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Doctoral Dissertation

Doctoral program in Material Science and Technology (39th Cycle)

Wood engineering: properties and durability improvement through innovative and sustainable processes

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Declaration

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Francesca Gullo

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Nature defines the structure. Science reveals its potential

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Abstract

The construction sector is transitioning to sustainable materials that combine energy efficiency with reduced environmental impact to achieve high performance and reduce the carbon footprint, in line with the Sustainable Development Goals (SDGs) of the 2030 Agenda. In this context, wood, a renewable and recyclable material characterized by a hierarchical porous structure, is configured as an engineerable platform for the development of highly engineered functional composites. Among these, Transparent Wood (TW), with its modular optical properties and easily functionalized nanostructure, opens up new perspectives for its application in sustainable construction, for example, in smart buildings with high energy savings. In this PhD thesis, developed as part of the PNRR NODES (Digital and Sustainable North West) project, the engineering of TW for building applications is studied, with the aim of improving its process sustainability and industrial transferability.

Chapter 1 introduces the theoretical and strategic framework of research: the role of the Sustainable Development Goals (SDGs) in European and national contexts is discussed. The thesis is, in fact, part of the PNRR NODES (Digital and Sustainable North West) project and falls under Spoke 4 – *Digital Innovation Toward Sustainable Mountain*. The research program is aligned with the objectives presented in the Spoke, which include: i) the enhancement of resources by using wood for the creation of multifunctional transparent composites; ii) the enhancement of energy efficiency through the design of wood based components to be integrated in e.g. into photovoltaic devices; iii) the improvement of durability, overcoming the natural degradation of wood through chemical and physical processes. Part of the chapter is dedicated to a critical review of the state of the art, with particular attention to the research gaps to be addressed to transition this product from the laboratory to industry. The steps to be taken in terms of chemical sustainability of processes, polymer consumption, industrial scalability, and control

of optical properties are mainly taken into account, as well as the definition of the thesis objectives, oriented towards rapid and sustainable production.

To achieve this goal, the work has been divided into three main objectives that will be presented in chapters 2, 3, and 4.

Chapter 2 is dedicated to objective 1, which focuses on developing a new whitening process derived from traditional treatments presented in the literature, but faster, more sustainable, and more efficient. The developed process allows for the production of mechanically stable bleached wood templates, with the possibility of recovering and reusing reagents until exhaustion, thereby reducing overall chemical consumption and process time and minimizing energy use. This work led to the publication of a scientific paper and the filing of a patent.

Chapter 3 is dedicated to objective 2, focusing on the development of TW, by impregnation of the bleached wood with suitable polymers. The Chapter mainly focuses on optimizing the polymer impregnation step to reduce resin consumption and studying its effect on optical properties through a Design of Experiments (DOE)-guided approach. This approach is used in particular to evaluate the potential tuning of light scattering by varying process parameters: the residual pressure and resin/wood ratio. Two thermocurable resins based on bisphenol A, crosslinkable at room temperature, were studied: one completely synthetic with UV-absorber and one partially biobased without UV-filter. The stability of both optical and structural properties was evaluated before and after 1 year of accelerated UV-Visible exposition in Solarbox. The results of this part of the study led to a publication currently unpublished.

Chapter 4, developed during the research period at the Royal Institute of Technology (KTH, Stockholm) and dedicated to objective 3, mainly focused on further improving the environmental sustainability of the whole process. In fact, it focuses on the use of a temperature-curable natural acrylic resin, derived from limonene (poly-limonene acrylate (PLIMA)), to obtain TW composites. This study allowed to evaluate the use of a lignin-rich white wood template, infiltrated with a completely biobased polymer matrix, to obtain high photostability values for future photovoltaic applications, which will be developed in collaboration with Uppsala University. Although the integration and evaluation of TWs' performance in photovoltaic devices are not presented in this thesis, the research establishes the basis for using TWs as an active substrate in perovskite solar cells synthesized at

low temperatures (150°C). The thesis is structured as a collection of articles and supplementary experimental sections and chapters. Chapter 5 concludes with a critical analysis of the results obtained and future perspectives. Overall, the work proposes transparent wood as an innovative and engineered material through the sustainable optimization of processes and the targeted control of properties, with a view to real industrial transferability.

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Chapter I

1.1. Sustainable Development Goals and the 2030 Agenda

Sustainable development was first defined in the 1980s by Brundtland as the “*development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Sustainable development means meeting basic needs to support long-term growth*”. (Brundtland, Gro Harlem 1987).

In 2015, the United Nations General Assembly adopted the document “*Transforming our world: the 2030 Agenda for Sustainable Development*” (United Nations 2015), which defines a global action plan structured around 17 Sustainable Development Goals (SDGs) and 169 associated goals. The Agenda represents a universal and integrated framework aimed at balancing the three fundamental dimensions of sustainable development: economic growth, social inclusion and environmental protection.

The SDGs, conceived as interconnected and indivisible goals, address global challenges such as climate change mitigation, responsible resource management, innovation, sustainable industrialization and resilient infrastructure. In particular, objectives such as:

1. *SDG 9 – Industry, Innovation and Infrastructure*
2. *SDG 11 – Sustainable cities and communities*
3. *SDG 12 – Responsible Consumption and Production*
4. *SDG 13 – Climate action*
5. *SDG 15 – Life on land*

are linked to the development of advanced, environmentally friendly materials for energy-efficient and circular applications in the construction sector.

The 2030 Agenda explicitly refers to the need for a transition to sustainable production models, promoting both resource efficiency and innovations that generate long-term environmental and socio-economic benefits. (United Nations 2015) In this context, the development of bio-based materials with a net negative carbon footprint, such as wood,

plays a strategic role. (Lippke et al. 2010; Montanari, Olsén, and Berglund 2021; Salazar and Meil (2009)

The work presented in this thesis aligns with this global vision and contributes to advancing sustainable materials engineering by designing and developing innovative wood-based composites, in line with some of the goals of the 2030 Agenda, as illustrated in Fig. 1.



Fig. 1 On the left, the 17 Sustainable Development Goals presented in the 2030 Agenda; on the right, the objectives considered for the TW platform.

1.2. The PNRR Framework and the NODES Innovation Ecosystem

In response to the European recovery strategy, Italy launched the National Recovery and Resilience Plan (PNRR) in 2021, under which Mission 4 – Education and Research, Component 2 – "From Research to Business" promotes the creation of territorial innovation ecosystems. (Presidency of the Council of Ministers 2021)

Among these, the NODES (*Digital and Sustainable North-West*) project was funded in October 2022, with the aim of strengthening research and innovation capacities in the Italian North-West. (Nodes | Digital and Sustainable North West)

The NODES ecosystem is structured as a HUB & SPOKE model and involves 24 partners, including universities, research centres, innovation clusters, incubators and competence centres, operating in Piedmont, Valle d'Aosta and part of Lombardy. The

project is organized into seven thematic Spokes that address strategic areas in the context of the digital and ecological transition (Fig. 2):

Spoke 1. Industry 4.0 for Sustainable Mobility and Aerospace — coordinated by the Politecnico di Torino (POLITO).

Spoke 2. Green Technologies and Sustainable Industry — coordinated by the University of Turin (UNITO).

Spoke 3. Industry of Culture and Tourism — coordinated by the University of Insubria (UNINSUBRIA).

Spoke 4. Digital innovation towards a sustainable mountain — coordinated by the University of Valle d'Aosta (UNIVDA)

Spoke 5. Industry for the health and economy of silver — coordinated by the University of Eastern Piedmont (UNIPO)

Spoke 6. Primary agro-industry — coordinated by the University of Pavia (UNIPV)

Spoke 7. Secondary agro-industry — coordinated by the University of Gastronomic Sciences (UNISG)

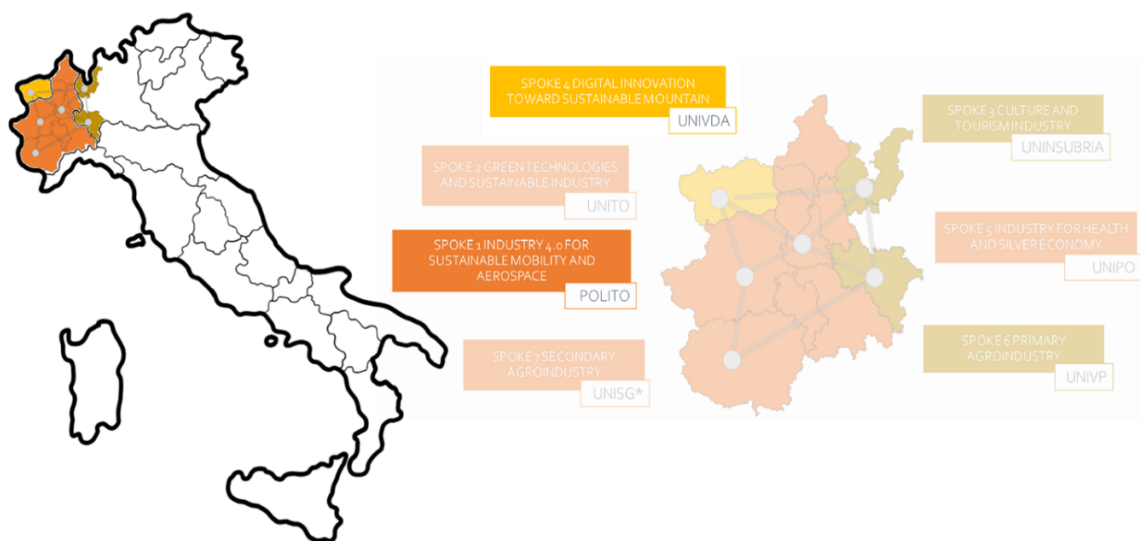


Fig. 2 NODES Innovation Ecosystem active in Piedmont, Valle d'Aosta, and in the provinces of Como, Varese, and Pavia, structured in seven thematic Spokes dedicated to the digital and ecological transition.

NODES' main ambition is to increase competitiveness, foster technology transfer, and accelerate digital and ecological transformation, to meet both the Regional Smart Specialisation Strategies (S3) and the broader objectives of the PNRR.

The research presented in this doctoral thesis was conducted within Spoke 4 – *Digital Innovation Towards Sustainable Mountain*.

Spoke 4 focuses on strengthening sustainability, resilience, and the ability to innovate in mountain territories through digital technologies, advanced materials, and sustainable solutions. (Nodes | Digital and Sustainable North West)

The mountain environment represents a complex socio-ecological system characterized by: i) fragile ecosystems; ii) climate vulnerability; iii) specific construction and energy challenges; iv) the need to sustainably exploit resources.

Specifically, the main objective of Spoke 4 is to enhance wood to guide the ecological transition of the mountain system of the North-West. The program aims to develop advanced biobased materials for applications in sustainable construction, enhancing local resources. Particular importance is attributed to the development of engineered wood components through compositional and structural modifications aimed at increasing, for example, dimensional and mechanical stability, durability, and fire behavior, or at combining these properties with new functionalities such as magnetic, optical, and electrical conductivity.

The use of wood, a renewable, biobased, locally available material that can sequester CO₂ from the atmosphere, is important for meeting these goals and addressing these challenges. (Gustavsson et al. 2017; Sathre and O'Connor 2010) However, traditional wood-based materials have limitations in durability, dimensional stability, and, sometimes, mechanical properties, making them useless for some structural and functional applications. (Evans, Urban, and Chowdhury 2008; Rowell 2005) In particular, applications, both indoor and outdoor, require reduced hygroscopicity, greater resistance to aging phenomena induced by exposure to light and atmospheric agents, and, moreover, adequate mechanical support properties. (Gullo et al. 2023; Hill 2007; Petrič 2013; Saha 2011; Song et al. 2018)

With this in mind, the research program of this PhD, entitled *"Wood Engineering: Properties and Durability Improvement through Innovative and Sustainable Processes"*, is directly aligned with the NODES Spoke 4 objectives. By developing Engineered Transparent Wood (TW), this research addresses specific Spoke 4 targets, such as: i) resource valorization by transforming wood into a multi-functional advanced composite; energy efficiency by integrating TW into building envelopes or photovoltaic systems to reduce energy consumption in mountain climates; and iii) durability by overcoming the

natural decay of bio-materials through sustainable chemical and physical modifications, ensuring a longer life cycle for mountain infrastructures.

1.3. Conventional wood-based engineered materials

Wood has been used since ancient times both for the manufacture of tools and as a structural material, thanks to its mechanical properties, in particular for its excellent tensile and compressive strength, high flexural strength, elasticity, and lightness. These values allow wood to compete with both modern metal alloys (e.g. magnesium or aluminum/lithium alloys) and structural polymers (e.g. liquid crystal polymers and high-density polyurethane foams), allowing the creation of lightweight architectures with high load-bearing capacity. (Edition and Ashby 2011; Kainer 2003; Rioja and Liu 2012)

However, the use of wood in large-scale, complex engineering has historically been limited by its biological nature. In particular, its anisotropy involves, for example, variations in mechanical properties in the longitudinal direction compared to the radial direction, and its hygroscopicity affects dimensional stability and susceptibility to both biological and physical degradation.

To overcome these limitations for some applications that today require strict standards of durability, stiffness, and safety, wood is engineered through new approaches in which the structure of the wood is reorganized on a macroscopic scale by processes of gluing, and controlled pressing. These systems enable the production of reproducible wood materials, improving both mechanical properties and dimensional stability. (Stark, Nicole; Cai, Zhiyong 2021)

Among the main engineered wood products we find:

- *Cross-Laminated Timber (CLT)*, consisting of layers of boards arranged orthogonally and glued together. Thanks to the cross-orientation of the fibers, a reduction in the anisotropy of solid wood is achieved with a resulting dimensional stability and a load-bearing capacity both flat and off-plane. This engineering makes CLT suitable for the construction of large structural panels; (Brandner et al. 2016; Younis and Dodoo 2022)
- *Glued Laminated Timber (Glulam)*, consisting of wooden slats oriented parallel and glued in the direction of the fiber. This arrangement allows for improved defect selection and distribution for the production of rigid, bending-resistant structural

elements, which allow the creation of curved and complex shapes; (Fink and Kohler 2014; Soriano, Pellis, and Mascia 2016)

- *Laminated Veneer Lumber (LVL)*, consisting of thin sheets of wood made (veneers) glued and then pressed, orientations generally in a direction parallel to the fiber. This engineering makes it possible to obtain materials with uniform, directional and easily calculable mechanical properties, suitable for use in load-bearing applications that require good structural performance. (Bal 2014; Gilbert, Zhang, and Bailleres 2019)

Despite the significant advances made by these systems, engineering remains predominantly confined to macroscopic and structural scales. The chemical composition and microstructure of the cell wall are not substantially modified, and the functionality of the material remains mainly of a mechanical nature, although with greater durability and fire resistance. (Popescu and Pfriem 2020; Rowell and Bongers 2017; Segmehl et al. 2018)

1.4. From structural engineering to cell wall engineering

Research on wood-based materials has gradually shifted the focus from structural modification on a macroscopic scale to micro- and nano-structure control. (Burgert et al. 2016; Chen et al. 2020)

In fact, wood is no longer considered just a building material but a natural biocomposite with a controllable hierarchical structure, consisting of cellulose microfibrils immersed in a matrix of hemicellulose and lignin, which together form a complex, interconnected network. (Fratzl and Weinkamer 2007) This multiscale architecture allows for selective intervention on the chemical composition, on the use of macro, meso, and microporosity, and on the void-cell wall interface for the creation of advanced multifunctional materials. (Zhou and Liu 2022)

The treatments studied to date include: i) the selective removal or modification of lignin; (Li et al. 2016; Li, Fu, et al. 2017; Zhu et al. 2016) ii) the functionalization of cell wall hydroxyl groups; (Montanari, Olsén, and Berglund 2020; Wang, Zhang, and Chu 2021) iii) the control of porous architecture and diffusion of fluids and gaseous substances; (Csiha 2024; Thybring et al. 2022; Thybring, Glass, and Zelinka 2019) iv) the infiltration of polymer matrices for cell wall swelling, dimensional stability control, or enhancement

of optical properties; (Chen et al. 2025; Olsen, Herrera, and Berglund 2019; Wang et al. 2018) and finally, v) the densification or restructuring of cellulose microfibrils for selective control of the micro-structure. (Luan et al. 2022; Qin et al. 2024)

All the listed strategies allow to integrate new properties or control existing ones, also opening the field to optically active wood composites and woods with thermal and functional properties for the development of partially or totally biobased high-performance composites. (Calovi, Zanardi, and Rossi 2024; Chen et al. 2020; Gao et al. 2024)

1.5. Transparent wood as an advanced engineered biocomposite

One of the wood-based materials that has attracted researchers' attention over the past decade is TW, which represents a paradigm shift in the engineering of wood-based materials.

Unlike the conventional products previously treated, TW composites do not involve an intervention on the macroscopic organization of the material, but a fine modification on a micro- and nano-scale of the cell wall. The preparation process of these materials involves two fundamental steps: i) the selective removal or modification of the lignin responsible for light absorption with preservation of the porous skeleton; (Ding et al. 2023; Kumar, Jyske, and Petrič 2021) ii) the infiltration of porosity with the use of a polymer matrix having a refractive index compatible with that of the cell wall. (Chen et al. 2020; Zhu et al. 2023)

This last step makes it possible to suppress light diffusion arising from the difference in refractive index between the air in the porosity and the hierarchical structure of the wood, yielding a material with high transmittance and modulable haze, while maintaining adequate mechanical support. (Jacucci et al. 2021) The cell wall, in fact, is able to act as a reinforcement in the wood-polymer composite, increasing the mechanical properties of both the wood and the starting polymer. (Jele et al. 2023)

The possibility of selectively modulating transmittance and light diffusion further expands the field of application, making it potentially suitable for integration into sustainable architectural systems, energy management components, and optically active devices. (Du et al. 2023; Li, Yu, et al. 2017; Mi et al. 2020)

In order to contextualize, rationalize the state of the art and outline the main lines of development of TW, below is presented the critical review of the scientific literature, with particular attention to the strategies for modifying the wooden template, the optical scattering mechanisms, the most promising applications in the field of construction and, finally, the critical issues related to scalability, to the reproducibility and sustainability of the process.

1.6. Published Paper: Transparent wood for a bio-based future: A critical review



Transparent wood for a bio-based future: A critical review

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ABSTRACT

Transparent wood (TW) is an emerging class of bio-based composites that combines high optical transmittance, mechanical strength, and tunable light scattering. This review provides a critical and integrated overview of recent advances in the design and processing of TW, with particular emphasis on how modifications of the wood template, through chemical, structural, and cell-wall engineering, govern optical and mechanical performance. Tailoring haze is highlighted as a key design parameter, enabling precise control of light diffusion and optical response for applications ranging from clear glazing to diffusive solar harvesting and smart window systems.

Beyond functional low- and high-haze TW, the review also addresses the emerging class of aesthetic TW, in which visual appearance, diffuse light transmission, and architectural integration are prioritized over maximum transparency. Dynamic and functionalized TW systems, including thermo- and photo-responsive structures, luminescent films, and composites incorporating micro- and nano-scale fillers, are discussed as routes toward adaptive and multifunctional materials.

Finally, the review critically examines the challenges associated with scalability, reproducibility, standardization, and sustainability, including processing bottlenecks, measurement comparability, and life-cycle considerations. By linking material design, optical scattering mechanisms, and manufacturing constraints, this work outlines a coherent pathway from laboratory-scale innovation to the development of industrially viable, bio-based, and circular TW materials.

1. Introduction

As the worldwide shift towards renewable and circular resources speeds up, wood has once again become a key element of sustainable design and practical materials engineering [1–3]. Beyond its long-standing role as a structural and aesthetic material, wood is increasingly viewed as a high-performance biocomposite platform, combining hierarchical porosity, anisotropic organization, and mechanical strength with natural abundance and its role as a net carbon-negative biocomposite [4–6]. The intricate, multiscale architecture of wood, composed primarily of cellulose, hemicellulose, and lignin, offers low density joined with high strength but also a naturally aligned, channelled microstructure that can be engineered to host new physical functionalities [7,8].

Pristine wood is optically opaque due to strong light absorption by lignin and intense scattering at air–cell wall interfaces arising from refractive index mismatch [6]. Modifying this optical feature has driven one of the most innovative developments in wood science: the creation

of Transparent Wood (TW). First introduced by Fink [9] and later refined by Li et al. [10] and Zhu et al. [6], TW represents a convergence of nature-inspired design and materials engineering, a composite that merges the anisotropic structure of wood with light-transmitting polymers, yielding a strong, lightweight, and partially transparent material.

In a broader context, TW can be considered a form of engineered wood, a class of materials in which natural wood is structurally and chemically modified to achieve tailored mechanical, optical, or functional properties [11]. Engineered woods include laminated, cross-laminated, densified, or chemically modified variants, with TW representing a prime example where delignification and polymer infiltration create a multifunctional, high-performance composite [12,13].

Since those pioneering works, the field has expanded dramatically, resulting in the development of various methods for preparing white wood templates and achieving resin infiltration. Early studies relied on complete delignification using sodium chlorite or peracetic acid [10,14], while more recent approaches have explored selective bleaching or lignin modification strategies that preserve the mechanical integrity of

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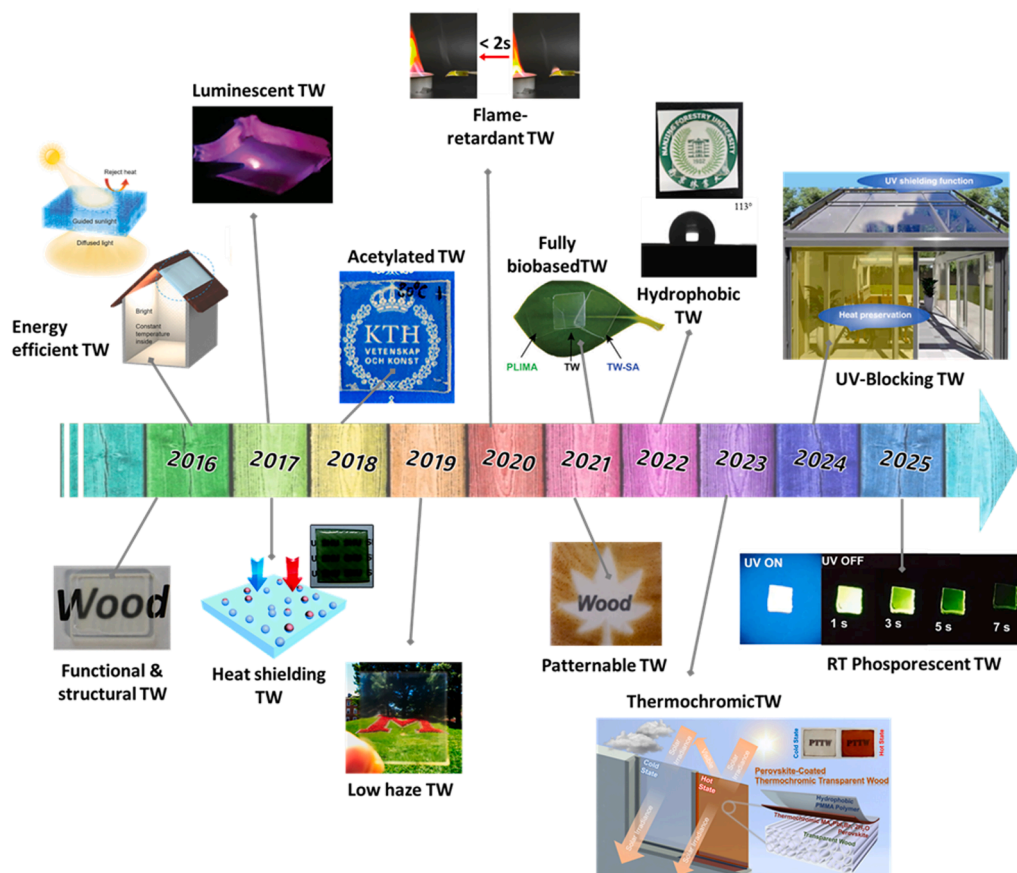


Fig. 1. Recent advances and representative applications of transparent wood composites. Copyright 2016: Reproduced from Li et al. [30] (above), reproduced with permission from Zhu et al. [6] (below); copyright 2017: Reproduced with permission from Li et al. [24] (above), reproduced with permission from Yu et al. [25] (below); reproduced from Li et al. [31]; copyright 2019: Reproduced with permission from Jia et al. [22]; copyright 2020: Reproduced with permission from Chen et al. [32]; reproduced from Montanari et al. [21] (above), reproduced from Xia et al. [17] (below); 2022: Reproduced from Ding et al. [33]; copyright 2023: Reproduced with permission from Du et al. [34]; copyright 2024: Reproduced with permission from Wu et al. [35]; 2025: Reproduced from Piao et al. [36].

the scaffold while reducing color and absorption [15]. Among these innovative treatments based on alkaline oxidation with hydrogen peroxide, there have been further reductions in environmental impact and processing time, offering promising routes toward scalable production [16,17].

Parallel to the development of these template preparation methods, increasing attention has been devoted to the choice of polymeric matrices and the functionalization of cell walls. Traditional polymers, such as poly(methyl methacrylate) (PMMA) and epoxy resin, have provided effective optical matching and structural reinforcement [6,10]. However, their fossil origin and poor compatibility with hydrophilic cellulose have prompted the search for alternative formulations. Recent works have compared polymers in terms of viscosity, refractive index, and interfacial compatibility [18,19], highlighting the importance of low-viscosity systems that enable deep infiltration without structural collapse. In this context, bio-based matrices such as poly(limonene acrylate) (PLIMA) and modified cellulose resins have emerged as sustainable candidates for developing fully renewable TW composites [20, 21].

In addition to polymer selection, the functionalization of the wood scaffold has become a powerful strategy to tailor optical behavior [7, 14]. Surface modification and coupling agents can enhance interfacial wetting, improve refractive index matching, and introduce new optical responses. The resulting materials exhibit a wide spectrum of tunable haze behaviors, from low-haze systems suitable for clear architectural glazing to high-haze composites optimized for daylighting or solar energy harvesting [22,23]. Moreover, the incorporation of inorganic or luminescent species, such as Cs_2WO_6 nanoparticles for NIR shielding,

quantum dots for photoluminescence, or phase-change materials for temperature-dependent transparency, has expanded the functional range of TW toward smart glazing and energy-adaptive materials [24–26].

Despite these advances, research on TW continues to face several challenges. Uniform resin infiltration, processing time, and the preservation of mechanical integrity in thick samples remain major bottlenecks. Thick TW panels (>5 mm) often exhibit high haze and low transmittance, even when wood–resin compatibility is improved through functionalization [7,14]. Furthermore, most processes are still conducted on laboratory scales, with limited consideration given to industrial reproducibility or cost efficiency. Addressing these issues will require advances in infiltration engineering, scalable chemical treatments, and the integration of in-line quality control to ensure reproducible optical and mechanical performance.

In this context, the present review aims to provide a comprehensive yet critical perspective on TW, covering the entire development chain from material fundamentals to application and scalability. Starting from wood structure and anisotropy, the review systematically examines template preparation strategies (delignification and selective bleaching), cell-wall modification approaches, and polymer infiltration routes, explicitly linking these processing choices to the resulting optical and mechanical behavior of transparent wood composites. Particular emphasis is placed on understanding how microstructural parameters, such as cellulose volume fraction, lignin retention, cell-wall accessibility, and interfacial design, govern light scattering, transmittance, haze, and mechanical integrity. While recent reviews have provided extensive overviews of transparent wood fabrication routes,

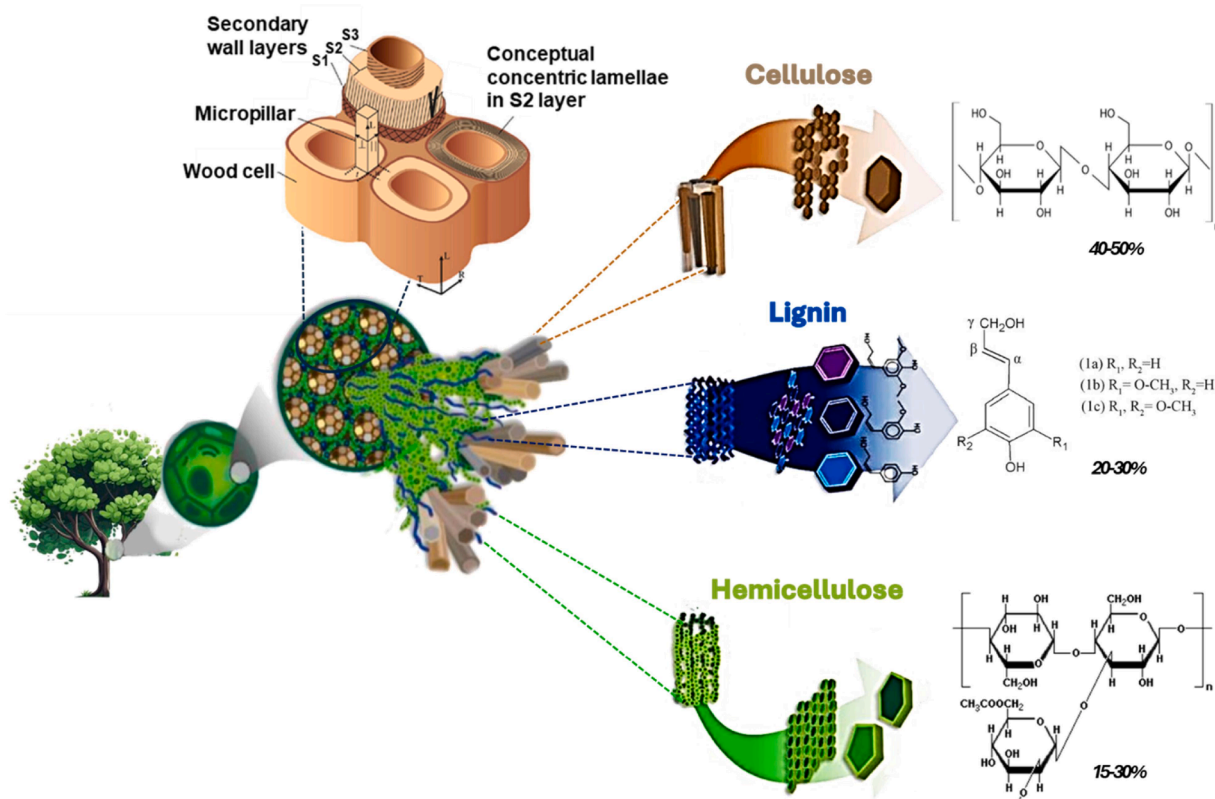


Fig. 2. Wood structure at different length scales. Copyright 2014: Adapted from Khan et al. [44] and with permission from Rafsanjani et al. [45].

functionalization strategies, and emerging applications, the present work distinguishes itself by systematically framing optical performance as a structure-driven and designable property rather than a secondary outcome [27–29]. By explicitly correlating processing-induced microstructural features with light–matter interactions, this review highlights how transmittance and haze can be rationally engineered through controlled template modification and interfacial design. In addition, beyond process-focused or chemistry-oriented perspectives, transparent wood is here discussed as an optically engineered composite system, with specific attention to scalability, reproducibility, and industrial relevance.

Emerging application scenarios, including thermally responsive glazing, UV- and NIR-blocking materials, photovoltaic integration, and light-management devices, are summarized in Fig. 1, which presents a timeline from 2016 to current developments in emerging applications. By connecting these elements, the review provides a critical framework for understanding transparent wood not merely as an experimental prototype, but as a tunable, multifunctional material platform with potential for industrial implementation and sustainable design.

2. Wood structure and properties

To understand how such a wide variety of functions can be engineered from a single natural precursor, it is essential to first examine the structure and intrinsic properties of wood, the hierarchical, anisotropic architecture that governs its optical behavior, mechanical response, and interaction with infiltrated polymers.

Wood, owing to its inherent sustainability, low environmental impact, and ability to sequester CO₂ and immobilize heavy metals, offers an excellent platform for engineering advanced bio-based materials.

What makes it unique is its porous structure that extends from the nanometric scale of the cell walls to the macroscopic scale of the wood trunk [6,37–41]. The image shown in Fig. 2 illustrates how, on a micrometric scale, the wood structure is related to the presence of pits,

lumina, and cell walls that serve supportive, conductive, and storage functions [42,43].

The microstructure of wood exhibits a hierarchical organization comprising cellulose, hemicellulose, and lignin (Fig. 2), which directly influences its physical and chemical properties, with varying concentration ranges during functionalization or composite fabrication [46–49]. At the nanometric scale, instead, the components that form the wood appear as a fibrous organic nanocomposite material. In fact, the lamellae of cellulose fibrils are immersed in a lignin matrix, which, through hemicelluloses, constitutes a mesh network and is connected to each other [41]. The secondary cell wall is composed of three main layers: S1, S2, and S3, each distinguished by its microfibril angle and thickness. Among these, the S2 layer is the most prominent and functionally critical, accounting for the majority of the wall thickness and exhibiting a low microfibril angle, which results in high tensile strength and stiffness [50,51]. The outer S1 and inner S3 layers, although thinner, contribute to the overall anisotropic behavior of the wall due to their distinct orientation of cellulose microfibrils. The cell wall thickness, fibre arrangement, and pit structure vary across species and within the growth cycle, influencing diffusivity, permeability, and surface reactivity [52,53]. A key feature of wood is its inherent heterogeneity across multiple scales, including seasonal growth patterns. Each annual ring consists of earlywood, formed at the beginning of the growing season, and latewood, formed later in the season. Earlywood cells typically have larger lumens and thinner walls, favoring water conduction, while latewood cells are denser with smaller lumens and thicker walls, enhancing mechanical resistance [54]. This intra-ring variation influences how liquids (such as water in nature or resins in modified wood) are transported via capillarity, as well as the drying process and the mechanical performance of treated or modified wood. At the species level, anatomical differences between softwoods and hardwoods introduce further variability. Softwoods are composed mainly of tracheids, which perform both structural and conductive functions [55]. In contrast, hardwoods show a more heterogeneous

Table 1

Values of density, porosity, and permeability along the longitudinal direction for wood of balsa, silver birch, poplar, spruce, and pine.

Wood type	Density [kg/m ³]	Porosity [%]	Longitudinal permeability [m ²]
Balsa	130–390 [58]	80–90 [59]	1.3×10^{-11} [60]
Silver Birch	550–650 [61]	54.5 [62]	1.0×10^{-13} – 1.0×10^{-12} [63]
Poplar	390 [64]	65–68 [65]	6.9×10^{-13} – 1.4×10^{-12} [66]
Spruce	232–588 [67]	60–80 [68]	1.0×10^{-14} – 2.5×10^{-14} [69]
Pine	350–450 [70]	63 [62]	2.0×10^{-15} – 3.5×10^{-14} [63]

structure, comprising distinct vessel elements, libriform fibres, and parenchyma cells [56]. This complexity influences the wood's porosity, directional permeability, and interaction with impregnating agents or coatings [53,57]. As a result, wood selection for advanced applications must account for these multiscale features not only for treatment compatibility but also for long-term performance.

In the design of TW-based composite materials, the choice of wood species plays a crucial role, as density, porosity, permeability, and volume fraction of the cell walls significantly influence the impregnation capacity, final transparency, and mechanical properties of the resulting material. The species conventionally used in the preparation of transparent woods, such as balsa, birch, poplar, and pine, display different anatomical characteristics; the most important of which are: density, porosity, and longitudinal permeability, as shown in Table 1, resulting in variable responses to chemical and physical treatments.

Balsa (*Ochroma pyramidale*) is known for being one of the lightest woods, with a density ranging from 130 to 390 kg/m³ depending on the trunk section. It also exhibits very high porosity, inversely related to density, between 80 and 90% by mass [7]. It features an open-pore cellular structure with large lumens and thin walls, promoting high longitudinal permeability that greatly facilitates resin infiltration [10]. However, its highly porous structure also makes it more prone to deformation and collapse during the delignification process [71]. In contrast, birch (*Betula pendula*) and poplar (*Populus* spp.) show medium density, around 550–650 kg/m³ for birch and 390 kg/m³ for poplar, and present lower porosity (50–70%); as a consequence, they also possess more compact structures. While these woods have open pores, they exhibit greater mechanical resistance and lower permeability, particularly in the radial direction. As a result, they require more aggressive impregnation methods or longer vacuum cycles [72,73].

Pinus (*Pinus* spp.), a typical example of a conifer, is a softwood with conductive tissue dominated by tracheids and elevated resin content [55,74]. It has a density ranging from 350 to 450 kg/m³, with moderate porosity and highly anisotropic directional permeability: high along the longitudinal axis but significantly reduced in the radial and tangential directions, owing to the lack of vessels and the presence of pit borders [75,76]. This anisotropic behaviour influences the uniform distribution of the resin and the optical quality of the resulting composite. In general, the infiltration efficiency is strongly affected by the volumetric fraction of the cell wall, which represents the solid part that cannot be replaced by resin and is calculated as the ratio between the volume of the cell wall

(excluding pores) and the total volume of the solid (including porosity and voids). For the mentioned woods, the volume fraction of the cell walls (from 7–10% for balsa to 40–50% for birch) determines not only the amount of resin needed but also the optical and mechanical properties of the composite [10,77]. In particular, a higher volumetric fraction of wood enhances mechanical performance by reinforcing the wooden structure combined with the resin. However, this significantly affects optical properties, which are strongly influenced by the anisotropic scattering of the wood.

Among the conifers most widely used in the production of engineered TW materials is also the spruce (*Abies* spp.) [78]. It is a softwood with a simple tissue structure, mainly consisting of tracheids and lacking vessels, similar to pine. Its dry density varies between 230 and 590 kg/m³, depending on its origin and position within the trunk (earlywood or latewood) [62,79].

The spruce exhibits an overall porosity that is medium to high, ranging from 60% to 80%. However, due to the closed nature of the tracheids and the presence of aspirated pits, it displays a highly anisotropic directional permeability: moderate in the longitudinal direction but significantly reduced in the radial and tangential directions, with values up to two orders of magnitude lower than in the main direction [80,81]. This indicates greater difficulty in achieving uniform infiltration on a macroscopic scale, particularly when using high-viscosity monomers or if extended and gradual vacuum cycles are not performed [78]. Despite these limitations, the fir tree can serve as a reasonable compromise regarding dimensional stability and availability. It has occasionally been employed in pilot studies for translucent materials [78], although it is generally less suitable than open-pore species like balsa or porous broadleaf trees such as *Paulownia* [82]. The cell wall's volumetric fraction is about 30–40% [83], which affects how much resin is needed to fully saturate the pore spaces.

Finally, the anisotropic permeability of wood, which varies significantly between the longitudinal (highest), radial, and tangential directions, must be considered in designing the functionalisation process to prevent impregnation gradients that could affect the transparency and uniformity of the final material [42,84].

A key consideration is differentiating between open-pore and closed-pore wood structures. Woods with open pores, such as balsa and many broadleaf species, allow easier monomer penetration. In contrast, woods with closed or denser, less interconnected structures hinder infiltration and may require process modifications, such as pre-treatments to boost porosity or the use of monomers with very low viscosity.

3. Wood modification strategies

In the process of obtaining TW, the initial treatment should be applied to lignin, the constituent chiefly responsible for the brown colouration of wood [85]. This polymer, characterised by a complex and conjugated aromatic structure, is responsible for absorbing approximately 80–90% of visible light. The remaining two principal components are colourless but appear white due to light scattering phenomena [6,86]. The primary cause of the scattering phenomena observed in

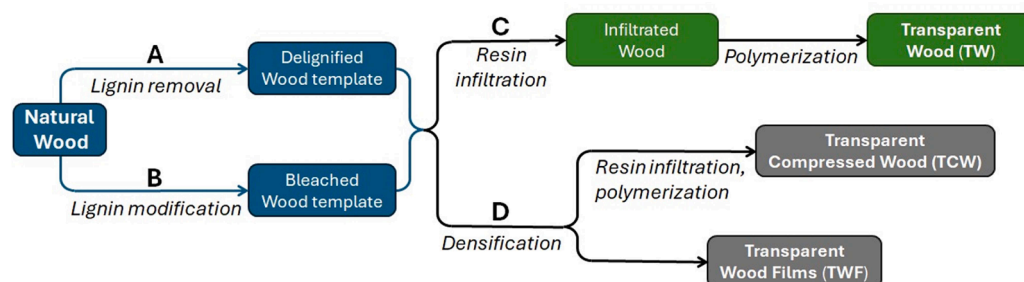


Fig. 3. Schematic of the strategies for preparing transparent wood.

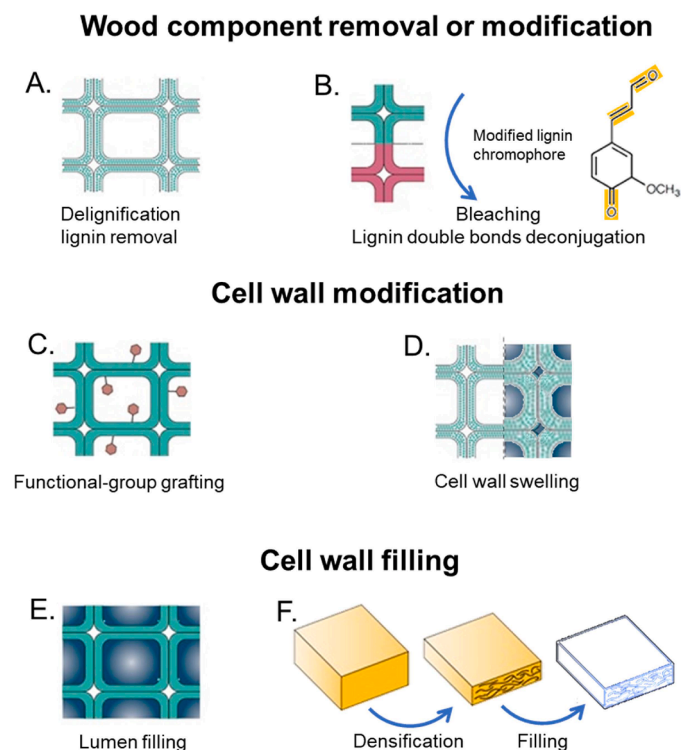


Fig. 4. Strategies for modifying the wood template include chemical treatments (delignification, A; bleaching, B); cell wall modifications (functional group grafting, C; cell wall swelling, D); and infiltration strategies (filling, E; densification before filling, F). Adapted with permission from C. Chen et al. [11].

wood is attributed to its hierarchical porous structure, which acts as a trap for air and diffusely transmits light due to the variation in refractive index between air ($RI = 1.00$) and wood ($RI = 1.54$) [87,88]. Without the removal of lignin, the wood would retain its transparency; however, it would exhibit a colouration ranging from straw yellow to dark brown. The precise shade is affected by the lignin content in the original wood and the extent of lignin conjugation [89]. There are two approaches to lignin treatment: a) delignification techniques that seek to eliminate nearly all lignin through highly aggressive oxidation or reduction processes adapted from the paper industry [6,10]; b) bleaching processes that modify lignin, particularly its chromophore groups such as benzene ring, quinonoid, vinyl, phenolic hydroxyl, and carbonyl groups, are conducted through milder procedures [12]. The subsequent step involves the elimination of air from the pores, which can be accomplished through three methods (Fig. 3): i) direct infiltration of resin having suitable RI to obtain TW [6,9,10]; ii) densification and subsequent

infiltration to obtain compressed transparent wood (CTW) [19,90]; iii) direct densification to obtain thin films (TWF) [91,92].

