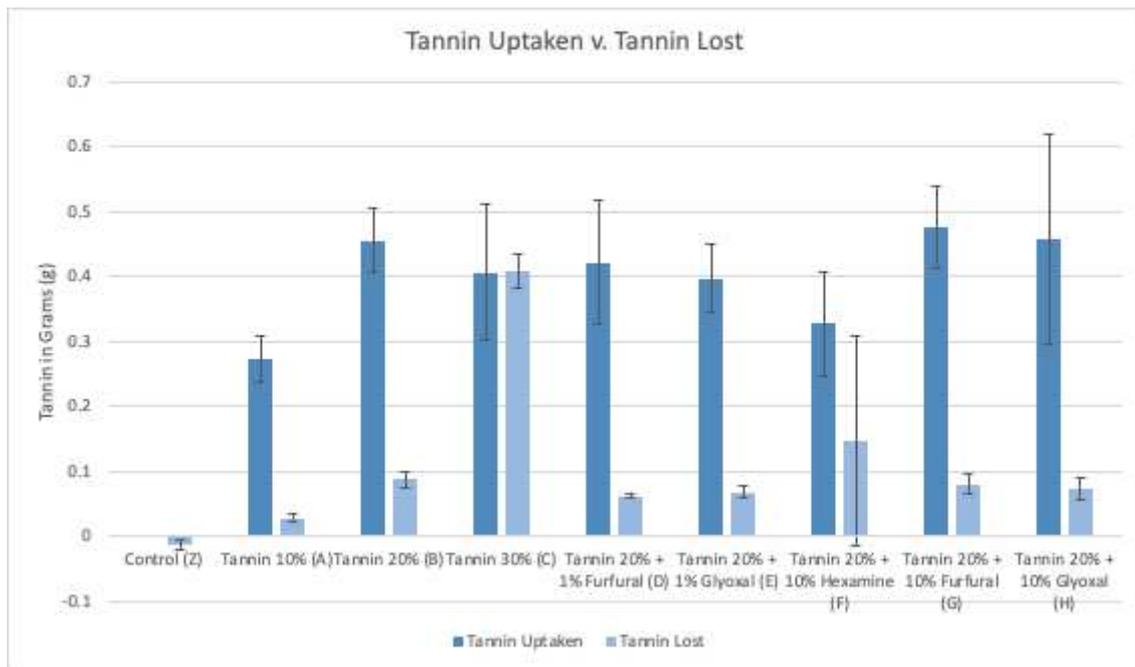
Figure 3. Shows the tannin uptaken in grams compared to tannin lost during leaching in grams.

Figure 4 shows the grams of tannin retained following leaching. The control was negligible. Formulations with both 1% and 10% furfural were top performers with retention values of 0.398 g and 0.42 g respectively. Tannin at 20% performed slightly better than glyoxal at 0.394, and just short of the glyoxal 1% formulation. Hexamine showed highly variable when observing the standard deviation, and retained slightly less tannin than the formulation of 10% tannin alone. Tannin 30% had the least retention.
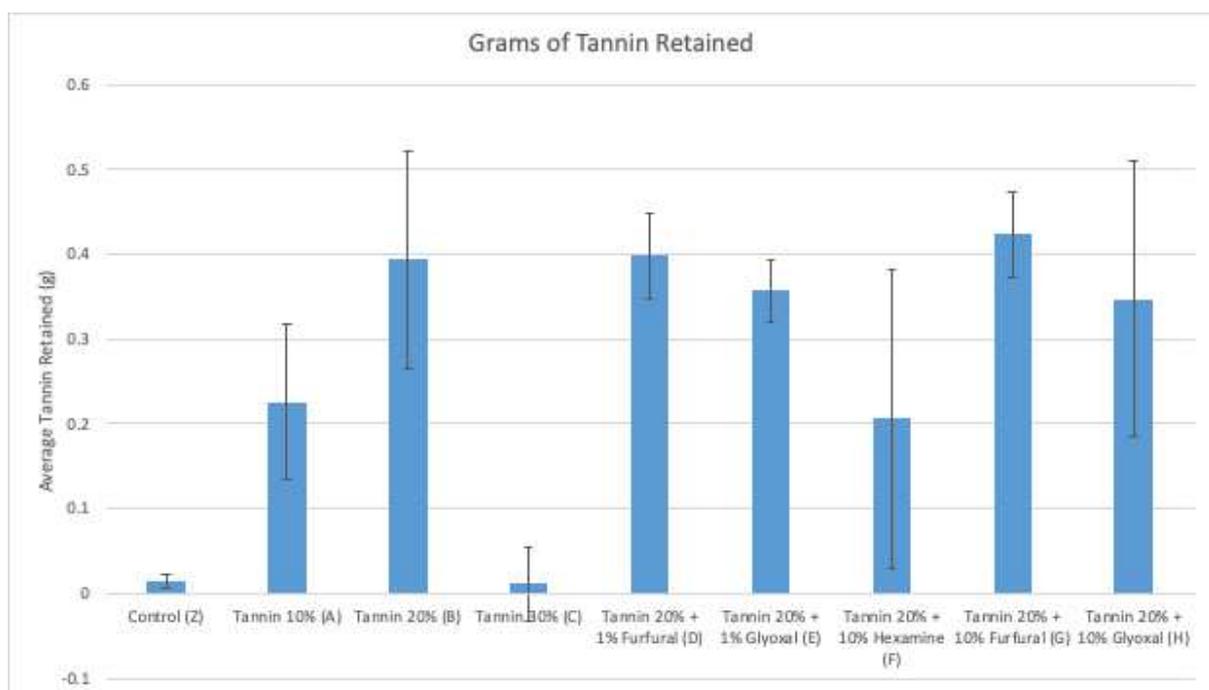

Figure 4. Shows the tannin in grams retained across all groups after leaching.

4.3 Brinell Hardness

Brinell Hardness (HB) values for all treatment groups are shown in Figure 5. The control recorded approximately 2.3 HB, while treated samples ranged from about 2.0 to 3.6. Among the concentration-only groups, tannin 10% (A) and tannin 30% (C) had the highest values, around 3.5 and 3.6 HB respectively. Tannin 20% (B) measured 3.1 HB, representing an increase of about 0.8 over the control.

When 20% tannin was combined with hardeners, hardness generally decreased. Tannin 20% + 1% glyoxal (E) recorded 2.8 HB, while 10% glyoxal (H) measured 2.7 HB. Furfural-treated groups were slightly lower, at 2.5 HB (1%) and 2.4 HB (10%). Hexamine produced the lowest values, with tannin 20% + 10% hexamine (F) at ~2.0 HB.
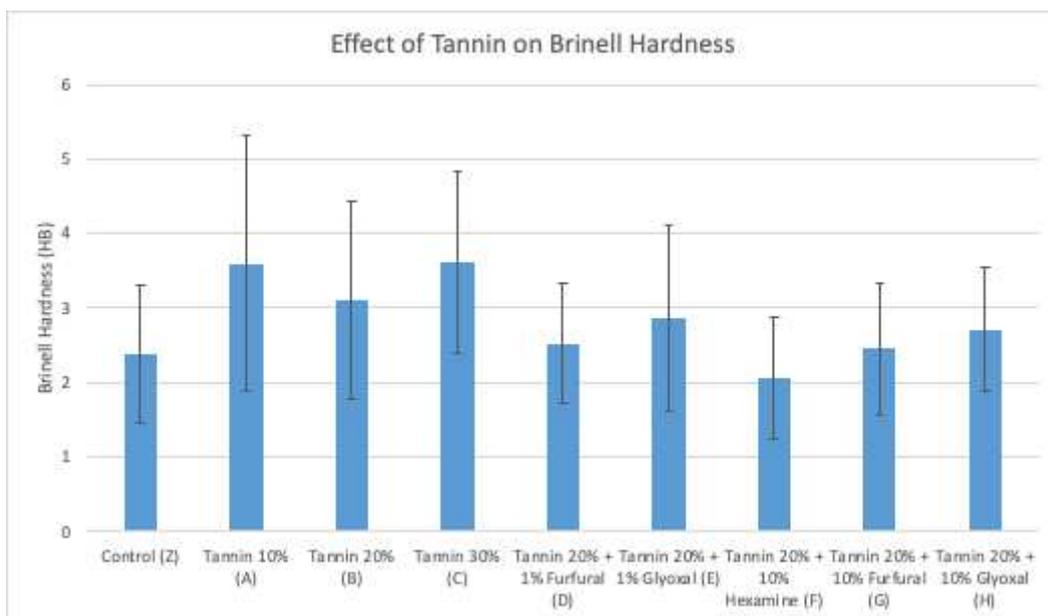

Figure 5. Presents the effect of tannin on the Brinell Hardness (HB) across all samples.

4.4 Tensile Strength

Figure 6 shows the effect of tannin concentration and hardener additives on tensile strength (Rm). The control measured approximately 48 N/mm², with treated samples ranging from about 45 to 50 N/mm². The highest value was observed in tannin 10% (A) (~50 N/mm²), while the lowest was in tannin 20% + 1% furfural (G) (~45 N/mm²). Among the concentration-only treatments, all tannin groups showed slightly higher Rm values than the

control: ~50 N/mm² for both 10% and 20% tannin, and ~49 N/mm² for 30% tannin. However, overlapping error bars suggest these differences are not statistically significant.

In the hardener series, tannin 20% + 1% and 10% glyoxal (E, H) both measured ~49 N/mm². Tannin 20% + 10% hexamine (F) was slightly lower at ~47 N/mm², while both 1% and 10% furfural (D, G) recorded the lowest values at ~45 N/mm².
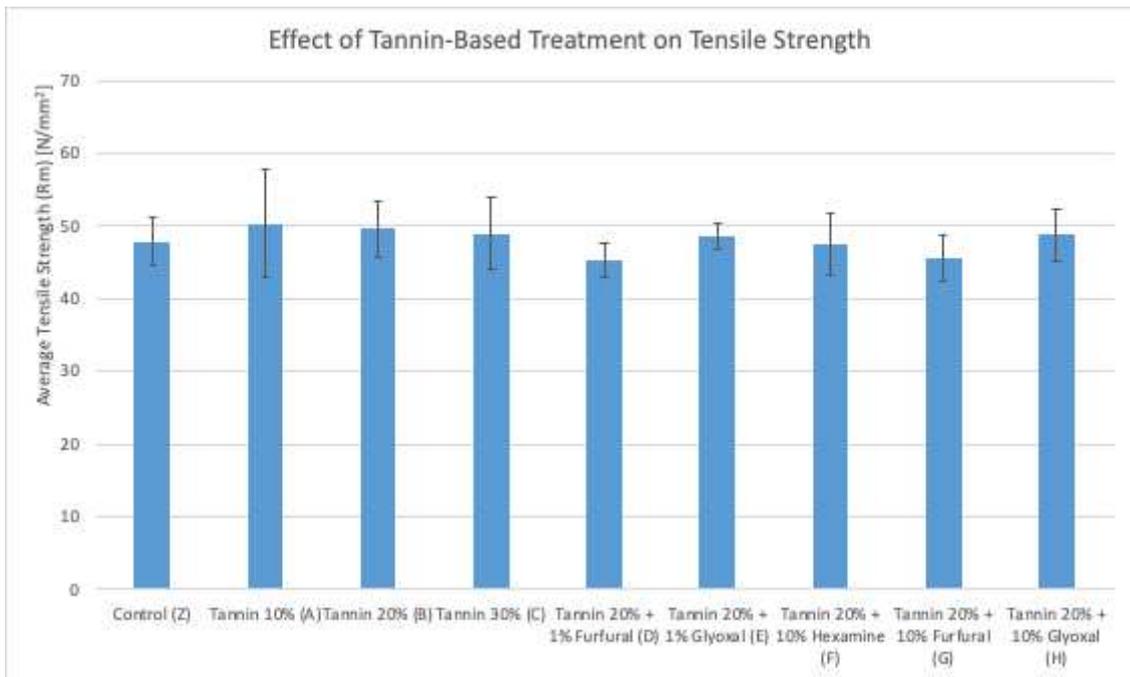