In the literature, TW, CTW, and TWF refer to distinct material classes. For clarity, these terms are defined as follows and used consistently throughout this review. TW refers to wood-based composites obtained by first rendering the wood template optically transparent through delignification or selective bleaching, followed by polymer infiltration to reduce refractive-index mismatch. TW typically retains the original wood thickness (from millimeters to centimeters).

CTW follows the same processing route as TW but includes an additional densification or compression step, applied before or after polymer infiltration. This step increases cellulose volume fraction and mechanical performance, at the cost of increased processing complexity.

TWF are ultrathin TW materials, typically in the micrometer-thick range. TWF can be fabricated with or without polymer infiltration and exhibits optical and mechanical behaviors distinct from bulk TW and CTW.

This review will consider the most common approach, which involves direct infiltration to obtain TW. The subsequent section provides a detailed examination of the predominant methodologies employed in lignin treatment, along with an exposition of selected strategies for modifying the cell wall. These strategies are utilised to effect changes in optical properties and the diffusion of solutions within the porous structure of native wood.

3.1. Modification of the wood nanostructure

Wood high strength-to-weight ratio, hierarchical porous structure, and modifiability through chemical or physical treatments make it suitable for both structural and functional applications [5,6,93,94].

Indeed, a key benefit of employing wooden templates is the capacity to customise the micro/nano-architecture through the targeted removal of undesired components [95], the strategic insertion of specific molecules grafted onto the hydroxyl groups of cellulose or directly into the cell wall, and the subsequent filling of the lumen with particular monomers, oligomers, or polymers in liquid form [11]. These properties are instrumental in enhancing the quality of TW, thereby improving its optical and mechanical properties [78,96–99], dimensional stability [97,100], and fire resistance [101]. Recent advances have demonstrated its potential in optics, electronics, thermal management, and packaging, especially when combined with polymeric matrices to form wood-based composites [30,73,102]. As illustrated in Fig. 4, the following sub-sections of the review will address the modification strategies that have been identified.

3.1.1. Wood component removal or modification

3.1.1.1. Delignification method. The chemical reactivity of lignin and its material properties are contingent upon the presence of specific

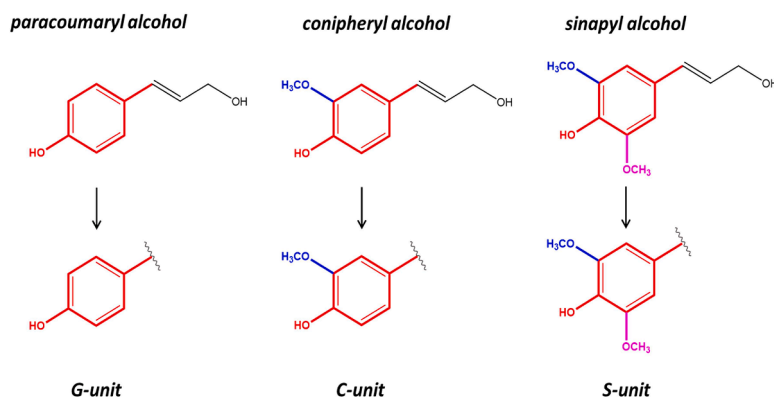


Fig. 5. Precursors and the basic unit in the lignin molecule.

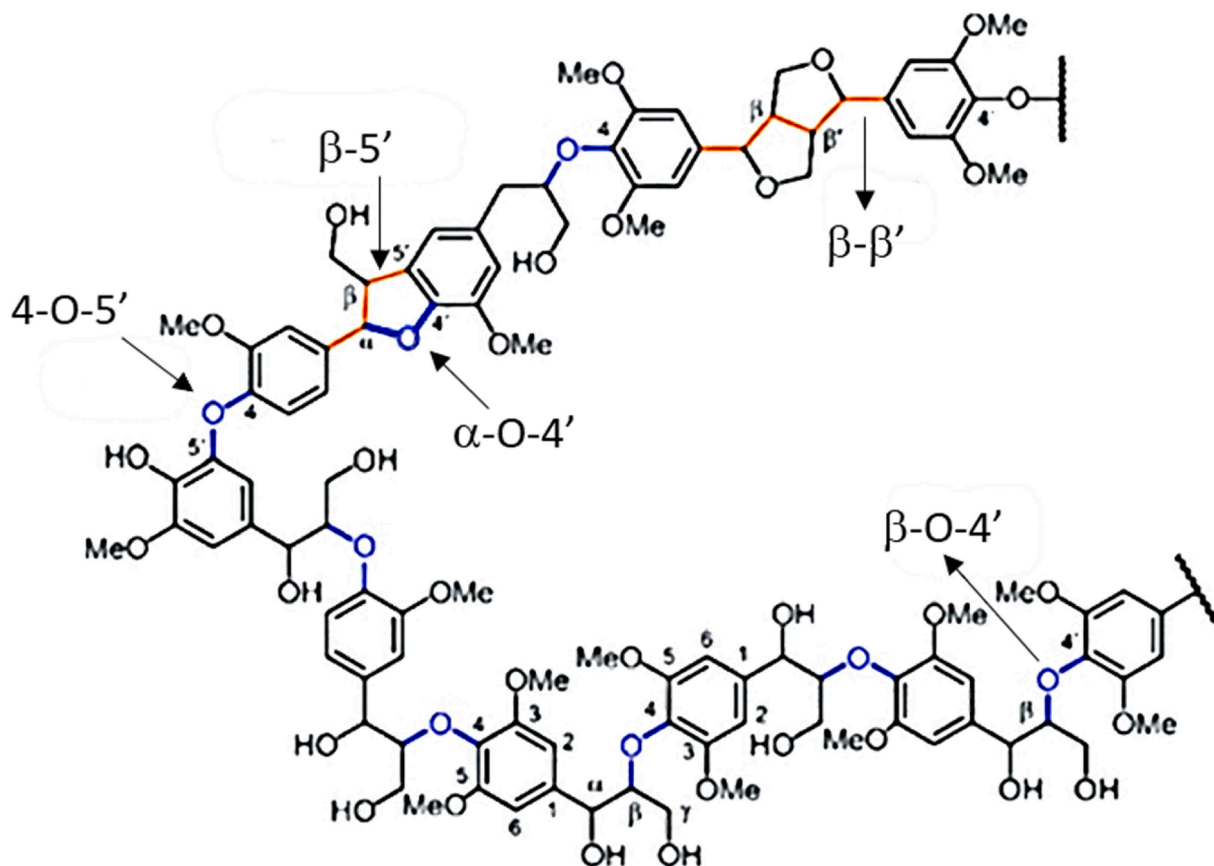


Fig. 6. Model structure of hardwood lignin with inter-unit ether bonds shown in blue and C-C bonds shown in orange. Adapted from Amiri et al. [114].

functional groups, notably hydroxyl groups (both aliphatic and phenolic) and methoxyl groups [103,104]. Its structural composition results from the polymerization of three phenylpropanoid alcohols (see Fig. 5): p-coumaryl, coniferyl, and sinapyl. The proportions of these vary according to species: in softwoods, coniferyl alcohol predominates at 90–95%, whereas in hardwoods, the content is more evenly distributed between coniferyl (25–50%) and sinapyl (50–75%) units [105,106].

This variation in composition directly affects the bond density and reactivity to chemical and physical treatments. Dense, lightweight woods contain a reduced amount of lignin, rendering them more susceptible to delignification processes [107]. In particular, balsa wood, characterized by its very low density (see Table 1), is among the most sensitive species to chemical treatments, especially to lignin removal through delignification processes [108]. This behavior is related to its high permeability, which facilitates the penetration and diffusion of delignifying solutions throughout its porous structure. Conversely, other species, such as pine and softwoods in general, tend to fracture or disintegrate into pieces during delignification treatments [15]. For this reason, it is crucial to carefully control reaction parameters, such as reagent concentration, treatment time, temperature, and pH, as these factors significantly influence the preservation of structural integrity [109].

At the molecular level, lignin exhibits a complex network of covalent C-C bonds (β -1, β -5, 5-5'), which are highly stable and resistant to breakage, and ether bonds (α -O-4', β -O-4', 4-O-5', 5-O-4'), which constitute the majority of the lignin matrix [41,110]. For instance, Fig. 6 illustrates the predominant ether and covalent bonds observed in hardwood. In particular, β -O-4 bonds account for approximately 50% in softwoods and 60% in hardwoods and are the most susceptible to attack in depolymerization processes [111]. The selective cleavage of these bonds is pivotal to the chemical transformation of lignin, thereby impacting the yield and efficiency of treatments such as delignification

[112,113].

The removal of lignin by delignification can be classified mainly into two processes: alkaline and acid, with respective reducing and oxidising actions [115,116]. In the context of industrial pulp production processes, lignin exhibits significantly higher solubility in alkaline systems compared to neutral aqueous media, where it is typically insoluble [41, 117]. The phenomenon can be attributed to the deprotonation of the phenolic hydroxyl groups, which promotes the attack on lignin-carbohydrate bonds, particularly β -O-4 bonds. This process consequently triggers fragmentation and depolymerisation of the macromolecule [118]. This increased reactivity enables more effective extraction, but concomitantly can lead to partial degradation of the cell walls, resulting in a loss of mechanical integrity [119,120].

Alkaline delignification comprises several pulping methods, with Kraft pulping being the most widely adopted [121]. This process enables the production of high-quality bleached pulp in the paper industry, achieving high brightness levels (up to 88% TAPPI), while also allowing partial recovery of chemicals and energy self-sufficiency [122,123]. First applied to preformed wood by Zhu et al. [6] the process involves treatment with an aqueous solution of sodium hydroxide (NaOH, 2.5 mol/L) and sodium sulfite (Na_2SO_3 , 0.4 mol/L) for 12 hours, followed by bleaching with hydrogen peroxide (H_2O_2 , 2.5 mol/L) until the characteristic yellow coloration is completely removed.

Acidic delignification, in contrast, encompasses several treatments, most commonly involving chlorinated reagents such as sodium hypochlorite (NaClO) or sodium chlorite (NaClO_2). For example, Li et al. [10] applied 1 wt% NaClO_2 in an acetate buffer (pH 4.6) at 80 °C, with treatment durations ranging from 6 to 12 hours depending on the wood thickness. Both alkaline and acid delignification processes often employ heat, which can accelerate the formation of toxic by-products, such as mercaptans in alkaline treatments or chlorinated compounds, including dioxins, in acid treatments [124,125].

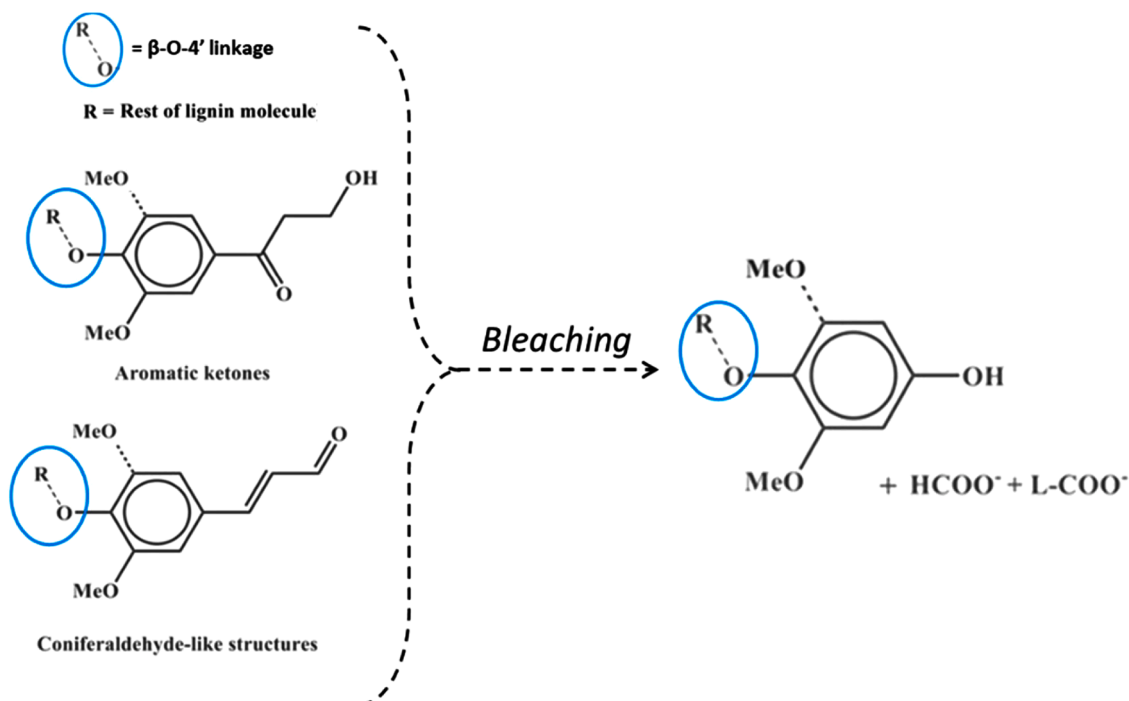


Fig. 7. Lignin structures involved in the bleaching process and the resulting product with preservation of the β -O-4' linkage. Adapted with permission from Li et al. [15].

To simplify delignification while avoiding chlorinated or sulfonated compounds, a universal and eco-friendly approach has been developed, utilizing H_2O_2 alone or in combination with acetic acid, which is brought to a boil to generate steam [126,127].

This method enhances wood meso- and microporosity by removing larger amounts of lignin, which facilitates resin infiltration, although uniform filling may be reduced if the majority of porosity is on the microscale [14,126]. The steam generated from heated H_2O_2 penetrates the cell wall, promoting deep and rapid removal of lignin. This suggests that vapor-phase diffusion, rather than liquid-phase diffusion, enables effective treatment of various wood species, including those that are typically challenging to process, such as linden and pine. While delignification effectively removes lignin to open the wood's porous structure and facilitate resin infiltration, it inevitably compromises structural integrity, particularly in species with light or dense anatomical features. Moreover, the harsh chemical and thermal conditions often required can induce unwanted degradation of cell walls, limiting the applicability to sensitive woods.

3.1.1.2. Bleaching method. Bleaching, in contrast to full delignification, provides a milder and more controlled approach. Rather than aiming at complete lignin removal, bleaching selectively targets lignin chromophores (conjugated aromatic and carbonyl structures) responsible for the characteristic brown color of wood [85]. By modifying these chromophoric groups, bleaching increases lightness and whiteness while largely preserving the lignin polymer and the hierarchical architecture of the cell wall [15]. This makes bleaching particularly suitable for softwoods and other anatomically challenging species, enabling subsequent functionalization or resin impregnation without the structural compromises associated with extensive lignin removal [16].

The bleaching mechanism relies on the oxidative modification of lignin chromophores, most commonly through the use of hydrogen peroxide (H_2O_2) in an alkaline environment [15–17,128,129]. The reactive radicals generated under these conditions selectively disrupt conjugated systems, such as ortho-/para-quinones, coniferaldehyde units, and quinone methides, without extensive depolymerization of the lignin β -O-4 ether backbone (Fig. 7).

Under alkaline conditions, the most widely applied bleaching system

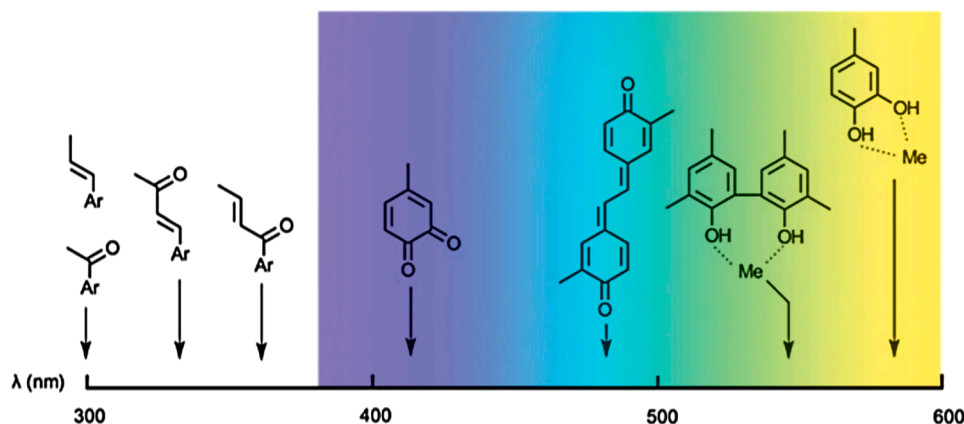


Fig. 8. Lignin-related chromophores and their absorption maxima wavelengths in the UV-visible spectrum. Adapted from Paulsson and Parkäs [137].

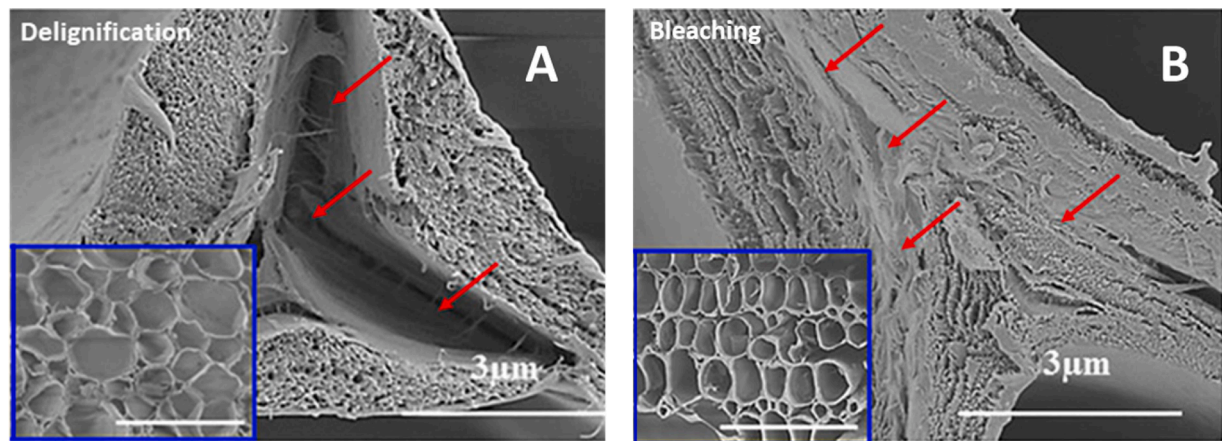


Fig. 9. SEM microstructures of delignified balsa wood (A) and bleached balsa wood (B). Reproduced with permission from Li et al. [15].

Table 2

Comparison between delignification and selective bleaching strategies for different wood species, highlighting the mechanical strength of the white wood templates, optical properties, advantages, limitations, and target applications.

Wood Type	Process Type	Mechanical strength of white wood template [MPa]	Optical properties	Pros	Cons	Target applications	REF
Balsa	Delignification	6.9 ± 1.3	85% (T) 70% (H)	High transmittance; moderate haze; good optical clarity	Low mechanical integrity; long reaction time; limited scalability	Photonic materials; optoelectronic substrates; low-haze optical components	[15]
	Bleaching	7.9 ± 1.2	83% (T) 75% (H)	Preserved structure; improved mechanical stability; short reaction time	Slightly reduced optical performance vs delignification	Light-diffusing panels; photovoltaic substrates; translucent interior elements	
	Delignification	~ 1	91% (T) 15% (H)	Excellent transparency; very low haze	Extremely weak template; poor processability; high waste	Photonic wood; photo-/electrochromic devices	[17, 129]
	Bleaching	~ 20	90% (T) 70% (H)	High mechanical robustness; scalable process; good optical diffusion	Higher haze due to residual lignin	Daylighting panels; diffuse light management systems	
Birch	Delignification	1.4 ± 0.4	80% (T) 70% (H)	Good optical performance; hardwood wood compatibility	Reduced mechanical strength; limited thickness scalability	Transparent optical substrates; low-haze panels	[7, 15]
	Bleaching	14.4 ± 3.3	64% (T) 80% (H)	Preserved hierarchical structure; high strength; good processability	Lower transmittance	Structural translucent panels; interior design; load-bearing TW	
Pine	Delignification	Not self-supporting	Non-representative (LW/EW mix)	High aesthetic transparency; strong visual light transmission	Low mechanical integrity; heterogeneous structure; optical data not representative for functional TW	Aesthetic transparent wood; decorative applications	[15, 139]
	Bleaching	14.4 ± 2.2	70% (T) 78% (H)	Preserved structure; compatible with softwood species; scalable	Moderate haze	Diffusive panels; photovoltaic substrates; translucent partitions	
Ash	Delignification	0.8 ± 1.4	—	Potential optical clarity	Severe loss of mechanical integrity	Aesthetic or proof-of-concept studies only	[15]
	Bleaching	13.9 ± 1.4	58% (T) 83% (H)	High haze; preserved mechanical support; robust template	Lower transmittance	High-haze architectural panels; diffuse light management	

Notes: Mechanical properties reported from Li, al. [15] were measured in the wet state, in order to simulate operative conditions during processing and infiltration. T = Transmittance; H = Haze, both reported at 550 nm, corresponding to the center of the visible spectrum, and commonly used as a reference wavelength, enabling comparison between different transparent materials.

for preparing white wood templates destined for TW is hydrogen peroxide, which can convert quinones into hydroxyquinones, making them more stable against aging [130–132]. Conversely, the use of transition-metal-based stabilizers, such as copper salts, may result in strongly colored complexes with phenolic and catecholic lignin moieties or extractives, like flavonoids. If not properly controlled, these reactions can lead to yellowing during storage or the service life [133,134].

The principal lignin-related chromophores and their approximate absorption maxima are shown in Fig. 8. Although reported values are

indicative, the absorption bands can shift in the solid state [132]. Stable phenoxyl radicals, persisting for days in lignocellulosic matrices, may also contribute to absorption in the 370–410 nm region [135,136]. The effect of light strongly depends on the spectral distribution: irradiation <385 nm favors photo-yellowing, whereas wavelengths >385 nm promote photo-bleaching.

This selective bleaching strategy highlights several contemporary methods for creating transparent and photonic wood, including lignin-retaining TW [15], and patternable photonic wood [17]. In these

approaches, mild oxidative treatments enable color modulation and optical functionality without eliminating lignin, thus demonstrating the potential of decoloration rather than delignification. A recent development builds on this concept by employing a one-pot $\text{H}_2\text{O}_2/\text{KOH}$ alkaline system at room temperature, achieving uniform chromophore removal while retaining lignin. Unlike prior multi-reagent systems that require external heating or UV light sources, this method enables treatment of thicker sections, ensures homogeneous bleaching, and preserves the hierarchical structure essential for TW applications [16].

Controlled oxidation is therefore the key to successful wood bleaching. Excessive reagent exposure, as in conventional delignification, promotes lignin solubilization, cleavage of aromatic structures, and new micro-porosity formation, ultimately compromising structural integrity (Fig. 9 A). In contrast, mild and targeted bleaching preserves the lignin backbone, maintains the native porosity and the mechanical support required for resin infiltration and template manipulation, and allows the fabrication of transparent or semi-transparent wood (Fig. 9B) [14,15,138].

3.1.1.3. Delignification vs. Bleaching. Delignification and selective bleaching should not be regarded as mutually exclusive strategies, but rather as complementary approaches for tailoring the optical and mechanical performance of TW according to the target application. A comparative overview of the two processes, including their effects on template strength, optical properties, advantages, limitations, and application domains for different wood species, is summarized in Table 2.

At a fundamental level, the distinction between these approaches lies in their different impact on lignin oligomerization. Highly aggressive delignification processes promote extensive cleavage of ether and carbon-carbon bonds within the lignin macromolecule, leading to de-oligomerization and solubilization of lignin fragments. This chemical pathway effectively removes chromophoric structures and reduces refractive-index heterogeneity, enabling superior optical properties such as high transmittance and low haze. However, the loss of the lignin network also disrupts the cell wall's mechanical cohesion, rendering the integrity of the white wood template secondary.

As a result, delignification is particularly suitable when optimal optical performance is required, and mechanical robustness is not the primary constraint. These conditions are typically needed for optoelectronic and photonic applications, including photochromic and electrochromic TW, where minimizing light scattering is critical. As shown in Table 2, delignified hardwood species such as birch can still retain acceptable optical performance, whereas softwoods often experience severe structural degradation due to their lower resistance to lignin de-oligomerization.

In contrast, selective bleaching strategies are based on preserving the oligomeric lignin backbone while selectively deconjugating chromophoric groups within the aromatic structure. In this case, lignin remains integrated within the cell wall as a continuous polymeric phase, maintaining crosslinking and mechanical support. Although this preservation introduces a larger optical mismatch and consequently higher scattering, manifested as increased haze, it prevents extensive microstructural collapse and preserves the wood's hierarchical architecture.

This difference in chemical pathways explains why bleached templates consistently exhibit higher mechanical retention and improved processability compared to fully delignified ones. Consequently, selective bleaching is particularly attractive for applications that benefit from high haze combined with mechanical robustness, such as photovoltaic substrates, light-diffusing panels, translucent partitions, and interior design elements for daylight management. These trends are consistently reflected in the comparative data reported in Table 2 across different wood species.

It is also important to note that delignification is not universally applicable to all wood types, especially from an industrial perspective.

Excessive lignin de-oligomerization in softwood species such as pine often leads to template collapse, reduced process yield, and loss of wood content in the final wood-polymer composite, thereby compromising both sustainability and process efficiency. In such cases, delignification may still be employed to produce so-called aesthetic TW, characterized by visual light transmission but non-representative optical and mechanical properties for functional applications, as highlighted in Table 2.

The effectiveness of both delignification and bleaching strategies is ultimately governed by the chemical accessibility of lignin and the availability of reactive functional groups within the cell wall. However, many current approaches remain limited when applied to thick wood sections, motivating the development of additional cell-wall modification strategies to improve processability, infiltration efficiency, and optical performance.

3.1.2. Cell wall modification

At this stage, it is important to clearly distinguish between chemical functionalization, primarily aimed at modifying surface energy and refractive index matching, and physical or chemical swelling processes, which primarily alter cell-wall accessibility, free volume, and diffusion pathways. In several reported systems, both effects coexist, and their contributions must be explicitly recognized to correctly interpret infiltration behavior and structure-property relationships.

The wood cell wall can be modified through both physical and chemical approaches. In the fabrication of TW composites, chemical treatments are generally preferred, as they enable functionalization of exposed hydroxyl groups, thereby imparting new properties [12,97]. Such modifications enhance compatibility between wood and resins, allowing for the customization of optical, mechanical, and physico-chemical properties. Since the chemical composition and physical features of the cell wall largely determine the properties of wood, chemical modifications are primarily designed to adjust the functionality of the wall matrix while preserving its hierarchical architecture and intrinsic stiffness. Two main strategies have been reported for the chemical modification of the wood cell wall. The first approach relies on the functionalization of hydroxyl groups, primarily in cellulose, which is typically achieved through esterification [14,31]. The second involves inducing cell wall swelling, either by grafting spacer-type polymers [140,141] or by applying alkaline pretreatments [31,142].

A key aspect is to optimize the interaction between modifying agents and the structural polysaccharides of the cell wall [143]. Functionalization of these polysaccharides can reduce the hygroscopic nature of cellulose fibers and improve stress transfer at the fiber-polymer interface [14].

3.1.2.1. Functional group grafting. The grafting of functional groups onto wood through acetylation or ring-opening esterification has emerged as a promising approach to enhance the dimensional stability, moisture resistance, and durability of TW, thereby expanding its applicability to more demanding environments. These strategies, first developed for traditional wood modification [144,145], have been reintroduced to optimize the wood-resin interface. Li et al. [31] reported the acetylation of cellulose hydroxyl groups using acetic anhydride in the presence of pyridine as a catalyst and N-methyl-2-pyrrolidone (NMP) as solvent, which yielded TW samples 3 mm thick with enhanced optical properties, namely an increase in transmittance from 60% to 89% and a reduction in haze from 80% to 55%. Building on this concept, Montanari et al. [14] proposed a greener ring-opening esterification route employing cyclic anhydrides. In particular, the proposed work is based on three cyclic anhydrides (maleic, itaconic, and succinic) under tailored time-temperature conditions specific to each anhydride, thereby forming covalent bonds between the acrylate-based polymer matrix and the wood cell wall. This chemical linkage leads to improved interfacial stability, reduced polymer shrinkage, and enhanced dimensional stability 3 mm-thick TW with

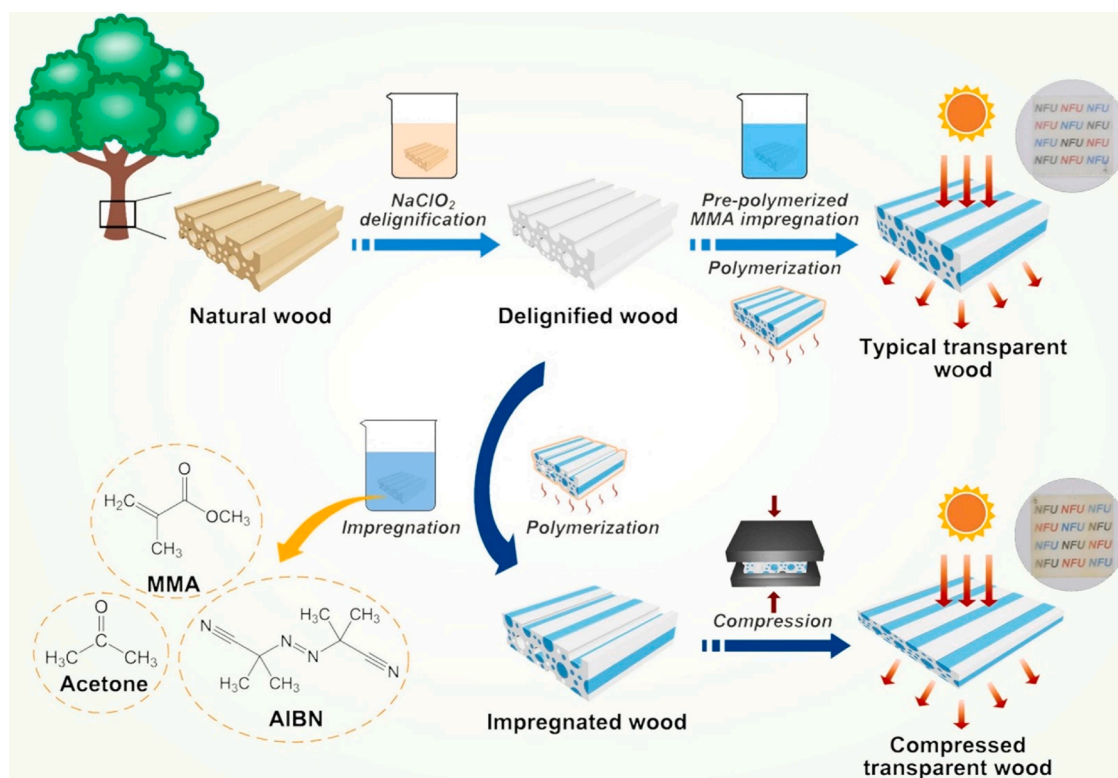


Fig. 10. Schematic comparison of the preparation process of vacuum-impregnated transparent wood (TW) and compressed transparent wood subsequently impregnated (CTW). Reproduced with permission from Wu et al. [151].

improved optical performance, increasing transmittance from 71% to 84% and reducing haze from 73% to 67%. While both strategies demonstrated improved interfacial compatibility, post-treatment yellowing was observed, requiring additional delignification under carefully optimized conditions to preserve the introduced functionalities. Beyond optical enhancement, acetylation and esterification significantly improved the durability of TW by reducing hygroscopicity and enhancing dimensional stability under variable environmental conditions. Such modifications mitigate swelling and shrinkage phenomena, limiting biological degradation and thereby broadening the potential for structural and long-term functional applications [146,147].

3.1.2.2. Cell wall swelling. Cell wall swelling is a complex phenomenon that occurs at the micro- and nanostructural levels of wood. It can naturally arise in native wood under environmental conditions such as moisture absorption or the presence of solutes, leading to dimensional changes that may compromise its structural and functional integrity [148]. However, when cell wall swelling is deliberately induced through chemical treatments, such as swelling solutions or the incorporation of small molecules directly into the cell wall, the resulting modification of intrinsic wood properties can be advantageous [141,142]. Such approaches have been investigated to obtain more homogeneous nanostructured composites from wood substrates. In this context, several studies combine swelling and chemical functionalization rather than relying on a single mechanism. For instance, swelling of wood fibers has been exploited to facilitate the grafting of monomers that can be subsequently polymerized within the cell wall. Cabane et al. [140] reported the use of dimethylformamide (DMF) as a swelling agent to enable the grafting of vinyl and acrylic monomers into the wood cell wall, while Olsen et al. [141] studied the swelling effects of different solvents, including acetic acid, on the density and extent of polycaprolactone grafting onto cellulose nanofibrils.

More recently, Chen et al. [142] introduced a greener nanotechnology approach, applying a 7% NaOH treatment at subzero

temperatures. This process was shown to significantly increase cell wall swelling, thereby improving accessibility for chemical impregnation and enabling the fabrication of thick TW with enhanced optical properties through the uniform distribution of acrylic-based polymers (PMMA) within the cell wall matrix.

While these studies provide valuable insights into the mechanisms of wood cell wall swelling, it remains crucial to balance the benefits of improved accessibility with the preservation of wood's natural structure and stability. Excessive swelling can weaken the mechanical integrity of the cell wall by generating microporosity during treatments; when this porosity becomes excessive, the material's cohesion is further compromised, making it fragile and difficult to handle during subsequent impregnation steps. In extreme cases, the substrate may lose its cohesive structure and approach a pulp-like state. Future research should focus on optimizing swelling-based modifications through more sustainable routes, thereby achieving improved dimensional stability and optical performance without compromising mechanical strength or ecological benefits.

3.1.3. Cell wall filling

3.1.3.1. Lumen filling. Lumen filling is a key step in preparing TW, as it enables the suppression of light scattering and achieves the desired optical performance in the composite. This is typically accomplished by infiltrating the porous wood structure with polymers whose refractive index is close to that of cellulose (1.53–1.54) [87]. By filling the lumina and intercellular spaces, the polymer acts as an index-matching medium, reducing heterogeneities at the cell wall–void interfaces and thereby enhancing both transmittance and transparency [6,9,10].

The most widely used fillers include acrylic-based polymers, such as PMMA and bio-based alternatives like PLIMA, alongside epoxy resins, most often based on bisphenol-A formulations [6,10,73]. The choice of polymer is not neutral: it strongly affects impregnation continuity, shrinkage during curing, and ultimately the interfacial adhesion with

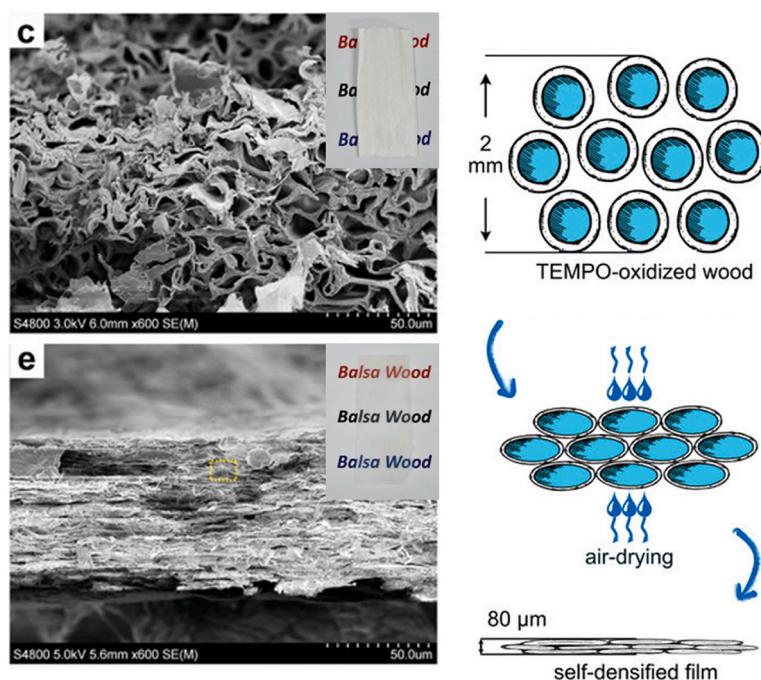


Fig. 11. Cross-sectional SEM images of the air-dried white wood template (c) and the self-densified wood (e) obtained after TEMPO-mediated oxidation. Adapted from Li et al. [91].

the cell walls. In untreated wood, lumen filling with acrylics can result in polymer detachment from the wall due to post-polymerization shrinkage, while epoxies, characterized by lower shrinkage, tend to maintain better cohesion even without preliminary functionalization of the substrate [14,31,149].

Acrylic resins, however, offer a crucial advantage when producing thick, TW. In fact, PMMA-based systems allow for fine control of viscosity during impregnation, as the polymerization of methyl methacrylate monomers can be tuned over longer time frames. This enables deep infiltration of denser samples without premature curing. Epoxy resins, by contrast, are generally prepared from predefined mixtures of resin and hardener, which cure rapidly, often at room temperature, leaving little flexibility for adjusting infiltration kinetics. For this reason, epoxy systems are typically not employed in the fabrication of thick TW, despite their favorable low shrinkage and adhesion properties.

Taken together, these considerations highlight that the lumen-filling stage is not only a matter of polymer choice, but also of processing strategy: achieving high optical quality requires balancing interfacial compatibility, shrinkage control, and curing dynamics with the target sample thickness.

3.1.3.2. Densification and filling. The densification process of wood is fundamental for the development of CTW with enhanced mechanical properties compared to TW. This approach for pre-formed wood was first introduced by Song et al. [94], who exploited hot pressing after partial delignification to induce hydrogen bonding among the exposed cellulose fibrils. The resulting densified wood achieved a specific strength of $422.2 \text{ MPa cm}^3 \text{ g}^{-1}$, defined as the tensile strength divided by the material's density, surpassing that of typical metals, including Fe–Al–Mn–C alloys and lightweight titanium alloy (Ti6Al4V), and demonstrating its potential as a high-performance structural material.

In a subsequent study, Gullo et al. [150] treated both softwood and hardwood, achieving up to a fourfold increase in tensile strength compared to the original samples (e.g., from 225 to 911 N), while using less environmentally harmful reagents. In this context, Wang et al. [90] investigated a compressed-then-impregnated route for TW fabrication. Their method involved delignification via sodium chlorite followed by

hydrogen peroxide bleaching, solvent dehydration, and hot pressing from 4 mm down to $110 \mu\text{m}$ before resin impregnation. This process differs from conventional vacuum impregnation and led to notable optical improvements, including a 34% increase in transmittance and a 28% increase in haze compared to uncompressed templates.

More recently, Wu et al. [151] introduced a clearer and more systematic comparison between traditional TW production and the fabrication CTW. As schematically illustrated in Fig. 10, delignified wood is first obtained through NaClO_2 treatment and then partially infiltrated with PMMA before undergoing densification. This approach contrasts with typical TW synthesis, where complete polymer impregnation is performed without compression. The CTW route significantly reduces polymer content (down to 58.8%, compared to 91.8% in typical TW) while improving both optical and mechanical performance. The resulting compressed TW achieves up to 77.9% optical transmittance and a haze of around 49%, alongside markedly enhanced tensile (85 MPa) and flexural (145 MPa) strengths. The process also offers notable sustainability advantages: a life-cycle assessment shows a 23% lower environmental impact than conventional TW and a 28% reduction compared to PMMA, highlighting CTW as a practical pathway for producing high-performance, low-polymer TW materials.

Moreover, Li et al. [91] proposed a method of self-densification of cellulose microfibrils, achieved through oxidation mediated by 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). This resulted in an ultrathin, $80 \mu\text{m}$ transparent film (TWF) (with 70% transmittance and controlled haze) starting from 2 mm thick balsa wood. As shown in Fig. 11, SEM images of the balsa wood cross-section highlight the structural differences between the air-dried white wood template and the self-densified wood obtained after TEMPO-mediated oxidation.

Advancements in wood densification and polymer filling have shown great potential for creating high-performance TW, CTW and TWF; however, significant challenges remain in balancing mechanical strength, optical clarity, and final thickness. In particular, densification generally produces very thin composite (from micrometers in the case of TWF to a few millimeters in the case of CTW) with superior mechanical properties, which are unsuitable for applications requiring thicker TW, such as interior and exterior construction.

Optical behavior, on the other hand, is influenced by multiple

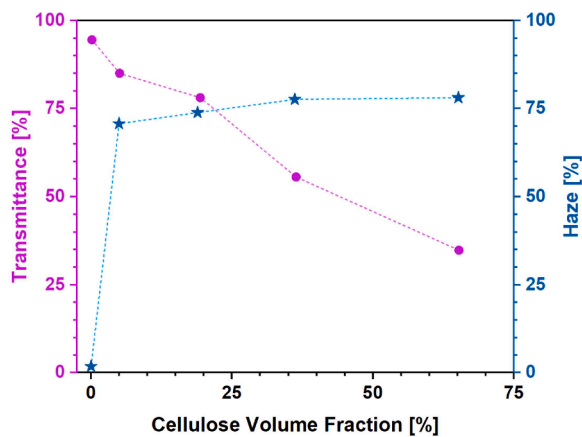


Fig. 12. Optical transmittance and haze as a function of cellulose volume fraction for 1.2 mm thick balsa wood. Data replotted from Li et al. [10].

factors, including lignin content, cell wall microstructure, and the compatibility between wood and infiltrated polymers. The next section thus focuses on infiltration processes and the role of the wood's anisotropic structure in light transmission, highlighting key considerations for optimizing transparency and haze in these composites.

4. Factors affecting wood transparency

In this review, optical transparency is discussed in terms of both optical transmittance and haze. Haze is defined as the ratio of diffusely transmitted light to the total transmitted light flux and quantifies the extent of light scattering within the material [152]. In contrast, opacity describes the overall attenuation of light transmission without distinguishing between absorption and scattering mechanisms [152]. Because TW systems are primarily characterized by strong light scattering rather than complete light blockage, haze represents the most relevant optical parameter for describing their functional behavior. For clarity and consistency, the term “haze” is therefore used throughout the manuscript. Once the white wood template is obtained, polymer infiltration becomes a crucial step to reduce the refractive index mismatch between the cell wall and the pore space, thereby lowering light scattering and enabling transparency. Several factors influence these optical characteristics. First, the cellulose volume fraction plays a central role. In contrast, wood density is defined as the mass of the material divided by its total volume, and therefore depends not only on the relative amount of solid cell wall material but also on factors such as moisture content and mineral inclusions. While density is commonly used in traditional wood science, it does not directly capture the relative fraction of solid versus void volume that governs light scattering. For instance, two samples with the same density could have different internal porosity or cell wall thickness, resulting in distinct optical behavior. Using cellulose volume fraction as a metric allows a more

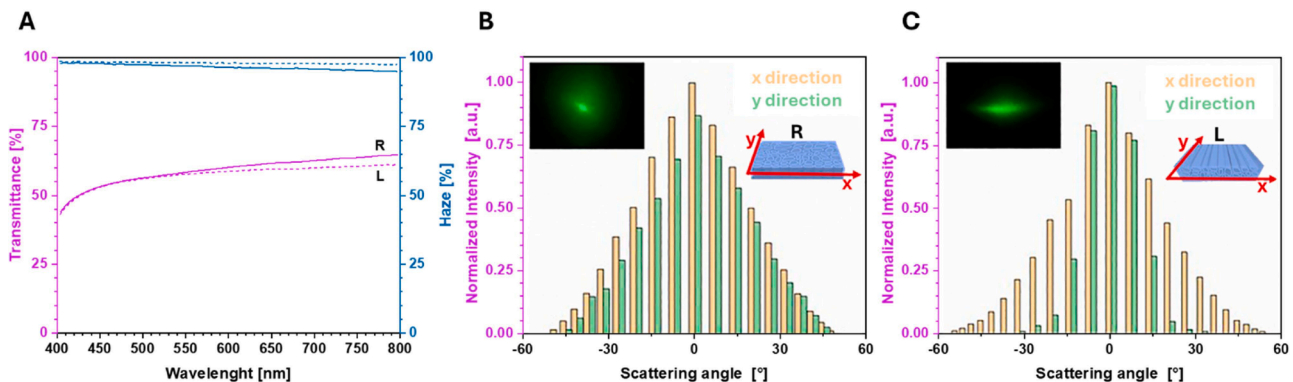


Fig. 13. Optical response of transparent wood with different cutting orientations.

(A) Optical transmittance and haze measured using an integrating sphere, showing comparable bulk optical properties for longitudinal and radial samples. Normalized angular intensity distributions of diffusely transmitted light for radial (B) and longitudinal (C) sections, revealing isotropic and anisotropic scattering behavior, respectively, as a function of wood channel orientation ($\lambda = 532$ nm). Data replotted from Wang et al. [153].

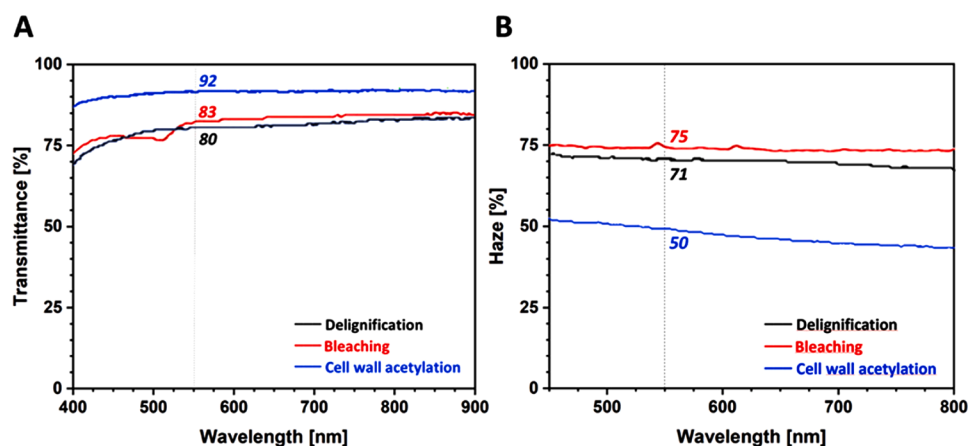


Fig. 14. Optical transmittance (A) and haze (B) of transparent wood prepared by different pretreatment methods: (black curve) delignification, (red curve) bleaching, and (blue curve) cell wall modification by acetylation. Data replotted from Li et al. [10,15,31].

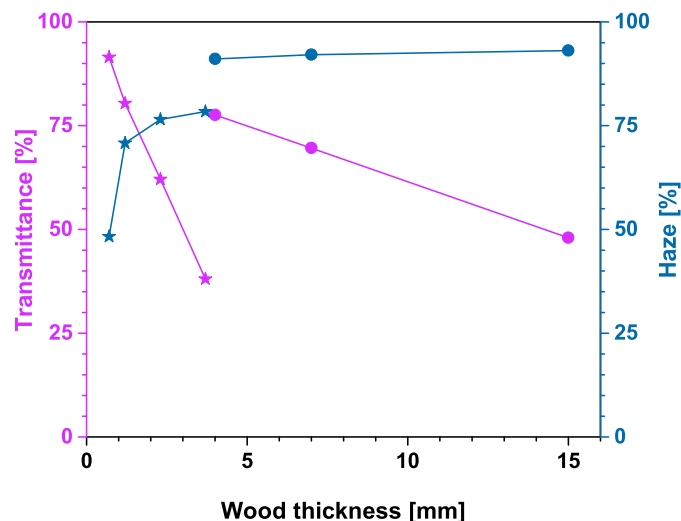


Fig. 15. Optical transmittance and haze of balsawood as a function of sample thickness. Data for samples with thicknesses between 0.7 and 3.7 mm (★) are from Y. Li et al. [10], while data for thicker samples between 4 and 15 mm (●) relate to balsawood pretreated with low-temperature NaOH-induced cell-wall swelling, as reported by Chen et al. [142]. Data replotted from Li et al. [10] and Chen et al. [142].

precise understanding of how the microstructure affects transmittance and haze. For example, balsawood, with a low cellulose volume fraction and thin fiber walls, generally exhibits higher transmittance than denser species like birch under similar treatment conditions [15]. Within the same wood species, an increase in cellulose volume fraction (i.e., a larger fraction of solid cell wall material) typically leads to lower transmittance and higher haze, as illustrated in Fig. 12.

Second, the sample's orientation strongly affects light scattering. Wang et al. [153] showed that TW can exhibit orientation-dependent light scattering even when bulk optical properties are similar. As shown in Fig. 13 A, optical transmittance and haze measured using an integrating sphere were comparable for longitudinally and transversely cut samples (~60% transmittance and ~95% haze). However, laser-based measurements ($\lambda = 532$ nm) revealed pronounced anisotropic scattering behavior. In particular, the normalized angular intensity distributions reported in Fig. 13 B and 13 C indicate that longitudinal samples exhibit broader light scattering perpendicular to the wood channel orientation (x direction) than parallel to it (y direction), whereas radially cut samples display a more isotropic scattering pattern. This anisotropic scattering was attributed to the preferential alignment of cellulose nanofibrils, demonstrating that sample orientation can govern directional light diffusion independently of average transmittance and haze values.

Third, the method used to modify the wood, such as delignification, bleaching, or other cell wall treatments, strongly affects its optical performance. As illustrated in Fig. 14 A, three distinct trends can be identified. Wood subjected to cell wall acetylation (blue curve) exhibits the highest transmittance across the visible spectrum (~92%), followed by bleaching (~83%) and delignification (~80%), indicating that direct chemical modification of the cellulose-rich cell wall more effectively reduces refractive index mismatches and light scattering than lignin removal alone. A similar pattern emerges for haze in Fig. 14 B. Acetylation produces the lowest haze (~50%), whereas bleaching and delignification result in higher haze values. Notably, bleaching yields a slightly lower haze (~75%) and a slightly higher transmittance compared to delignification (~70%), suggesting that bleaching, despite preserving most of the lignin, may promote a more homogeneous redistribution or chemical alteration of chromophoric groups, reducing micro-scale refractive index gradients within the cell wall. Overall, all treatments show relatively flat spectral profiles between 400 and 900

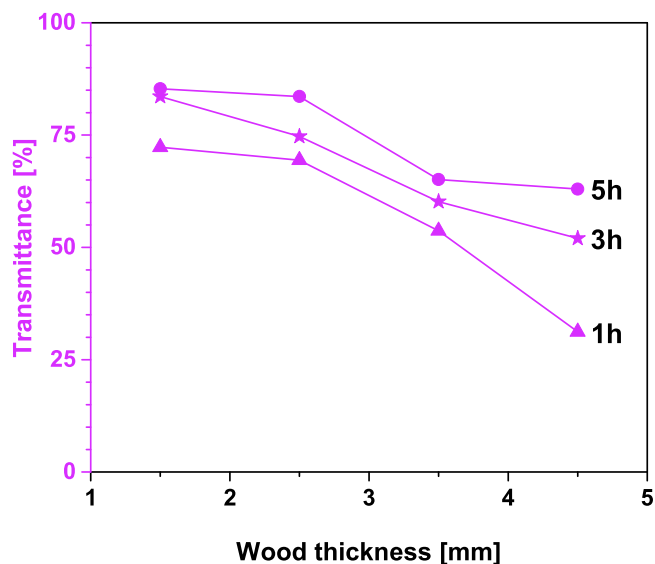


Fig. 16. Optical transmittance at 550 nm of poplar TW with thicknesses of 1.5, 2.5, 3.5, and 4.5 mm processed using different bleaching durations: 5 h (●), 3 h (★), and 1 h (▲). Data replotted from Bisht et al. [154].

nm, implying that these optical effects are largely wavelength-independent [10,15,31].

Fourth, sample thickness directly impacts scattering: thicker specimens generally exhibit increased haze and reduced transmittance, as observed in studies involving balsawood sheets with different thicknesses (Fig. 15). In the study by Li et al. [10], delignified balsawood samples with thicknesses ranging from 0.7 to 3.7 mm and infiltrated with PMMA show a pronounced decrease in optical transmittance, from approximately 92% down to 35%, accompanied by a substantial increase in haze from about 45% to 77% as thickness increases. This behavior reflects the expected effect of increasing cellulose content and wood mass, which increases the number of scattering centers along the optical path.

In contrast, Chen et al. [142] reported a markedly different thickness dependence for thicker balsawood samples (4–15 mm) subjected to a low-temperature NaOH pretreatment prior to delignification and PMMA infiltration. As shown in Fig. 15, these samples exhibit a more moderate decrease in transmittance, from ~75% at 4 mm to ~50% at 15 mm, while haze remains relatively stable, increasing only slightly from ~80 to ~85%. This improved optical performance at larger thicknesses was attributed to cell-wall swelling induced by the alkaline pretreatment, which enhances reagent diffusion, promotes more homogeneous delignification and polymer infiltration, and reduces microstructural heterogeneities responsible for excessive scattering.

Fifth, treatment time is an additional parameter that influences the optical response of TW. In a study on TW composites prepared from transverse sections of poplar Bisht et al. [154] showed that increasing the bleaching treatment duration results in higher, more stable optical transmittance (Fig. 16). In particular, samples treated for extended durations (5 h) exhibit relatively similar transmittance values at low and intermediate thicknesses, as well as a moderate decrease at larger thicknesses, indicating a more homogeneous optical response throughout the bulk material. In contrast, shorter treatment times result in systematically lower transmittance values and a much steeper decline with increasing thickness.

This behavior can be attributed to the degree of homogeneity achieved during the chemical treatment. Longer treatment times promote more uniform lignin modification throughout the wood thickness, thereby reducing local refractive index mismatches and minimizing the formation of poorly treated regions that act as strong scattering centers. Conversely, insufficient treatment times (1 h) result in incomplete or spatially heterogeneous lignin modification, particularly in the inner

Table 3

Optical properties of polymers and results reported in the literature for transparent wood as a function of the type of polymer, viscosity, and compatibility with the cell wall.

Wood Type	Thickness [mm]	Resin Type	Viscosity [mPa · s]	Refractive Index	Cell Wall Compatibility	Transmittance [%]	Work REF
Balsa	1.0–3.0	Epoxy Resin	500–5000	1.50–1.60 [155]	Good epoxy filling of lumens, mechanical reinforcement (MOE: 4613.5 → 6089.9 MPa)	70 at 1.0 and 2.0 mm 40 at 3 mm	[149]
Balsa	0.8	Polyvinyl alcohol	1.5–15	1.53–1.54	Good wettability on cellulose, mechanical reinforcement	91	[93]
Balsa	1.0	Cellulose Acetate	300–500	1.47 [156]	Good wettability on cellulose	87	[127]
Balsa	1.5	PMMA	Tunable	1.490–1.492 [157]	Interface manipulation through acetylation removes debonding gaps.	92	[31]
Birch	1.5					90	
Balsa	0.7; 1.2	PLIMA	-	1.52	Need to perform interface manipulation to eliminate debonding gaps less than PMMA	95.1; 88.6	[21]
Alder	0.7					89.6	
Birch	0.7					91.6	
Beech	0.7					88.6	

Notes: Transmittance values refer to optical transmittance at 550 nm, the center of the visible spectrum, and a commonly used reference wavelength for comparing transparent materials.

regions of thicker samples. As thickness increases, these untreated or partially treated domains accumulate along the optical path, giving rise to enhanced scattering and a rapid loss of transmittance.

Taken together, these observations indicate that thickness-dependent optical losses are not solely governed by geometry, but also by the combined effects of sample thickness, pretreatment strategy, and treatment kinetics. Adequate treatment duration is therefore essential to ensure uniform modification throughout the wood template and to preserve high optical performance, particularly in thicker TW composites.

Finally, the properties of the polymer matrix and the quality of infiltration, such as refractive index matching, viscosity, and wetting behaviour, strongly affect uniformity and optical performance. For example, infiltration with good wetting of cell walls, such as using epoxy resins, results in higher transmittance than other polymers, such as acrylic resins or PVA. These polymers poorly penetrate the wood structure and require modifications to the cell walls, as shown in Table 3.

A comparative analysis of the literature (as summarized in Table 3) highlights several key parameters that cannot be rationalized by a single parameter but instead emerge from the combined effects of polymer-wood interactions, infiltration efficiency, and microstructural constraints.

First, ensuring that the refractive indices (RIs) match between wood and polymer is crucial to reducing interfacial scattering, but it is not a sufficient condition for achieving high transparency. Delignified wood scaffolds typically have RI values between 1.525 and 1.538, so polymers with similar RI are needed to reduce interfacial scattering. However, Table 3 shows that polymers with comparable RI can yield markedly different transmittance values, indicating that RI matching alone does not fully capture the optical response. For instance, PMMA and PLIMA, despite a residual RI mismatch (1.490–1.492), can achieve high transmittance when interfacial debonding is mitigated through acetylation or surface modification, whereas epoxy resins benefit from a broader RI window (1.50–1.60) and stronger adhesion to the cell wall. These observations underscore the interplay between RI matching and interfacial continuity. Additionally, hybrid systems incorporating nanofillers such as ZnO, ZrO₂, or TiO₂ can help adjust the polymer's RI over a wide range, offering a promising direction for future enhancements [158–160].

Second, the viscosity of polymers strongly affects infiltration depth and homogeneity. While low-viscosity systems (<100 mPa · s) facilitate penetration into small lumina and submicrometric voids, Table 3 reveals that high transmittance can also be achieved with medium-viscosity polymers (100–1000 mPa · s), when wetting and interfacial compatibility are optimized. Conversely, higher-viscosity systems (>1000 mPa · s) often require additional processing steps, such as vacuum cycles,

elevated temperatures, or solvent assistance to avoid residual voids that act as scattering centers [161–163]. These trends illustrate that viscosity must be considered alongside wetting behavior and processing conditions, rather than as an isolated descriptor.

Third, the wood thickness introduces an additional constraint, exposing contradictions in the reported data. High transmittance values (87–95%) are generally achieved in thin samples (0.8–1.2 mm), whereas thicker samples (3 mm) increasingly promote internal scattering and haze. Nevertheless, selected studies demonstrate that optimized infiltration and interfacial manipulation can partially mitigate this limitation, enabling transmittance values above 70% even at thicknesses approaching 7 mm in balsa wood [31]. This variability highlights that thickness scaling is not governed by geometry alone, but by the combined effectiveness of infiltration (diffusion and accessibility), interfacial continuity, and structural preservation.

Finally, wood-polymer interfacial compatibility emerges as a decisive factor that reconciles many of the apparent discrepancies in Table 3. Strategies such as chemical functionalization (acetylation or succinylation), use of silane coupling agents, and selective surface treatments have proven effective in eliminating debonding gaps and stabilizing optical performance, especially in hydrophobic polymer systems [21,31,164].

Despite these developments, several key unresolved issues limit the predictive comparison of different polymer systems. These include: i) limited data for softwood species such as pine and spruce; ii) insufficient reporting and standardization of polymer viscosity; iii) absence of standardized parameters describing the chemical and physical affinity between wood cell walls and polymers (i.e., interfacial energy, contact angle during infiltration, or diffusion coefficients which would enable direct comparison and predictive modelling); iv) the need to expand the use of fully bio-based polymers, whose optical performance and infiltration behavior are still largely unexplored; and v) the limited comparability of optical transmittance and haze values reported in the literature. These values are strongly influenced by sample thickness, measurement geometry, and instrumentation. Even when standardized protocols are employed, such as ASTM D1003–21 (“Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics”), which is commonly used in both academic and industrial contexts, differences in specimen thickness, surface finish, light source, detector configuration, and scattering geometry can lead to significant variations in the measured optical properties. As a result, optical data should be interpreted with caution, and meaningful comparisons across studies should only be made when measurement conditions and sample dimensions are clearly aligned. Moreover, the effects of scalability and thickness must be better characterized to advance TW toward industrial applicability.

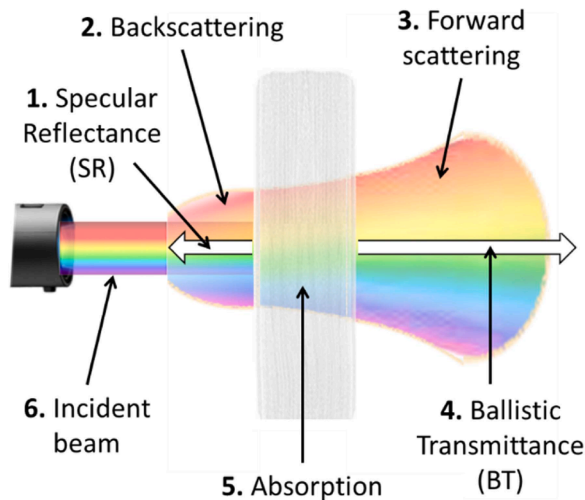


Fig. 17. Scheme of light interactions with transparent wood as a turbid material. Adapted from Chen et al. [165].

Overall, these findings demonstrate that optical transparency in wood results from a complex interplay of factors, including refractive index matching, polymer viscosity, interfacial engineering, and macro-to nano-scale structural features, all of which are closely linked to the light-material interaction mechanisms described in the next section. Overcoming the lack of standardized descriptors and systematically separating these intertwined effects is a crucial step toward advancing TW toward reliable, scalable applications.

4.1. Wood-light interaction

Understanding the interaction between light and TW is crucial for designing materials with controlled transmittance and haze. The TW, as previously described, is a hierarchically structured material characterized by complex multiscale features and non-periodic heterogeneity, which makes it challenging to apply classic optical models based on average scattering and absorption coefficients, commonly used for homogeneous turbid media such as air, water, or transparent plastics [165].

For this reason, in TW, the photon behaviour is influenced by the anisotropic and porous nature of the starting wood, by the cellular morphology, and by the optical compatibility between the lignocellulosic wall and the infiltrating polymer [165]. The anatomical structure of the wood, composed of vessels and fibers oriented longitudinally and rays arranged radially, creates different optical paths depending on the angle of incident light [10,140,147]. Inside the cell wall, the presence of residual cellulose, hemicellulose, and lignin affects the local optical behaviour: cellulose microfibrils, in fact, are birefringent, and their refractive index (RI) depends on the orientation (microfibril angle, MFA), lignin content, and humidity level [87,166–168]. The experimental measurements conducted in the work of Chen et al. [87] employed liquid immersion methods to demonstrate RI values perpendicular to the fibers, ranging from 1.535 to 1.538 at 589 nm, thereby enabling the targeted selection of the infiltrating polymer to achieve effective optical matching and reduce unwanted scattering.

The interaction of light with the TW primarily occurs through three physical mechanisms: reflection, scattering, and absorption. Reflection at the outer air-polymer or air-wood interface is generally limited (about 4–10%), so most photons penetrate the material [10]. Inside the composite, light scattering is the main phenomenon responsible for haze formation. It results from discontinuities in the refractive index at the wood-polymer interfaces and from the presence of voids or nanopores in the cell wall, which act as scattering centers. Depending on the size of these centers relative to the wavelength of incident light, three regimes

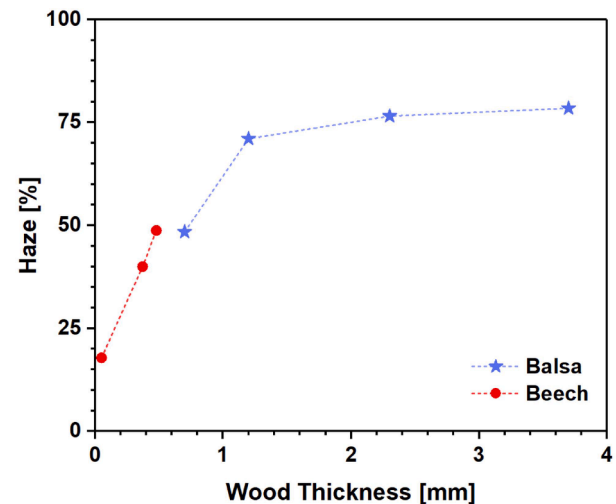


Fig. 18. Haze values for beech wood [169] and balsa wood [10], illustrating how the haze varies with the sample thickness.

are distinguished: Rayleigh scattering (on a nanometric scale, nearly isotropic), Mie scattering (on an intermediate scale, characterized by directional scattering), and the geometric regime (on a micrometric scale), in which photons undergo limited deviations and tend to propagate forward [165]. Absorption, although less pronounced than scattering, plays a crucial role in modulating the intensity of the transmitted light. This is mainly due to residual lignin and chromophores generated during chemical treatments. Therefore, processes such as delignification or chemical modifications of the cell wall enable a significant increase in the material's transparency [10,15,31]. From a quantitative perspective, as described in the work of Chen et al. [165], the light-material interaction can be described through fundamental optical quantities shown in Fig. 17: ballistic transmittance (BT), which represents the fraction of photons that pass through the sample without deflections or absorption (4); total transmittance (TT), which includes both ballistic and scattered components (2, 3 and 4); specular reflectance (SR), associated with photons reflected from the surface without internal interaction (1); and backscattering, generated by multiple scattering and amplified by voids or interfacial defects (2).

Variations in haze and transmittance depend on multiple factors, including sample thickness, wood species, cellulose and lignin content, the presence of voids, and the quality of polymeric infiltration. For thicknesses below the Transport Mean Free Path (TMFP), haze tends to increase in proportion to the thickness. For thicker samples, saturation is observed, indicating a shift to a diffuse transport regime [7]. However, two previous studies, one by Yaddanapudi et al. [169] on beech wood and the other by Li et al. [10] on balsa wood, show two opposite trends in the variation of haze as the thickness of the considered wood type changes. In particular, as shown in Fig. 18, the values obtained by varying the thickness of balsa wood indicate that density and cellulosic volume fraction have a relatively modest influence on haze, confirming that interfaces, nanostructure, and the quality of the contact between wood and polymer are the main factors determining optical behaviour.

In contrast, as the thickness of beech wood varies, a strong dependency between wood thickness and measured haze is observed. This is likely due to the greater density and more compact cell structure of beech, which increases the absorption and internal scattering of photons, thereby amplifying the effect of thickness on optical behavior. In other words, while in light wood, such as balsa, the interfaces and the quality of infiltration dominate optical transport, in dense wood, such as beech, the thickness itself and the cellular morphology play a decisive role in increasing haze.

Ultimately, TW presents a complex interplay among ballistic transmission, multiple scattering, backscattering, and absorption, whose

interaction critically depends on the material's hierarchical architecture and the optical properties of its components. An in-depth understanding of these phenomena, supported by structural analyses, photonic models, and optical measurements, is essential for designing advanced transparent biocomposites with tailored optical performance for applications in construction, optics, and sustainability [10].

It is important to note that similar optical transmittance values reported in the literature do not necessarily arise from the same physical mechanisms. In TW, light transport results from a balance between ballistic transmission through aligned cell-wall domains and multiple scattering events arising from refractive-index mismatches at cell walls, lumen interfaces, and polymer-filled pores. As a consequence, high transmittance may be achieved either by reducing scattering (low haze) or by strong forward scattering accompanied by high haze, depending on the microstructural configuration. This distinction helps rationalize apparent contradictions in the literature, where materials with comparable transmittance exhibit markedly different haze values, mechanical integrity, or thickness limits. For example, delignified templates with extensive pore collapse can exhibit high transmittance at small thicknesses but rapidly lose optical performance as thickness increases, whereas lignin-retaining or selectively bleached systems maintain higher haze yet offer greater structural stability and more robust optical behavior over larger dimensions. Accordingly, the factors discussed in this section should be interpreted as interconnected rather than independent variables. Cellulose volume fraction, orientation, treatment route, polymer infiltration, and thickness jointly define the dominant light-transport regime, underscoring the need to evaluate optical data in conjunction with microstructural and mechanical considerations.

5. Limitations and bottlenecks

Although TW offers high optical clarity and mechanical reinforcement due to the presence of the transparent template, its fabrication still undergoes several challenges. PMMA remains the most commonly used acrylate polymer in composite production, owing to its transparency, compatibility with cellulose, and controllable viscosity via prepolymerization time [10]. However, its fossil-based origin and slow curing and diffusion kinetics limit its use in sustainable and scalable processes. Among acrylates, PLIMA is a particularly promising biobased alternative, as it shows improved compatibility with the cellulose cell wall and exhibits less post-polymerization shrinkage than PMMA [14,138]. Nevertheless, like PMMA, it requires long curing times at around 70 °C and does not allow versatile viscosity control, even though it is less viscous than PMMA and therefore has a higher diffusion rate [138,21].

Epoxy resins, another widely used class, are often based on bisphenol A. They provide strong adhesion and low shrinkage, and importantly, they show an excellent refractive index match with white wood templates, improving optical transparency [6,96,149]. However, they can yellow over time, frequently require toxic cross-linkers, and currently, the development of biobased epoxy alternatives remains limited [20]. Their processing generally occurs at room temperature without the need for heat, allowing for long polymerisation times and making them more sustainable in terms of energy and infrastructure costs [6]. Nevertheless, a significant limitation of both acrylate and epoxy resins in TW fabrication is that a substantial amount of the resin is wasted, as it cannot be recovered or reused after the infiltration process.

Despite extensive research, resin infiltration remains one of the primary limitations for the fabrication of TW, particularly for large or thick samples. High polymer viscosity can impede deep penetration into the wood scaffold, while incomplete infiltration can lead to microvoids, optical defects, and weak interfaces. Some of these issues can be partially mitigated through chemical modification of the cell wall, such as acetylation of hydroxyl groups, as previously mentioned. However, these strategies are still limited in their sustainability due to the chemicals involved and the lengthy process. Poor wetting of the hydrophilic cellulose matrix by most hydrophobic resins, along with the potential

deformation or degradation of the wood structure during thermal curing cycles, further complicates the process. Additionally, most polymers reported in the literature are petroleum-based, non-renewable, and exhibit low recyclability, raising concerns about the environmental sustainability of the final material. Beyond resource concerns, their use raises environmental and chemical issues. For example, bisphenol A-based epoxy resins can degrade over time or under certain processing conditions, forming potentially toxic byproducts. Similarly, many acrylate monomers, such as methyl methacrylate (MMA), are volatile and chemically reactive, posing challenges for safe handling, containment, and waste management. Incomplete polymerization or improper disposal can release unreacted monomers or other hazardous substances into the environment, contributing to pollution and complicating the development of sustainable TW composites.

Another critical aspect to consider is the sustainability and life-cycle perspective, since the environmental performance of TW cannot be assessed solely by the bio-based content of the polymer matrix. Although several Life Cycle Assessment (LCA) studies have been reported, they are often limited to specific laboratory-scale demonstrators or assume the direct scalability of batch processes without accounting for industry constraints [170,171]. In many cases, these evaluations implicitly assume that the laboratory protocol is industrially transferable, leading to scenarios characterized by a high consumption of chemical reagents and polymer resins, which are unlikely to represent continuous or semi-continuous processes based on chemical recovery and resource reuse. In particular, delignification and infiltration-based pathways often overlook the impacts of reagent recovery, resin losses, and waste streams generated during processing. The absence of closed-loop strategies for the recovery of solvents and polymers significantly affects both the environmental footprint and the economic feasibility. As a result, current LCAs may overestimate the sustainability of some laboratory-developed approaches while underestimating the challenges associated with industrialization. In addition, the adoption of bio-based polymers introduces further trade-offs that go beyond the material's origin. Polymers such as PLIMA, poly(vinyl alcohol), or cellulose acetate show promising optical performance and compatibility with cellulose-rich models; however, their long-term optical stability, moisture sensitivity, and durability under in-service conditions remain insufficiently addressed. Bio-based systems are often more susceptible to hydrolytic degradation, plasticization, or photo-induced degradation during use, which can progressively change haze and transmittance over time, potentially offsetting their initial sustainability benefits in applications requiring a long operational life. These considerations highlight that the sustainability of TW must be assessed within an integrated framework that combines optical performance, mechanical durability, process efficiency, and realistic life cycle inventories. Future studies should therefore incorporate comparative LCA and techno-economic assessments based on scalable processing scenarios, including chemical recovery, resin reuse, and long-term performance stability, rather than focusing solely on material substitution. An additional, largely neglected aspect concerns the end-of-life management of TW composites. To date, only a very limited number of studies explicitly address disposal, recycling, or reuse scenarios for TW-polymer composites [172, 173]. The intimate integration between lignocellulosic models and infiltrated polymers, while beneficial for optical and mechanical performance, poses significant challenges for material separation, recyclability, and circular reuse at the end of their operational life. In most of the systems reported, clear wood is implicitly treated as a single-use or recyclable material, with limited discussion of recovery routes or secondary applications.

Addressing end-of-life strategies, such as mechanical reuse, controlled separation, chemical recycling, or energy recovery, will be essential to fully assess the environmental sustainability of TW and align its development with the principles of the circular economy.

However, the TW model remains a promising material, with among its main advantages the exploitation and enhancement of its

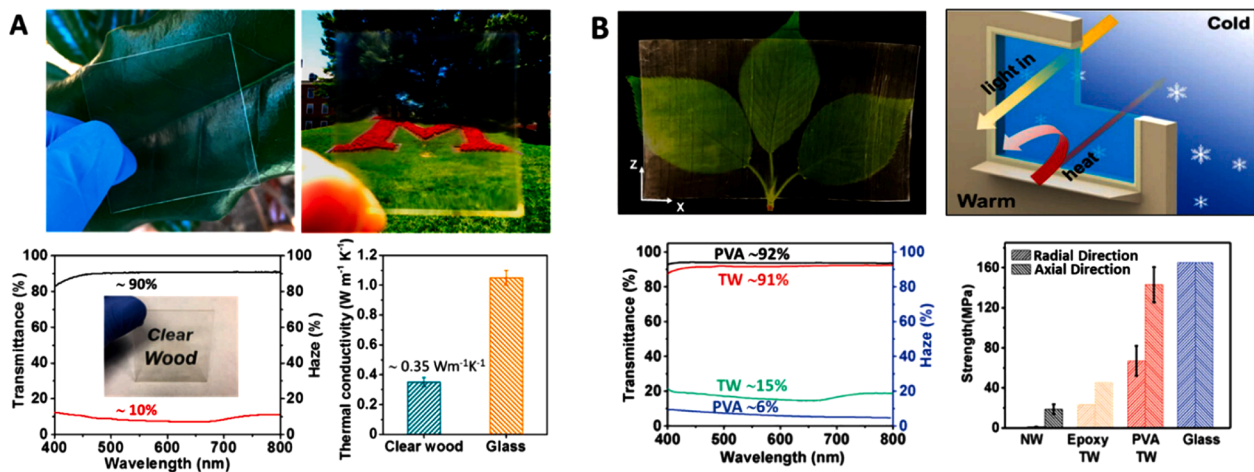


Fig. 19. A) Images of low-haze wood highlighting its optical properties and thermal conductivity. Adapted with permission from Jia et al. [22] B) Schematic illustration of the energy-saving mechanism when using low-haze transparent wood for exterior windows in cold climates, and comparison of strength and toughness among natural wood, epoxy transparent wood, and glass. Adapted with permission from Mi et al. [93].

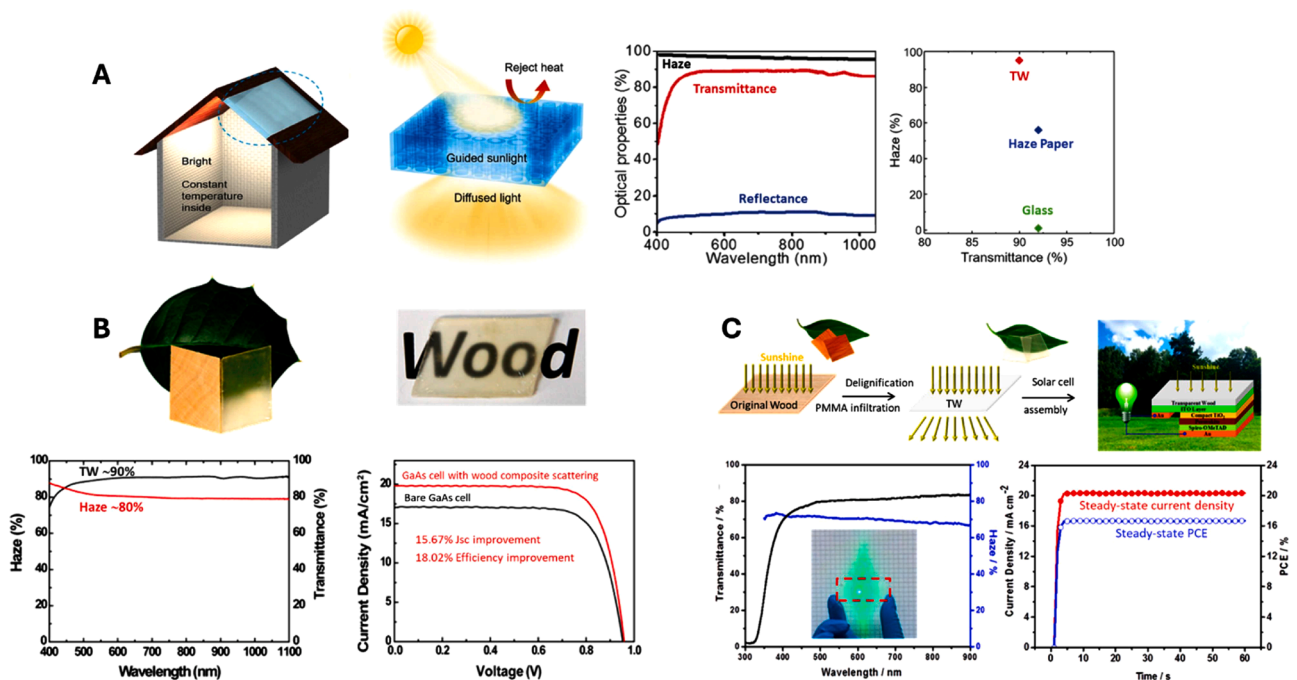


Fig. 20. A) Diffuse illumination and thermal stability of transparent wood; optical properties and haze comparison with glass and haze paper. Adapted from Li et al. [30] B) Optical properties of transparent wood and enhanced performance of a GaAs cell coated with light-managing wood compared to the bare cell. Adapted with permission from Zhu et al. [23] C) Preparation of transparent wood, solar cell integration, optical properties, and performance (power conversion efficiency at 0.82 V). Adapted with permission from Li et al. [174].

hierarchical, oriented structure, which can be modified to modulate its optical properties. In particular, as highlighted in the previous paragraphs, by controlling the orientation of the wood fibers and the architecture of the cell wall, it is possible to tune both transmittance and haze: light can propagate more directly along the fiber direction, while diffusion is enhanced in the transverse direction. This structural control not only facilitates the mechanical reinforcement of impregnating polymers but also enables the design of materials with tailor-made optical, thermal, and hydrophobic properties. By highlighting these multifunctional capabilities, the model offers a natural bridge to exploring the different applications of TW, ranging from building applications to optically functional composites.

6. Applications and functional requirements

Building on this idea, the ability to tune haze stands out as one of the most unique and adaptable characteristics of transparent materials wood. By adjusting the wood microstructure, the degree of lignin removal, or the refractive index match between the wood template and the impregnating polymer, it is possible to control light scattering and obtain a broad spectrum of optical performances. This structural tunability has opened a wide range of applications in building materials, from low-haze transparent windows to high-haze diffusive panels for energy-efficient or photonic architectures. Jia et al. [22] demonstrated one of the first examples of clear wood suitable for clear wood windows in energy-efficient buildings (Fig. 19 A), achieving high transmittance (~90% at a 1.2 mm thickness) and low haze (~10%) by infiltrating

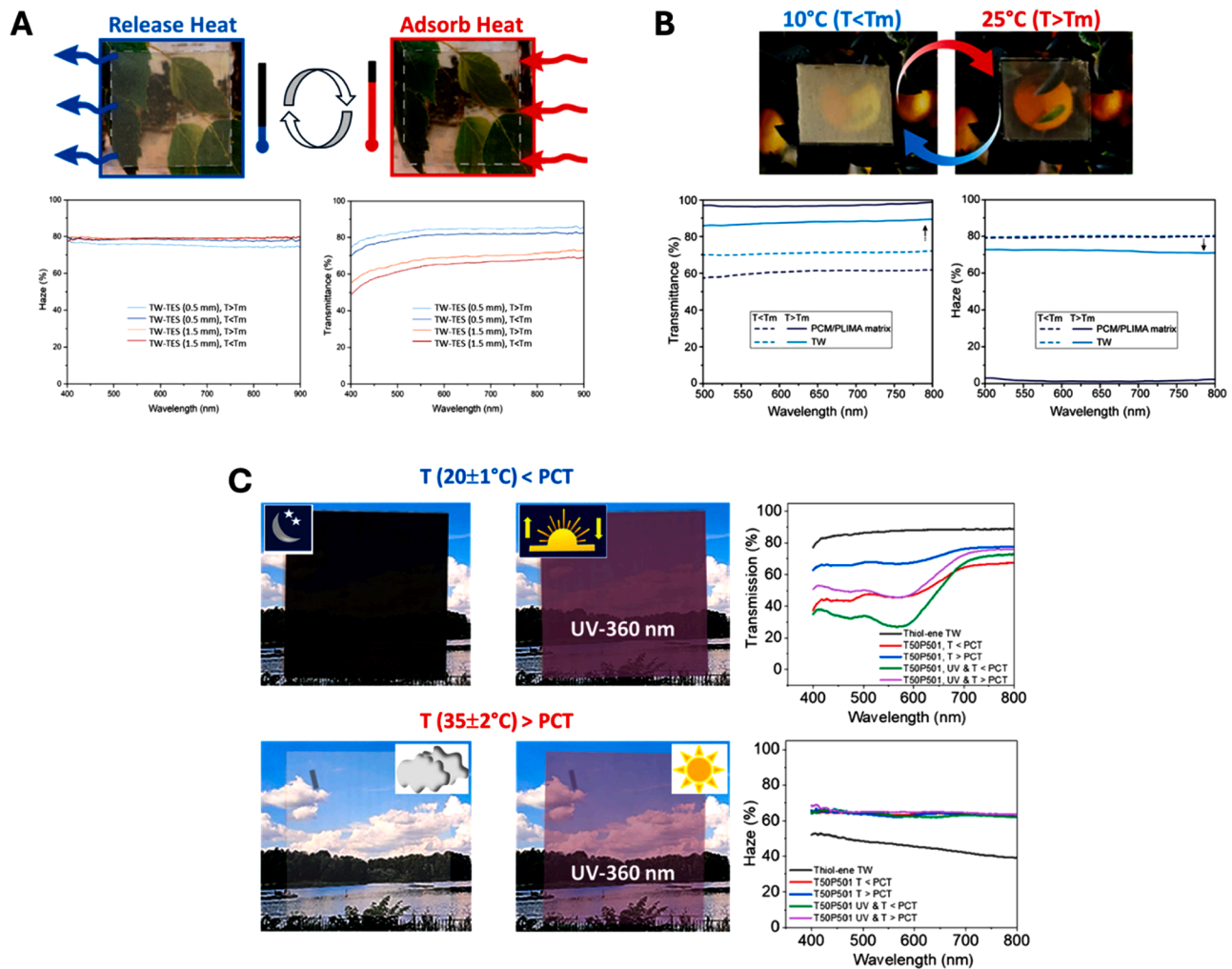


Fig. 21. A) Images showing PMMA-PEG-based TW with the transition from haze to transparency with increasing temperature and the optical properties (transmittance and haze) of samples with different thicknesses. Adapted from Montanari et al. [73] B) Photographs of the TW PCM/PLIMA-based matrix during phase transitions; transmittance can be tuned by varying the ambient temperature. Optical properties (transmittance and haze) of the phase change material (PCM) and transparent wood (TW) at temperatures above T_m and below T_c . Adapted from Montanari et al. [138] C) Optical properties and images of the sample at temperatures below (20 °C) and above (35 °C) the PCT, with or without UV exposure, showing changes in color, transparency, and haze. Adapted from Samanta et al. [175].

delignified wood with refractive index-matched PMMA. The resulting material combined optical clarity with a strength of ~ 45 MPa and a thermal conductivity of only $0.32 \text{ W m}^{-1} \text{ K}^{-1}$, outperforming glass in insulation efficiency. However, the study did not include a comprehensive characterization of UV resistance, which remains a critical issue that must be addressed before TW can be reliably used in outdoor applications. Mi et al. [93] further advanced this concept (Fig. 19 B) by fabricating a strong and thermally insulating TW, achieving transmittance values of 85% and haze levels below 15%, while maintaining high mechanical performance (flexural strength ~ 50 MPa) and reduced infrared transmittance for energy-saving window systems. Their work established TW as a promising candidate for low-energy buildings, capable of simultaneously transmitting visible light and blocking near-infrared radiation.