Figure 6. Shows the tensile strength across all groups.

4.5 Exposure & Color Analysis

4.5.1 Color Analysis- Lightness Axis

The lightness data over time (L*) is presented in Figure 7 and demonstrates interpretable trends across the treatment groups. Scatter plots with linear trendlines and R² values provide insight into the directional changes in surface lightness over the 125-day exposure period.

As expected, all treated samples exhibited a general increase in lightness over time, while the control group consistently decreased in lightness. The control followed a clear downward trend ($R^2 = 0.789$), indicating surface darkening likely caused by natural weathering and photodegradation processes. This effect may be attributed to the development of an increasingly ashen or silvery surface that was observed, which would lead to a decrease in L* values. This interpretation is further supported by the b* values (yellow-blue axis) in Figure

9, in which the control group showed a decrease over time, indicating a relative increase in blue tones consistent with surface graying.

In contrast, the tannin-treated samples generally followed positive linear trends with stronger correlation coefficients. The sample treated with 20% tannin + 10% hexamine (F) showed the most consistent increase in lightness, with the highest R^2 value (0.976). This suggests a highly reliable bleaching or lightening effect, though the sample still displayed some variability, due to inconsistencies in the impregnation process. Sample F had the most inconsistent color deposit during the treatment process, which is reflected in the presence of several outlying points. Similarly, the control group had some scattered values, likely due to darker surface spots like knots that skewed lightness measurements.

Sample C, treated with 30% tannin, showed a notable and abrupt increase in lightness between the first and second sampling points. This jump may be explained by a high concentration of tannins at the surface level, with poor penetration into the wood. As a result, much of the surface-bound tannin may have been lost or degraded early on, as early days of the exposure were accompanied with a rainy period, contributing to a rapid initial shift in appearance.

A strong trend line has presented itself by day 49, where it can be seen that the untreated group is darkening, while the treated groups are growing in lightness. At day 90, 20% tannin and 1% glyoxal (E) begins to equalize with the day 49 control (Z) measurement. This sign of divergence reinforces the overall pattern in which treated groups continue to lighten over time, while the untreated control darkens. The presence of tannins and tannin derivatives likely contributes to a more uniform lightening or bleaching process across the surface. In contrast, the control sample, without any added protective compounds, appears to weather unevenly, resulting in a reduction in lightness and a more muted, silver-gray tone.

Although some variability exists within individual sample sets, particularly in F and C, the overall trends are strong and internally consistent. This is confirmed by the generally high R^2 values across most treatments, with the exception of the 20% Tannin + 10% Glyoxal group (H), which showed a weaker correlation ($R^2 = 0.632$).