Li et al. [30] explored the opposite regime (Fig. 20 A) by utilizing high-haze TW for roofing elements that enable uniform light diffusion. Their composite, with an optical transmittance of around 80% and haze close to 95%, acted as an efficient daylight distributor, enabling guided sunlight transmittance and reduced glare, thus improving indoor light uniformity and energy balance. Similar high-haze architectures were exploited by Zhu et al. [23] (Fig. 20 B) and Li et al. [174] (Fig. 20 C) in photovoltaic applications. Zhu and co-workers used transparent and haze-controlled wood composites to enhance light trapping in gallium

arsenide (GaAs) solar cells, increasing the optical path length and achieving an 18.02% improvement in power conversion efficiency compared to bare devices. Li et al. employed a high-haze wood substrate for perovskite solar cells, demonstrating that diffuse light propagation within the device led to higher absorption and improved efficiency ($\sim 16.2\%$) compared to conventional glass-based cells. The scattering nature of the TW effectively prolonged photon residence time within the active layer, thus boosting photovoltaic conversion.

In addition to static haze control, dynamic optical behavior has been achieved through thermo-responsive and dual-stimuli TW systems. Montanari et al. [73] (Fig. 21 A) incorporated polyethylene glycol (PEG) as a phase-change material within the polymer matrix, creating a TW that can store thermal energy and switch between reversible transmittance states of 85% (below the melting point) and 40% (above the melting point). This concept was further developed by the same group, Montanari et al. [138], (Fig. 21 B), who created a fully bio-based TW energy battery using PEG and limonene acrylate, achieving a reversible optical transition of $\sim 50\%$ and excellent heat storage, thereby combining sustainability with smart functionality. Samanta et al. [175] (Fig. 21 C) designed dual-stimuli chromic TWs responsive to both temperature and UV irradiation, with reversible color change and transmittance modulation between 80% and 30%, enabling smart windows capable of regulating both light and heat. These materials exemplify the

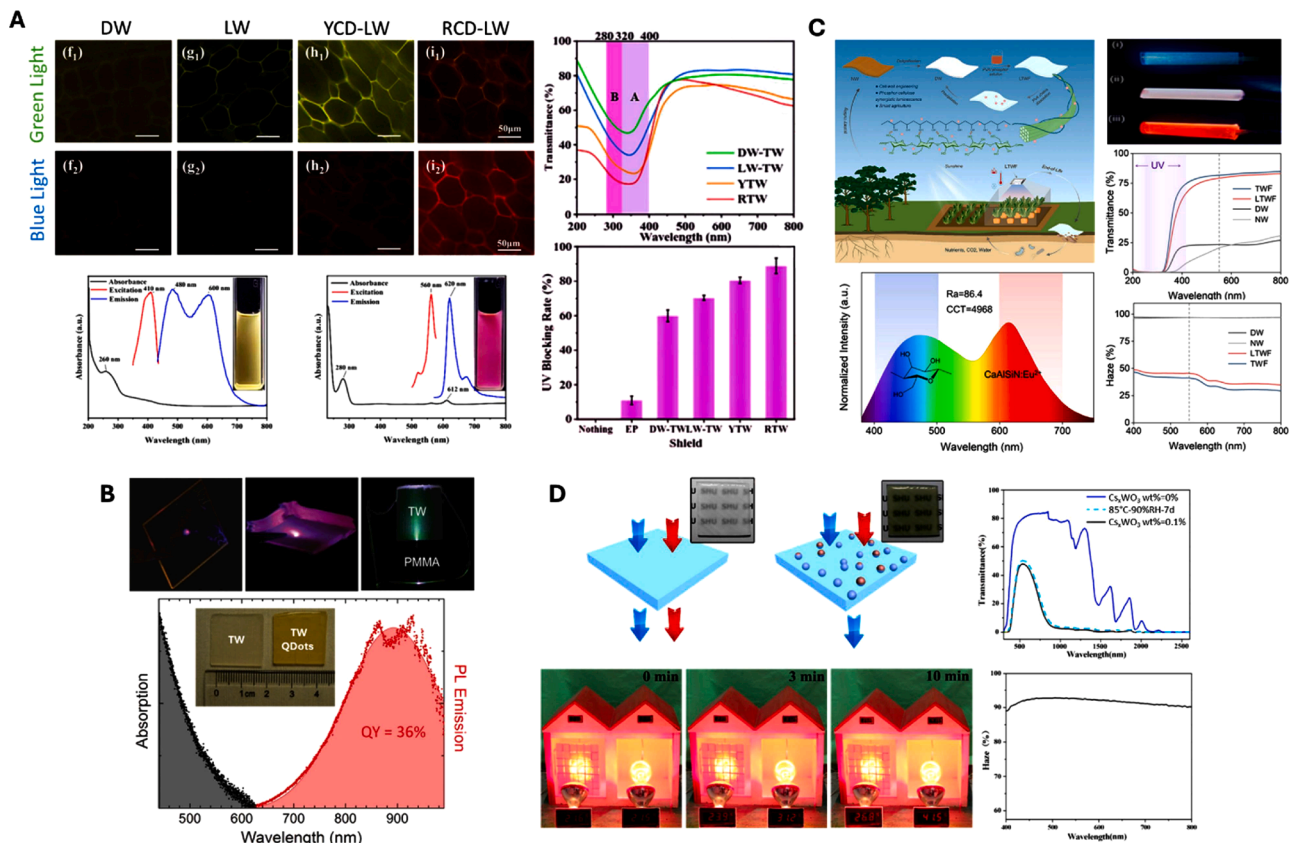


Fig. 22. A) UV–Vis absorption and fluorescence spectra of YCD (bottom left) and RCD (bottom right), and fluorescence microscopy images (blue/green light) of cross-sections of delignified wood (DW), bleached wood (LW), and LW infiltrated with YCD (YCD–LW) and RCD (RCD–LW) after 50 min capillary infiltration. Adapted with permission from Zhou et al. [26] B) Top left: Si-QDs embedded in glass under 405 nm laser excitation; center: TW incorporating Si-QDs showing homogeneous diffuse luminescence; top right: TW with CdSe-QDs integrated into a larger PMMA piece exhibiting both waveguiding and diffuse emission; bottom: absorption and PL emission spectra of Si-QD–TW in the near-infrared region. Adapted with permission from Li et al. [24] C) Top left: schematic illustration of the fabrication and application of luminescent transparent wood films (LTWF); top right: photographs of transparent wood (TW) and LTWFs exhibiting blue, white, and red emission under 365 nm UV excitation; bottom left: room-temperature photoluminescence (PL) spectra of w-LED devices encapsulated with LTWFs; bottom right: optical transmittance and haze of natural wood (NW), delignified wood (DW), transparent wood films (TWF), and luminescent transparent wood films (LTWF). Adapted with permission from Chen et al. [172] D) Top left: image of Cs_xWO_3 /transparent wood (TW) sample; top right: transmittance spectra of Cs_xWO_3 /TW (Cs_xWO_3 wt% = 0.1%) and variation of TW (Cs_xWO_3 wt% = 0%) transmittance profiles after heating under 85 °C and 90% RH; bottom right: TW haze; bottom left: model house showing temperature change under continuous simulated solar irradiation with Cs_xWO_3 /TW after 0 min (left), 3 min (center), and 10 min (right). Adapted with permission from Yu et al. [25].

potential of TW for adaptive building envelopes that autonomously react to environmental stimuli.

Functionalization with inorganic nanoparticles further expands the multifunctional landscape of TW by enabling simultaneous optical, thermal, and photonic functionalities. Zhou et al. [26] demonstrated carbon dot-embedded TW (Fig. 22 A) combining efficient ultraviolet shielding (blocking >95% of UV radiation) with thermal insulation, while maintaining high visible transmittance (~80%) and haze values around 60%, making this system particularly attractive for energy-efficient glazing applications. Li et al. [24] introduced luminescent silicon nanoparticles into the polymer matrix (Fig. 22 B), yielding a photoluminescent TW capable of converting UV radiation into visible light with a quantum yield of approximately 65%, thus enabling light-conversion functionalities suitable for optical or decorative building components. Similarly, Yu et al. [25] reported the incorporation of Cs_xWO_3 nanoparticles within PMMA (Fig. 22 D), achieving near-infrared shielding while preserving visible transparency (~75%), thereby improving both thermal comfort and structural performance.

More recently, Chen et al. [172] reported a fully recyclable luminescent TW film incorporating inorganic phosphor nanoparticles (Fig. 22 C), which enables a bifunctional platform combining color-tunable wavelength conversion under UV excitation with optical

temperature sensing. As illustrated in the figure, these Luminescent Transparent Wood Films (LTWF) exhibit high visible transmittance and controlled haze, as well as stable photoluminescence spectra suitable for plant growth lighting. Importantly, thin-film architectures significantly reduce optical losses associated with bulk scattering while maintaining sufficient mechanical integrity for handling and integration in thermal sensor systems. In addition, the LTWF is recyclable, biodegradable, and can be converted into plant nutrients, supporting a closed-loop, sustainable system for smart agriculture.

All these studies highlight that nanoparticle functionalization enables TW systems with high optical efficiency, multifunctional light management, and enhanced energy performance. At the same time, key challenges remain in long-term durability, photostability, and nanoparticle dispersion uniformity, particularly under prolonged UV exposure and in humid environments. Addressing these aspects, along with scalable processing and environmental compatibility of inorganic additives, will be essential to translate nanoparticle-functionalized TW from laboratory demonstrations to reliable, long-term applications in building and optoelectronic systems.

Ultimately, an increasing amount of research focuses on aesthetic TW for architectural uses, emphasizing diffuse light transmission and visual appeal rather than absolute optical clarity.

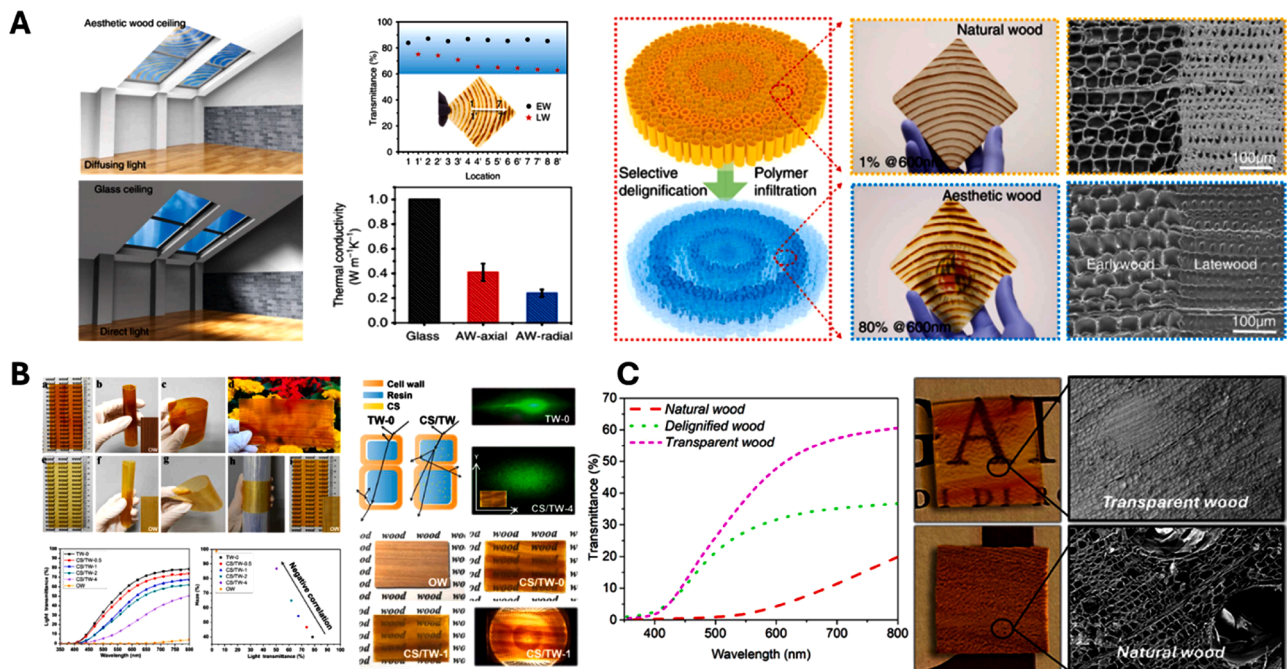


Fig. 23. A) Left: schematic illustration of light distribution and aesthetic performance in a building using aesthetic wood (AW); center: optical transmittance of earlywood (EW) and latewood (LW) regions (positions 1–8 and 1'–8', respectively) and comparison of thermal conductivity between glass and AW along axial and radial directions; right: fabrication scheme of aesthetic wood, cross-sectional SEM images of natural wood and polymer-filled dense aesthetic wood-R showing the EW/LW boundary, and photograph of a large-scale aesthetic wood-R panel derived from Douglas fir. Adapted from Miet et al. [139] B) Top left: logs and corresponding transparent wood samples from multiple tree species (cedar on top, basswood on bottom), prepared with chitosan contents of 1–2%; bottom left: optical transmittance and haze of original wood (OW), transparent wood without chitosan (TW-0), and chitosan-modified transparent wood with increasing chitosan content (CS/TW-0.5, CS/TW-1, CS/TW-2, CS/TW-4); top right: laser scattering patterns of TW-0 and CS/TW-4; bottom right: photographs showing the visual appearance of TW-0 and CS/TW samples. Request with permission from Zhou and Xu [176] C) Optical transmittance of natural paulownia wood, delignified wood, and transparent wood, together with photographs at natural scale and SEM microstructural comparison between transparent wood and the corresponding natural wood. Reproduced from Bolognesi et al. [177].

In the work by Mi et al. [139] (Fig. 23 A) spatially selective delignification was employed to preserve earlywood-latewood contrast and natural growth-ring patterns. After polymer infiltration, the resulting aesthetic TW exhibited a high average visible transmittance of ~80% at 600 nm, with locally higher transmittance in earlywood (~86%) than in latewood (~68%). In addition to optical performance, this material showed good mechanical integrity and low thermal conductivity (~0.24 W m⁻¹ K⁻¹ in the radial direction), making it attractive for energy-efficient architectural elements such as patterned ceilings and interior panels.

Furthermore, Zhou and Xu [176] demonstrated that controlled incorporation of chitosan into the polymer matrix enabled the production of TW panels with tunable transmittance and haze (Fig. 23 B). At 550 nm, optical transmittance increased by up to ~50% compared to the original wood, then decreased with increasing chitosan content. Higher chitosan concentrations led to increased opacity, reaching haze values of ~87%, while maintaining near-zero transmittance in the 200–400 nm range, thus providing effective UV shielding. These properties make aesthetic TW suitable for applications requiring privacy, diffuse daylighting, and UV protection. Moreover, the addition of chitosan was shown to suppress the anisotropic scattering observed in pristine TW by enhancing interfacial filling and light diffusion.

A complementary strategy reported by Bolognesi et al. [177], in Fig. 23 C, where aesthetic TW was fabricated from paulownia wood. For 1 mm thick samples, optical transmittance reached ~60% at 800 nm (~50% at 600 nm) for longitudinal sections, while transversely cut samples exhibited lower values (~20% at 800 nm), highlighting the combined influence of wood species, cutting direction, and residual lignin content. More broadly, this study situates aesthetic TW within the typical transparency window of most TW systems, where transmittance commonly ranges between 60% and 85%.

Overall, these studies establish aesthetic TW as a distinct application class, in which controlled haze, spatially heterogeneous transmittance, and preserved wood textures enable diffuse light management, privacy, and visual appeal, while offering thermal insulation and mechanical performance superior to conventional glass-based solutions.

Collectively, these studies demonstrate how the tunable haze of TW, including low-haze, high-haze, luminescent, and aesthetic TW systems, serves as the key parameter enabling its adaptation to diverse architectural scenarios. From transparent panels that maximize daylight transmission, to high-haze diffusive or photothermal structures for energy harvesting and comfort regulation, and to aesthetic TW where visual appearance and privacy are prioritized, the intrinsic anisotropy of wood provides a unique natural scaffold for the development of multifunctional building materials. At the same time, translating these laboratory-scale demonstrations into reliable, scalable products requires addressing challenges in process control, standardization, and industrial implementation, which are discussed in the following section.

7. Bridging laboratory-scale development and industrial applications of transparent wood

Despite significant progress at the laboratory scale, transitioning TW from proof-of-concept demonstrations to industrially viable materials remains a critical challenge. As discussed in [Section 5](#) (“Limitations and Bottlenecks”), many reported fabrication routes rely on batch processing, simplified assumptions about reagent consumption, and long template modification and polymerization times. While these approaches are suitable for fundamental studies, they do not fully reflect industrial constraints. Bridging this gap requires a systematic evaluation of how material design, processing strategies, and testing protocols evolve from laboratory-scale development toward scalable production.

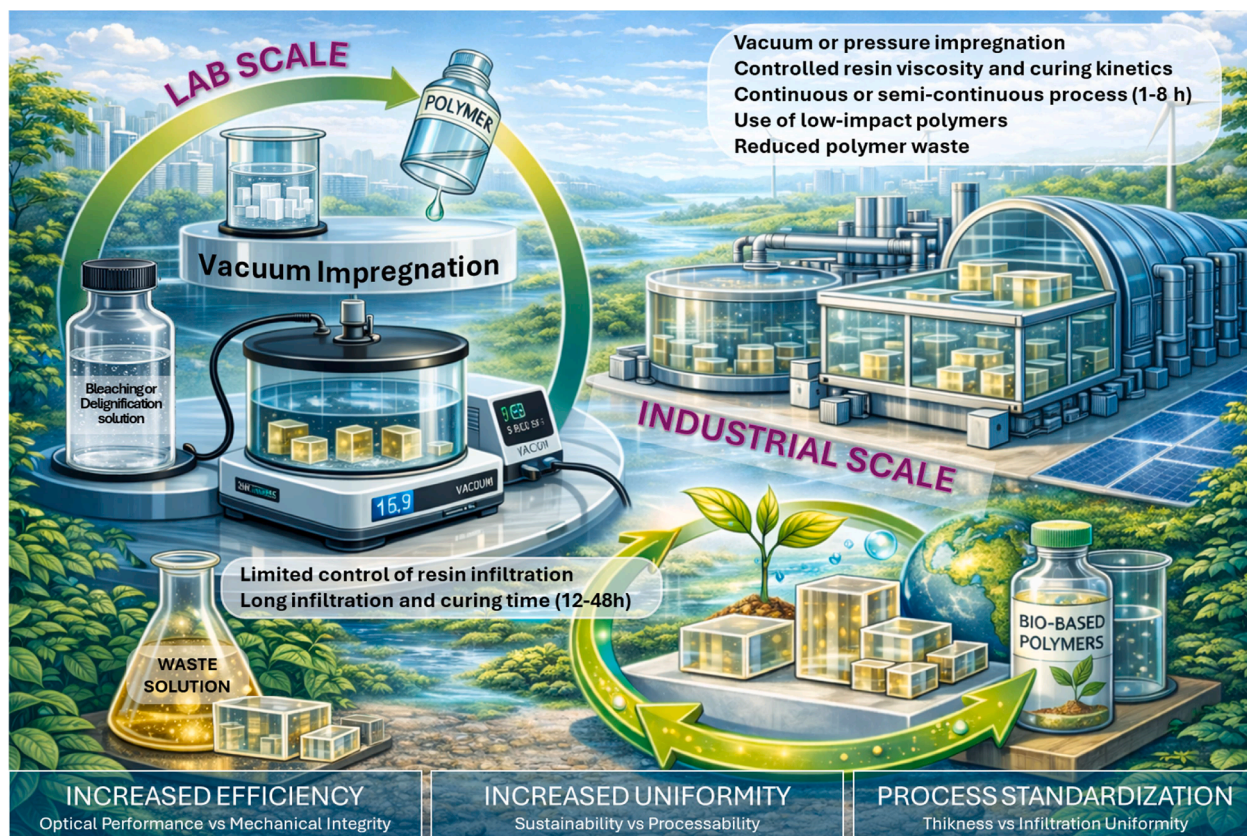


Fig. 24. Illustrative comparison between laboratory-scale and industrial-scale impregnation processes for transparent wood fabrication. The figure highlights key challenges related to scalability, uniformity, sustainability, and process standardization. Conceptual illustration partially generated using artificial intelligence and subsequently modified by the authors.

Fig. 24 schematically compares laboratory-scale and industrial-scale impregnation processes for TW fabrication. At the laboratory scale, production typically relies on batch vacuum impregnation, limited control over resin infiltration, and curing times ranging from several hours to days. These conditions often result in infiltration gradients and thickness-dependent variability. In contrast, industrial implementation requires combined vacuum-pressure impregnation systems, precise control over resin viscosity and curing kinetics, and continuous or semi-continuous operation. Importantly, industrial processes must integrate chemical recovery and resource reuse to reduce environmental impact and ensure economic feasibility, aspects that are often overlooked in laboratory-scale studies.

This evolution from laboratory to industrial scale is summarized in Table 4, which compares the main equipment, processing steps, and testing protocols currently employed at laboratory scale with those required or adaptable for industrial production. Although industrial impregnation technologies already exist and could be partially repurposed for the fabrication of TW, several bottlenecks remain. Among these, the development of infiltration gradients in thick panels represents a major limitation, as incomplete resin penetration directly affects both optical uniformity and mechanical integrity. In addition, curing kinetics often conflict with industrial throughput: polymers that exhibit excellent optical performance at laboratory scale frequently require processing times incompatible with continuous manufacturing.

Standardization of testing protocols represents an additional challenge. Optical properties are commonly measured according to ASTM D1003–21, which is widely adopted in both academic and industrial contexts; however, variations in sample thickness, surface finish, and measurement geometry can still compromise direct comparability. Mechanical testing is even less standardized: while wood-based standards such as ISO 13,061–6 are suitable for evaluating the mechanical

behavior of white wood templates, composite-oriented standards must be adapted to account for the hybrid nature of polymer-infiltrated TW. Moreover, standardized protocols for humidity exposure, UV aging, and long-term durability are largely absent for this emerging class of materials. Existing plastic standards are often overly stringent, whereas wood standards may underestimate degradation phenomena in polymer-modified systems.

Within this framework, a roadmap toward industrially relevant TW applications can be defined by linking wood preparation strategies to targeted optical regimes. Highly delignified hardwood templates, which offer low haze and high transmittance, are best suited for applications where optical clarity is the primary requirement. Selectively bleached, lignin-retaining systems enable mechanically stable, high-haze materials compatible with a wider range of wood species and are therefore more suitable for scalable, load-bearing, or light-diffusing applications. Given the current level of technological maturity, high-haze TW for photovoltaic substrates, daylighting panels, and translucent interior elements represents one of the most promising early industrialization scenarios, as these applications tolerate moderate thickness and benefit from optical diffusion combined with mechanical robustness.

Furthermore, this analysis highlights the need for future comparative studies explicitly designed around industrially relevant constraints, including systematic investigations on softwood species and on blended or partially bio-based polymer systems under standardized processing and testing conditions. Such studies are essential to close current data gaps and to enable predictive material-process optimization beyond laboratory-scale demonstrations.

Overall, these considerations indicate that successful industrialization of TW requires integrated design rules that simultaneously address material chemistry, microstructure, process scalability, and standardized testing. Moving beyond isolated laboratory optimization toward

Table 4

Comparison between laboratory-scale and industrial-scale requirements for transparent wood fabrication, including equipment, processing steps, and testing protocols.

Aspect	Laboratory scale	Industrial/pre-industrial scale	Status
Wood preparation	Small samples, batch bleaching/delignification	Continuous or semi-continuous treatment, chemical recovery	Adaptation required
Impregnation equipment	Vacuum chamber, batch process	Vacuum implant mimics the composite existing technologies, pressure autoclaves, roll-to-roll, or panel-based systems	Existing (to be adapted)
Resin viscosity control	Manual tuning, long curing times	Inline viscosity control, kinetic matching with throughput	To be implemented
Curing strategy	Thermal curing (12–48 h)	Accelerated curing (UV/RT/dual cure)	To be optimized
Thickness control	≤3–5 mm typical	Up to 10 mm panels with uniform infiltration	Major bottleneck
Chemical recovery	Rarely implemented	Mandatory for sustainability and cost	To be developed
Optical testing	ASTM D1003–21 (lab conditions)	ASTM D1003–21 with thickness and geometry normalized protocols	Partial
Mechanical testing (template)	ISO 13,061–6 (wood specimens)	ISO 13,061–6 adapted to treated templates	Available
Mechanical testing (composites)	Adapted wood or plastic standards	Composite-oriented ASTM/ISO standards to be tailored	To be adapted
Humidity/aging tests	Wood or plastic standards	New hybrid protocols are required	Missing
UV/weathering tests	Sporadic, non-uniform	Accelerated aging (ISO/ASTM) adapted to TW	Missing

material–process co-design is therefore essential to translate TW from a laboratory curiosity into a viable industrial material platform.

8. Conclusion and future perspectives

This review highlights that TW is not a single material concept, but a design space defined by trade-offs between optical transparency, light scattering, mechanical integrity, and processability. The optical response of TW emerges from the coupled effects of wood anisotropy, cellulose volume fraction, lignin modification, cell-wall accessibility, and polymer infiltration, rather than from refractive-index matching alone. As a result, similar transmittance values reported in the literature may originate from fundamentally different light-transport regimes, with distinct implications for haze, thickness scalability, and mechanical performance. Moreover, direct comparisons of optical properties are often complicated by differences in measurement standards, geometries, and experimental setups, as transmittance and haze are not always evaluated using the same protocols, underscoring the need for caution when benchmarking reported values.

Delignification and selective bleaching should therefore be regarded as complementary strategies rather than competing routes. While aggressive delignification enables low-haze, high-transparency materials suitable for photonic or optoelectronic applications, lignin-retaining and selectively bleached systems offer superior mechanical stability, higher haze, and greater scalability, making them more appropriate for architectural, photovoltaic, and light-diffusing applications. Likewise, cell-wall functionalization, swelling, densification, and polymer filling should be viewed as interconnected design tools that must be balanced to achieve targeted relationships among structure, properties, and processing.

From a sustainability perspective, this review emphasizes that the environmental performance of TW cannot be assessed solely on the basis of its bio-based content. Realistic life-cycle and techno-economic evaluations must account for chemical recovery, resin losses, durability, and end-of-life scenarios, which remain largely unexplored. Developing fully bio-based, recyclable resins represents a key step toward sustainable, high-performance TW composites, but must be accompanied by process scalability, long-term stability, and standardized testing.

Ultimately, the development of TW as a practical, eco-friendly alternative to glass will rely on integrating green chemistry, materials engineering, and architectural design into a unified, truly transparent vision of the future.

CRediT authorship contribution statement

Francesca Gullo: Writing – review & editing, Writing – original draft, Conceptualization. **Massimo Messori:** Writing – review & editing, Validation, Supervision. **Paola Palermo:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

References

- [1] T. Farid, M. Imran Rafiq, A. Ali, W. Tang, Transforming wood as next-generation structural and functional materials for a sustainable future, *EcoMat.* 4 (1) (2022) e12154.
- [2] S. He, X. Zhao, E.Q. Wang, G.S. Chen, P. Chen, L. Hu, Engineered wood: sustainable technologies and applications, *Annu. Rev. Mater. Res.* 53 (1) (2023) 195–223.
- [3] İlker, Usta, The value and functionality of wood as a sustainable and inexhaustible renewable natural material, in: The 29th International Conference Research For Furniture Industry, Ankara, Turkey, 2019, pp. 233–239. 19–20 September 2019 *Proceedings Book*.
- [4] C. Montanari, P. Olsén, L.A. Berglund, Sustainable wood nanotechnologies for wood composites processed by in-situ polymerization, *Front. Chem.* 9 (2021) 682883.
- [5] H. Zhu, W. Luo, P.N. Ciesielski, Z. Fang, J.Y. Zhu, G. Henriksson, M.E. Himmel, L. Hu, Wood-derived materials for green electronics, biological devices, and energy applications, *Chem. Rev.* 116 (16) (2016) 9305–9374.
- [6] M. Zhu, J. Song, T. Li, A. Gong, Y. Wang, J. Dai, Y. Yao, W. Luo, D. Henderson, L. Hu, Highly anisotropic, Highly transparent wood composites, *Adv. Mater.* 28 (26) (2016) 5181–5187, <https://doi.org/10.1002/adma.201600427>.
- [7] Y. Li, Q. Fu, X. Yang, L. Berglund, Transparent wood for functional and structural applications, *Philos. Trans. R. Soc. A* 376 (2112) (2018) 20170182.
- [8] Y. Li, E. Vasileva, I. Sychugov, S. Popov, L. Berglund, Optically Transparent Wood: recent progress, opportunities, and challenges, *Adv. Opt. Mater.* 6 (14) (2018) 1800059.
- [9] Siegfried. Fink, Transparent wood – A new approach in the functional study of wood structure, *Holzforschung.* 46 (5) (1992) 403–408, <https://doi.org/10.1515/hfsg.1992.46.5.403>.
- [10] Y. Li, Q. Fu, S. Yu, M. Yan, L. Berglund, Optically transparent wood from a nanoporous cellulosic template: combining functional and structural performance, *Biomacromolecules.* 17 (4) (2016) 1358–1364, <https://doi.org/10.1021/acs.biomac.6b00145>.
- [11] C. Chen, Y. Kuang, S. Zhu, I. Burgert, T. Keplinger, A. Gong, T. Li, L. Berglund, S. J. Eichhorn, L. Hu, Structure–Property–Function relationships of natural and

- engineered wood, *Nat. Rev. Mater.* 5 (9) (2020) 642–666, <https://doi.org/10.1038/s41578-020-0195-z>.
- [12] Y. Ding, Z. Pang, K. Lan, Y. Yao, G. Panzarasa, L. Xu, M. Lo Ricco, D.R. Rammer, J. Y. Zhu, M. Hu, Emerging engineered wood for building applications, *Chem. Rev.* 123 (5) (2022) 1843–1888.
 - [13] D. Sandberg, G. Gorbacheva, H. Lichtenegger, P. Niemz, A. Teischinger, Advanced engineered wood-material concepts. Springer Handbook of Wood Science and Technology, Springer, 2023, pp. 1835–1888.
 - [14] C. Montanari, P. Olsén, L.A. Berglund, Interface tailoring by a versatile functionalization platform for nanostructured wood biocomposites, *Green Chem.* 22 (22) (2020) 8012–8023, <https://doi.org/10.1039/D0GC02768E>.
 - [15] Y. Li, Q. Fu, R. Rojas, M. Yan, M. Lawoko, L. Berglund, Lignin-retaining transparent wood, *ChemSusChem*. 10 (17) (2017) 3445–3451, <https://doi.org/10.1002/cssc.201701089>.
 - [16] F. Gullo, M. Messori, P. Palmero, Preservation of wood structure using stabilized alkaline bleaching agents: A novel and mild approach to enhance whitening for lignin-rich wood template, *Wood. Sci. Technol.* 60 (1) (2026) 12, <https://doi.org/10.1007/s00226-025-01725-8>.
 - [17] Q. Xia, C. Chen, T. Li, S. He, J. Gao, X. Wang, L. Hu, Solar-assisted fabrication of large-scale, patternable transparent wood, *Sci. Adv.* 7 (5) (2021) eabd7342, <https://doi.org/10.1126/sciadv.abd7342>.
 - [18] L. Hu, M. Zhu, T. Li, A.S. Gong, J. Song, Transparent Wood Composite, Systems and Method of Fabrication, Google Patents, 2024.
 - [19] S. Wang, L. Li, L. Zha, S. Koskela, L.A. Berglund, Q. Zhou, Wood Xerogel for fabrication of high-performance transparent Wood, *Nat. Commun.* 14 (1) (2023) 2827.
 - [20] L. Antony, A. Giuri, S. Bruno, S. Pal, S. Carallo, I. Tarantini, A. Licciulli, M. Pugliese, V. Maiorano, C.E. Corcione, Fully plant-based and optically transparent wood substrates with improved thermal insulating properties, *Adv. Sustain. Syst.* (2025) e00564.
 - [21] C. Montanari, Y. Ogawa, P. Olsén, L.A. Berglund, High performance, fully Bio-based, and optically transparent wood biocomposites, *Adv. Sci.* 8 (12) (2021) 2100559.
 - [22] C. Jia, C. Chen, R. Mi, T. Li, J. Dai, Z. Yang, Y. Pei, S. He, H. Bian, S. Jang, Clear wood toward high-performance building materials, *ACS. Nano* 13 (9) (2019) 9993–10001.
 - [23] M. Zhu, T. Li, C.S. Davis, Y. Yao, J. Dai, Y. Wang, F. AlQatari, J.W. Gilman, L. Hu, Transparent and haze wood composites for highly efficient broadband light management in solar cells, *Nano Energy* 26 (2016) 332–339, <https://doi.org/10.1016/j.nanoen.2016.05.020>.
 - [24] Y. Li, S. Yu, J.G. Veinot, J. Linnros, L. Berglund, I. Sychugov, Luminescent transparent wood, *Adv. Opt. Mater.* 5 (1) (2017).
 - [25] Z. Yu, Y. Yao, J. Yao, L. Zhang, Z. Chen, Y. Gao, H. Luo, Transparent wood containing Cs x WO 3 nanoparticles for heat-shielding window applications, *J. Mater. Chem. A* 5 (13) (2017) 6019–6024.
 - [26] N. Zhou, S. Long, D. Song, B. Hui, X. Cui, C. An, M. Zhang, Fabrication of carbon dots-embedded luminescent transparent wood with ultraviolet blocking and thermal insulating capacities towards smart window application, *Int. J. Biol. Macromol.* 259 (2024) 129358.
 - [27] X. Hu, R. Yu, F. Wang, Z. Liu, H. Yang, C. Chen, Y. Li, N. Noor, B. Fei, Fabrication, functionalities and applications of transparent wood: A review, *Adv. Funct. Mater.* 33 (37) (2023) 2303278.
 - [28] J. Li, C. Chen, J.Y. Zhu, A.J. Ragauskas, L. Hu, In situ wood delignification toward sustainable applications, *Acc. Mater. Res.* 2 (8) (2021) 606–620.
 - [29] S. Zhu, S. Kumar Biswas, Z. Qiu, Y. Yue, Q. Fu, F. Jiang, J. Han, Transparent wood-based functional materials via a top-down approach, *Prog. Mater. Sci.* 132 (2023) 101025.
 - [30] T. Li, M. Zhu, Z. Yang, J. Song, J. Dai, Y. Yao, W. Luo, G. Pastel, B. Yang, L. Hu, Wood composite as an energy efficient building material: guided sunlight transmittance and effective thermal insulation, *Adv. Energy Mater.* 6 (22) (2016) 1601122, <https://doi.org/10.1002/aenm.201601122>.
 - [31] Y. Li, X. Yang, Q. Fu, R. Rojas, M. Yan, L. Berglund, Towards centimeter thick transparent wood through interface manipulation, *J. Mater. Chem. A* 6 (3) (2018) 1094–1101, <https://doi.org/10.1039/C7TA09973H>.
 - [32] L. Chen, Z. Xu, F. Wang, G. Duan, W. Xu, G. Zhang, H. Yang, J. Liu, S. Jiang, A flame-retardant and transparent wood/polyimide composite with excellent mechanical strength, *Compos. Commun.* 20 (2020) 100355.
 - [33] L. Ding, X. Han, L. Chen, S. Jiang, Preparation and properties of hydrophobic and transparent wood, *J. Bioresources Bioproducts* 7 (4) (2022) 295–305.
 - [34] Y. Du, S. Liu, Y. Li, X. Chen, T.C. Ho, L.C. Chao, C.Y. Tso, Perovskite-coated thermochromic transparent wood: A novel material for smart windows in energy-efficient and sustainable buildings, *ACS. Appl. Mater. Interfaces*. 15 (42) (2023) 49665–49677.
 - [35] J. Wu, Y. Shi, X. Wen, W. Zhang, D. Zhao, L. Liu, J. Duan, Ultraviolet-shielded transparent wood with improved interface for insulating windows, *ACS. Appl. Mater. Interfaces*. 17 (2) (2024) 3866–3875.
 - [36] X. Piao, T. Wang, X. Chen, G. Wang, X. Zhai, K. Zhang, Room-temperature phosphorescent transparent wood, *Nat. Commun.* 16 (1) (2025) 868.
 - [37] P. Fratzl, R. Weinkamer, Nature's hierarchical materials, *Prog. Mater. Sci.* 52 (8) (2007) 1263–1334.
 - [38] L.J. Gibson, M.F. Ashby, B.A. Harley, Cellular Materials in Nature and Medicine, Cambridge University Press, 2010.
 - [39] S. Ling, D.L. Kaplan, M.J. Buehler, Nanofibrils in nature and materials engineering, *Nat. Rev. Mater.* 3 (4) (2018) 1–15.
 - [40] M.A. Meyers, P. Chen, A.Y. Lin, Y. Seki, Biological materials: structure and mechanical properties, *Prog. Mater. Sci.* 53 (1) (2008) 1–206.
 - [41] Eero. Sjöström, Wood Chemistry: Fundamentals and Applications, Gulf professional publishing, 1993.
 - [42] A.J. Stamm, The dimensional stability of wood, *For. Prod. J.* 9 (10) (1959) 375–381.
 - [43] E.E. Thybring, M. Fredriksson, Wood modification as a tool to understand moisture in Wood, *Forests*. 12 (3) (2021) 372.
 - [44] M.U. Khan, M. Usman, M.A. Ashraf, N. Dutta, G. Luo, S. Zhang, A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas production: opportunities and limitations, *Chem. Eng. J. Adv.* 10 (2022) 100263.
 - [45] A. Rafsanjani, M. Stiefel, K. Jefimovs, R. Mokso, D. Derome, J. Carmeliet, Hygroscopic swelling and shrinkage of latewood cell wall micropillars reveal ultrastructural anisotropy, *J. R. Soc. Interf.* 11 (95) (2014) 20140126.
 - [46] M.S. Doblin, F. Pettolino, A. Bacic, Plant cell walls: the skeleton of the Plant world, *Funct. Plant Biol.* 37 (5) (2010) 357–381.
 - [47] H. Nishimura, A. Kamiya, T. Nagata, M. Katahira, T. Watanabe, Direct evidence for α ether linkage between lignin and carbohydrates in wood cell walls, *Sci. Rep.* 8 (1) (2018) 6538.
 - [48] R.F. Service, Biofuel Researchers Prepare to Reap a New Harvest, American Association for the Advancement of Science, 2007.
 - [49] C. Somerville, H. Youngs, C. Taylor, S.C. Davis, S.P. Long, Feedstocks for Lignocellulosic biofuels, *Science* 329 (5993) (2010) 790–792.
 - [50] Lloyd. Donaldson, Microfibril angle: measurement, variation and relationships—a review, *IAWA J.* 29 (4) (2008) 345–386.
 - [51] C. Plomion, G. Leprovost, A. Stokes, Wood formation in trees, *Plant Physiol.* 127 (4) (2001) 1513–1523.
 - [52] D. Fengel, G. Wegener, Wood: Chemistry, Ultrastructure, Reactions, Walter de Gruyter, 2011.
 - [53] M. Zauer, A. Pfriem, A. Wagenführ, Toward improved understanding of the cell-wall density and porosity of wood determined by gas pycnometry, *Wood. Sci. Technol.* 47 (6) (2013) 1197–1211.
 - [54] O. Bouriaud, J.M. Leban, D. Bert, C. Deleuze, Intra-annual variations in climate influence growth and wood density of Norway spruce, *Tree Physiol.* 25 (6) (2005) 651–660.
 - [55] B.G. Butterfield, B.A. Meylan, The structure of softwoods. Three-dimensional Structure of wood: An Ultrastructural Approach, Springer, 1980, pp. 28–47.
 - [56] D.G. Hepworth, J.F. Vincent, G. Stringer, G. Jeronimidis, Variations in the morphology of wood structure can explain why hardwood species of similar density have very different resistances to impact and compressive loading, *Philos. Trans. R. Soc. London Ser. A* 360 (1791) (2002) 255–272.
 - [57] Panshin, A.J., and C. de Zeeuw. 1981. *Textbook of Wood Technology*.
 - [58] M. Borrega, P. Ahvenainen, R. Serimaa, L. Gibson, Composition and structure of balsa (Ochroma Pyramidale) wood, *Wood. Sci. Technol.* 49 (2) (2015) 403–420.
 - [59] E. Jang, C. Kang, Porosity analysis of three types of balsa (Ochroma Pyramidale) wood depending on density, *J. Wood Sci.* 68 (1) (2022) 31.
 - [60] J. Kawabe, M. Mori, Longitudinal air permeability in fifteen wood species, *J. Soc. Mater. Sci.* 30 (334) (1981) 666–672, <https://doi.org/10.2472/jms.30.666>. Japan.
 - [61] B. Šilinskis, I. Varnagiryte-Kabasišienė, L. Beniusienė, M. Aleinikovas, M. Škema, V. Baliuckas, Evaluation of mechanical wood properties of silver birch (Betula Pendula L. Roth.) of half-sib genetic families, *Forests*. 15 (5) (2024) 845.
 - [62] Z. Zhu, F. Lv, J. Lv, R. Huang, C. Mao, Y. Cai, W. Cheng, A. Sánchez-Ferrer, J. Zhao, Modelling and validation of wood permeability: combining fractal theory with mercury intrusion porosimetry method, *Wood. Sci. Technol.* 59 (5) (2025) 79.
 - [63] J. Pokki, V.V. Laakso, P. Tikka, J. Aittamaa, Specific permeability of wood to water part 2: perpendicular Specific permeability of steamed, impregnated, and kraft-cooked wood, *Ind. Eng. Chem. Res.* 49 (5) (2010) 2155–2160.
 - [64] M. Bao, X. Huang, M. Jiang, W. Yu, Y. Yu, Effect of thermo-hydro-mechanical densification on microstructure and properties of Poplar wood (Populus Tomentosa), *J. Wood Sci.* 63 (6) (2017) 591–605.
 - [65] Scholz, G., M. Zauer, J. Van den Bulcke, D. Van Loo, A. Pfriem, J. Van Acker, and H. Militz. 2010. "Investigation on wax-impregnated wood. Part 2: study of void spaces filled with air by He pycnometry, Hg intrusion porosimetry, and 3D X-ray imaging".
 - [66] H.R. Taghiyari, A. Karimi, D. Parsapajouh, K. Pourtahmasi, Study on the longitudinal gas permeability of juvenile wood and mature wood, *Special Topics Rev. Porous Media* 1 (1) (2010) 31–38, <https://doi.org/10.1615/specialtopicsrevporousmedia.v1.i1.30>.
 - [67] A. Milks, J. Lehmann, D. Leder, M. Sietz, T. Koddenberg, U. Böhner, V. Wachtendorf, T. Terberger, A double-pointed wooden throwing stick from Schöningen, Germany: results and new insights from a multianalytical study, *PLoS. One* 18 (7) (2023) e0287719.
 - [68] M. Plötze, P. Niemz, Porosity and pore size distribution of different wood types as determined by mercury intrusion porosimetry, *Eur. J. Wood Wood Products* 69 (4) (2011) 649–657.
 - [69] R.W. Rice, M. D'Onofrio, Wood Fiber Sci., "longitudinal gas permeability measurements from Eastern White pine, Red Spruce Balsam Fir (1996) 301–308.
 - [70] Y. Tsapko, N. Buisiukh, R. Likhnyovskiy, O. Horbachova, A. Tsapko, S. Mazurchuk, A. Matviichuk, M. Sukhanevych, Establishing regularities in the application of dry pine wood, *Eastern-Eur. J. Enterprise Technol.* 4 (118) (2022) 51–59, <https://doi.org/10.15587/1729-4061.2022.262203>, 10.
 - [71] Y. Liu, B. Li, W. Mao, W. Hu, G. Chen, Y. Liu, Z. Fang, Strong cellulose-based materials by coupling sodium hydroxide–Anthraquinone (NaOH–AQ) pulping with hot pressing from wood, *ACS. Omega* 4 (4) (2019) 7861–7865.
 - [72] A. García-Iruela, L.G. Esteban, F.G. Fernández, Paloma de Palacios, A. B. Rodríguez-Navarro, R. Martín-Sampedro, M.E. Eugenio, Effect of vacuum/