Taken together, the lightness data provides a robust and interpretable set of trends. These findings offer strong support for the effectiveness of tannin-based treatments in altering and stabilizing the aesthetic behavior of wood surfaces over time.
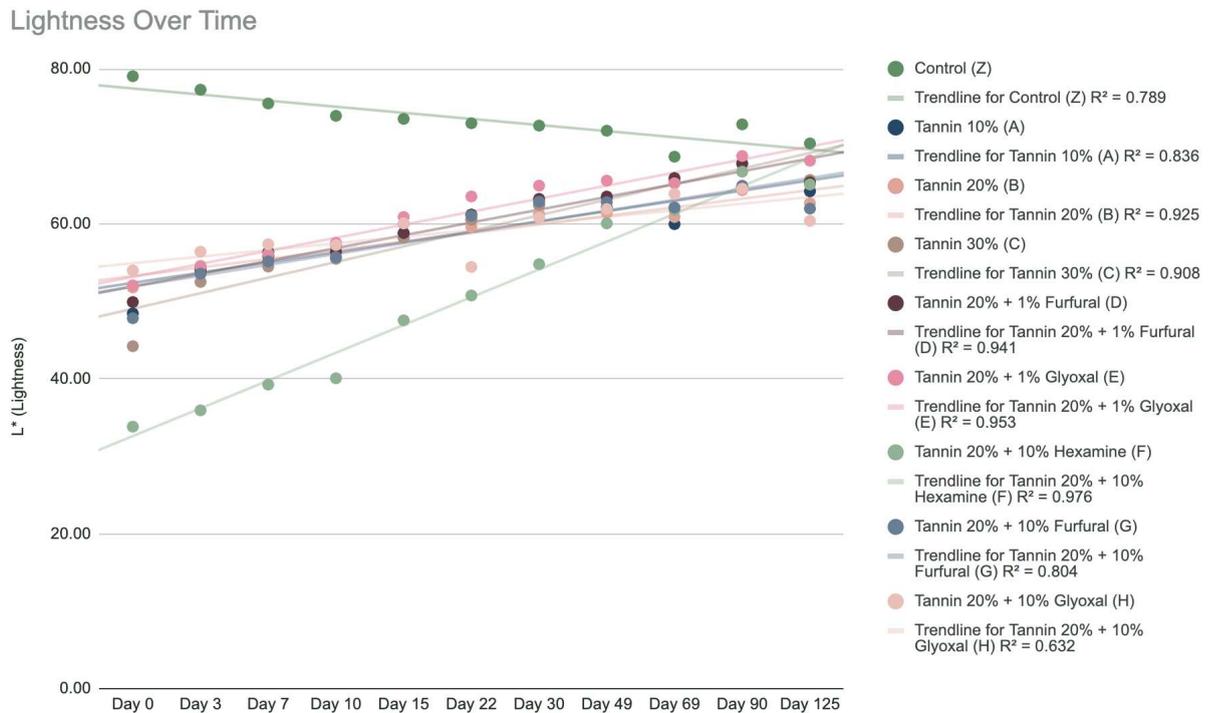
Figure 7. Changes in surface lightness (L*) over time for treated and untreated wood samples.

4.5.2 Color Analysis- Red-Green Axis

The a* values over time, representing shifts along the red-green color axis, are shown in Figure 8. In contrast to the clear linear trends observed in lightness (L*), the a* parameter displays more variation, with overall trends towards green (cooler) tones. While most treatment groups remain relatively stable over the 125-day exposure period, a few samples stand out with more pronounced responses.

The most significant change was observed in the sample treated with 20% tannin and 1% furfural (D), which showed a marked increase in a* values over time. This suggests a strong shift toward red tones initially, followed by a gradual return toward the starting values later in the study. Sample F, 20% tannin + 10% hexamine, also exhibited a more elevated a* curve compared to most others, although its changes were less extreme than sample D.

The control sample followed a less consistent trajectory, with some deviation from the relatively flat profiles of other treatment groups.

Despite these isolated differences, most treatment groups clustered closely around a* values between approximately 6 and 9, showing minimal red-green drift. Overall, the most interpretable observation is a subtle shift in most samples from warmer to cooler tones over time, consistent with a slow reduction in red saturation and a relative shift to green hues.
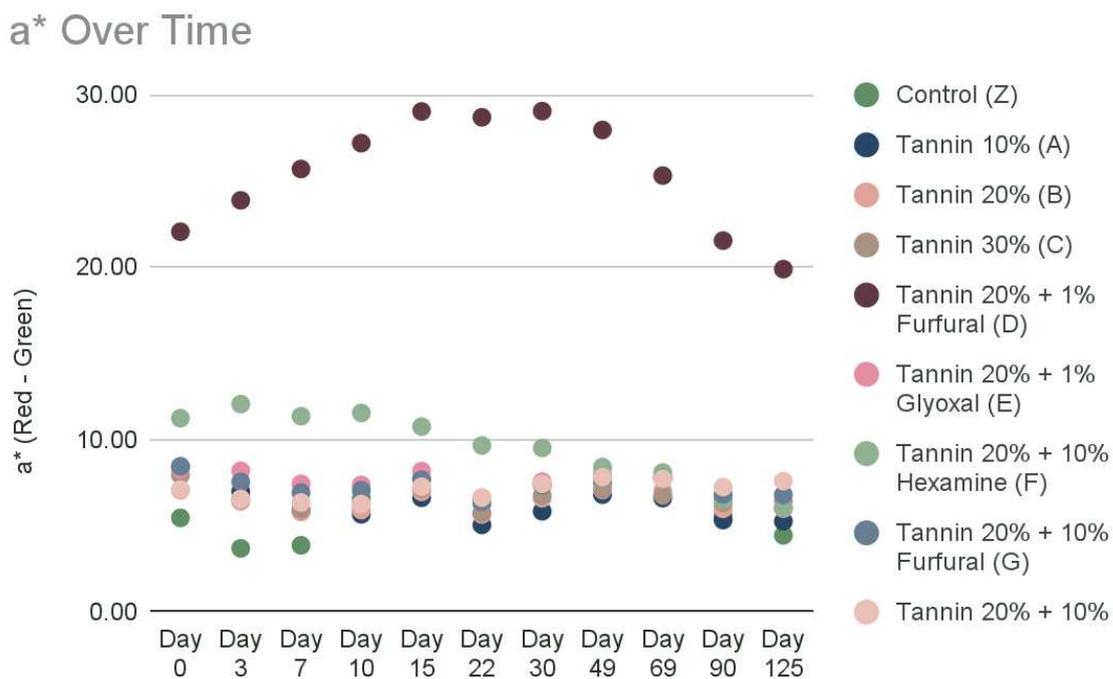

Figure 8. a* Values over time on the red-green axis.

4.5.3 Color Analysis- Yellow-Blue Axis

The b* values over time, representing the yellow-blue component of color, are shown in Figure 9. Overall, the data suggests an early trend of yellowing across most samples, followed by a gradual decline, indicating a shift toward cooler tones. This aligns with what is seen in a general sense from the a* trends.

Initially, several samples, including both treated and untreated groups, exhibited increases in b* values, suggesting a warming of tone toward yellow. However, as the exposure period progressed, a majority of samples began to show a decline in b*, indicating a cooling trend as yellow tones faded and an observed bluish-gray cast became more apparent. This trend was

most evident in the control sample, which underwent a sharper and more distinct drop in b* values than the treated groups.

This observation aligns with the behavior described in the lightness data, where the control sample exhibited a more pronounced darkening and developed a silvery or ashen surface tone over time. The decline in b* values in the control group support this interpretation, reflecting a loss of yellow coloration and a shift toward the blue end of the spectrum, consistent with surface weathering and oxidative graying. The treated samples, while also trending cooler over time, exhibited a less dramatic change in b*, suggesting that tannin treatments may have helped retain surface warmth and delayed the onset of gray discoloration.
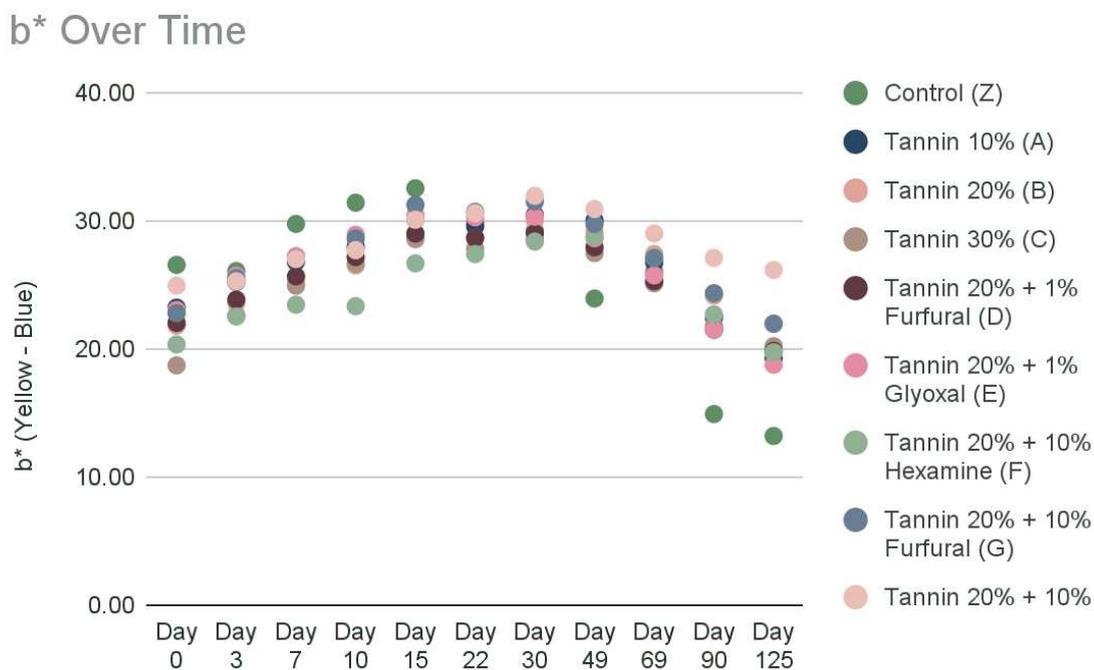

Figure 9. b* Values over time on the yellow-blue axis.

Discussion

5.1 Impregnation

The impregnation results demonstrate that both tannin concentration and hardener selection strongly influenced uptake. It was concluded that 20% represents an optimal threshold under the constraints of this series; being sufficient to achieve deep penetration without the viscosity-related inhibition that accompanies higher concentrations. Similar reductions in

penetration at elevated tannin levels have been reported in preservative systems where viscosity limited fluid flow into wood lumina (Thevenon et al., 2009).

The addition of hardeners introduced some variation. At 1%, both furfural and glyoxal slightly reduced uptake compared to the 20% tannin baseline. However, when applied at 10%, both hardeners increased uptake to values equal to or greater than the control, suggesting that higher levels facilitated penetration rather than obstructing it. This is consistent with reports that aldehydes such as furfural provide effective crosslinking of tannins while maintaining relatively low viscosity, thereby supporting mobility of the resin within the wood (Cesprini et al., 2022a). Furfural produced the strong results, the success of which demonstrates the potential for leveraging furan chemistry not only in adhesives but also in preservative systems. In addition, glyoxal promoted effective fixation, consistent with its prior success as a non-toxic aldehyde substitute in tannin adhesives (Ballerini et al., 2005). Its bifunctional aldehyde groups appear to provide stable cross-linking under the treatment conditions, which supports earlier findings that glyoxal is a viable alternative to formaldehyde for stabilizing tannin-based systems (Trosa and Pizzi, 2001).

By contrast, hexamine at 10% produced a marked decline in uptake. Unlike aldehydes, hexamine reacts rapidly with tannins, forming a rigid network early in the impregnation process. In this study, the solution was not pH-adjusted, which exacerbated the problem by inducing foaming during treatment (Pichelin et al., 2006). Previous work has demonstrated that condensation reactions between tannins and aldehydes are highly pH-dependent (Pizzi, 2008). The result was a layer of deposited tannin at the wood surface rather than uniform penetration into the structure. This outcome explains why hexamine, typically a strong and durable hardener, underperformed in terms of uptake and other tests.