- pressure cycles on cell wall composition and structure of poplar wood, *Cellulose* 26 (16) (2019) 8543–8556.
- [73] C. Montanari, Y. Li, H. Chen, M. Yan, L.A. Berglund, Transparent wood for thermal energy storage and reversible optical transmittance, *ACS. Appl. Mater. Interfaces*. 11 (22) (2019) 20465–20472, <https://doi.org/10.1021/acsaami.9b05525>.
- [74] A. Rodríguez-García, J.A. Martín, L. Gil, M. Menéndez-Gutiérrez, R. Díaz, Resin canal traits variation in *Pinus* spp. With different susceptibility to the pine wood nematode, *Forests*. 14 (5) (2023) 925.
- [75] G.L. Comstock, Directional permeability of softwoods, *Wood Fiber Sci.* (1970) 283–289.
- [76] F. Scholz, J. Bauch, Anatomical and physiological investigations concerning movement of water in needles of *Pinus*, *Planta* 109 (2) (1973) 105–119.
- [77] T. Saito, R. Kuramae, J. Wohler, L.A. Berglund, A. Isogai, An ultrastrong nanofibrillar biomaterial: the strength of single cellulose nanofibrils revealed via sonication-induced fragmentation, *Biomacromolecules*. 14 (1) (2013) 248–253.
- [78] H. Bradai, A. Koubaa, J. Zhang, N.R. Demarquette, Effect of wood species on lignin-retaining high-transmittance transparent wood biocomposites, *Polymers* 16 (17) (2024) 2493.
- [79] Glass, S., and S. Zelinka. 2021. "Moisture relations and physical properties of wood." *Chapter 4 in FPL-GTR-282 4-1-4-22*.
- [80] J.F. Siau, Transport Processes in Wood, 2, Springer Science & Business Media, 2012.
- [81] C.H.G. Wimmer, A. Teischinger, Permeability of wood—a review, *Wood Research* 47 (4) (2002) 1–16.
- [82] Q. Jiankun, B. Tian, S. Yali, Z. Xin, L. Shuai, H. Yingcheng, Fabrication and characterization of multilayer transparent wood of different species, *Journal of Beijing Forestry University* 40 (7) (2018) 113–120.
- [83] W.A. Côté, Chemical composition of wood. Principles of Wood Science and Technology: I Solid Wood, Springer, 1968, pp. 55–78.
- [84] R.E. Booker, J. Sell, The nanostructure of the cell wall of softwoods and its functions in a living tree, *Holz Als Roh-Und Werkstoff* 56 (1) (1998) 1–8.
- [85] R.S. Davidson, The photodegradation of some naturally occurring polymers, *J. Photochem. Photobiol. B* 33 (1) (1996) 3–25.
- [86] A.L. Andrad, S.H. Hamid, X. Hu, A. Torikai, Effects of increased solar ultraviolet radiation on materials, *J. Photochem. Photobiol. B* 46 (1–3) (1998) 96–103.
- [87] H. Chen, C. Montanari, M. Yan, S. Popov, Y. Li, I. Sychugov, L.A. Berglund, Refractive index of delignified wood for transparent biocomposites, *RSC. Adv.* 10 (67) (2020) 40719–40724.
- [88] M.J. Madsen, D.R. Brown, S.R. Krutz, M.J. Milliman, Measuring the molecular polarizability of air, *Am. J. Phys.* 79 (4) (2011) 428–430.
- [89] Y. Wu, J. Zhou, Q. Huang, F. Yang, Y. Wang, J. Wang, Study on the properties of partially transparent wood under different delignification processes, *Polymers* 12 (3) (2020) 661.
- [90] Y. Wang, Y. Wu, F. Yang, L. Yang, J. Wang, J. Zhou, J. Wang, A highly transparent compressed wood prepared by cell wall densification, *Wood. Sci. Technol.* 56 (2) (2022) 669–686.
- [91] K. Li, S. Wang, H. Chen, X. Yang, L.A. Berglund, Q. Zhou, Self-densification of highly mesoporous wood structure into a strong and transparent film, *Adv. Mater.* 32 (42) (2020) 2003653.
- [92] G.G. Mastantuoni, L. Li, H. Chen, L.A. Berglund, Q. Zhou, High-strength and UV-shielding transparent thin films from hot-pressed sulfonated wood, *ACS. Sustain. Chem. Eng.* 11 (34) (2023) 12646–12655.
- [93] R. Mi, T. Li, D. Dalgo, C. Chen, Y. Kuang, S. He, X. Zhao, W. Xie, W. Gan, J. Zhu, J. Srebric, R. Yang, L. Hu, A clear, strong, and thermally insulated transparent wood for energy efficient windows, *Adv. Funct. Mater.* 30 (1) (2020), <https://doi.org/10.1002/adfm.201907511>.
- [94] J. Song, C. Chen, S. Zhu, M. Zhu, J. Dai, U. Ray, Y. Li, Y. Kuang, Y. Li, N. Qispe, Processing bulk natural wood into a high-performance structural material, *Nature* 554 (7691) (2018) 224–228.
- [95] C. Wang, H. Wang, B. Dang, Y. Yang, L. Zhou, Y. Li, Q. Sun, A versatile 2D cellulose platform strategy from natural wood scaffold, *ACS. Nano* 17 (13) (2023) 12663–12672.
- [96] H. Cai, Z. Wang, D. Xie, P. Zhao, J. Sun, D. Qin, F. Cheng, Flexible transparent wood enabled by epoxy resin and ethylene glycol diglycidyl ether, *J. For. Res.* 32 (4) (2021) 1779–1787.
- [97] T.B. Jele, J. Andrew, M. John, B. Sithole, Engineered Transparent Wood Composites: A review, *Cellulose* 30 (9) (2023) 5447–5471.
- [98] N.P. Simelane, O.S. Olatunji, M.J. John, J. Andrew, Engineered transparent wood with cellulose matrix for glass applications: A review, *Carbohydr. Polym. Technol. Appl.* 7 (2024) 100487.
- [99] J. Wu, Y. Wu, F. Yang, C. Tang, Q. Huang, J. Zhang, Impact of delignification on morphological, optical and mechanical properties of transparent wood, *Compos. Part A* 117 (2019) 324–331.
- [100] L. Hu, M. Zhu, T. Li, A. Gong, J. Song, Transparent Wood Composite, Systems and Method of Fabrication, 2017.
- [101] P. Samanta, A. Samanta, C. Montanari, Y. Li, L. Maddalena, F. Carosio, L. A. Berglund, Fire-retardant and transparent wood biocomposite based on commercial thermoset, *Compos. Part A* 156 (2022) 106863.
- [102] Z. Fang, H. Zhu, Y. Yuan, D. Ha, S. Zhu, C. Preston, Q. Chen, Y. Li, X. Han, S. Lee, Novel nanostructured paper with ultrahigh transparency and ultrahigh haze for solar cells, *Nano Lett.* 14 (2) (2014) 765–773.
- [103] C. Cateto, M. Andreia, F. Barreiro, A.E. Rodrigues, M.N. Belgacem, Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams, *Ind. Eng. Chem. Res.* 48 (5) (2009) 2583–2589.
- [104] M.P. Pandey, C.S. Kim, Lignin depolymerization and conversion: A review of thermochemical methods, *Chem. Eng. Technol.* 34 (1) (2011) 29–41.
- [105] E. Dorrestijn, L. J.J. Laarhoven, I.W. Arends, P. Mulder, The occurrence and reactivity of phenoxyl linkages in lignin and low rank coal, *J. Anal. Appl. Pyrolysis*. 54 (1–2) (2000) 153–192.
- [106] L. ZhongZheng, L. ZhongZheng. 2012. "Research on renewable biomass resource-lignin".
- [107] S. Wei, C. Wan, Y. Wu, Recent advances in wood-based electrode materials for supercapacitors, *Green Chem.* 25 (9) (2023) 3322–3353.
- [108] H. Alqrinawi, B. Ahmed, Q. Wu, H. Lin, S. Kameshwar, M. Shayan, Effect of partial delignification and densification on chemical, morphological, and mechanical properties of wood: structural property evolution, *Ind. Crops. Prod.* 213 (2024) 118430.
- [109] A. Mariani, G. Malucelli, Transparent wood-based materials: A new step toward sustainability and circularity, *Next Mater.* 5 (2024) 100255.
- [110] P. Bocchini, G.C. Galletti, R. Seraglia, P. Traldi, S. Camarero, A.T. Martinez, Matrix-assisted laser desorption/ionization mass spectrometry of natural and synthetic lignin, *Rapid Commun. Mass Spectrom.* 10 (9) (1996) 1144–1147.
- [111] Z. Chen, C. Wan, Biological valorization strategies for converting lignin into fuels and chemicals, *Renew. Sustain. Energy Rev.* 73 (2017) 610–621.
- [112] Y. Pu, D. Zhang, P.M. Singh, A.J. Ragauskas, The new forestry biofuels sector, *Biofuels Bioprod. Bioref.* 2 (1) (2008) 58–73.
- [113] J. Reiter, H. Strittmatter, L.O. Wiemann, D. Schieder, V. Sieber, Enzymatic cleavage of lignin β -O-4 aryl ether bonds via net internal hydrogen transfer, *Green Chem.* 15 (5) (2013) 1373–1381.
- [114] M.T. Amiri, S. Bertella, Y.M. Questell-Santiago, J.S. Luterbacher, Establishing lignin structure-upgradeability relationships using quantitative ^1H – ^{13}C heteronuclear single quantum coherence nuclear magnetic resonance (HSQC-NMR) spectroscopy, *Chem. Sci.* 10 (35) (2019) 8135–8142.
- [115] M.B. Ocreto, Delignification of lignocellulosic biomass for bioethanol production, *USM R&D J.* 21 (1) (2013) 1–20.
- [116] Xiao, K., H. Li, L. Liu, X. Liu, and Y. Lian. 2022. "Quantitative comparison on delignification performance of pretreatment technologies of lignocellulosic biomass for enzymatic saccharification".
- [117] Wegener, G., M. Przyklenk, and D. Fengel. 1983. "Hexafluoropropanol as valuable solvent for lignin in UV and IR spectroscopy".
- [118] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, *Ind. Crops. Prod.* 20 (2) (2004) 131–141.
- [119] E.I. Evstigneyev, S.M. Shevchenko, Structure, chemical reactivity and solubility of lignin: A fresh look, *Wood. Sci. Technol.* 53 (1) (2019) 7–47.
- [120] U. Shakeel, X. Li, B. Wang, F. Geng, Q. Zhang, K. Zhang, X. Xu, J. Xu, Structure and integrity of sequentially extracted lignin during Poplar (Alkaline) pretreatment, *Process Biochem.* 117 (2022) 198–208.
- [121] A. Kumar, T. Jyske, M. Petrić, Delignified wood from understanding the hierarchically aligned cellulosic structures to creating novel functional materials: A review, *Adv. Sustain. Syst.* 5 (5) (2021) 2000251, <https://doi.org/10.1002/advs.202000251>.
- [122] J.J. Klemeš, Handbook of Process Integration (PI): Minimisation of Energy and Waste, Waste and Emissions, Woodhead Publishing, 2022.
- [123] Puthson, P., O. Kordsachia, J. Odermatt, M. Zimmermann, and R. Patt. 1997. "ASAM pulping of Eucalyptus Camaldulensis and TCF bleaching of the resulting pulps".
- [124] V. Tarvo, T. Lehtimaa, S. Kuitunen, V. Alopaus, T. Vuorinen, Chlorate formation in chlorine dioxide delignification—An analysis via elementary kinetic modeling, *J. Wood Chem. Technol.* 29 (3) (2009) 191–213, <https://doi.org/10.1080/02773810802650351>.
- [125] J.Y. Zhu, X.S. Chai, X.J. Pan, Q. Luo, J. Li, Quantification and reduction of organic sulfur compound formation in a commercial wood pulping process, *Environ. Sci. Technol.* 36 (10) (2002) 2269–2272.
- [126] H. Li, X. Guo, Y. He, R. Zheng, A green steam-modified delignification method to prepare low-lignin delignified wood for thick, large highly transparent wood composites, *J. Mater. Res.* 34 (6) (2019) 932–940.
- [127] J. Zhang, Y. Ying, X. Yi, W. Han, L. Yin, Y. Zheng, R. Zheng, H₂O₂ Solution steaming combined method to cellulose skeleton for transparent wood infiltrated with cellulose acetate, *Polymers* 15 (7) (2023) 1733.
- [128] R.B. Santos, E.A. Capanema, M.Y. Balakshin, H. Jameel, Effect of hardwoods characteristics on kraft pulping process: emphasis on lignin structure, *BioResources* 6 (4) (2011).
- [129] Q. Xia, C. Chen, Y. Yao, S. He, X. Wang, J. Li, J. Gao, W. Gan, B. Jiang, M. Cui, L. Hu, Situ lignin modification toward photonic wood, *Adv. Mater.* 33 (8) (2021) 2001588, <https://doi.org/10.1002/adma.202001588>.
- [130] J. Abbot, Reactions of Ortho-quinones and the model compound 4-*t*-butyl-1, 2-benzo-quinone in alkaline peroxide, *Res. Chem. Interm.* 21 (3) (1995) 535–562.
- [131] E.S. Rundlöf, E. Zhang, L. Zhang, G. Gellerstedt, The behavior of chromophoric structures in softwood mechanical pulp on bleaching with alkaline hydrogen peroxide, *Nord. Pulp. Paper. Res. J.* 21 (3) (2006) 359–364.
- [132] L. Zhang, G. Gellerstedt, Quinoid lignin chromophores and their contribution to photobleaching. 3rd European Workshop On Lignocellulosics and Pulp, 1994, pp. 28–31.
- [133] Y. Ni, A. Ng, M. Mosher, A model compound study: the formation of colored metallic extractive complexes and their effect on the brightness of TMP pulp, *J. Wood Chem. Technol.* 19 (3) (1999) 213–223.
- [134] A. Wuorimaa, R. Jokela, R. Aksela, Recent developments in the stabilization of hydrogen peroxide bleaching of pulps: an overview, *Nord. Pulp. Paper. Res. J.* 21 (4) (2006) 435–443.

- [135] K. Kónya, J.C. Scaiano, High-intensity laser generation of ortho-quinones from 2-methoxyphenols; relevance to the question of color reversion in pulp and paper, *J. Photochem. Photobiol. A* 100 (1–3) (1996) 119–124.
- [136] J.K.S. Wan, M.C. Depew, Some mechanistic insights in the behaviour of thiol containing antioxidant polymers in lignin oxidation processes, *Res. Chem. Interim.* 22 (3) (1996) 241–253.
- [137] M. Paulsson, J. Parkäs, Light-induced yellowing of lignocellulosic pulps—mechanisms and preventive methods, *BioResources* 7 (4) (2012) 5995–6040.
- [138] C. Montanari, H. Chen, M. Lidfeldt, J. Gunnarsson, P. Olsén, L.A. Berglund, Sustainable thermal energy batteries from fully Bio-based transparent wood, *Small* 19 (28) (2023) 2301262.
- [139] R. Mi, C. Chen, T. Keplinger, Y. Pei, S. He, D. Liu, J. Li, J. Dai, E. Hitz, B. Yang, Scalable aesthetic transparent wood for energy efficient buildings, *Nat. Commun.* 11 (1) (2020) 3836.
- [140] E. Cabane, T. Keplinger, V. Merk, P. Hass, I. Burgert, Renewable and functional wood materials by grafting polymerization within cell walls, *ChemSusChem* 7 (4) (2014) 1020–1025.
- [141] P. Olsen, N. Herrera, L.A. Berglund, Polymer grafting inside wood cellulose fibers by improved hydroxyl accessibility from Fiber swelling, *Biomacromolecules* 21 (2) (2019) 597–603.
- [142] H. Chen, J. Garemark, L. Li, M. Nero, M. Ritter, O. Cheung, T. Willhammar, I. Sychugov, Y. Li, L.A. Berglund, Green nanotechnology of cell wall swelling for nanostructured transparent wood of high optical performance, *Small* 21 (5) (2025) 2406749, <https://doi.org/10.1002/sml.202406749>.
- [143] Y. Dong, K. Wang, J. Li, S. Zhang, S.Q. Shi, Environmentally benign wood modifications: a review, *ACS Sustain. Chem. Eng.* 8 (9) (2020) 3532–3540.
- [144] E.P.J. Beckers, H. Militz, Acetylation of solid wood. Initial trials on lab and semi industrial scale, in: *Second Pacific Rim bio-based composites symposium*, Vancouver Canada, 1994, pp. 125–135.
- [145] M. Jebrane, G. Sèbe, I. Cullis, P.D. Evans, Photostabilisation of wood using aromatic vinyl esters, *Polym. Degrad. Stab.* 94 (2) (2009) 151–157.
- [146] Roger. Rowell, Dimensional Stability and Fungal Durability of Acetylated Wood, *Drewno: Prace Naukowe, Doniesienia, Komunikaty*, 2016, p. 59.
- [147] R.M. Rowell, R.E. Ibach, J. McSweeney, T. Nilsson, Understanding decay resistance, dimensional stability and strength changes in heat-treated and acetylated wood, *Wood Mater. Sci. Eng.* 4 (1–2) (2009) 14–22.
- [148] A. Barbetta, L. Bertinetti, J. Lautru, R. Podor, T. Zemb, Nano-, meso- and macro-swelling characterization of impregnated compression wood cell walls, *Wood. Sci. Technol.* 52 (2) (2018) 421–443.
- [149] T. Le Duc, N. Thanh-Long, N.T.M. Huong, N.T. Hai, C.N. Thang, T.T.T. Huong, Fabrication of transparent wood by impregnation of epoxy resin into modified balsa wood for application in energy saving materials, *Vietnam J. Catal. Adsorpt.* 14 (1) (2025) 45–50.
- [150] F. Gullo, A. Marangon, A. Croce, G. Gatti, M. Aceto, From natural woods to high density materials: an ecofriendly approach, *Sustainability* 15 (3) (2023) 2055.
- [151] J. Wu, Y. Wang, Y. Vasseghian, Y. Du, H. Kamyab, H. Hashim, C. Xia, Minimizing the polymer content of compressed transparent synthetic wood from renewable biomass sources: A comparative life cycle assessment, *Sustainable Mater. Technol.* 40 (2024) e00977.
- [152] S. Pane, M. Caporusso, H. Hakemi, Haze and opacity control in polymer dispersed liquid crystal (PDLC) films with phase separation method, *Liq. Cryst.* 23 (6) (1997) 861–867.
- [153] K. Wang, X. Liu, Y. Dong, Z. Ling, Y. Cai, D. Tian, Z. Fang, J. Li, Editable shape-memory transparent wood based on epoxy-based dynamic covalent polymer with excellent optical and thermal management for smart building materials, *Cellulose* 29 (14) (2022) 7955–7972.
- [154] P. Bisht, K.K. Pandey, G. Srinivas, Optical properties of transparent wood composites prepared using transverse sections of Poplar wood, *Holzforschung* 76 (7) (2022) 658–667.
- [155] H. Tsuda, K. Urabe, Characterization of long-period grating refractive index sensors and their applications, *Sensors* 9 (6) (2009) 4559–4571.
- [156] T.S. Kleine, L. Ruiz Diaz, K.M. Konopka, L.E. Anderson, N.G. Pavlopoulos, N. P. Lyons, E.T. Kim, Y. Kim, R.S. Glass, K. Char, One dimensional photonic crystals using ultrahigh refractive index chalcogenide hybrid inorganic/organic polymers, *ACS. Macro Lett.* 7 (7) (2018) 875–880.
- [157] N. Sultanova, S. Kasarova, I. Nikolov, Dispersion properties of optical polymers, *Acta Physica Polonica A* 116 (4) (2009) 585–587.
- [158] P. Kim, C. Li, R.E. Riman, J. Watkins, Refractive index tuning of hybrid materials for highly transmissive luminescent lanthanide particle–Polymer composites, *ACS. Appl. Mater. Interfaces* 10 (10) (2018) 9038–9047.
- [159] A.W. Ritchie, H.J. Cox, H.I. Gonabadi, S.J. Bull, J.P.S. Badyal, Tunable high refractive index polymer hybrid and polymer–Inorganic nanocomposite coatings, *ACS. Appl. Mater. Interfaces* 13 (28) (2021) 33477–33484.
- [160] Z. Wang, Z. Lu, C. Mahoney, J. Yan, R. Ferebee, D. Luo, K. Matyjaszewski, M. R. Bockstaller, Transparent and high refractive index thermoplastic polymer glasses using evaporative ligand exchange of hybrid particle fillers, *ACS. Appl. Mater. Interfaces* 9 (8) (2017) 7515–7522.
- [161] I. Gavrilovic-Grmus, M. Dunky, J. Miljkovic, M. Djiporovic-Momcilovic, Influence of the viscosity of UF resins on the radial and tangential penetration into poplar wood and on the shear strength of adhesive joints, *Holzforschung* 66 (7) (2012) 849.
- [162] M. de Meijer, K. Thurich, H. Militz, Quantitative measurements of capillary coating penetration in relation to wood and coating properties. *Holz als Roh und Werkstoff* 59, 2001, pp. 35–45.
- [163] G. Tondi, M.F. Thévenon, B. Mies, G. Standfest, A. Petutschnigg, S. Wieland, Impregnation of Scots pine and beech with tannin solutions: effect of viscosity and wood anatomy in wood infiltration, *Wood Sci. Technol.* 47 (3) (2013) 615–626.
- [164] D. Guo, X. Shen, F. Fu, S. Yang, G. Li, F. Chu, Improving physical properties of wood–Polymer composites by building stable interface structure between swelled cell walls and hydrophobic polymer, *Wood. Sci. Technol.* 55 (5) (2021) 1401–1417.
- [165] H. Chen, C. Montanari, R. Shanker, S. Marcinkevicius, L.A. Berglund, I. Sychugov, Photon walk in transparent wood: scattering and absorption in hierarchically structured materials, *Adv. Opt. Mater.* 10 (8) (2022) 2102732.
- [166] P.H. Hermans, J.J. Hermans, D. Vermaas, Optical properties of the system cellulose-water: A contribution to the optics of swollen gels, *J. Colloid. Sci.* 1 (3) (1946) 251–260.
- [167] M. Meyer, A. Frey-Wyssling, P. Jaccard, Das lichtbrechungsvermögen der cellulose in funktion des quellungsgrades, *Helv. Chim. Acta* 18 (1) (1935) 1428–1435.
- [168] E. Vasileva, A. Baitenov, H. Chen, Y. Li, I. Sychugov, M. Yan, L. Berglund, S. Popov, Effect of transparent wood on the polarization degree of light, *Opt. Lett.* 44 (12) (2019) 2962–2965.
- [169] H.S. Yaddanapudi, N. Hickerson, S. Saini, A. Tiwari, Fabrication and characterization of transparent wood for next generation smart building applications, *Vacuum* 146 (2017) 649–654.
- [170] R. Rai, R. Ranjan, P. Dhar, Life cycle assessment of transparent wood production using emerging technologies and strategic scale-up framework, *Sci. Total Environ.* 846 (2022) 157301.
- [171] J. Wu, H. Ye, S. Li, Z. Que, Y. Peng, L. Cai, C. Xia, Life cycle assessment of transparent wood in building industry: A sustainable solution for global warming mitigation, *Constr. Build. Mater.* 438 (2024) 137303.
- [172] H. Chen, J. Chen, R. Mi, Y. Liu, L. Mei, X. Min, M. Fang, X. Wu, Z. Huang, C. Chen, Toward recyclable, luminescent transparent wood film via synergistic light responses of lignocellulose and phosphors for plant growth lighting and optical thermometer, *Adv. Funct. Mater.* (2025) 2423874.
- [173] N. Pan, X. Sheng, R. Shi, H. Jia, J. Zhang, N. Li, H. Shi, B. Wang, Q. Ping, Synthesis of lignin-based resin and fabrication of sustainable transparent wood based on bio-recycling concept, *Int. J. Biol. Macromol.* 268 (2024) 131620.
- [174] Y. Li, M. Cheng, E. Jungstedt, B. Xu, L. Sun, L. Berglund, Optically transparent wood substrate for perovskite solar cells, *ACS. Sustain. Chem. Eng.* 7 (6) (2019) 6061–6067, <https://doi.org/10.1021/acssuschemeng.8b06248>.
- [175] A. Samanta, H. Chen, P. Samanta, S. Popov, I. Sychugov, L.A. Berglund, Reversible dual-stimuli-responsive chromic transparent wood biocomposites for smart window applications, *ACS. Appl. Mater. Interfaces* 13 (2) (2021) 3270–3277.
- [176] J. Zhou, W. Xu, An aesthetic transparent wood resistant to *Escherichia Coli* based on interface optimization, *Eur. J. Wood Wood Products* 81 (6) (2023) 1569–1579.
- [177] F. Bolognesi, E. Galvanetto, L. Duranti, A. Bianco, M. Togni, A. Bianco, Toward Sustainable Aesthetic Transparent Wood from a Fast-Growing Hardwood Species: Paulownia Wood Templates Infused With Epoxy Bioresin, *ACS Omega*, 2026.

Chapter I References

- Bal, Bekir Cihad. 2014. "Some Physical and Mechanical Properties of Reinforced Laminated Veneer Lumber." *Construction and Building Materials* 68:120–26. doi:10.1016/j.conbuildmat.2014.06.042.
- Brandner, R., G. Flatscher, A. Ringhofer, G. Schickhofer, and A. Thiel. 2016. "Cross Laminated Timber (CLT): Overview and Development." *European Journal of Wood and Wood Products* 74(3):331–51. doi:10.1007/s00107-015-0999-5.
- Brundtland, Gro Harlem. 1987. *Our Common Future World Commission on Environment and Development*.
- Burgert, Ingo, Tobias Keplinger, Etienne Cabane, Vivian Merk, and Markus Rüggeberg. 2016. "Biomaterial Wood: Wood-Based and Bioinspired Materials." Pp. 259–81 in *Secondary Xylem Biology*. Elsevier.
- Calovi, Massimo, Alessia Zanardi, and Stefano Rossi. 2024. "Recent Advances in Bio-Based Wood Protective Systems: A Comprehensive Review." *Applied Sciences* 14(2):736.
- Chen, Chaoji, Yudi Kuang, Shuze Zhu, Ingo Burgert, Tobias Keplinger, Amy Gong, Teng Li, Lars Berglund, Stephen J. Eichhorn, and Liangbing Hu. 2020. "Structure–Property–Function Relationships of Natural and Engineered Wood." *Nature Reviews Materials* 5(9):642–66.
- Chen, Hui, Jonas Garemark, Lengwan Li, Mathias Nero, Maximilian Ritter, Ocean Cheung, Tom Willhammar, Ilya Sychugov, Yuanyuan Li, and Lars A. Berglund. 2025. "Green Nanotechnology of Cell Wall Swelling for Nanostructured Transparent Wood of High Optical Performance." *Small* 21(5):2406749.
- Csiha, Csilla. 2024. "Review on Water Vapor Diffusion through Wood Adhesive Layer." *Journal of the Korean Wood Science and Technology* 52(4):301–18.
- Ding, Yu, Zhenqian Pang, Kai Lan, Yuan Yao, Guido Panzarasa, Lin Xu, Marco Lo Ricco, Douglas R. Rammer, J. Y. Zhu, Ming Hu, Xuejun Pan, Teng Li, Ingo Burgert, and Liangbing Hu. 2023. "Emerging Engineered Wood for Building Applications." *Chemical Reviews* 123(5):1843–88. doi:10.1021/acs.chemrev.2c00450.
- Du, Yuwei, Sai Liu, Yang Li, Xu Chen, Tsz Chung Ho, Luke Christopher Chao, and Chi Yan Tso. 2023. "Perovskite-Coated Thermochromic Transparent Wood: A Novel Material for Smart Windows in Energy-Efficient and Sustainable Buildings." *ACS Applied Materials & Interfaces* 15(42):49665–77. doi:10.1021/acsami.3c11706.
- Edition, Fourth, and Michael F. Ashby. 2011. *Material Selection in Mechanical Design*. Elsevier Ltd.: Burlington, MA, USA.

- Evans, P. D., K. Urban, and M. J. A. Chowdhury. 2008. "Surface Checking of Wood Is Increased by Photodegradation Caused by Ultraviolet and Visible Light." *Wood Science and Technology* 42(3):251–65.
- Fink, Gerhard, and Jochen Kohler. 2014. "Model for the Prediction of the Tensile Strength and Tensile Stiffness of Knot Clusters within Structural Timber." *European Journal of Wood and Wood Products* 72(3):331–41. doi:10.1007/s00107-014-0781-0.
- Fratzl, Peter, and Richard Weinkamer. 2007. "Nature's Hierarchical Materials." *Progress in Materials Science* 52(8):1263–1334. doi:10.1016/j.pmatsci.2007.06.001.
- Gao, He, Ying Li, Yanjun Xie, Daxin Liang, Jian Li, Yonggui Wang, Zefang Xiao, Haigang Wang, Wentao Gan, and Lorenzo Pattelli. 2024. "Optical Wood with Switchable Solar Transmittance for All-Round Thermal Management." *Composites Part B: Engineering* 275:111287.
- Gilbert, Benoit P., Hao Zhang, and Henri Bailleres. 2019. "Reliability of Laminated Veneer Lumber (LVL) Beams Manufactured from Early to Mid-Rotation Subtropical Hardwood Plantation Logs." *Structural Safety* 78:88–99. doi:10.1016/j.strusafe.2019.02.001.
- Gullo, Francesca, Andrea Marangon, Alessandro Croce, Giorgio Gatti, and Maurizio Aceto. 2023. "From Natural Woods to High Density Materials: An Ecofriendly Approach." *Sustainability* 15(3):2055.
- Gustavsson, Leif, Sylvia Haus, Mattias Lundblad, Anders Lundström, Carina A. Ortiz, Roger Sathre, Nguyen Le Truong, and Per-Erik Wikberg. 2017. "Climate Change Effects of Forestry and Substitution of Carbon-Intensive Materials and Fossil Fuels." *Renewable and Sustainable Energy Reviews* 67:612–24.
- Hill, Callum AS. 2007. *Wood Modification: Chemical, Thermal and Other Processes*. John Wiley & Sons.
- Jacucci, Gianni, Lukas Schertel, Yating Zhang, Han Yang, and Silvia Vignolini. 2021. "Light Management with Natural Materials: From Whiteness to Transparency." *Advanced Materials* 33(28):2001215. doi:10.1002/adma.202001215.
- Jele, Thabisile Brightwell, Jerome Andrew, Maya John, and Bruce Sithole. 2023. "Engineered Transparent Wood Composites: A Review." *Cellulose* 30(9):5447–71. doi:10.1007/s10570-023-05239-z.
- Kainer, Karl U. 2003. *Magnesium Alloys and Technology*. John Wiley & Sons.
- Kumar, Anuj, Tuula Jyske, and Marko Petrič. 2021. "Delignified Wood from Understanding the Hierarchically Aligned Cellulosic Structures to Creating Novel Functional Materials: A Review." *Advanced Sustainable Systems* 5(5):2000251. doi:10.1002/adsu.202000251.
- Li, Yuanyuan, Qiliang Fu, Ramiro Rojas, Min Yan, Martin Lawoko, and Lars Berglund. 2017. "Lignin-retaining Transparent Wood." *ChemSusChem* 10(17):3445–51.

- Li, Yuanyuan, Qiliang Fu, Shun Yu, Min Yan, and Lars Berglund. 2016. "Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance." *Biomacromolecules* 17(4):1358–64.
- Li, Yuanyuan, Shun Yu, J. G. C. Veinot, Jan Linnros, Lars Berglund, and Ilya Sychugov. 2017. "Luminescent Transparent Wood." *Advanced Optical Materials* 5(1). <https://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-202236>.
- Lippke, Bruce, Jim Wilson, Jamie Meil, and Adam Taylor. 2010. "Characterizing the Importance of Carbon Stored in Wood Products." *Wood and Fiber Science* 5–14.
- Luan, Yu, Chang-Hua Fang, Yi-Fan Ma, and Ben-Hua Fei. 2022. "Wood Mechanical Densification: A Review on Processing." *Materials and Manufacturing Processes* 37(4):359–71.
- Mi, Ruiyu, Chaoji Chen, Tobias Keplinger, Yong Pei, Shuaiming He, Dapeng Liu, Jianguo Li, Jiaqi Dai, Emily Hitz, Bao Yang, Ingo Burgert, and Liangbing Hu. 2020. "Scalable Aesthetic Transparent Wood for Energy Efficient Buildings." *Nature Communications* 11(1):3836. doi:10.1038/s41467-020-17513-w.
- Montanari, Céline, Peter Olsén, and Lars A. Berglund. 2020. "Interface Tailoring by a Versatile Functionalization Platform for Nanostructured Wood Biocomposites." *Green Chemistry* 22(22):8012–23.
- Montanari, Céline, Peter Olsén, and Lars A. Berglund. 2021. "Sustainable Wood Nanotechnologies for Wood Composites Processed by In-Situ Polymerization." *Frontiers in Chemistry* 9:682883.
- Nodes | Nord Ovest Digitale e Sostenibile. n.d. <https://ecs-nodes.eu/>.
- Olsen, Peter, Natalia Herrera, and Lars A. Berglund. 2019. "Polymer Grafting inside Wood Cellulose Fibers by Improved Hydroxyl Accessibility from Fiber Swelling." *Biomacromolecules* 21(2):597–603.
- Petrič, Marko. 2013. "Surface Modification of Wood." *Reviews of Adhesion and Adhesives* 1(2):216–47.
- Popescu, Carmen-Mihaela, and Alexander Pfriem. 2020. "Treatments and Modification to Improve the Reaction to Fire of Wood and Wood Based Products—An Overview." *Fire and Materials* 44(1):100–111. doi:10.1002/fam.2779.
- Presidenza del Consiglio dei Ministri. 2021. *Piano Nazionale Di Ripresa e Resilienza (PNRR)*. Roma.
- Qin, Qin, Shiyi Zeng, Gaigai Duan, Yanbo Liu, Xiaoshuai Han, Ruizhi Yu, Yong Huang, Chunmei Zhang, Jingquan Han, and Shaohua Jiang. 2024. "'Bottom-up' and 'Top-down' Strategies toward Strong Cellulose-Based Materials." *Chemical Society Reviews* 53(18):9306–43.
- Rioja, Roberto J., and John Liu. 2012. "The Evolution of Al-Li Base Products for Aerospace and Space Applications." *Metallurgical and Materials Transactions A* 43(9):3325–37.

- Rowell, Roger, and Ferry Bongers. 2017. "Role of Moisture in the Failure of Coatings on Wood." *Coatings* 7(12):219. doi:10.3390/coatings7120219.
- Rowell, Roger M. 2005. *Handbook of Wood Chemistry and Wood Composites*. CRC press.
- Saha, Sudeshna. 2011. "Study on the Color Change of Heat-Treated Wood Caused by UV Light: Coating Development." Université du Québec à Chicoutimi.
- Salazar, James, and Jamie Meil. 2009. "Prospects for Carbon-Neutral Housing: The Influence of Greater Wood Use on the Carbon Footprint of a Single-Family Residence." *Journal of Cleaner Production* 17(17):1563–71.
- Sathre, Roger, and Jennifer O'Connor. 2010. "Meta-Analysis of Greenhouse Gas Displacement Factors of Wood Product Substitution." *Environmental Science & Policy* 13(2):104–14.
- Segmehl, Jana, Vanessa Studer, Tobias Keplinger, and Ingo Burgert. 2018. "Characterization of Wood Derived Hierarchical Cellulose Scaffolds for Multifunctional Applications." *Materials* 11(4):517. doi:10.3390/ma11040517.
- Song, Jianwei, Chaoji Chen, Shuze Zhu, Mingwei Zhu, Jiaqi Dai, Upamanyu Ray, Yiju Li, Yudi Kuang, Yongfeng Li, and Nelson Quispe. 2018. "Processing Bulk Natural Wood into a High-Performance Structural Material." *Nature* 554(7691):224–28.
- Soriano, Julio, Bruno Piva Pellis, and Nilson Tadeu Mascia. 2016. "Mechanical Performance of Glued-Laminated Timber Beams Symmetrically Reinforced with Steel Bars." *Composite Structures* 150:200–207. doi:10.1016/j.compstruct.2016.05.016.
- Stark, Nicole; Cai, Zhiyong. 2021. *Wood-Based Composite Materials: Panel Products, Glued Laminated Timber, Structural Composite Lumber, and Wood–Nonwood Composites*. Vols. 11–1. Chapter 11. Washington, Wash.: United States Department of agriculture. Forest products laboratory.
- Thybring, Emil Engelund, Maria Fredriksson, Samuel L. Zelinka, and Samuel V. Glass. 2022. "Water in Wood: A Review of Current Understanding and Knowledge Gaps." *Forests* 13(12):2051.
- Thybring, Emil Engelund, Samuel V. Glass, and Samuel L. Zelinka. 2019. "Kinetics of Water Vapor Sorption in Wood Cell Walls: State of the Art and Research Needs." *Forests* 10(8):704.
- United Nations. 2015. *Transforming Our World: The 2030 Agenda for Sustainable Development*. A/RES/70/1.
- Wang, Jifu, Daihui Zhang, and Fuxiang Chu. 2021. "Wood-derived Functional Polymeric Materials." *Advanced Materials* 33(28):2001135.
- Wang, Kaili, Youming Dong, Yutao Yan, Shifeng Zhang, and Jianzhang Li. 2018. "Improving Dimensional Stability and Durability of Wood Polymer Composites

by Grafting Polystyrene onto Wood Cell Walls.” *Polymer Composites* 39(1):119–25.

Younis, Adel, and Ambrose Dodoo. 2022. “Cross-Laminated Timber for Building Construction: A Life-Cycle-Assessment Overview.” *Journal of Building Engineering* 52:104482. doi:10.1016/j.job.2022.104482.

Zhou, Ting, and Honghai Liu. 2022. “Research Progress of Wood Cell Wall Modification and Functional Improvement: A Review.” *Materials* 15(4):1598.

Zhu, Mingwei, Jianwei Song, Tian Li, Amy Gong, Yanbin Wang, Jiaqi Dai, Yonggang Yao, Wei Luo, Doug Henderson, and Liangbing Hu. 2016. “Highly Anisotropic, Highly Transparent Wood Composites.” *Advanced Materials (Deerfield Beach, Fla.)* 28(26):5181–87.

Zhu, Sailing, Subir Kumar Biswas, Zhe Qiu, Yiying Yue, Qiliang Fu, Feng Jiang, and Jingquan Han. 2023. “Transparent Wood-Based Functional Materials via a Top-down Approach.” *Progress in Materials Science* 132:101025. doi:10.1016/j.pmatsci.2022.101025.