The findings suggest that successful impregnation depends on maintaining a balance between reactivity and solution flow. Furfural and glyoxal, particularly at higher dosages, appear to achieve this balance, allowing tannins to penetrate deeply before curing reactions dominate. Comparable success has been demonstrated in tannin–boron–aldehyde treatments, where adequate penetration was a prerequisite for long-term preservative performance (Tondi et al., 2012a). The poor performance of hexamine in this study highlights the importance of treatment conditions, especially pH control. Overall, these results establish that a 20% tannin solution provides a penetration threshold sufficient for effective uptake, and that furfural and glyoxal additions at higher concentrations enhance this process. Conversely, unadjusted

hexamine hinders penetration by driving surface deposition, underlining the need to tailor both concentration and hardener chemistry to optimize impregnation.

5.2 Leaching

The leaching results underline that retention is governed more by fixation chemistry than by tannin loading. While higher concentrations increased uptake, they also magnified losses, reflecting the difficulty of stabilizing unmodified tannins against solubilization (Sen, 2009). Among the samples with hardeners, furfural and glyoxal both improved retention relative to tannin alone, even though their absolute performance did not exceed that of the 20% tannin formulation in terms of uptake. This pattern suggests that these aldehydes contributed to fixing tannins within the wood matrix, reducing the amount that was leached. Similar effects have been reported in quebracho–aldehyde systems, where low levels of hardeners increased resistance to water exposure without significantly altering penetration behavior (Cesprini et al., 2022b).

Between the two, furfural showed stronger performance at both concentrations, retaining more tannin than the equivalent glyoxal formulations. This indicates that furfural may form more effective condensation products with tannins under the impregnation conditions used, paralleling results in other preservative systems where the specific reactivity of the crosslinker was critical to reducing losses (Lyon et al., 2007).

Hexamine presented the weakest and most variable outcomes, which can be attributed to the lack of pH adjustment during formulation. Since hexamine requires alkaline conditions to initiate the methylene bridge formation that stabilizes tannin networks, its performance was expected to be limited here. Earlier studies confirm that tannin–hexamine systems provide enhanced durability only when properly cured under controlled conditions (Tondi et al., 2012a).

Taken together, the results show that while neither furfural nor glyoxal substantially enhanced uptake, both contributed to improved fixation, with furfural clearly outperforming glyoxal. Hexamine's underperformance reinforces the importance of formulation conditions such as pH in determining the efficacy of tannin-based treatments. This supports the broader conclusion that effective retention depends on optimized crosslinking chemistry rather than increased tannin loading (Tondi et al., 2012b).

5.3 Hardness

The improved hardness of the tannin-only treatments suggests that tannins themselves contribute directly to strengthening the wood. This supports earlier findings that tannin formulations can reinforce cell walls and increase resistance to indentation (Tondi et al., 2012b). Data from section 4.3 shows higher concentrations further enhanced hardness, indicating that tannin uptake plays a central role in mechanical improvement. In contrast, when hardeners such as glyoxal, furfural, or hexamine were added, hardness values dropped. This indicates that while these crosslinkers are known to improve the durability of tannin formulations by reducing leaching (Thevenon, 2009), their effect on mechanical properties may be less favorable. The rigid networks formed could reduce the wood's ability to absorb localized stresses, explaining why treated samples were softer despite the added stabilizers. This would be particularly evident for the sample treated with hexamine as most of the surface received deposition of tannin with incomplete penetration. This could suggest that without full penetration soft spots inside the wood can be exacerbated as it is less able to move uniformly and thus absorb localized force effectively.

Another factor in the variability of hardness across treatments may lie in the natural structure of the wood itself. Features such as knots and grain deviations can strongly influence local measurements. This is consistent with observations that wood anatomy plays an important role in determining the performance of preservative treatments (Järvinen et al., 2022)

Overall, tannin concentration is the primary driver of improved hardness, while the addition of hardeners can serve a different function such as enhancing stability and resistance to leaching but at the cost of reduced mechanical performance. This trade-off highlights the need to balance mechanical enhancement with durability when developing tannin-based wood treatments (Tondi et al., 2012a).

5.4 Compression

The tensile strength results indicate that tannin-only treatments produced values comparable to or slightly above the control, but the overlapping error bars suggest no statistically significant difference. This agrees with previous reports that tannin impregnation tends to improve mechanical properties modestly but not drastically, since the primary effect is structural reinforcement rather than chemical bonding (Cesprini et al., 2022a).

The addition of glyoxal maintained tensile strength at control levels, showing that this hardener does not compromise performance. This is consistent with studies on tannin–glyoxal systems in adhesives, where glyoxal crosslinking produced stable, low-emission networks without negatively affecting bond strength (Ballerini et al., 2005). In contrast, furfural-treated samples exhibited the lowest tensile strength in this study. This parallels findings where tannin–furfural adhesives showed weaker mechanical properties compared to other bio-based formulations, requiring optimization or additives to reach standard performance (Cesprini et al., 2022a).

Finally, hexamine reduced tensile strength slightly below the control, suggesting that while it enhances durability against leaching in other contexts, it may form rigid crosslinked networks that do not contribute positively to tensile load-bearing capacity (Thevenon et al., 2009). However, it is more likely due to the lack of penetration for proper cross-linkage to occur. Together, these patterns suggest that tannin concentration alone does not significantly influence tensile strength, while hardeners play a more complex role in stabilizing chemistry in some cases but reducing mechanical performance in others.