Chapter II

2.1. Development and optimization of a new selective bleaching process for lignin

Within the chapter, an innovative, selective bleaching process for lignin will be described, developed to overcome the limitations of traditional delignification treatments, preserve the structural integrity of the resulting wood template, minimize mass loss, and make the treatment applicable in the industrial field.

As described in the review presented in the previous chapter, two approaches are adopted in the literature for obtaining white woods, used individually or in combination before the next infiltration step: i) the complete or almost complete removal of lignin by delignification, which requires high temperatures and concentrations of the reagents; (Li et al. 2016; Zhu et al. 2016) and ii) the preservation of lignin through mild bleaching processes activated by temperature or UV irradiation. (Li et al. 2017; Xia, Chen, Li, et al. 2021; Xia, Chen, Yao, et al. 2021)

Both processes, presented in the literature, present critical issues. The first leads to an 80% removal of lignin by heat application, which results in mechanically bleached, weak, and difficult-to-handle templates, which can degrade into pieces, exhibiting individual cellulose fibrils completely disconnected from each other, as well as the formation of secondary micro- or nanoporosities, which are more difficult to infiltrate under vacuum. (Gullo, Messori, and Palmero 2026; Montanari et al. 2023; Montanari, Olsén, and Berglund 2020) The second, on the other hand, while requiring external activation sources such as heat or UV radiation, removes a smaller amount of lignin and is effective for samples less than 2 mm thick, due to the uneven diffusion of the reagents in the bulk of the material. (Li et al. 2017; Xia, Chen, Li, et al. 2021; Xia, Chen, Yao, et al. 2021)

To overcome the limitations of the literature, the process developed in this work allows a selective, stable, and homogeneous deconjugation of the chromophore groups of lignin,

preserving their aromatic skeleton and guaranteeing their natural glue function in the cell wall. The experimental development led to the filing of the Italian patent IT102024000023808 presented in Appendix B (p. 170). Commonly used reagents such as hydrogen peroxide (H_2O_2), potassium hydroxide (KOH), and sodium bicarbonate (NaHCO_3) were used to develop this process at room temperature.

2.2. Bleached Wood Template Engineering: Optimization of Process Parameters

The development of the wooden template, with permanent white coloring and stable over time, was achieved after a preliminary phase of process optimization aimed at defining the balance between delignification effectiveness and the maintenance of cell wall structural integrity.

The experimental conditions explored combined variations in reagent concentration and reaction times, with the aim of overcoming the limitations of traditional treatments. In particular, the explored matrix is shown in Fig. 3, which presents different combinations of molarity (0–3 M) and treatment times (0–3 h), associated with the evaluation of color variation (from B to S) relative to the starting wood (A).

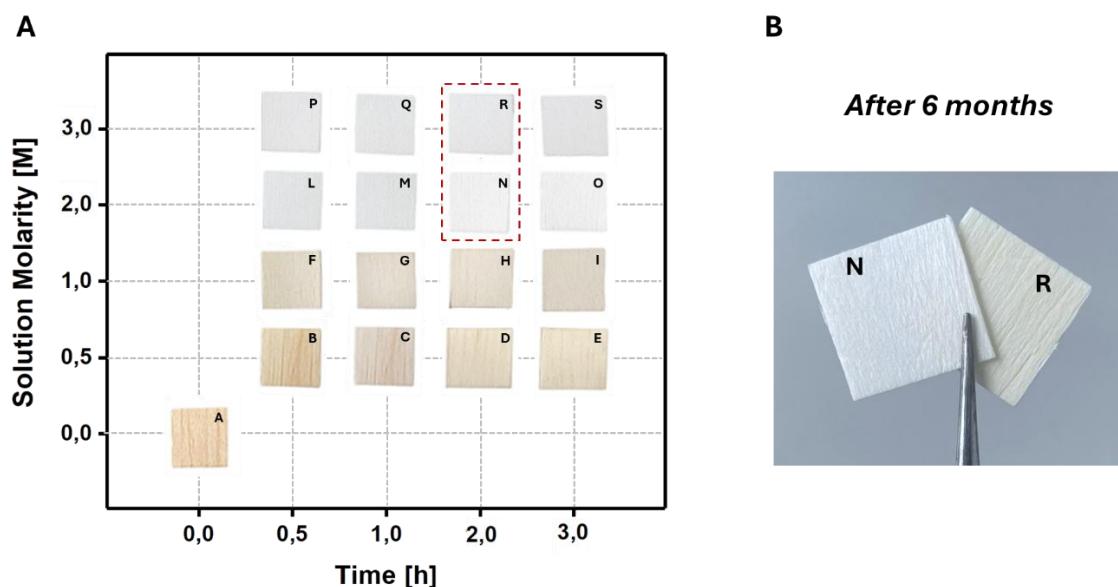


Fig. 3 A) Graph of the experimental conditions used for the development of the bleaching treatment explored as a function of the molarity of the alkaline solution (0–3 M) and the treatment time (0–3 h), with images relating to the treated samples (B–S) and the natural

wood sample (A); B) comparison of the stain stability of N and R samples after 6 months of exposure to natural light.

The analysis of the chromatic variation as a function of concentration and treatment time (Fig. 3A) allowed to study the balance between reaction kinetics and lignin oxidation, the diffusion of the solution in the bulk of the samples, and, finally, the stability of the residual aromatic systems in the final staining (Fig. 3B).

At low concentrations (0.5 M), even after prolonged periods (up to 3 h), the samples (B-E) exhibit partial discoloration compared to natural wood (A), with a straw-yellow color maintained. Under these conditions, the concentration of oxidizing species generated by the decomposition of H_2O_2 in an alkaline environment is insufficient to favor an extensive deconjugation of the lignin chromophore groups. In fact, as we can see from the photos, the discoloration is mainly limited to the most accessible surface, resulting in a coloring that is not suitable for composites intended for advanced optical applications such as TW. At intermediate concentrations (1 M), a more homogeneous discoloration is observed even at shorter times, suggesting that the alkaline H_2O_2 solution, richer in free radicals, is more effective at breaking up conjugate systems, such as coniferaldehyde and quinone structures. (Ding et al. 2022) However, as the treatment time increases, no appreciable color variations are observed. This indicates that a plateau in the effectiveness of the reaction has been reached due to diffusion-limited solution conditions or the depletion of easily accessible chromophoric species.

At higher concentrations (2 and 3 M) a significant variation in the coloration of the wooden templates (L-S) is observed. In fact, a marked whitening of the template is observed, reaching a uniform white color, especially in the N and R samples. In these conditions, the strongly alkaline environment favors the formation of active radical species capable of deeply and effectively deconjugating the aromatic systems responsible for the dark color of the wood.

To optimize the process for subsequent industrialization, the selected operating conditions are a concentration of 2 M and a treatment time of 2 h. The selection of optimal parameters enables good process efficiency by avoiding excessively aggressive conditions and minimizing chemical consumption.

In fact, stricter parameters (3 M, longer times) did not show significant advantages in final staining, but rather highlighted a potential increase in structural alteration of the sample. If we look at the two optimized samples (N and R) in Fig. 3B, we can observe

that N shows greater stain stability over time, even after six months of exposure to natural light. This behavior can be explained by the fact that a lower concentration of KOH reduces secondary rejugations in the aromatic structure of lignin. (Brebu and Vasile 2010; Rundlöf et al. 2006) Higher concentrations, in fact, can destabilize the residual lignin, which remains more susceptible to photooxidation and chromophore rejugation over time, especially following sun exposure. (Paulsson and Parkås 2012; Teacă and Bodîrlău 2016) This is followed by the publication on bleaching, which adopts the optimized parameters applied to balsa and birch woods at two different thicknesses: 1 and 3 mm.

2.3. Published Paper: Preservation of wood structure using stabilized alkaline bleaching agents: a novel and mild approach to enhance whitening for lignin-rich wood template



Preservation of wood structure using stabilized alkaline bleaching agents: a novel and mild approach to enhance whitening for lignin-rich wood template

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Abstract

Preservation and enhancement of wood properties have become increasingly important due to the growing demand for sustainable materials in the construction and manufacturing industries. This study focuses on bleaching processes as an alternative to conventional delignification, aiming to retain a significant amount of lignin while achieving the desired whiteness of the wood template. In particular, stabilized alkaline hydrogen peroxide is investigated as a bleaching agent under mild conditions. The treatment preserves more than 90% of the native mass in both balsa and birch, ensuring that most of the wood's structural components are maintained. This results in a high wood volume fraction, corresponding to reduced porosity and a structure closely resembling that of unbleached wood. Fourier Transform Infrared spectroscopy (FTIR) semi-quantitative analysis further confirms that the relative lignin content is retained, ranging between 70 and 80% depending on the species. Unlike conventional approaches that often degrade the wood structure and require long treatment times at high temperatures, the proposed process is performed at room temperature under mild conditions and completed in less than 2–4 h, thus reducing energy demand and avoiding harmful byproducts. Overall, this work provides a bleaching strategy that combines efficiency, structural integrity, and sustainability, offering bleached wood templates suitable for further characterization and advanced applications.

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Introduction

Wood has been extensively used since ancient times in construction, furniture, and tool-making due to its versatility and mechanical properties. The complexity of wood's hierarchical structure, combined with the variability of its biological composition, has been further enhanced by several technological advancements that promote more efficient use of this resource. In recent decades, increasing attention has been directed toward modifying and selectively controlling wood's microstructure to enhance its optical properties, enabling the development of transparent wood composites with diverse applications spanning structural and functional use, energy efficiency, solar energy harvesting, and advanced light management systems (Zhu et al. 2016a, b; Li et al. 2016a, 2019).

For this purpose, the properties of wood can be controlled and modified through physical and chemical treatments that aim to overcome the weaknesses of native wood by acting on the chemical and physical properties of its primary components: cellulose, hemicellulose, and lignin. In particular, by modifying and adjusting the lignin content in wood via an initial chemical treatment, white wood templates can be created that have a non-transparent appearance, due to light scattering within the wood's porous structure. Subsequently, by infiltrating these porosities with polymers that closely match cellulose in refractive index, most light can pass through the wood-polymer composite, resulting in either a transparent or translucent appearance, depending on the sample's haze level. This phenomenon arises from the wood's intrinsic anisotropic structure, which diffuses some light within the composite.

To perform the first step, there are two strategies to modify the color of the wood and increase its whiteness: (i) delignification and (ii) bleaching.

Most wood treatment processes focus on achieving nearly complete removal of lignin, with reductions of over 80% through delignification methods (Li et al. 2016b). The dark color of the wood is primarily attributed to lignin, which accounts for 80–95% of light absorption (Davidson 1996). In the absence of lignin, cellulose and hemicellulose are colorless. However, they appear white due to light scattering phenomena within the hierarchical porous structure of wood (Zhu et al. 2016a).

The initial method for delignifying wood and producing bleached templates was introduced by Fink, (1992), who used a 5% aqueous solution of sodium hypochlorite for 24 to 48 h to eliminate colour-causing compounds, particularly lignin and extractives. In a study by Li et al. (2016b) delignification was achieved by treating wood with sodium chlorite at 80 °C for 6 to 12 h, significantly reducing lignin content from approximately 25 to less than 3%. Zhu et al. (2016a) proposed a method for removing lignin that involved wood immersion in a boiling solution of NaOH and Na₂SO₃ for 12 h, followed by bleaching with hot H₂O₂, which also resulted in a lignin content of less than 3%. In another study, Zhang et al. (2023) demonstrated that the lignin content could be reduced from 22 to 1% using a highly concentrated H₂O₂ vapor at 95 °C for 10 h. However, these lignin removal processes result in weakened wood structures that can entirely disintegrate the hierarchical organization and lead to the separation of cellulose fibers, which become unbonded (Sirviö et al. 2023). For instance, following delignification, pine breaks down into pieces containing condensed cellulose fibers (Li et al. 2017). In fact, lignin, constituting approximately

30 wt% of wood, plays a vital structural role by cross-linking with polysaccharides to reinforce the cell wall and maintain mechanical integrity (Vanholme et al. 2010). Therefore, preserving lignin within the wood matrix through alternative approaches to complete removal is essential to maintain structural integrity.

Moreover, the delignification processes are often characterized by long processing times and poor environmental compatibility. As the temperature increases during the treatments with chlorinated agents, toxic by-products, such as chlorinated dioxins, could form (Tarvo et al. 2009). To avoid and control the formation of these by-products during delignification processes, chlorinated reagents must be prevented and operated at lower temperatures.

Recent studies have focused on optimizing the preparation of white wood by modifying the lignin structure using mild oxidizing agents. This approach overcomes these processing issues while achieving desirable optical and mechanical properties (Li et al. 2017; Xia et al. 2021a).

The second strategy implies bleaching, meaning selective lignin modification to target the chromophore units responsible for the wood's color. Only a few studies have utilized hydrogen peroxide as a key reagent in chemical modification processes while retaining most of the lignin. For example, Li et al. (2017) treated various types of wood with an alkaline hydrogen peroxide solution at 70 °C, incorporating different reagents, including magnesium sulfate. This resulted in bleached wood that retained about 80% of its lignin, creating 1.5 mm thick samples that maintained a structure similar to natural wood. Subsequently, Xia et al. (2021a) created a solar-assisted white wood template with a thickness of 1 mm by applying a hydrogen peroxide solution to balsa coated with a small amount of alkali powder. This resulted in 80% lignin preservation.

While these studies have demonstrated the feasibility of producing white wood templates, they also present significant drawbacks. The method reported by Li et al. generates sulfur compounds (e.g., methyl mercaptan, dimethyl sulfide, hydrogen sulfide) upon heating, raising concerns about environmental impact and process safety. The approach by Xia et al., although milder, is ineffective for thicker and denser samples and requires a UV source to enhance the action of hydrogen peroxide. However, this reliance on UV not only produces ozone, with associated risks to human health and the environment, but also limits the scalability of the process in industrial applications. More generally, bleaching strategies considered more sustainable in terms of energy demand still depend on external activation sources (e.g., high temperatures or UV) and remain effective only for thin samples (<2 mm). This limitation arises from the challenging diffusion of the bleaching solution within the hierarchical wood structure, which restricts whitening to the surface rather than the bulk.

In light of these concerns, we introduce an innovative bleaching method designed to overcome the inefficiencies of conventional processes by enhancing optical reflectivity, preserving structural integrity, and retaining most of the native lignin. The novelty of our treatment lies in achieving bulk and surface whitening under mild conditions, without the need for external heating or sulfur-based reagents, such as those used in Kraft pulping. The synergistic action of hydrogen peroxide and potassium hydroxide at the reported concentrations enables efficient penetration into the wood matrix at room temperature within a shorter time frame (2–4 h), eliminating the need

for additional activation sources (e.g., heat or UV). This effective penetration makes it possible to treat wood species of different densities and thicknesses—up to 3 mm for both balsa and birch, and up to 1 cm for balsa wood—thus overcoming the limitations reported in the literature, where low-density woods were typically restricted to thicknesses below 2 mm. This one-pot process, followed by a simple sodium bicarbonate washing step, selectively modifies lignin chromophores while preserving the mechanical integrity of the substrate. Importantly, potassium hydroxide can be recovered and reused, thereby lowering chemical demand and operational costs in industrial applications. As a result, the treatment can be defined as an eco-friendly, non-delignifying bleaching approach that minimizes waste and energy consumption while providing a scalable route for producing bleached wood across different species and thicknesses.

To further highlight the versatility of the method, two hardwood species with markedly different characteristics were selected: low-density balsa and high-density birch, each tested at thicknesses of 1 and 3 mm. Their contrasting hierarchical structures, pore connectivity, and densities, together with the extensive availability of data on their chemical and physical properties in the literature, made them suitable model systems for validating the scalability and general applicability of the proposed treatment (Borrega et al. 2015; Luostarinen et al. 2000).

Therefore, this study aims to establish a mild alkaline bleaching process that enhances wood whitening while preserving lignin within the cell wall, where it continues to function as a natural structural binder. We hypothesize that stabilized hydrogen peroxide under alkaline conditions at room temperature can selectively deconjugate chromophoric groups in lignin without significantly altering the native structure.

Materials and methods

Materials and chemicals

Raw balsa wood was purchased from Specialized Balsa Wood, LLC in the USA in two different thicknesses: 1 and 3 mm. The density of the balsa wood ranges from 0.15 to 0.17 g/cm³. Raw birch wood with a thickness of 1 mm was provided from VNT Trinciati S.p.a (Italy), with a density of 0.70 g/cm³. Birch wood with a thickness of 3 mm was sourced from Woodenave in China, with a density of 0.70 g/cm³. Both species were cut into two sets of 50 sample units, with known dimensions of 25 × 25 × 1 mm³ and 25 × 25 × 3 mm³ (tangential x longitudinal x radial). This was done to guarantee an accurate comparison between the two wood species.

For the bleaching process, a 30% v/v hydrogen peroxide (H₂O₂) solution (supplied by Sigma Aldrich), potassium hydroxide (KOH) granules (Sigma Aldrich, purity ≥ 85%), and sodium bicarbonate (NaHCO₃) powder (Solvay S.p.a, purity: 99%) were used.

Alkaline H₂O₂ bleaching for Balsa wood

An alkaline H₂O₂ solution was prepared by dissolving KOH granules in 30% v/v H₂O₂ to reach a 2 M concentration. Sheets of balsa wood, with thicknesses of 1 and 3 mm, were immersed in 20 mL of such solution at room temperature. The wood: solution ratio was 1:10 g/mL (1:16 v/v). The samples were left to soak at room temperature in a 60 mm diameter glass crystallizer under the action of a glass weight for 2 h, until completely bleached. Then, they were immersed in a 0.5 M NaHCO₃ solution to wash and stabilize the final color. Afterwards, the samples were rinsed thoroughly with deionized water to remove residual components and dried in an oven at 65 °C overnight.

Alkaline H₂O₂ bleaching for Birch wood

The procedure used for balsa wood was applied to birch specimens, with the difference that samples were treated twice with the alkaline H₂O₂ solution for 4 h, until complete bleaching. The wood: solution ratio was 1:3 g/mL (1:16 v/v).

Characterisation

The morphological analysis was performed using Field-emission Scanning Electron Microscopy (FESEM, Hitachi S4000, Tokyo, Japan) to analyze the wood's hierarchical structure and porosity features before and after bleaching.

The percentage of lignin removed was determined gravimetrically using an analytical balance ED224S Extend (Sartorius), with measurements repeated on five samples of each type. For each sample, the weight before and after treatment was measured after drying in an oven at 105 °C for 4 h. The percentage of lignin removed was calculated using Eq. 1:

$$\text{Removed lignin \%} = 100 - \frac{\text{White wood sample weight}}{\text{Raw wood sample weight} - \text{moisture content}} * 100 \quad (1)$$

The UV-visible analysis was conducted using an Avantes AvaSpec-ULS2048XLUSB2 model spectrophotometer (Apeldoorn, The Netherlands) alongside an AvaLight HAL-S-IND tungsten halogen light source. The detector and light source were linked via fibre optic cables to a probe with a 1.5 mm diameter FCR-7UV200-2-1.5 × 100. The incident and detecting angles were both set at 45° from the surface normal to eliminate specular reflectance. The spectral range of the detector was from 350 to 1100 nm, and the analysis was collected from 400 to 750 nm.

The ATR-FTIR structural analyses were performed on bleached and raw wood sheets using a Nicolet IS50 IR spectrometer (Thermo Fisher Scientific). The spectra of the analyzed samples were collected at an IR beam temperature of 35 °C, with 32 scans performed at a 4 cm⁻¹ resolution in a spectral range of 4000 to 550 cm⁻¹.

The relative lignin content was estimated from FTIR spectra by calculating the ratio between the intensity of the aromatic skeletal vibration of lignin at 1509 cm⁻¹ (I₁₅₀₉) and the intensity of the C–H deformation in cellulose at 893 cm⁻¹ (I₈₉₃). The

relative lignin content for each treated sample was then expressed as a percentage with respect to the corresponding untreated native wood, considered as 100%, according to the Eq. 2:

$$\text{Relative lignin content } \% = \frac{\left(\frac{I_{1509}}{I_{893}}\right)_{\text{Bleached wood}}}{\left(\frac{I_{1509}}{I_{893}}\right)_{\text{Natural wood}}} \times 100 \quad (2)$$

For each specimen, spectra were collected on three different points of the sample surface, and the reported values correspond to the average of these measurements.

The relative crystallinity percentage was determined using an Empyrean X-Ray Diffractometer (XRD) from Malvern Panalytical, equipped with a Cu source at 40 kV and 40 mA. The samples were tested in the 2θ range of $5\text{--}40^\circ$ with a scan rate of $3^\circ/\text{min}$. The diffractometer was equipped with soller slits (0.04°), anti-scatter slit (P7.5), beam mask (10 mm), divergence ($\frac{1}{4}^\circ$), and axial ($\frac{1}{2}^\circ$) slits. All wood slices were dried at 60°C for 24 h before analysis. In particular, through Segal's method, the crystallinity percentage was determined using Eq. 3:

$$C_r I = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (3)$$

Where: (i) $C_r I$ is the percentage of relative crystallinity; (ii) I_{002} represents the maximum intensity of the diffraction angle for the cellulose I_{002} lattice; (Popescu2009) and (iii) I_{am} is the scattering intensity of the amorphous background diffraction at 2θ , which is approximately 18° .

The diffractograms were deconvoluted using a fitting procedure with the OPUS V. 5.5 software to calculate the entire crystalline contribution. Multiple runs were performed to achieve the minimal residual error, with a Root Mean Square Error (RMSE) of less than 2×10^{-4} . Five components were included, utilising five Gaussian bands to deconvolve the crystalline phases (101, 10–1, 012, and 200) and the amorphous halo. The resulting fitting curve closely matches the experimental curve. Following the deconvolution, the crystalline index was successfully determined using Eq. 4:

$$C_r I = \frac{I_c}{I_c + I_{am}} \times 100 \quad (4)$$

where the term I_c , which replaces I_{002} , indicates the total area of the crystalline component. This value is derived from the sum of the integral contributions attributed to the deconvoluted crystallographic planes 101, 10–1, 012, and 200.

The specific surface area (SSA) of the wood samples was analyzed utilizing N_2 physisorption measurements performed at 77 K. Before analysis, the samples were outgassed at 70°C for 16 h, resulting in a residual pressure lower than 10^{-6} Torr. The N_2 measurements were performed in the relative pressure range from 5×10^{-5} to 1 P/P_0 using a Quantachrome Autosorb IMP instrument. The apparent surface areas were determined using the Brunauer-Emmett-Teller (BET) equation within the relative pressure range from 0.05 to 0.25 P/P_0 . Pore size distributions and cumulative pore volume were obtained by applying the QSDFT model of N_2 at 77 K on carbon (slit pore, equilibrium model).

The tensile strength of the samples was determined using a Shimadzu AGSX tensile/compressive machine. A total of twenty samples measuring $10 \times 100 \times 1 \text{ mm}^3$ and twenty samples $10 \times 100 \times 3 \text{ mm}^3$ (tangential x longitudinal x radial) were tested. The twenty samples, consisting of ten balsa wood and ten birch wood, were divided into two sets of five samples each. One of these sample sets for the two chosen species was treated with a whitening solution before testing. Sample preparation and tensile tests were performed in accordance with ISO 13061-6. Tests on treated and untreated balsa and birch samples are the average of five measurements conducted for each sample. The displacement rate was 1 mm/min, with the clamp distance ranging from 60 to 70 mm. A 1 kN force sensor was used for the thinner samples, while a 50 kN force sensor was employed for the thicker samples. Strain was measured as the ratio of cross-head displacement to the initial distance between the grips. Stress was calculated as a ratio of force to the cross-sectional area.

Results and discussion

The discoloring process

The pictures of the 3-mm samples obtained by the discoloring process are shown in Fig. 1, both in the fiber direction and in the inner cross-section. These images confirm a homogeneous bleaching, with a uniform white color characterizing both surface and bulk of the specimens, overcoming the thickness limitations reported in previous studies ($< 2 \text{ mm}$) (Li et al. 2017; Xia et al. 2021a).

The color of the wood may vary depending on the treatment conditions. In an alkaline environment, lignin may undergo chromogenic reactions, leading to darkening (Liu et al. 2023). However, when combined with a mild oxidizing agent, such as H_2O_2 , chromophore units, including benzene rings, quinoids, vinyl groups, phenolic hydroxyls, and carbonyls, are deconjugated (Ding et al. 2022), generating inter-

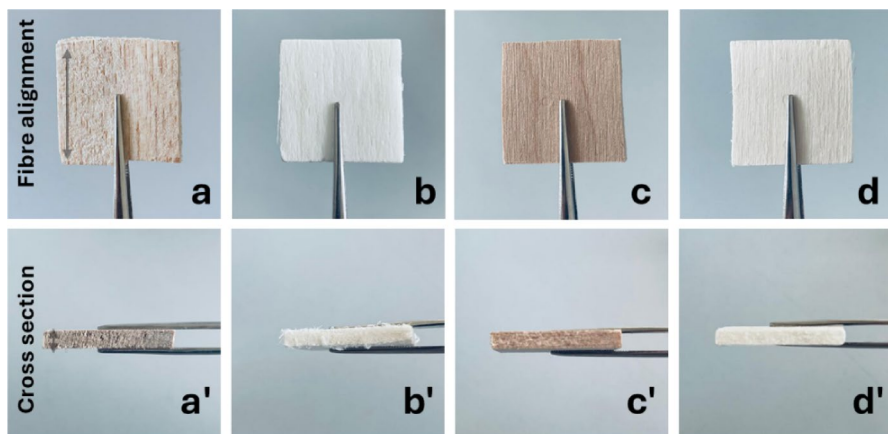


Fig. 1 Images 0.6x of: Natural and bleached balsa (a–b) and birch (c–d) wood in fiber direction; Natural and bleached balsa (a'–b') and birch (c'–d') wood in cross section

mediates such as coniferaldehyde and quinones while preserving the overall lignin macrostructure.

This effect is achieved through the synergistic combination of H_2O_2 and the basic activator KOH, without the need for external energy sources.

KOH's high solubility in concentrated H_2O_2 ensures uniform distribution of the reagents, while careful control of reaction conditions prevents instability, uncontrolled exothermic reactions, or hazardous byproduct formation, preserving the structural integrity of the wood. The optimized combination of reagents allows deep penetration into both low-density and high-density structures of the sample, enabling effective treatment of wood species with thicknesses from 1 to 3 mm, and up to 1 cm for balsa, far exceeding previous thickness limitations (Li et al. 2017; Xia et al. 2021a). Operating at room temperature with carefully selected concentrations balances penetration efficiency and safety, minimizing the risk of lignin or cellulose degradation and preventing premature H_2O_2 decomposition. Treatment times of 2–4 h ensure complete saturation of the wood, promoting uniform bleaching throughout the sample.

During the process, chromophore structures are selectively reacted or removed while non-participating lignin is preserved.

The bleaching protocol involves two steps (Fig. 2): (i) immersion in an alkaline H_2O_2 solution until complete bleaching (2–4 h); (ii) a subsequent washing phase with aqueous NaHCO_3 , which stabilizes the pH and the final color. This step acts as a buffer: as H_2O_2 is gradually consumed, NaHCO_3 prevents KOH from promoting the reconnection of previously deconjugated lignin chromophores. By maintaining a controlled pH, this washing phase ensures uniform whitening and preserves the integrity of the bleached wood.

To validate the predicted penetration and bleaching uniformity, this method was applied to wood types with different densities and hierarchical structures. The results confirm the effective diffusion of reagents across various wood architectures, achieving uniform lignin modification while maintaining structural integrity, and demonstrating the versatility and scalability of the proposed treatment.

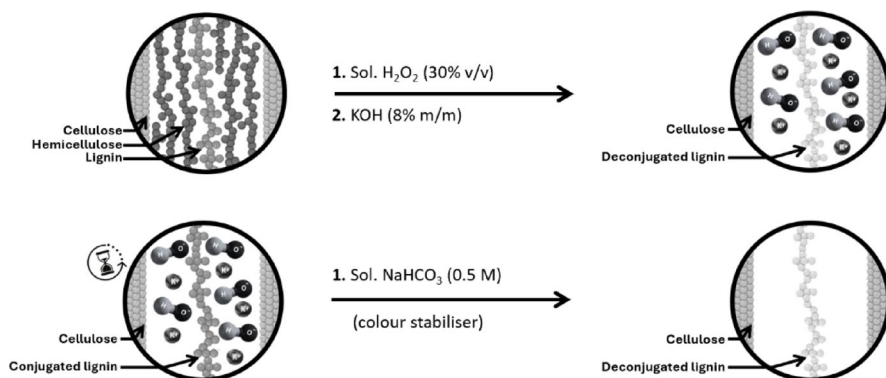


Fig. 2 Two-step proposed reaction scheme for the H_2O_2 alkaline whitening process

FE-SEM analysis

The influence of the bleaching treatment on the microstructure was evaluated through FE-SEM analysis. Figure 3 shows balsa wood (a–d) and Fig. 4 birch wood (a–d) before and after treatment.

The balsa wood sample was chosen as the representative example because it is the most sensitive wood species to chemical treatments. Specifically, its lower density, reduced lignin content, high porosity, and thinner cell walls permit easier access to the lignin within its hierarchical structure (Alqrinawi et al. 2024).

As shown in Fig. 3 at the microscopic level, low-magnification images (a and c) reveal that both samples exhibit the typical structure of balsa wood fibers, characterized by porosity with irregular polygonal shapes resembling hexagons (Borrega et al. 2015). The orientation of wood fibers is parallel to the tree's growth direction, creating an orderly structure.

The pore diameters of both samples, at the microporous hierarchical level, range from 10 to 50 μm . As a result, no significant structural changes are observed before and after treatment, nor is there any fiber collapse during the delignification process (Liu et al. 2019).

A combination of lignin and hemicellulose mainly causes strong adhesion between neighboring fibers. The images at high magnifications (see images b and d, Fig. 3)

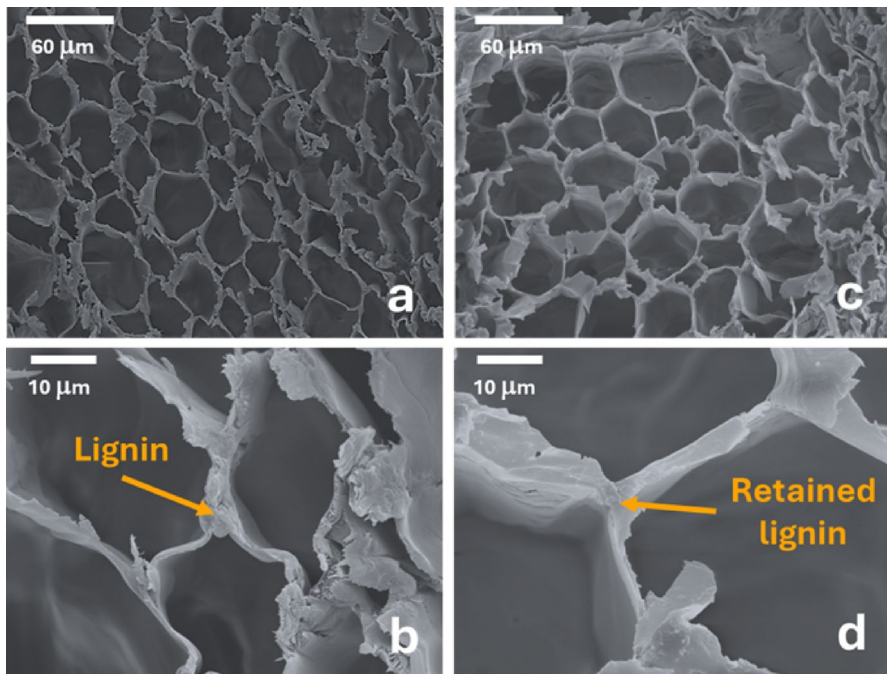


Fig. 3 FE-SEM images at 400x and 1800x of natural balsa wood (a and b) and bleached balsa wood (c and d)

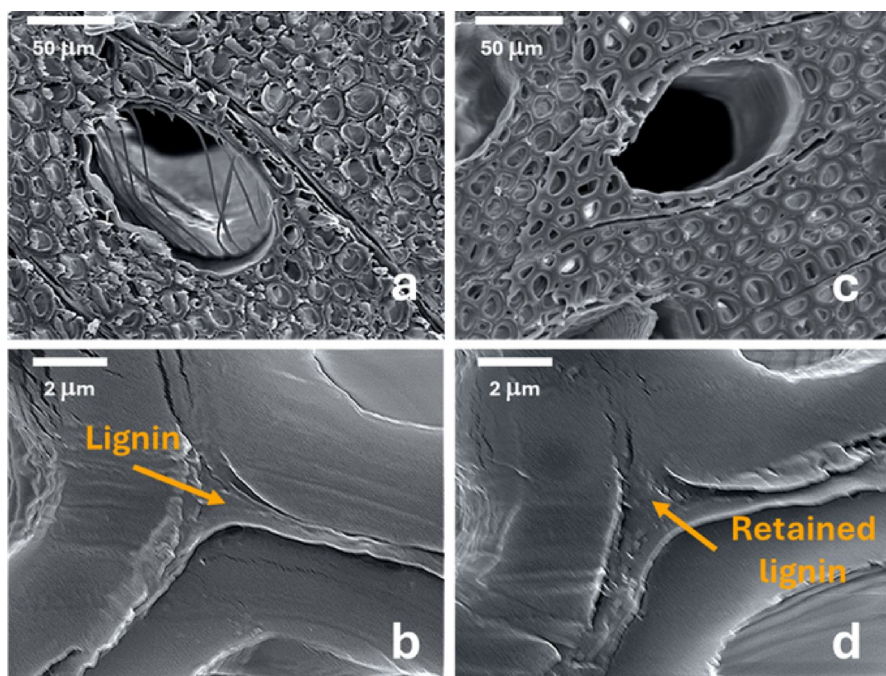


Fig. 4 FE-SEM images at 500x and 10000x of natural birch wood (**a** and **b**) and bleached birch wood (**c** and **d**)

show that the lignin, which is predominantly located in the middle lamella between the cell walls, has been preserved.

In contrast, the birch samples (Fig. 4a–d) exhibit a denser and more compact structure, with smaller and more uniformly distributed lumina compared to balsa. At low magnification (Fig. 4a and c), the characteristic arrangement of hardwood vessels is evident, showing no evidence of collapse or major structural alterations after bleaching. High-magnification images (Fig. 4b and d) confirm that lignin remains preserved in the middle lamella, ensuring adhesion between fibers and maintaining the integrity of the wood structure.

This observation confirms that the bleaching treatment with alkaline H_2O_2 effectively maintains the wood's structure without creating new microporosities that occur with traditional delignification methods (Zhu et al. 2016a; Li et al. 2016b; Wu et al. 2019; Montanari et al. 2020).

Optical properties and total mass loss

The effect of lignin removal can be observed by monitoring changes in the colour of the wood surface and measuring the percentage of mass loss.

A UV-visible analysis was conducted to measure the reflectivity of the white template after the bleaching treatment and is reported in Fig. 5. Every treated sample shows a high reflectance level at 550 nm (92–97%), indicating that the samples produced using this approach are suitable for creating transparent composites (Li et al.

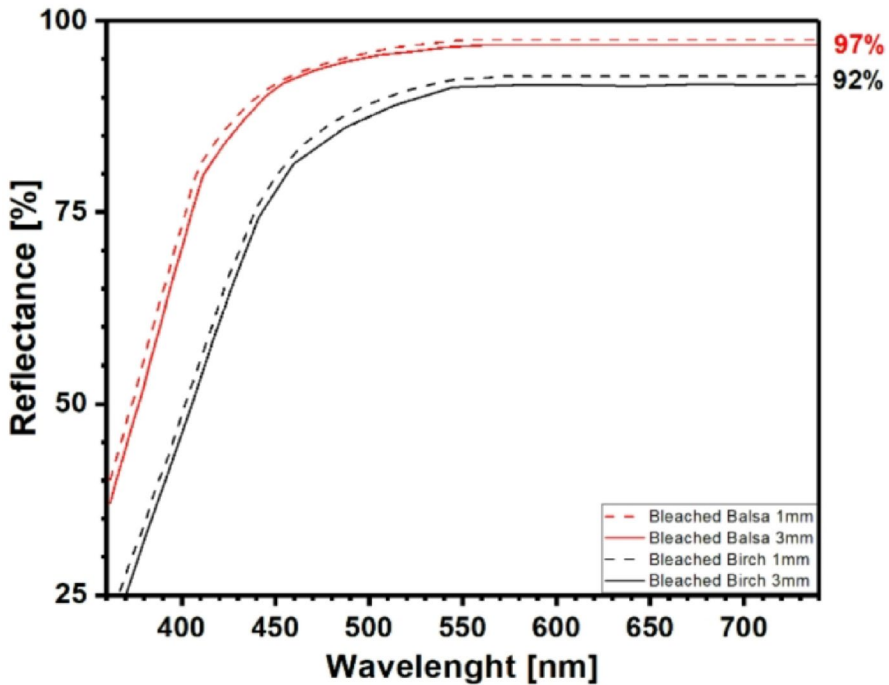


Fig. 5 Reflectance from 360 to 740 nm of the low-density and high-density wood species, 1 mm and 3 mm thick

2017). Additionally, the samples made with this method demonstrate superior reflectance compared to the previously used bleaching techniques. For example, Xia et al. (2021b) reported an average reflectance of 93% for balsa wood.

The difference in measured reflectance values was smaller for birch wood than for balsa wood. This outcome may be attributed to the lower diffusion of the solution in birch wood, which has a higher density and lower porosity than balsa wood. As a result, the deeper chromophore groups in the lignin may be less accessible, reducing bleaching efficiency.

A gravimetric analysis was conducted to evaluate the effectiveness of the bleaching process in performing a semi-quantitative assessment of the percentage of all the removed components compared to the untreated sample. This treatment allows for the retention of most of the lignin, unlike conventional delignification methods, which typically result in the removal of over 80% of lignin and a total mass loss of around 25–26% for both balsa and birch wood (Li et al. 2017; Zhang et al. 2024; Alves-Ferreira et al. 2021).

In addition to lignin removal, certain cellulose, hemicellulose, and extractives in the raw sample may also be removed during extraction. Thus, lignin preservation is evaluated with further structural analysis. Table 1 presents the weight loss from both types of wood studied for the two thicknesses (1 and 3 mm).

The data presented in Table 1 demonstrates a similar trend for both balsa and birch samples. Specifically, as the wood's thickness increases, the percentage of mass loss decreases. This percentage decreases from 9.6 to 8.6% for the balsa samples, while for the birch samples, from 7.0 to 6.4%. This result is due to a reduced diffusion of reagents within the bulk of the material, which leads to a less complete deconjugation of lignin and a lower solubilization of hemicellulose, resulting from the more challenging access to components in the central zone from the basic solution.

The higher mass losses for low-density wood confirm that balsa is more susceptible to overall structural modifications under the treatment conditions, due to its lower density, lower lignin content, and higher cellulose ratio. In contrast, denser hardwoods like birch necessitate more aggressive treatment conditions to achieve comparable overall modification of wood components (Alqrinawi et al. 2024; Santos et al. 2011). Nevertheless, the total weight loss varies between 9.5 and 6.5% for both wood species under mild room temperature conditions. These results are lower than the previous bleaching treatment proposed by Li et al. (2017), ranging from 12 for balsa to 10.6% for birch. In addition, the lower weight loss with our treatment could lead to a further high volume fraction transparent wood composite because a higher initial wood content in the white wood template leads to a lower resin content after infiltration and polymerization. It is crucial to consider the final composite's sustainability and mechanical properties. Many resins used are petroleum-based, (Zhu et al. 2016b; Li et al. 2016b) and incorporating a wood template enhances the mechanical properties of the infiltrating resin (Li et al. 2016b).

IR analysis

Fourier-transform infrared spectroscopy in attenuated total reflectance (FTIR-ATR) was performed to assess the impact of the bleaching process on the chemical and physical structure of the treated balsa and birch samples. This assessment was conducted by analyzing the changes in signals related to the functional groups present before and after the lignin deconjugation process.

The analyses, as shown in Fig. 6, allowed for identifying the peaks corresponding to the lignocellulosic components present in the materials.

For clarity, the band's assignments are presented in Table 2.

Due to wood's significant structural and compositional variability, it is highly complex to correlate the vibrational mode of the functional groups that compose only

Table 1 Percentage of all the removed components from balsa and birch samples based on the pre- and post-treatment weight ratio, using a 2 M KOH solution in H₂O₂

Sample	Weight [g]		Weight loss [wt%]	
	1 mm	3 mm	1 mm	3 mm
Thickness				
Natural Balsa ^a	0.052±0.007	0.151±0.009		
Bleached Balsa	0.047±0.005	0.138±0.007	9.6±1.1	8.6±0.9
Natural Birch ^a	0.387±0.015	1.339±0.014		
Bleached Birch	0.360±0.012	1.253±0.015	7.0±1.0	6.4±0.8

^aThe value is relative to the weight of the sample from which the percentage moisture content has been subtracted

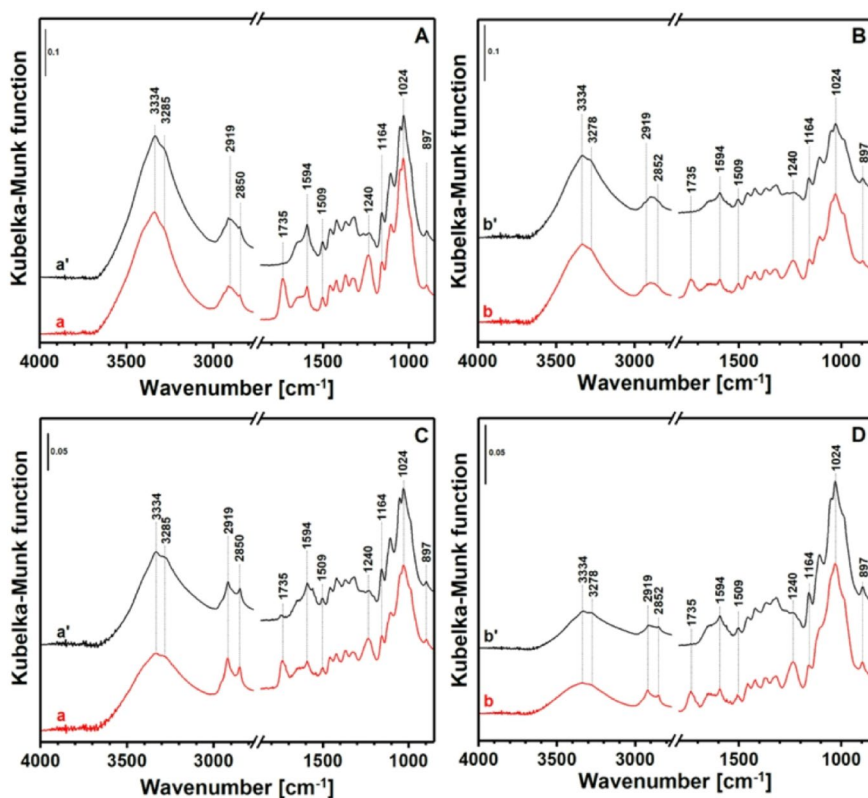


Fig. 6 ATR-FTIR analysis in the range 4000–850 cm^{-1} for: **(A)** balsa, 1 mm thick; **(B)** birch, 1 mm thick; **(C)** balsa, 3 mm thick; and **(D)** birch, 3 mm thick. In all the figures, red curves refer to natural wood, and the black ones to the bleached wood

lignin with the corresponding peaks. However, some of the distinguishable peaks can be associated with aromatic rings and can be compared to understand whether there are structural changes before and after treatment. By comparing the spectra of balsa and birch woods, both in their natural and bleached states, for the two thicknesses (see Fig. 6A–D), we observe that the intensity and shape of the broadband between 4000 and 2750 cm^{-1} , which is related to the stretching of -OH groups, remain consistent. The peaks at 2919 and 2852 cm^{-1} , which correspond to the stretching of the -CH₂ bonds in holocellulose, are also preserved. This behaviour indicates that the structure of the cellulose and hemicellulose skeleton remains unchanged after treatment with alkaline H₂O₂ (Yang et al. 2018).