5.5 Color Analysis

The color analysis highlights how tannin-based treatments shift the trajectory of wood surface weathering. The steady darkening of the control confirms that unprotected wood surfaces undergo oxidative and photochemical degradation, leading to reduced lightness and the characteristic gray appearance of aged timber (Tondi et al., 2012a). Such behavior has been linked to the breakdown of phenolic extractives, particularly ellagitannins, which accelerate darkening when exposed to UV light (Zahri et al., 2007). In contrast, the upward lightness trends in the tannin-treated groups indicate that the treatments interfered with these degradation pathways, creating a surface that weathers differently than untreated wood.

The particularly strong linear increase in lightness for the tannin + hexamine formulation suggests that crosslinked networks provide a stabilizing effect, producing a more uniform bleaching pattern. This stability could be interpreted as an advantage where consistent appearance is important, though the bleaching itself may not be desirable in all applications. Meanwhile, the abrupt jump in lightness observed in the high-concentration tannin treatment suggests that excess tannin at the surface may be unstable, leaching or degrading early in exposure and producing unpredictable aesthetic changes. This points to a treatment limitation: higher concentrations do not necessarily translate to greater long-term stability,

echoing broader findings that tannin polymers can be susceptible to weathering stresses if not well-fixed (Tondi et al., 2012a).

On the red–green axis, the relative stability of most treatments compared to the more pronounced drift of the furfural formulation implies that hardener chemistry has a direct influence on chromophore transformations. Furfural's shift toward red tones may reflect the formation of conjugated structures under UV exposure, a phenomenon that parallels observations in nanocomposite coatings, where additives altered optical response to light and accelerated hue changes (Sow et al., 2011). This highlights the need to consider not only durability but also how specific additives shape the color evolution of treated wood.

The yellow–blue axis reinforces these interpretations. The control's steep decline in b* confirms the strong cooling and graying typical of weathered wood, while treated groups showed a slower loss of yellow tones. This suggests that tannins helped moderate oxidative pathways, delaying the onset of the silvery-gray appearance.

Taken together, these findings suggest that tannin treatments do not simply prevent darkening but fundamentally redirect the optical aging of wood, creating surfaces that lighten and stabilize rather than gray unevenly. While variability in impregnation remains a practical challenge, especially at higher concentrations, the overall patterns indicate that tannins can provide both aesthetic and sustainability benefits if optimized for weathering conditions.

Conclusions

This work investigated the influence of tannin concentration and cross-linking agents on impregnation, leaching resistance, mechanical properties, and color stability of Norway spruce (*Picea abies*). The results demonstrated that while increasing tannin concentration enhances uptake, excessively high viscosities limit penetration. A 20% tannin solution emerged as the most effective balance between depth of impregnation and ease of processing.

The choice of hardener proved equally important. Furfural consistently produced the strongest performance, yielding high impregnation, strong leaching resistance, improved hardness, and resistance to ultraviolet-induced discoloration. Glyoxal delivered moderate improvements, particularly in retention and strength, though with less consistency. Hexamine performed poorly under the conditions tested, but this outcome was strongly influenced by the absence of pH adjustment during treatment. Given its known reactivity under more

favorable conditions, hexamine remains a candidate worth further exploration, particularly in long-term exposure studies. Importantly, across all treatments, tensile strength was maintained, confirming that tannin modification does not compromise structural integrity.

The inclusion of colorimetric analysis highlighted an important but often overlooked aspect of wood preservation. While untreated spruce darkened unevenly over time, tannin-based treatments— especially those with furfural— lightened more uniformly and resisted surface degradation. This combination of functional durability and improved visual stability highlights the potential for tannins to enhance both the performance and the aesthetic appeal of timber products.

Much attention in wood science is directed toward engineered materials such as particleboard, glulam, and cross-laminated timber. However, the intersection of sustainability, structural integrity, and visual appeal represents an equally compelling frontier. Lowering costs, maintaining aesthetic quality, and reducing emissions together chart a path for the success of future wood products. Within this context, the potential role of tannins, particularly in applications that address ultraviolet stability, offer a promising and exciting direction for further research.

References

Ballerini, A., Despres, A., & Pizzi, A. (2005). Non-toxic, zero emission tannin-glyoxal adhesives for wood panels. *Holz Als Roh- Und Werkstoff*, *63*(6), 477–478. https://doi.org/10.1007/s00107-005-0048-x

Cesprini, E., Baccini, R., Urso, T., Zanetti, M., & Tondi, G. (2022). Quebracho-based wood preservatives: Effect of concentration and hardener on timber properties. *Coatings*, *12*(5), 568. https://doi.org/10.3390/coatings12050568

Cesprini, E., Causin, V., De Iseppi, A., Zanetti, M., Marangon, M., Barbu, M. C., & Tondi, G. (2022). Renewable tannin-based adhesive from quebracho extract and furfural for particleboards. *Forests*, *13*(11), 1781. https://doi.org/10.3390/f13111781

Ciriminna, R., Meneguzzo, F., Petri, G. L., Meneguzzo, C., Angellotti, G., & Pagliaro, M. (2024). Chestnut tannin: New use, research and Bioeconomy. *Journal of Bioresources and Bioproducts*, *9*(3), 246–252. https://doi.org/10.1016/j.jobab.2024.05.001

Comandini, P., Lerma-García, M. J., Simó-Alfonso, E. F., & Toschi, T. G. (2014). Tannin analysis of chestnut bark samples (Castanea sativa mill.) by HPLC-Dad–MS. *Food Chemistry*, *157*, 290–295. https://doi.org/10.1016/j.foodchem.2014.02.003