The band at 1737 cm^{-1} , associated with the balsa sample (Fig. 6A and C) and the birch sample (Fig. 6B and D), is attributed to hemicellulose and/or lignin and is absent after bleaching. This result is due to the cleavage of the lignin and hemicellulose ester groups due to the alkaline hydrolysis induced by KOH in the bleaching solution (Agarwal and McSweeney 1997; Horikawa et al. 2013). The bands at 1594 and 1509 cm^{-1} , related to the aromatic ring stretching of lignin, remain stable before and after treatment for both types of wood. This demonstrates that most of the lignin

Table 2 Assigned mode of infrared bands for balsa and birch wood samples

Band [cm ⁻¹]	Assigned mode	REF
4000–2750	n -OH	(Adel et al. 2011)
2919	n _{as} CH ₂ in cellulose, hemicellulose, and sugars	(Adel et al. 2011, Schwanninger et al. 2004)
2852	n _a CH ₂ in cellulose, hemicellulose, and sugars	(Adel et al. 2011, Schwanninger et al. 2004)
1735	Acetyl and uronic ester groups of hemicellulose Ester bonding of carboxylic groups of phenuryl and p-coumaric acids of lignin and/or hemicellulose	(Chen et al. 2011a, b; Sain et al. 2006, Sun et al. 2000)
1594	n _{C=C} aromatic ring skeletal	(Liu et al. 2020)
1509	n _{C-C} aromatic ring skeleton of flavonoids	(Schwanninger et al. 2004; Chen et al. 2011a, b; Sain et al. 2006, Sun et al. 2000, Liu et al. 2020)
1240	n _{-CO} hemicellulose	(Schwanninger et al. 2004)
1164	n _{C-O-C} cellulose	(Szymanska-Chargot and Zdunek 2013; Peng et al. 2019; Canteri et al. 2019)
1024	n _{C-O} ester in methoxyl and β-O-4 linkages in lignin	(Popescu et al. 2013)
897	d _{CH} in the plane aromatic lignin	(Schwanninger et al. 2004; Chen et al. 2011a, b; Sain et al. 2006, Sun et al. 2000, Gullo et al. 2023)

has been deconjugated through the action of H₂O₂, which selectively acts on the chromophore groups while preserving its aromatic structure (Li et al. 2017; Wójciak et al. 2010). In addition to the qualitative observations, a semi-quantitative evaluation of the residual lignin was conducted by calculating the ratio of absorbance at 1509 cm⁻¹ to the absorbance at 893 cm⁻¹, which is associated with the β-glycosidic vibrations of cellulose, as reported in the literature (Kostyukov et al. 2022; Sun et al. 1997; Tryjarski et al. 2022). The analysis revealed that the relative lignin content decreased by approximately 18% in the balsa samples (1 and 3 mm) and by 27% in the 1 mm birch samples, and by 26% in the 3 mm birch samples, respectively (see Table S1). The differences in relative lignin loss between balsa and birch can be attributed to the distinct structural properties of the two species: balsa's lower density, higher porosity, and thinner cell walls facilitate easier penetration of the bleaching solution, whereas birch's denser structure and thicker cell walls limit diffusion,

leading to variations in the degree of lignin deconjugation as detected by the surface-sensitive FTIR measurements.

The band at 1240 cm⁻¹, associated with the stretching of the C-O bond in hemicellulose, is absent after treatment of both the balsa and birch bleached samples. This confirms the occurrence of alkaline hydrolysis in the presence of the basic agent. Finally, the bands at 1024 and 897 cm⁻¹ related to the C-O ester stretching vibrations in methoxyl and β -O-4 linkages in lignin and the bending in the plane of the aromatic -CH groups of the lignin macromolecule, respectively, appear unchanged for all bleached materials, confirming the occurrence of deconjugation and not the complete removal of lignin, leaving the aromatic skeleton intact. The analyses shown indicate that after our process, a large part of the hemicellulose was removed through basic attack, while the lignin structure was only deconjugated. Furthermore, it can be assumed that the original molecular structure of cellulose was maintained even after the chemical treatment at room temperature. This behaviour may suggest that the treatment with H₂O₂ at basic pH is more selective for the deconjugation of lignin and the removal of hemicellulose, and does not degrade cellulose, in contrast to the delignification treatments. It is also important to note that the relative lignin values obtained from FTIR analysis are semi-quantitative and sensitive to surface changes. Therefore, they cannot be directly compared to the absolute Klason lignin contents reported in the literature. Instead, these values provide insights into structural modifications and relative compositional changes.

XRD analysis

An X-ray diffraction analysis was conducted to assess the impact of bleaching treatment on the crystalline structure of wood samples.

Figure 7 presents the X-ray diffraction patterns for two types of wood samples at two thicknesses: raw and bleached balsa (diffractograms A and C for raw samples at 1 mm and 3 mm, respectively, and diffractograms A' and C' for bleached samples at the same thicknesses). Diffractograms B and D relate to raw birch samples at 1 mm and 3 mm, respectively, and diffractograms B' and D' for the corresponding bleached samples.

To evaluate the relative crystallinity of the samples, both the Segal method (Segal et al. 1959) and the Rietveld method (Rietveld 1967, 1969) were applied, as reported in the literature (Xu et al. 2013). The Segal method, which provides a general estimation of the crystallinity index, is reported in Table 3 together with Fig. S1 (Supporting Information). The Rietveld method, instead, involves deconvolution with Gaussian curves designed to refine and model the peaks, thus considering contributions from the entire crystalline component. This analysis is presented in Fig. 7; Table 3.

Table 3 reports the crystalline content of the wood samples calculated using both selected methods.

As demonstrated in Fig. 7, an analysis of the data reveals that the position of diffraction peak 200 in the area related to the presence of crystalline cellulose I remains unchanged for the bleaching of both balsa (Figs A' and C') and birch wood (Figs B' and D'). This observation indicates that the bleaching process does not affect the crystallinity of cellulose type I (Lionetto et al. 2012). This type of cellulose is asso-

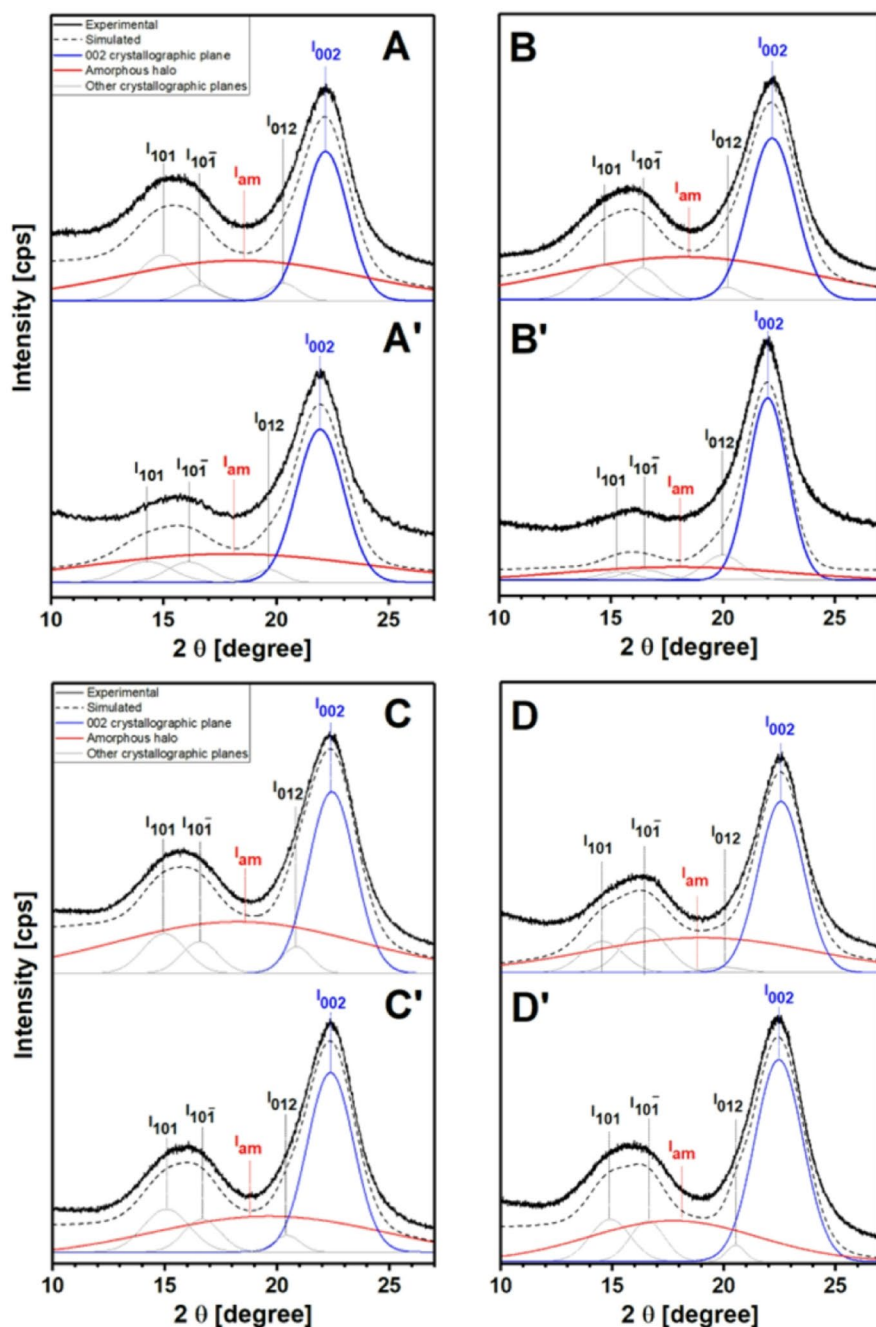


Fig. 7 Deconvoluted X-ray diffractograms for: Natural balsa 1 and 3 mm thick (A and C); Bleached balsa 1 and 3 mm thick (A' and C'); Natural birch 1 and 3 mm thick (B and D) and Bleached birch 1 and 3 mm thick (B' and D'). Line plot: — Experimental; --- Simulated; blue line: 002 crystallographic plane; red line: amorphous halo and grey line: other crystallographic planes

Table 3 Calculation of the crystallinity index from X-ray diffraction patterns using the method proposed by Segal et al. (1959) and the method proposed by Rietveld (1967, 1969)

Sample	Size [mm]	I_{002}	Segal method		Rietveld method		
			I_{am}	Crystallinity [%]	I_c	I_{am}	Crystallinity [%]
Natural Balsa	1	2566.1	439.3	82.9	8545.4	5601.4	60.4
	3	6295.9	1182.4	81.2	21003.0	15572.1	57.4
Bleached Balsa	1	2842.0	461.1	83.8	8674.1	7181.8	54.7
	3	4354.1	677.5	84.4	14340.3	8243.9	63.5
Natural Birch	1	6765.8	2302.1	66.0	21189.5	20983.4	50.2
	3	6503.4	1934.9	70.2	29224.3	10542.1	73.5
Bleached Birch	1	5715.1	349.3	93.9	14873.9	2835.2	84.0
	3	4087.4	778.4	80.9	14874.0	2835.2	84.0

ciated with the most intense peak in the diffractogram, as it is the most abundant, ordered and stable crystalline organisation of cellulose in wood and plants. (Newman 1994; Kulasinski et al. 2014) However, an increase in both relative and total crystallinity was observed and calculated using the Segal and Rietveld methods for all the samples except for balsa wood with 1 mm thickness. This finding suggests that the treatment influenced the amorphous regions by partially removing most of the hemicellulose and a small part of the lignin (9.6–6.4%, see Table 1) and rearranging the remaining hemicellulose, cellulose and lignin components (Xu et al. 2013). The results indicate that lignin and hemicellulose in the cell walls were partially degraded during bleaching due to basic attack at room temperature. As previously mentioned, KOH facilitates the hydrolysis of amorphous cellulose by breaking the ether bonds in the molecular chains, allowing the exposed hydroxyl groups to recombine through hydrogen bonding (Liu et al. 2023; Xu et al. 2013). As demonstrated in Table 3, which utilizes the Segal method to estimate the degree of crystallinity of cellulose type I, divergent responses may be observed between the two types of wood following treatment. These findings are consistent with results reported in the literature for balsa wood, which shows a crystallinity degree of 80–90% (Borrega et al. 2015), and birch wood, which ranges from 40 to 60% (Wikberg and Maunu 2004). The percentage of crystallinity in balsa wood remains stable before (82.9 and 81.2%) and after treatment (83.8 and 84.4%) for the two analyzed thicknesses. In contrast, birch exhibits a significant increase in crystallinity after bleaching, rising from 66.0 to 70.2% to 93.9 and 80.9% for 1 and 3 mm, respectively. Utilising the Rietveld method, which incorporates the contributions of all crystalline components, a discernible discrepancy in the behaviour of the two wood types upon treatment is evident (see Table 3). For the thicker balsa, an increase in crystalline content is shown, while a decline in crystalline content is evident in thinner balsa wood, decreasing from 64.4 to 54.7%. This reduction can be attributed to the bleaching solution's strongly oxidizing action in the thinner and lower-density balsa wood, which leads to the unselective deconjugation/removal of part of the amorphous component and causes partial damage to the crystalline component (Alqrinawi et al. 2024; Quintana et al. 2015). On the contrary, for the two birch wood samples, an increase in the degree of crystallinity was observed even when utilizing the Rietveld method. The percentage increases from 50.2 to 84.0% at 1 mm and from 73.5 to 84.0% at 3 mm. This fact is attributed

to the more orderly arrangement of cellulose microfibrils in the amorphous region following basic treatment (Tyufekchiev et al. 2019). In this instance, the amorphous lignin component exhibits enhanced resistance, making it more difficult to modify or remove while simultaneously protecting the crystalline part from degradation (Higuchi et al. 1977; Lourenço and Pereira 2018). Consequently, the oxidizing alkaline solution is an effective preservation agent for the cellulose component, achieving this by selectively targeting the amorphous fractions and as a consequence, the crystalline content associated with cellulose is enhanced (Lionetto et al. 2012). The assessment of the material's crystallinity post-treatment was monitored, as higher crystallinity in the bleaching treatments indicates superior fibre orientation and less amorphous loss, which could lead to enhanced mechanical properties (e.g., fracture toughness) compared to the weak delignified woody materials (Frey et al. 2019).

Since the Rietveld method considers the entire contribution of all crystalline phases, unlike the Segal method that primarily targets the 002 diffraction plane, the results from the Rietveld refinement were deemed more reliable. Consequently, these results were used for further correlation with the mechanical properties discussed in Sect. "Mechanical properties".

N₂ physisorption analysis at 77 K

The textural properties of the materials before and after treatment were analyzed to assess the impact of the process on pore size and distribution. Nitrogen (N₂) physisorption analysis was conducted at 77 K on wood samples, each 3 mm thick, including natural and bleached balsa and birch. The resulting isotherms are presented in Fig. S2 (Supporting Information). The N₂ physisorption isotherms for these wood materials are classified as type V. All hysteresis loops extend to low relative pressures (below 0.4 P/P₀) and remain visibly open throughout desorption.

In woody materials, Wang et al. (2023) suggest that the open hysteresis loops of N₂ at cryogenic conditions result from the weak interaction between the gas and the particular hierarchical structure of wood as indicated by the low value of the constant C (Table 4) calculated from BET model applied on the isotherms and which limits the accessibility of nitrogen in porosity (Lowell et al. 2012; Fukuzumi et al. 2013). Indeed, using the constant C derived from the BET model, it is possible to describe the intensity of the interaction between the adsorbed gas and the material's surface. When the values of C are <10, as in this case, the gas adsorption on the surface is unselective, resembling a liquid-like condensation (Lowell et al. 2012). Nevertheless, the C values can still be deemed reliable for applying the BET model (Lowell et al. 2012).

Table 4 Specific surface area calculated with BET method and total pore volume of the raw and bleached wood

Sample	SSA _{BET} [m ² g ⁻¹]	C _{BET}	V _{Total} [cc g ⁻¹]
Natural Balsa	8.7	2.233	0.024
Bleached Balsa	44.3	2.198	0.054
Natural Birch	4.8	5.429	0.018
Bleached Birch	41.8	3.278	0.066

The analysis of the pore size distribution curves in Fig. 8 reveals the presence of micro- and mesopores in all the materials examined. These pores exhibit a dimensionality that varies uniformly between 15 and 100 Å, with a maximum distribution centred at approximately 20 Å in all cases. However, when the total porous volumes are considered, it becomes evident that the values related to the pore distributions are negligible (Fig. 8A; Table 4).

In particular, the overall quantity of adsorbed N_2 is lower for natural birch and balsa wood, at approximately 4.8 and 8.7 m^2/g , in accordance with the literature data (Garemark et al. 2023; Montanari et al. 2020). The specific surface area calculated by the BET method for bleached balsa and birch wood is assessed at 44.3 and 41.8 m^2/g , respectively (Table 4), with a total pore volume of 0.054 and 0.066 cc/g , respectively (Fig. 8B; Table 4). In addition, the overall pore volume of the two materials was observed to be lower than that of the two treated materials analyzed, with values of 0.018 and 0.024 cc/g , respectively (see Fig. 8B; Table 4). The slight variation in surface area aligns with the treatment applied to the materials, which aims to modify lignin in situ rather than remove it. This approach helps prevent microporosity formation in the cell wall, which could lead to partial detachment of the cellulose fibres and structural weakening (Liu et al. 2019). Deep delignification treatments can significantly increase the surface area and microporous volume of the resulting wood (Montanari et al. 2020, 2023). Consequently, the excessive increase in microporosity of white wood templates may create greater challenges for later infiltration with transparent resins, leading to longer processing times to achieve optimal performance in terms of high transmittance and low haze.

Mechanical properties

Tensile strength tests were conducted to evaluate the mechanical behaviour before and after treatment. The stress-strain curve of the treated and untreated wood is shown in Fig. S3 (Supporting Information). This analysis is important because the proper-

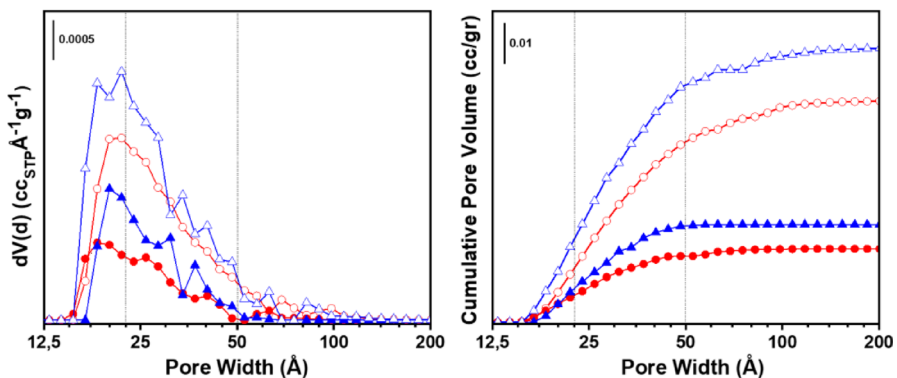


Fig. 8 Pore size distribution (A) and cumulative pore volume (B) of: natural balsa (filled blue triangle); natural birch (filled red circle); bleached balsa (unfilled blue triangle) and bleached birch (unfilled red circle)

ties, interactions, and arrangement of components in wood materials directly affect their mechanical properties. Treatments designed to modify or selectively remove specific components, such as lignin and hemicelluloses, can significantly alter the mechanical characteristics of natural wood (Zhang et al. 2013). Bleaching treatments can notably increase the crystallinity of cellulose microfibrils, which strongly adhere to each other due to rigid lignin, leading to enhanced mechanical properties (Ottesen et al. 2019; Wang et al. 2014).

Figure 9 illustrates the ultimate tensile strength of the two types of wood examined in this study, comparing results before and after treatment at two different thicknesses: 1 mm and 3 mm.

Table 5 shows a clear correlation between cellulose crystallinity (CrI) and the mechanical behaviour of the wood species studied (see Table 3). The crystallinity values discussed in this section, and reported in Table 3, are derived from the Rietveld method, which was selected as the most reliable approach since it considers the entire crystalline contribution rather than only the intensity of the 002 reflection. For 1 mm birch, CrI increased significantly from 50% to 84% after treatment, resulting in a higher tensile strength of ~196 MPa compared to ~162 MPa in the native wood. This improvement is attributed to better alignment of cellulose fibrils and partial removal of amorphous lignin and hemicellulose (~7% of the total). In contrast, 1 mm

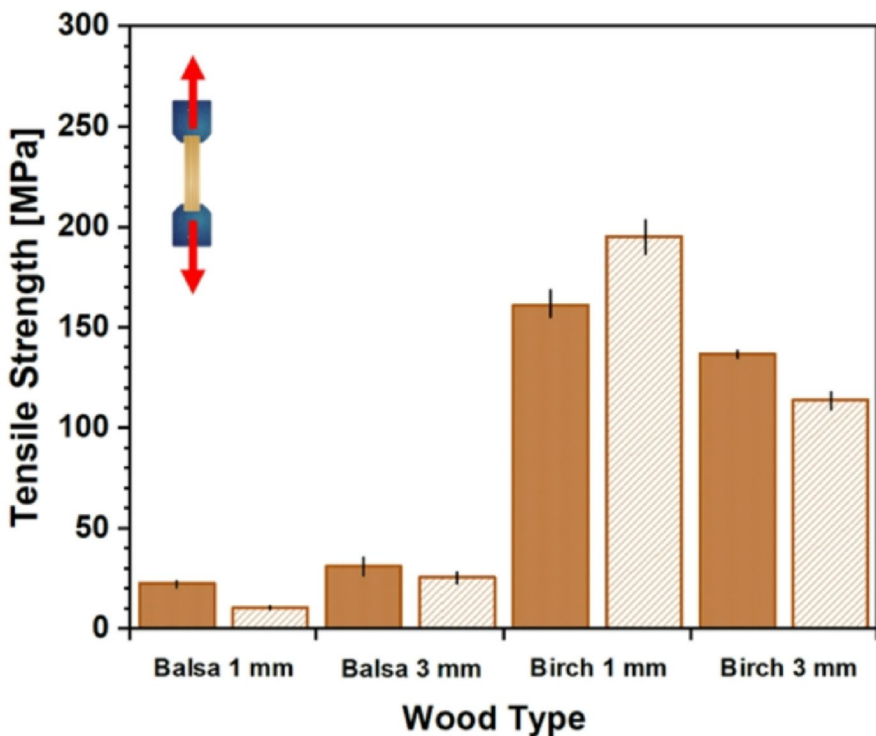


Fig. 9 Tensile strength of natural (solid brown) and bleached (hatched brown) balsa and birch wood with 1 mm and 3 mm thicknesses

Table 5 Comparison of the ultimate strength of the bleached and natural wood types at different thicknesses. Natural woods are identified with N and treated ones with W

Wood		Process	Thickness [mm]	Treatment Time [h]	Weight Loss [wt%]	Crystal- linity [%]	Ultimate Strength [MPa]
Balsa	N	-	1.0	-	-	60.4	22.7±3.3
	W	Lignin deconjugation	1.0	2	9.6	54.7	10.4±2.0
	N	-	3.0	-	-	57.4	30.5±7.7
	W	Lignin deconjugation	3.0	2	8.6	63.5	25.6±5.9
Birch	N	-	1.0	-	-	50.2	161.5±13.5
	W	Lignin deconjugation	1.0	4	7.0	84.0	195.7±17.0
	N	-	3.0	-	-	73.5	137.1±9.1
	W	Lignin deconjugation	3.0	4	6.4	84.0	114.4±3.3

balsa showed a slight decrease in CrI from 60% to 55%, while both birch and balsa exhibited a small increase in relative crystallinity via the Rietveld method, accompanied by a corresponding decrease in ultimate strength.

The effects of the bleaching treatment on mechanical properties correlate with changes in cellulose crystallinity (C_rI). Three trends were observed: (i) decreased properties when C_rI decreases; (ii) preserved properties when C_rI slightly increases; and (iii) improved properties when C_rI significantly increases.

Both 1 mm birch and 1 mm balsa samples were selected for this study. The thin 1 mm thickness allows the chemical solution to access the entire structure, making any modifications to the cellulose–lignin network more pronounced.

For 1 mm birch, selective deconjugation of lignin at room temperature preserves cellulose, promotes fibril alignment, and maintains lignin as a natural binder, enhancing rigidity and strength while supporting stress transfer along the fibers. Its rigid structure complements the flexibility of cellulose, allowing stress to be effectively transferred along the wood cell walls, which enhances compressive strength and dimensional stability (Kurei et al. 2024; Salmén et al. 2016). During processing, structural changes in lignin can further improve its bonding capabilities, illustrating its versatility as a binder (Wang et al. 2016). Unlike traditional delignification, which removes most lignin and compromises mechanical support (Li et al. 2017; Wu et al. 2019; Xia et al. 2021b; Bolognesi et al. 2024), this approach retains structural integrity.

In contrast, 1 mm balsa exhibited a moderate reduction in CrI (from 60% to 55%) and a corresponding decrease in tensile strength (from 22.7 to 10.4 MPa). Despite the preservation of about 80% of lignin and the absence of visible structural collapse in SEM images, the lower density and higher porosity of balsa make it more sensitive to slight changes in the cellulose–lignin network. The partial removal and redistribution of amorphous domains may induce local heterogeneities and a weaker inter-fibrillar interface, reducing stress transfer efficiency (Alqrinawi et al. 2024; Li et al. 2017). In low-density woods such as balsa, even mild chemical modification can lead to disproportionate mechanical losses, as mechanical strength relies more on cell wall cohesion than on overall lignin content (Alqrinawi et al. 2024).

In thicker or denser samples (3 mm birch), limited solution diffusion reduced fibril alignment, slightly decreasing mechanical performance, while balsa, being more

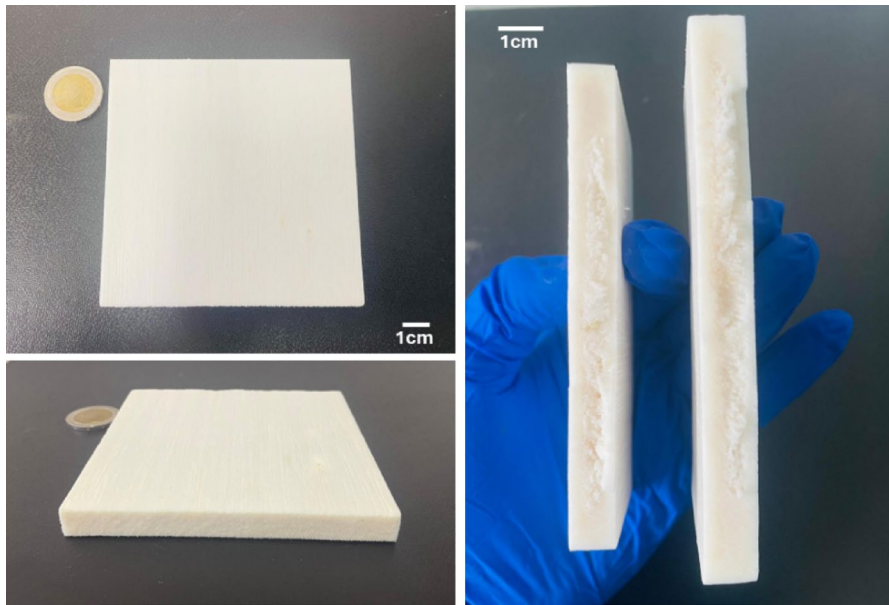


Fig. 10 Optical image of balsa wood template with dimensions of $100 \times 100 \times 10 \text{ mm}^3$

porous, showed smaller differences. These results indicate that both CrI and lignin retention are crucial for maintaining mechanical integrity, and that optimizing solution penetration could further improve the properties of thicker samples.

Moreover, our approach to delignification and bleaching presents several advantages over traditional methods: (i) it is eco-sustainable, utilizing minimal hydrogen peroxide, avoiding using on external energy sources (like light or UV), and resulting in alkaline water as a by-product that can be readily purified for future applications of the recovered base (KOH) until it is completely exhausted. Additionally, it generates no toxic gases during H_2O_2 decomposition, unlike delignification or other bleaching techniques that emit volatile chlorine, sulfur compounds or ozone; (ii) the oxidation of chromophore groups is enhanced by the base's more penetrating action, which releases K^+ ions, occurring faster than in previously mentioned delignification and bleaching methods. Additionally, this method preserves the wood volume fraction with a total weight loss of less than 10%. To showcase the scalability of our process and the simplicity of solution diffusion at room temperature, we prepared a sample measuring $100 \times 100 \times 10 \text{ mm}^3$ (longitudinal $\times$ tangential $\times$ radial) in just 3 hours of treatment performed on a dry sample, as shown in Fig. 10. Balsa was selected for this demonstration because its lower density facilitates homogeneous bleaching at larger thicknesses, allowing us to highlight the feasibility of extending the process to centimeter-scale specimens.

Conventionally, preparation times for samples of this thickness range from 6 to 14 h and are generally conducted on wet samples. Additionally, retaining a significant portion of lignin as a binder facilitates the creation of mechanically durable wood samples compared to traditional techniques, resulting in improved optical properties (92–97% reflectance) for both low- and high-density wood types after bleaching.

Conclusion

This study presents an innovative method for producing a white wood template using stabilized alkaline bleaching agents without an external heating source. The wood samples were successfully bleached by targeting the deconjugation of chromophore groups in lignin. This scalable method enables wood bleaching at room temperature, resulting in extremely white wood products (with a reflectivity of 97%) that, unlike other preparation methods, essentially preserve the wood's component content (>90%) as well as the mechanical properties of the original wood.

Scanning Electron Microscopy analysis confirmed that the lignin remained intact within the cell wall. Fourier Transform Infrared and X-ray Diffraction analyses demonstrated that the treatment primarily affected the amorphous components of lignin, resulting in their deconjugation and the removal of hemicelluloses, leaving the crystalline cellulose structure unaffected.

Semi-quantification of residual lignin by FTIR, using the aromatic peak at 1509 cm^{-1} relative to the cellulose peak at 893 cm^{-1} , confirmed that a large fraction of lignin was retained after treatment, supporting the preservation of wood's structural integrity.

N_2 physisorption analysis at 77 K indicated that the shape and distribution of meso- and microporosities were similar before and after treatment. However, there was a partial increase in both porous volume and surface area due to the complete removal of hemicellulose and partial removal of lignin, resulting from the alkaline action of KOH.

The mechanical properties of wood, especially its tensile strength, are closely linked to the degree of crystallinity. A higher alignment of cellulose fibres is associated with improved tensile strength. Conversely, a lower alignment of the cellulose fibres may be related to the varying diffusion of the solution into the thicker network.

Future research should explore the applicability of this method to different types of wood. It should focus on enhancing diffusion as thickness increases and assess the long-term implications of these treatments in large-scale industrial. Overall, this study contributes to ongoing efforts toward more sustainable and eco-friendly practices in wood processing to obtain fully transparent wood.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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References

- Adel AM, El-Wahab A, Ibrahim ZH, A. A., Al-Shemy MT (2011) Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: physicochemical properties. *Carbohydr Polym* 83(2):676–687
- Agarwal UP, McSweeney JD (1997) Photoyellowing of thermomechanical pulps: looking beyond α -carbonyl and ethylenic groups as the initiating structures. *J Wood Chem Technol* 17(1–2):1–26
- Alqrinawi H, Ahmed B, Wu Q, Kameshwar S, Shayan M (2024) Effect of partial delignification and densification on wood's chemical. Structural property evolution, morphological, and mechanical properties. *Ind Crops Prod* 213:118430
- Alves-Ferreira J, Lourenço A, Morgado F, Duarte LC, Roseiro LB, Fernandes MC, Pereira H, Carvalho F (2021) Delignification of cistus ladanifer biomass by organosolv and alkali processes. *Energies* 14(4):1127
- Bolognesi F, Duranti L, Bertollini V, Bianco A, Lamastra FR, Togni M, Bianco A (2024) Cellulose-rich templates from naturally found and cultivation woods diffused in the South-European area: a comprehensive investigation for novel wood-polymer hybrids. *Cellulose* pp 1–21
- Borrega M, Ahvenainen P, Serimaa R, Gibson L (2015) Composition and structure of Balsa (*Ochroma pyramidale*) wood. *Wood Sci Technol* 49:403–420
- Canteri MH, Renard CM, Le Bourvellec C, Bureau S (2019) ATR-FTIR spectroscopy to determine cell wall composition: application on a large diversity of fruits and vegetables. *Carbohydr Polym* 212:186–196
- Chen W, Yu H, Liu Y, Chen P, Zhang M, Hai Y (2011a) Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. *Carbohydr Polym* 83(4):1804–1811
- Chen W, Yu H, Liu Y, Hai Y, Zhang M, Chen P (2011b) Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. *Cellulose* 18:433–442
- Davidson RS (1996) The photodegradation of some naturally occurring polymers. *J Photochem Photobiol B* 33(1):3–25
- Ding Y, Pang Z, Lan K, Yao Y, Panzarasa G, Xu L, Hu L (2022) Emerging engineered wood for building applications. *Chem Rev* 123(5):1843–1888
- Fink S (1992) Transparent wood—a new approach in the functional study of wood structure. *Holzforschung* 46(5):403–408
- Frey M, Schneider L, Masania K, Keplinger T, Burgert I (2019) Delignified wood–polymer interpenetrating composites exceeding the rule of mixtures. *ACS Appl Mater Interfaces* 11(38):35305–35311
- Fukuzumi H, Fujisawa S, Saito T, Isogai A (2013) Selective permeation of hydrogen gas using cellulose nanofibril film. *Biomacromolecules* 14(5):1705–1709
- Garemark J, Perea-Buceta JE, Felhofer M, Chen B, Ruiz C, Sapouna MF, Li I, Y (2023) Strong, shape-memory lignocellulosic aerogel via wood cell wall nanoscale reassembly. *ACS Nano* 17(5):4775–4789

- Gullo F, Marangon A, Croce A, Gatti G, Aceto M (2023) From natural woods to high density materials: an ecofriendly approach. *Sustainability*, 15(3), 2055
- Higuchi T, Shimada M, Nakatsubo F, Tanahashi M (1977) Differences in biosyntheses of guaiacyl and syringyl lignins in woods. *Wood Sci Technol* 11:153–167
- Horikawa Y, Konakahara N, Imai T, Kentaro A, Kobayashi Y, Sugiyama J (2013) The structural changes in crystalline cellulose and effects on enzymatic digestibility. *Polym Degrad Stab* 98(11):2351–2356
- Kostiryukov SG, Malov NA, Matyakubov KB, Konushkin IA (2022) Quantitative determination of lignin in plant materials using IR spectroscopy. *Bull Perm Univ Series: Chem* 12(1):5–16
- Kulasinski K, Keten S, Churakov SV, Derome D, Carmeliet J (2014) A comparative molecular dynamics study of crystalline, paracrystalline and amorphous states of cellulose. *Cellulose* 21:1103–1116
- Kurei T, Sakai S, Nakaba S, Funada R, Horikawa Y (2024) Structural and mechanical roles of wood polymer assemblies in softwood revealed by gradual removal of polysaccharides or lignin. *Int J Biol Macromol* 259:129270
- Li T, Zhu M, Yang Z, Song J, Dai J, Yao Y, Hu L (2016a) Wood composite as an energy efficient building material: guided sunlight transmittance and effective thermal insulation. *Adv Energy Mater* 6(22):1601122
- Li Y, Fu Q, Yu S, Yan M, Berglund L (2016b) Optically transparent wood from a nanoporous cellulosic template: combining functional and structural performance. *Biomacromolecules* 17(4):1358–1364
- Li Y, Fu Q, Rojas R, Yan M, Lawoko M, Berglund L (2017) Lignin-retaining transparent wood. *Chemsuschem* 10(17):3445–3451
- Li Y, Cheng M, Jungstedt E, Xu B, Sun L, Berglund L (2019) Optically transparent wood substrate for perovskite solar cells. *ACS Sustain Chem Eng* 7(6):6061–6067
- Lionetto F, Del Sole R, Cannoletta D, Vasapollo G, Maffezzoli A (2012) Monitoring wood degradation during weathering by cellulose crystallinity. *Materials* 5(10):1910–1922
- Liu Y, Li B, Mao W, Hu W, Chen G, Liu Y, Fang Z (2019) Strong cellulose-based materials by coupling sodium hydroxide–anthraquinone (NaOH–AQ) pulping with hot pressing from wood. *ACS Omega* 4(4):7861–7865
- Liu J, Zhang QH, Ma F, Zhang SF, Zhou Q, Huang AM (2020) Three-step identification of infrared spectra of similar tree species to *pterocarpus Santalinus* covered with beeswax. *J Mol Struct* 1218:128484
- Liu W, Zhang Y, Li P, Wu Y, Li X, Zuo Y (2023) Exploring the effect of lignin on the chemical structure and microstructure of Chinese fir wood by segmental delignification. *Wood Sci Technol* 57(2):329–344
- Lourengo A, Pereira H (2018) Compositional variability of lignin in biomass. *Lignin-trends Appl* pp. 65–98. IntechOpen
- Lowell S, Shields JE, Thomas MA, Thommes M (2012) Characterization of porous solids and powders: surface area, pore size and density, vol 16. Springer Science & Business Media
- Luostarinen K, Verkasalo E (2000) Birch as sawn timber and in mechanical further processing in Finland. A literature study. Finnish Forest Research Institute. Research Papers No. 781
- Montanari C, Olsén P, Berglund LA (2020) Interface tailoring by a versatile functionalization platform for nanostructured wood biocomposites. *Green Chem* 22(22):8012–8023
- Montanari C, Chen H, Lidfeldt M, Gunnarsson J, Olsén P, Berglund LA (2023) Sustainable thermal energy batteries from fully bio-based transparent wood. *Small* 19(28):2301262
- Newman RH (1994) Crystalline forms of cellulose in softwoods and hardwoods. *J Wood Chem Technol* 14(3):451–466
- Ottesen V, Larsson PT, Chinga-Carrasco G, Syverud K, Gregersen ØW (2019) Mechanical properties of cellulose nanofibril films: effects of crystallinity and its modification by treatment with liquid anhydrous ammonia. *Cellulose* 26:6615–6627
- Peng H, Salmén L, Stevanic JS, Lu J (2019) Structural organization of the cell wall polymers in compression wood as revealed by FTIR microspectroscopy. *Planta* 250:163–171
- Popescu CM, Singurel G, Popescu MC, Vasile C, Argyropoulos DS, Willför S (2009) Vibrational spectroscopy and X-ray diffraction methods to establish the differences between hardwood and softwood. *Carbohydr Polym* 77(4):851–857
- Popescu MC, Froidevaux J, Navi P, Popescu CM (2013) Structural modifications of *tilia cordata* wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. *J Mol Struct* 1033:176–186
- Quintana E, Valls C, Barneto AG, Vidal T, Ariza J, Roncero MB (2015) Studying the effects of laccase treatment in a softwood dissolving pulp: cellulose reactivity and crystallinity. *Carbohydr Polym* 119:53–61

- Rietveld HM (1967) Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Crystallogr A* 22(1):151–152
- Rietveld HM (1969) A profile refinement method for nuclear and magnetic structures. *Appl Crystallogr* 2(2): 65–71.
- Sain M, Panthapulakkal S (2006). Bioprocess preparation of wheat straw fibers and their characterization. *Ind Crops Prod.* 23(1): 1–8
- Salmén L, Stevanic JS, Olsson AM (2016) Contribution of lignin to the strength properties in wood fibres studied by dynamic FTIR spectroscopy and dynamic mechanical analysis (DMA). *Holzforschung* 70(12):1155–1163
- Santos RB, Capanema EA, Balakshin MY, Jameel H (2011) Effect of hardwoods characteristics on kraft pulping process: emphasis on lignin structure. *BioResources* 6(4):3623–363
- Schwanninger MJCR, Rodrigues JC, Pereira H, Hinterstoisser B (2004) Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib Spectrosc* 36(1):23–40
- Segal LGJMA, Creely JJ, Jr M, A. E., Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text Res J* 29(10):786–794
- Sirviö JA, Kantola AM, Ämmälä (2023) A Cellulose nanofibers from nonbleached and hydrogen peroxide bleached acidic thiourea treated sawdust. *J Clean Prod* 423: 138824.
- Sun Z, Ibrahim A, Oldham PB, Schultz TP, Connors TE (1997) Rapid lignin measurement in hardwood pulp samples by near-infrared fourier transform Raman spectroscopy. *J Agric Food Chem* 45(8):3088–3091
- Sun RC, et al. (2000) Physico-chemical and structural characterization of hemicelluloses from wheat straw by alkaline peroxide extraction. *Polymer*, 41(7), 2647–2656
- Szymanska-Chargot M, Zdunek A (2013) Use of FT-IR spectra and PCA to the bulk characterization of cell wall residues of fruits and vegetables along a fraction process. *Food Biophys* 8:29–42
- Tarvo V, Lehtimaa T, Kuitunen S, Alopaeus V, Vuorinen T (2009) Chlorate formation in chlorine dioxide delignification—an analysis via elementary kinetic modeling. *J Wood Chem Technol* 29(3):191–213
- Tryjarski P, Gawron J, Andres B, Obiedzińska A, Lisowski A (2022) FTIR analysis of changes in chip-board properties after pretreatment with *pleurotus ostreatus* (Jacq.) P. Kumm. *Energies* 15(23):9101
- Tyufekchiev M, Kolodziejczak A, Duan P, Foston M, Schmidt-Rohr K, Timko MT (2019) Reaction engineering implications of cellulose crystallinity and water-promoted recrystallization. *Green Chem* 21(20):5541–5555
- Vanholme R, Demedts B, Morreel K, Ralph J, Boerjan W (2010) Lignin biosynthesis and structure. *Plant Physiol* 153(3):895–905
- Wang H, Li D, Yano H, Abe K (2014) Preparation of tough cellulose II nanofibers with high thermal stability from wood. *Cellulose* 21: 1505–1515
- Wang B, Li DL, Chen TY, Qin ZY, Peng WX, Wen JL (2017) Understanding the mechanism of self-bonding of bamboo binderless boards: investigating the structural changes of lignin macromolecule during the molding pressing process. *BioResources* 12(1):514–532
- Wang S, Li L, Zha L, Koskela S, Berglund LA, Zhou Q (2023) Wood xerogel for fabrication of high-performance transparent wood. *Nat Commun* 14(1): 2827
- Wikberg H, Maunu SL (2004) Characterisation of thermally modified hard-and softwoods by ¹³C CPMAS NMR. *Carbohydr Polym* 58(4):461–466
- Wójciak A, Kasprzyk H, Sikorska E, Khmelinskii I, Krawczyk A, Oliveira AS, Sikorski M (2010) Changes in chromophoric composition of high-yield mechanical pulps due to hydrogen peroxide bleaching under acidic and alkaline conditions
- Wu J, Wu Y, Yang F, Tang C, Huang Q, Zhang J (2019) Impact of delignification on morphological, optical and mechanical properties of transparent wood. *Compos Part A: Appl Sci Manufac* 117:324–331
- Xia Q, Chen C, Li T, He S, Gao J, Wang X, Hu L (2021a) Solar-assisted fabrication of large-scale, patternable transparent wood. *Sci Adv* 7(5):eabd7342
- Xia Q, Chen C, Yao Y, He S, Wang X, Li J, Hu L (2021b) Situ lignin modification toward photonic wood. *Adv Mater* 33(8):2001588
- Xu F, Shi YC, Wang D (2013) X-ray scattering studies of lignocellulosic biomass: a review. *Carbohydr Polym* 94(2):904–917
- Yang X, Berthold F, Berglund LA (2018) Preserving cellulose structure: delignified wood fibers for paper structures of high strength and transparency. *Biomacromolecules* 19(7):3020–3029
- Zhang SY, Wang CG, Fei BH, Yu Y, Cheng HT, Tian GL (2013) Mechanical function of lignin and hemicelluloses in wood cell wall revealed with microtension of single wood fiber. *BioResources* 8(2):2376–2385

- Zhang J, Ying Y, Yi X, Han W, Yin L, Zheng Y, Zheng R (2023) H₂O₂ solution steaming combined method to cellulose skeleton for transparent wood infiltrated with cellulose acetate. *Polymers* 15(7):1733
- Zhang Y, Wang Y, Li W, Liu S, Tan X, Zhang Q, Zhuang X (2024) Valorization of lignocellulose with One-Step acidified monophasic phenoxylethanol fractionation. *Chemsuschem*. 17(19): e202400487
- Zhu M, Song J, Li T, Gong A, Wang Y, Dai J, Hu L (2016a) Highly anisotropic, highly transparent wood composites. *Adv Mater (Deerfield Beach Fla)* 28(26):5181–5187
- Zhu M, Li T, Davis CS, Yao Y, Dai J, Wang Y, Hu L (2016b) Transparent and haze wood composites for highly efficient broadband light management in solar cells. *Nano Energy* 26:332–339

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2.4. Additional analytical and physico-chemical characterizations: compositional and accessibility investigation of hydroxyl groups

Following the bleaching process covered by the patent in Appendix X and the publication presented in paragraph 2.3, further analytical and chemical-physical investigations were conducted. In particular, a quantitative analysis was performed to determine the lignocellulosic composition of bleached and natural wood (Section 2.5), and a chemical-physical characterization was performed to assess the accessibility of hydroxyl groups via isotopic exchange with D₂O (Section 2.6).