Hildebrandt, J., Hagemann, N., & Thrän, D. (2017). The contribution of wood-based construction materials for leveraging a low carbon building sector in Europe. *Sustainable Cities and Society*, *34*, 405–418. https://doi.org/10.1016/j.scs.2017.06.013

Järvinen, J., Ilgın, H. E., & Karjalainen, M. (2022). Wood preservation practices and future outlook: Perspectives of experts from Finland. *Forests*, *13*(7), 1044. https://doi.org/10.3390/f13071044

Lyon, F., Pizzi, A., Imamura, Y., Thevenon, M.-F., Kartal, S. N., & Gril, J. (2007). Leachability and termite resistance of wood treated with a new preservative: Ammonium borate oleate. *Holz Als Roh- Und Werkstoff*, *65*(5), 359–366. https://doi.org/10.1007/s00107-007-0192-6

Panagopoulos, T. (2009). Linking forestry, sustainability and aesthetics. *Ecological Economics*, *68*(10), 2485–2489. https://doi.org/10.1016/j.ecolecon.2009.05.006

Peng, Y., Wang, Y., Zhang, R., Wang, W., & Cao, J. (2021). Improvement of wood against UV weathering and decay by using plant origin substances: Tannin acid and tung oil. *Industrial Crops and Products*, *168*, 113606. https://doi.org/10.1016/j.indcrop.2021.113606

Pichelin, F., Nakatani, M., Pizzi, A., Wieland, S., Despres, A., & Rigolet, S. (2006). Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives. *Forest Products*, *56*(5).

Pizzi, A. (2008). Tannins: Major sources, properties and applications. *Monomers, Polymers and Composites from Renewable Resources*, 179–199. https://doi.org/10.1016/b978-0-08-045316-3.00008-9

Pizzi, A. (2016). Wood products and Green Chemistry. *Annals of Forest Science*, *73*(1), 185–203. https://doi.org/10.1007/s13595-014-0448-3

Pizzi, A. (2019). Tannins: Prospectives and actual industrial applications. *Biomolecules*, *9*(8), 344. https://doi.org/10.3390/biom9080344

Sen, S., Tascioglu, C., & Tırak, K. (2009). Fixation, leachability, and decay resistance of wood treated with some commercial extracts and wood preservative salts. *International Biodeterioration & Biodegradation*, *63*(2), 135–141. https://doi.org/10.1016/j.ibiod.2008.07.007

Sow, C., Riedl, B., & Blanchet, P. (2010). UV-waterborne polyurethane-acrylate nanocomposite coatings containing alumina and silica nanoparticles for wood: Mechanical, optical, and Thermal Properties Assessment. *Journal of Coatings Technology and Research*, *8*(2), 211–221. https://doi.org/10.1007/s11998-010-9298-6

Teshome, D. T., Zharare, G. E., & Naidoo, S. (2020). The threat of the combined effect of biotic and abiotic stress factors in forestry under a changing climate. *Frontiers in Plant Science*, *11*. https://doi.org/10.3389/fpls.2020.601009

Thevenon, M.-F., Tondi, G., & Pizzi, A. (2008). High performance tannin resin-boron wood preservatives for outdoor end-uses. *European Journal of Wood and Wood Products*, *67*(1), 89–93. https://doi.org/10.1007/s00107-008-0290-0

Tondi, G., Wieland, S., Wimmer, T., Thevenon, M. F., Pizzi, A., & Petutschnigg, A. (2012). Tannin-boron preservatives for wood buildings: Mechanical and fire properties. *European Journal of Wood and Wood Products*, *70*(5), 689–696. https://doi.org/10.1007/s00107-012-0603-1

Tondi, Gianluca, Palanti, S., Wieland, S., Thevenon, M.-F., Petutschnigg, A., & Schnabel, T. (2012). Durability of tannin-boron-treated timber. *BioResources*, *7*(4). https://doi.org/10.15376/biores.7.4.5138-5151

Trosa, A., & Pizzi, A. (2001). A no-aldehyde emission hardener for tannin-based wood adhesives for exterior panels. *Holz Als Roh- Und Werkstoff*, *59*(4), 266–271. https://doi.org/10.1007/s001070100200

Valenzuela, J., von Leyser, E., Pizzi, A., Westermeyer, C., & Gorrini, B. (2012). Industrial production of pine tannin-bonded particleboard and MDF. *European Journal of Wood and Wood Products*, *70*(5), 735–740. https://doi.org/10.1007/s00107-012-0610-2

Viriot, C., Scalbert, A., Hervé du Penhoat, C. L. M., & Moutounet, M. (1994). Ellagitannins in woods of sessile oak and sweet chestnut dimerization and hydrolysis during wood ageing. *Phytochemistry*, *36*(5), 1253–1260. https://doi.org/10.1016/s0031-9422(00)89647-8

Winandy, J. E., & Morrell, J. J. (2017). Improving the utility, performance, and durability of wood- and bio-based composites. *Annals of Forest Science*, *74*(1). https://doi.org/10.1007/s13595-017-0625-2

Zahri, S., Belloncle, C., Charrier, F., Pardon, P., Quideau, S., & Charrier, B. (2007). UV light impact on ellagitannins and wood surface colour of European oak (Quercus petraea and Quercus robur). *Applied Surface Science*, *253*(11), 4985–4989. https://doi.org/10.1016/j.apsusc.2006.11.005