As for the analysis of the sugar composition (Klason lignin and sugar analysis), the activity was carried out at the KTH laboratories in Stockholm, using a different batch of balsa wood with a nominal density of about 150 kg/m³. Despite variation in the starting material and the sources of chemicals, the adoption of standardized protocols for the determination of carbohydrates and lignin has enabled the collection of comparable, representative data on the effectiveness of the treatment. The insoluble lignin content in natural and bleached balsa wood was determined according to the Klason lignin TAPPI T 222 om-02 method. The wood samples were pulverized using a Wiley Mini-Mill 3383-L70 (Thomas Scientific, USA) with a 60 µm mesh. 200 mg of dried powder (105°C) was used for each sample, and the results are the average of 6 replicates.

For hydrolysis and determination of insoluble lignin (Klason method), samples were subjected to an acidic attack with concentrated sulfuric acid (H₂SO₄, 72%). The mixture was treated in an autoclave at 125°C for 60 min. The suspension was vacuum-filtered using fiberglass filters that had been weighed and dried at 105°C. The insoluble residue (Klason lignin) was first washed with hot deionized water and then with cold water, dried at 105 °C overnight, and weighed gravimetrically.

The filtrate was collected, diluted, and used for carbohydrate determination performed using a Dionex ICS-3000 ion chromatography system (Thermo Fisher Scientific, USA). The main monosaccharides identified are arabinose, galactose, xylose, mannose, and glucose. The cellulose content was assumed to be the same as the glucose content, while the hemicellulose content was taken as the sum of the other four.

The evaluation of the accessibility of hydroxyl groups, discussed in Section 2.6, was carried out by ATR-FTIR spectroscopy through isotope exchange with deuterated water

(D₂O) on the same balsa samples described in the publication (Materials and Methods p. 46). The exchange in D₂O was monitored via IR spectroscopy using a Thermo Nicolet IS50 IR spectrometer in transmission mode. The spectra were collected at 35°C (beam temperature) using 64 scans with a spectral resolution of 4 cm⁻¹. To allow dosing, a Pyrex cell designed for gases was used, consisting of a reserve zone in which pressure is monitored, permanently connected to a vacuum system via a valve, and a measuring area equipped with a vacuum gauge for pressure measurement. The two zones communicate via a valve. The experiment consists of dosing D₂O at 26 mbar (saturation pressure at 35°C), waiting 15 min, and recording the saturation spectrum. Subsequently, the excess D₂O is degassed up to 1*10⁻⁴ mbar, and a second spectrum is recorded. The procedure is repeated 4 times.

2.4.1. Compositional analysis of the pre- and post-treatment balsa wood template (Klason lignin and sugar analysis)

Following publication, a quantitative analysis of the composition of 1 mm-thick natural and bleached balsa wood was conducted. This sample was chosen as representative to validate the effectiveness of the chemical treatment, as its high sensitivity to delignification processes, already highlighted in the literature, ensures clear and reliable compositional data. (Alqrinawi et al. 2024) In fact, both its hierarchical structure and low density, as well as low lignin content, allow easier penetration of the whitening solution into the bulk making it an ideal substrate for accurately quantifying lignin removal via Klason analysis. (Alqrinawi et al. 2024)

The analysis was conducted at the laboratories of the Wallenberg Wood Science Centre (WWSC) department at the Royal Institute of Technology in Stockholm (KTH).

Through sugar analysis and the determination of Klason lignin, the composition, in grams, of the three structural components of the wood was determined: i) cellulose; ii) hemicellulose; iii) lignin. (Walker 1993)

Fig. 4 shows both the compositional comparison of the pre- and post-treatment balsa wood species (Fig. 4A) and a comparison between the percentage of residual post-treatment lignin and the main bleaching and delignification treatments present in the literature (Fig. 4B). As can be seen from the graph shown in Fig. 4A, natural balsa wood has a holocellulose and lignin composition consistent with the data reported in the

literature for this species, characterized by a high fraction of cellulose and a moderate lignin content. (Alqrinawi et al. 2024; Xu et al. 2024)

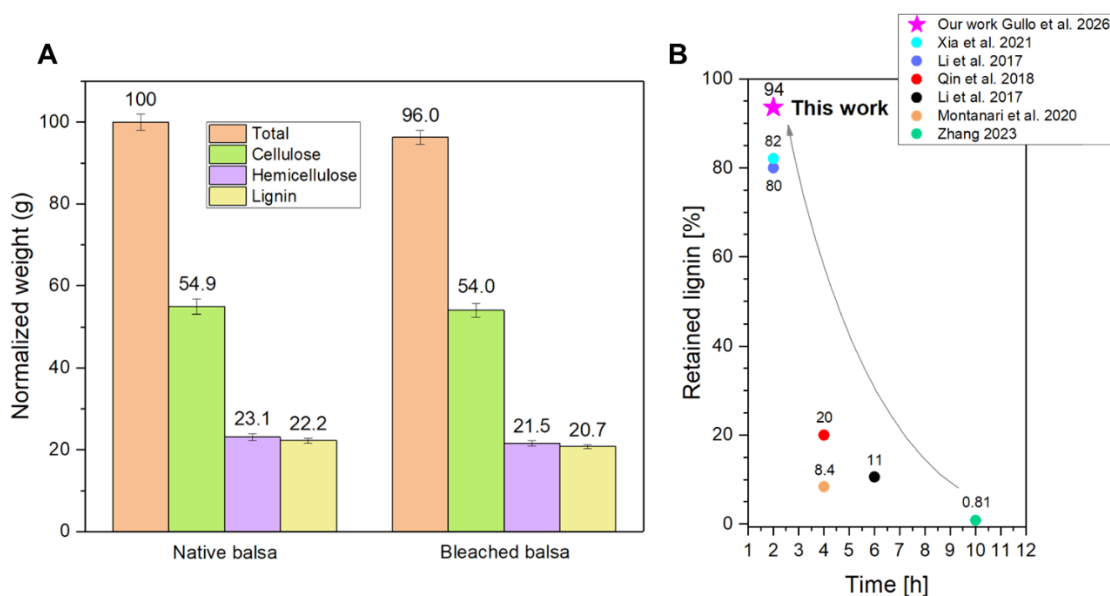


Fig. 4 A) Wood composition of the balsa wood before (native balsa) and after the bleaching process (bleached balsa) using hydrogen peroxide (H_2O_2) and potassium hydroxide (KOH); B) comparison of the percentage of lignin removed in the literature vs the new bleaching process. (Gullo et al. 2026; Li et al. 2017; Montanari et al. 2020; Qin et al. 2018; Xia, Chen, Yao, et al. 2021; Zhang et al. 2023)

Following the bleaching treatment, the percentage changes in the individual components were calculated as the proportions of the content, in grams, of the natural and bleached wood components. The results show a smaller percentage change in cellulose (2%), as expected, and a more significant change in hemicellulose and lignin (7 and 6%, respectively). (Lionetto et al. 2012)

The recorded lignin loss is the lowest value so far reported in the literature, both for comparable bleaching treatments and for deeper delignification treatments, as can be seen in Fig. 4B. (Li et al. 2017; Xia, Chen, Yao, et al. 2021)

This quantitative difference underlines the mild nature of the treatment, which acts on the target modification of lignin, preserving it as much as possible within the structure.

These results could be compared with those presented in the paper regarding ATR-FTIR structural analysis, XRD, and mechanical properties, taking into account the use of significantly different methodologies and technologies. Therefore, the analyses will be compared with the results of the compositional analysis below.

The FTIR analysis reported on p. 55 showed the disappearance of the band at 1735 cm^{-1} , associated with the ester groups of hemicellulose, and the significant reduction of the band at 1240 cm^{-1} , associated with the vibration of the carbonyl groups of hemicellulose. At the same time, the maintenance of the bands at 1594 and 1509 cm^{-1} , associated with the vibration of the aromatic skeleton, was observed. Furthermore, comparing the latter band (1509 cm^{-1}) to that of cellulose (893 cm^{-1}), associated with the vibration of the β -glycosidic bond, it was possible to determine, with a semi-quantitative analysis, the loss of lignin resulting in 18%. (Kostryukov et al. 2022; Sun et al. 1997; Tryjarski et al. 2022) These data could suggest an apparent discrepancy between the change in hemicellulose and lignin recorded by sugar analysis and that detected by structural IR analysis. However, as already highlighted in the publication, the two techniques yield completely different results: sugar analysis provides quantitative data for the entire mass of the sample, while ATR-FTIR detects a surface response, more sensitive to changes in the first layers of the material rather than the entire bulk. (Nakamoto 2009)

During the process, the strongly alkaline environment induces a hydrolysis of the hemicellulose ester groups and a breakdown of the side bonds and acetyl groups, which does not necessarily result in a complete solubilization of the hemicellulose fraction, but in a predominantly superficial break. (Nakamoto 2009) Suppression of the 1735 cm^{-1} band signal could therefore indicate a surface chemical change (hydrolysis/deacetylation) rather than a total removal from the bulk material.

If we consider the semi-quantitative loss of lignin estimated by ATR-FTIR, we obtain a relative change in the ratio of aromatic rings/surface cellulose fraction. (Popescu et al. 2007; Tryjarski et al. 2022) Sugar analysis, on the other hand, shows a smaller percentage loss. This result supports the hypothesis that the treatment involves deconjugation, rather than extensive depolymerization, of the aromatic backbone of lignin.

The crystallinity index, calculated from XRD data using the Rietveld method (Table 3, p. 59), shows a moderate decrease in crystallinity in the treated balsa samples (1 mm), attributed to the partial removal of more accessible or less-ordered cellulosic fractions. (Andersson et al. 2003)

In an alkaline environment, in fact, the following can occur: i) swelling phenomena of the cell wall; ii) partial disorganization of the microfibrils; and iii) selective removal of more exposed crystalline domains. (Chen et al. 2025; Ding et al. 2016; Eronen, Österberg, and Jääskeläinen 2009; Ishikura and Nakano 2005; Ji, Ma, and Xu 2014)

The reduction observed is, however, limited and consistent with the limited loss of cellulose detected by the sugar analysis (2%). In addition, no phase transformation of cellulose I to cellulose II is observed from XRD. This result confirms that the treatment remains non-destructive to crystalline cellulose. (French 2014)

Finally, if we look at the mechanical properties recorded for thin balsa samples (p. 62), we find a 50% decrease in ultimate strength compared to natural wood. This behavior can be interpreted by considering three competing factors:

- *Partial removal of hemicellulose*, which plays a fundamental role in the transfer of cargo between cellulose and lignin. (Salmén 2015) In fact, its partial removal can reduce the efficiency of interfibrillar bridging. (Nagy 2010)
- *Change in lignin*, which is preserved, but deconjugation with the consequent formation of more hydroxyl groups, can alter its rigidity and ability to transfer stresses. (Winandy and Lebow 2001)
- *Reduction of crystallinity in thinner samples* in which the diffusion of the reagent is more complete and can induce greater local alteration of amorphous and partially crystalline regions, negatively affecting ultimate strength. (Andersson et al. 2003)

It is important to underline that the reduction in tensile strength is not attributable to structural collapse or macroscopic fibrillation, as occurs in aggressive delignification processes. (Li et al. 2016, 2017) The matrix remains cohesive and structurally intact, thanks to the extensive presence of lignin, but exhibits reduced load capacity, probably due to chemical modification of the amorphous phases.

2.4.2. *Evaluation of the accessibility of hydroxyl groups by ATR-FTIR spectroscopy and D₂O isotope exchange*

The study of the nature of the hydroxyl groups present in balsa wood (NB) and bleached wood (WB) was carried out by isotopic exchange with D₂O in the gas phase. To distinguish, in natural and bleached wood, the contribution of the lignocellulose component, a cellulose and a lignin standard were used.

This technique enables the distinction between the hydroxyl groups (-OH) of the amorphous and crystalline components, both in bulk and on the surface. The latter represents the -OH chemically accessible to external molecules and, in this case, to D₂O.

Fig. 5 A shows the spectra of the cellulose standard before isotope exchange (curve a), after the sending of 26 mbar of D₂O (curve b), and after the complete desorption of the fine gas phase (residual pressure of 1·10⁻⁴ mbar). In order to appreciate the spectral variations starting from Fig. 5 A, Fig. 5 B was obtained, as better described in the following. Fig. 5 B, in fact, shows the spectra presented in subtraction mode where (b') represents the subtraction between curve b and curve a in Fig. 5 A, (c') the subtraction between curve c and curve a in Fig. 5 A and finally (d) the subtraction between curve b and curve c in Fig. 5 A.

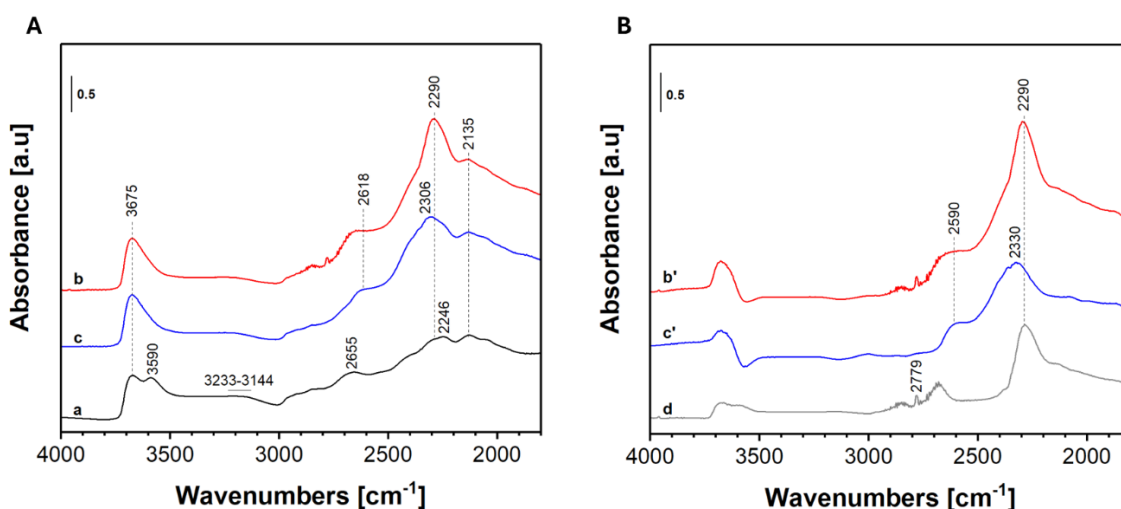


Fig. 5 FTIR spectra in transmission of pure cellulose. A) after degassing (a), after 26 mbar of D₂O (b), and subsequent degassing for 24 h (c). B) Pure cellulose spectra shown in subtraction: (b') spectrum resulting from subtraction between curves b and a in Fig. A, (c') between curves c and a in Fig. A, (d) between curves b and c in Fig. A.

The band originally present in cellulose (Fig. 5 A (a)) at 3590 cm⁻¹ is attributable to the primary hydroxyls bonded to the C2 and C3 carbons of the glucose unit, which are mainly involved in intramolecular hydrogen bonds, while the broad band with a maximum between 3233 and 3144 cm⁻¹ is associated with the stretches of C6 carbon-bound hydroxyls participating in intermolecular hydrogen bonds. (Hofstetter, Hinterstoisser, and Salmén 2006) The fact that these bands are negative after exchange with D₂O (Fig 5 b' e c') indicates that a portion of these hydroxyl groups is willing to exchange their protons for deuterium and therefore that the sites are accessible to D₂O molecules.

The exchange is further confirmed by the formation of bands related to the stretching of the -OD groups in the region between 2600 and 1800 cm⁻¹. In particular, a less intense band at 2590 cm⁻¹, related to the -OD stretches involved in weaker or more accessible

hydrogen bonds, such as intermolecular ones; and a band at 2330 cm⁻¹, related to the formation of -OD groups involved in stronger hydrogen bonds, such as intramolecular ones. (Hofstetter et al. 2006) By observing the subtraction spectrum (d) in Fig. 5 B it is possible to distinguish the contribution of the gas phase at about 2779 cm⁻¹ and the contribution at 2290 cm⁻¹, linked to the liquid-like phase of the deuterated water trapped in the material through physisorption processes. (Kondo 2005)

For clarity, Table 1 shows the positions of the bands observed in the spectra, the attribution to functional groups and the interaction with D₂O, as well as the diagnostic significance of the observed bands.

Assignment	Wavenumber [cm ⁻¹]	Diagnostic significance	REF
v -OH	3300 - 3400	Original cellulose hydroxyl -OH groups (crystalline and amorphous domain) involved in a large cluster of hydrogen bonds.	(Blackwell 1977; Maréchal 1997)
	3675	Monomeric D--HO molecules/isolates generated as a by-product of isotopic exchange, or surface -OH groups no longer interacting due to solvent-induced structural changes.	(Hofstetter et al. 2006; Liang and Marchessault (1959)
v -OD	2618 / 2590	-OD groups of exchanged cellulose or D ₂ O molecules weakly bound to hydrogen.	(Mann and Marrinan 1956)
	2330 / 2306	Chemically exchanged cellulose -OD groups, strongly involved in intra- and intermolecular hydrogen bonds.	(Hofstetter et al. 2006; Liang and Marchessault 1959; Mann and Marrinan (1956)
	2290	Physisorbed D ₂ O molecules strongly interacting with the polymer matrix ("liquid-like" structures or solvent clusters).	(Maréchal 1997)
Combination	2135	Combination bands of adsorbed D ₂ O.	(Maréchal 1997)

Table 1 Assignment of IR bands for pure cellulosa standard in the range 4000-400 cm⁻¹. The table shows the main bands related to -OH and -OD stretching and combination and the interpretative notes relating to the contributions of the interaction between cellulose and (deuterated) water.

Fig. 6 A shows the spectra related to the lignin standard with the same order and color code used and described for Fig. 5 A. Fig. 6 B shows the spectra related to the lignin standard in subtraction mode with the same order and color code used in Fig. 5 B.

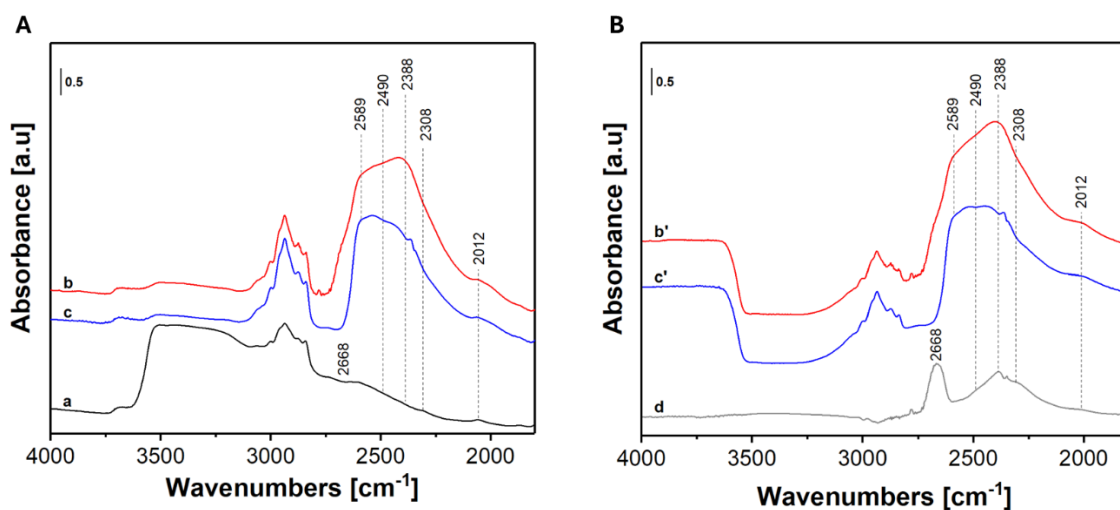


Fig. 6 FTIR spectra in transmission of pure Kraft lignin. A) After degassing (a), after 26 mbar of D₂O (b), and subsequent degassing for 24 hours (c). B) Spectra of the lignin standard shown in subtraction: (b') spectrum resulting from the subtraction between curve b and a in Fig. A, (c') between curve c and a in Fig. A, (d) between curve b and c in Fig. A.

Unlike cellulose, which is a linear semicrystalline polymer consisting of repeated units of glucose and organized into crystalline and amorphous domains, lignin is a highly amorphous and disordered three-dimensional aromatic biopolymer, formed by interconnected phenylpropanoid units. (Boerjan, Ralph, and Baucher 2003) This structural difference is fundamental to understanding the behavior of the two materials during isotope exchange with D₂O. While in cellulose a significant part of the hydroxyl groups is involved in an ordered network of hydrogen bonds within the crystal domains, in lignin the functional groups are more heterogeneously distributed within an amorphous matrix. (Salmén 2015)

In particular, hydroxyl groups exchangeable in lignin can be divided mainly into two categories: i) aliphatic groups located on the propyl side chains of phenylpropanoid units and ii) phenolic groups directly linked to aromatic rings. (Schoemaker et al. 1991) This variety of chemical sites is reflected in the increased complexity and width of the bands observed in infrared spectra.

Comparing the results obtained for lignin with those observed for cellulose, the differences related to the different structural organization of the two biopolymers clearly emerge. Lignin, being essentially amorphous and lacking a compact crystalline nucleus like that found in cellulose, has hydroxyl groups that are, in principle, almost completely accessible to D₂O molecules. The accessibility of these sites is therefore mainly controlled by the ability of the solvent to diffuse into the matrix and cause it to swell. (Taniguchi, Harada, and Nakato 1978)

This feature results in a distinctly different interaction with D₂O than that observed in cellulose. Analyzing the spectra, it is observed that lignin retains significant amounts of D₂O through physisorption phenomena (Fig. 6B (a')). Despite the presence of numerous hydroxyl groups, lignin is globally more hydrophobic than cellulose due to the high density of aromatic rings present in its structure. As a result, water molecules tend to form clusters or accumulate in the pores and cavities of the structure rather than fully integrating into a network of hydrogen bonds with the polymer matrix. (Kang et al. 2019; Kirui et al. 2022)

The isotopic exchange of protons with deuterium on lignin functional groups (Fig. 6B) is therefore more pronounced than in cellulose. The band associated with isotopic exchange appears to be wider and more complex due to the overlap of contributions from -OD groups related to both aliphatic and phenolic sites. This behavior is indicative of a high accessibility of the hydroxyl groups present in the lignin structure.

In the literature, the band observed around 2668 cm⁻¹ (Fig. 6B (c')) is generally attributed to isolated deuterated hydroxyls, i.e., -OD groups that have very weak or virtually no hydrogen interactions. This signal differs from the broader and more intense band centered between 2450 and 2550 cm⁻¹, which instead corresponds to the -OD groups involved in the polymer's hydrogen-bond network. (Lourençon et al. 2022)

The pioneering studies of Mann and Marchessault on wood accessibility use this band as a probe of the amorphous fraction of lignocellulosic materials. (Liang and Marchessault 1959; Mann and Marrinan 1956) Since lignin is inherently amorphous, most of its hydroxyl groups are potentially accessible to isotopic exchange with D₂O. The presence of the band at 2668 cm⁻¹ therefore reflects those hydroxyl groups which, although accessible, are found in microstructural cavities or in steric configurations that prevent the formation of strong hydrogen bonds with other nearby oxygen atoms. (Lourençon et al. 2022; Pönni 2014)

This type of interaction is commonly described as "deuterium-bonded isolated OD". (Murby and Pullin 1979) These groups can be isolated by the action of the aromatic, rigid structure of lignin, which locks some -OH groups in oriented positions that are not suitable for the formation of hydrogen bonds. This phenomenon is accentuated in lignin obtained by aggressive chemical processes, such as insoluble lignin obtained by Klason, which uses concentrated sulphuric acid, or the Kraft process, which combines an aggressive basic treatment with bleaching agents. During these processes, the lignin macromolecule can undergo structural rearrangements that affect the distribution of hydroxyl sites.

The main bands observed in the spectra and their assignments to the functional groups involved in isotopic exchange with D₂O are summarized in Table 2, which also reports their diagnostic significance.

Assignment	Wavenumber [cm ⁻¹]	Diagnostic significance	RIF
v -OH	3550 - 3100	Aliphatic and phenolic -OH groups	(Faix 1991)
	2668	Isolated -OD groups with weak or no hydrogen interactions	(Pönni 2014)
	2650 - 2450	D ₂ O liquid like physisorbed in the meso and macropores and in the cavities of the three-dimensional structure	(Tarmian, Burgert, and Thybring 2017)
v -OD	2450 - 2350	Aliphatic and phenolic -OD groups exchanged	(Tarmian et al. 2017)

Table 2 Assignment of FTIR bands of -OH and -OD groups in lignin standard after isotope exchange with D₂O and related diagnostic significance.

Fig. 7 shows the spectra related to the interaction of natural (NB) and bleached (WB) balsa wood with D₂O. In particular, Fig. 7 A and B show the spectra obtained for NB and WB, respectively, before the sending of D₂O in the gas phase (a), after the sending of 26 mbar (b), and after complete degassing (c). Fig. 7 C and D show the subtraction spectra of NB (red curve) and WB (blue curve) obtained by subtraction of curves (b) and (c) and (b) and (c) (Fig. 7 A and B), respectively.

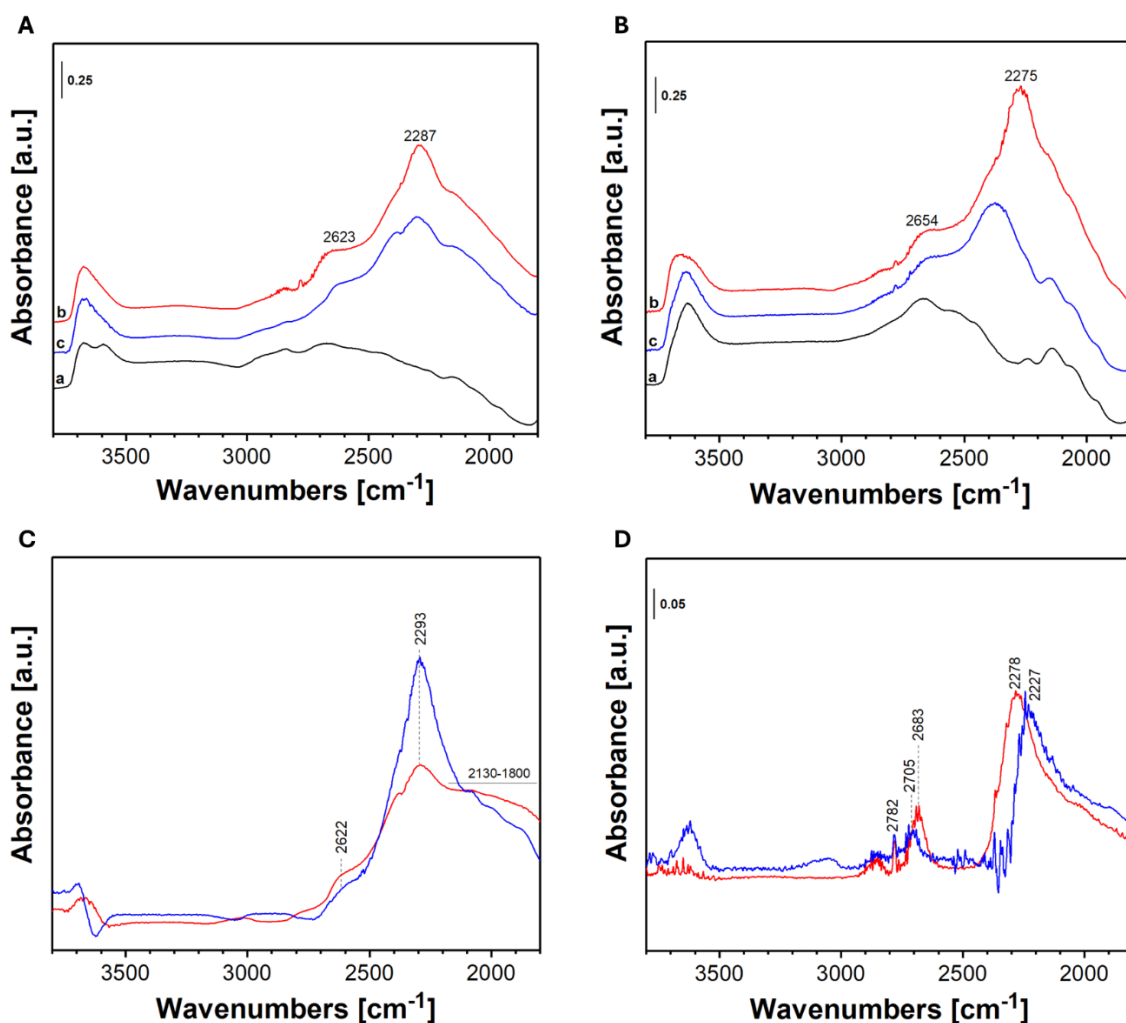


Fig. 7 FTIR spectra in transmission of NB and WB samples. A) NB sample after degassing (a), after sending 26 mbar of D₂O (b), and subsequent degassing for 24h (c). B) sample WB after degassing (a), after sending 26 mbar of D₂O (b) and subsequent degassing for 24 h C) NB (red curve) and WB (blue curve) spectra obtained by subtraction of the curve c and a (Fig. A-B), D) NB (red curve) and WB (blue curve) spectra obtained by subtraction of the b and c curves (Fig. A-B).

From the analysis in Fig. 7, it is possible to verify how the structures of natural balsa wood (NB) and bleached wood (WB) interact with D₂O molecules at the molecular level. In Fig. 7 A and B, it can be observed that the behavior in the experimental sequence does not differ from that of the previous experiments. Also in this case, the process highlights the ability of the samples to exchange protons with deuterium, transforming the original -OH groups into -OD groups. Analyzing Fig. 7 C and D, which show the spectra in subtraction mode to highlight the variations induced by the exchange, the difference between the natural component (red curve) and the bleached component (blue curve)

clearly emerges. The appearance of signals in the region between 2700 and 1800 cm^{-1} confirms that deuteration has taken place. In particular, the bands observed at 2623 cm^{-1} for the NB sample and at 2622 cm^{-1} for the WB (Fig. 7 C) are attributable to isolated -OD groups, i.e., sites that fail to establish strong hydrogen bonds with the surrounding oxygen atoms due to structural rigidity or their position within microcavities.

These signals are more pronounced in natural wood due to the presence of lignin, which sterically blocks some hydroxyls. A crucial aspect is related to the physisorbed deuterated water, whose presence is signaled by the intense peaks at 2287 cm^{-1} for NB and at 2293 cm^{-1} for WB (Fig. 7 C). These bands indicate the formation of liquid-like structures or solvent clusters trapped in the pores of the lignocellulosic matrix. In Fig. 7 D, the detail at 2278 and 2227 cm^{-1} further emphasizes how the physisorbed water interacts with the three-dimensional structure of the material. Interestingly, the lignin in the NB sample, despite its more hydrophobic nature than cellulose, favors the accumulation of D_2O in cavities and pores rather than integration into an ordered network of hydrogen bonds, leading to a broader, more complex exchange band due to the overlap of aliphatic and phenolic sites. Finally, the presence of the signals at 2782 cm^{-1} in panel D is attributable to the gas phase of D_2O , while the region between 2130 and 1800 cm^{-1} (Fig. 7 C) shows the presence of the combination bands of adsorbed deuterated water.

From this information we can verify, as demonstrated by the comparison between NB and WB in Fig. 7, that the bleaching process modifies the lignin and consequently alters the accessibility of the sites and the way in which the water is retained in the wood bulk, making the spectroscopic profile of the WB more similar to that of pure cellulose described earlier in the published paper.

This increase in the accessibility of hydroxyl groups in WB has direct implications for the wood-polymer interface. First of all, the increased abundance of free sites allows the formation of a dense network of hydrogen bonds between cellulose chains and the polar groups of the epoxy resin, such as oxiranic rings and secondary hydroxyls. (Olsen, Herrera, and Berglund 2019) A higher density of these bonds, even if weak, improves the affinity at the interface by facilitating, on the one hand, the wettability of the template and, on the other hand, reducing the formation of micro-voids that would lead to greater detachment and optical scattering. (Chen et al. 2022; Li et al. 2018) In this way, the WB is not only an inert template but also actively binds to the matrix to create a composite with a continuous interface. In addition to ensuring natural compatibility, the greater availability of sites, due to the higher surface area of the most accessible -OH, could

enable their chemical functionalization using strategies already consolidated and studied in the literature for porous inorganic materials with high surface area, such as zeolites, bentonites, and saponites. In these materials, functionalization of active sites with pendant -OH groups is exploited to tune surface reactivity. (Athens, Shayib, and Chmelka 2009; Cauvel et al. 1995; Huo 2011) Applying this approach to TW, free -OH groups could serve as graft sites for functional molecules (e.g., silanes). (Gullo et al. 2023) These changes would allow the wood template to be used as a chemically reactive platform to improve specific properties and achieve intrinsic hydrophobicity and fire resistance to enhance the hierarchical and accessible structure of wood, combined with the versatility of the polymer phase. (Fang et al. 2025; Wang et al. 2011)

2.5. Conclusions

In this chapter, a new selective bleaching process for chromophore groups has been presented as fast and eco-friendly, aimed at overcoming the limits of other processes, both delignification and bleaching, already reported in the literature. The effectiveness of the process and the preservation of lignin with an alkaline H_2O_2 solution enabled the retention of 96% of the total mass compared to natural balsa and 93%, as evidenced by Klason lignin determination. In fact, as confirmed by the mechanical properties, lignin continues to perform its structural and hydrophobic binding function within the cell wall. Through sugar analysis, it was possible to confirm that the ratio of holocelluloses (hemicellulose and cellulose) remained unchanged compared to natural wood, indicating that the process was selective for the chromophore groups of lignin only. Through isotope exchange with D_2O monitored via ATR-FTIR, the hydroxyl groups accessible to D_2O in the WB have shown that the bleaching process does not reduce access to the reactive sites of the cellulose. On the contrary, the accessibility of the -OH groups is enhanced, thanks to the modification of the lignin, which makes the template more similar to pure cellulose while preserving its structural integrity. This is very important for enhancing both wettability and interactions between the polymer template and the subsequent infiltration step. In addition, monitoring concentrations and reaction times to control color stability during bleaching enabled optimization of the parameters, reducing both the energy and environmental impact of the treatment, in line with the sustainable innovation objectives of the PNRR NODES project. In conclusion, the proposed approach, the subject of the

IT102024000023808 patent, allowed the production of a white wood template that preserves the integrity of the original material and has the optical properties necessary for its use as a template for the production of TW.

Chapter II References

- Alqrinawi, Hussein, Bulbul Ahmed, Qinglin Wu, Hai Lin, Sabarethinam Kameshwar, and Mohammad Shayan. 2024. "Effect of Partial Delignification and Densification on Chemical, Morphological, and Mechanical Properties of Wood: Structural Property Evolution." *Industrial Crops and Products* 213:118430.
- Andersson, Seppo, Ritva Serimaa, Timo Paakkari, Pekka Saranpää, and Erkki Pesonen. 2003. "Crystallinity of Wood and the Size of Cellulose Crystallites in Norway Spruce (*Picea Abies*)." *Journal of Wood Science* 49(6):531–37.
- Athens, George L., Ramzy M. Shayib, and Bradley F. Chmelka. 2009. "Functionalization of Mesoporous Inorganic–Organic and Porous Inorganic Materials." *Current Opinion in Colloid & Interface Science* 14(4):281–92.
- Blackwell, John. 1977. "Infrared and Raman Spectroscopy of Polysaccharides." ACS Publications.
- Boerjan, Wout, John Ralph, and Marie Baucher. 2003. "Lignin Biosynthesis." *Annual Review of Plant Biology* 54(1):519–46.
- Brebu, Mihai, and Cornelia Vasile. 2010. "Thermal Degradation of Lignin—a Review." *Cellulose Chemistry & Technology* 44(9):353.
- Cauvel, A., D. Brunel, F. Di Renzo, P. Moreau, and F. Fajula. 1995. "Functionalization of Y Zeolites with Organosilane Reagents." Pp. 286–93 in *Studies in Surface Science and Catalysis*. Vol. 94. Elsevier.
- Chen, Hui, Jonas Garemark, Lengwan Li, Mathias Nero, Maximilian Ritter, Ocean Cheung, Tom Willhammar, Ilya Sychugov, Yuanyuan Li, and Lars A. Berglund. 2025. "Green Nanotechnology of Cell Wall Swelling for Nanostructured Transparent Wood of High Optical Performance." *Small* 21(5):2406749.
- Chen, Hui, Céline Montanari, Ravi Shanker, Saulius Marcinkevicius, Lars A. Berglund, and Ilya Sychugov. 2022. "Photon Walk in Transparent Wood: Scattering and Absorption in Hierarchically Structured Materials." *Advanced Optical Materials* 10(8):2102732.
- Ding, Dayong, Xia Zhou, Zhe Ji, Tingting You, and Feng Xu. 2016. "How Does Hemicelluloses Removal Alter Plant Cell Wall Nanoscale Architecture and Correlate with Enzymatic Digestibility?" *BioEnergy Research* 9(2):601–9.
- Ding, Yu, Zhenqian Pang, Kai Lan, Yuan Yao, Guido Panzarasa, Lin Xu, Marco Lo Ricco, Douglas R. Rammer, J. Y. Zhu, and Ming Hu. 2022. "Emerging Engineered Wood for Building Applications." *Chemical Reviews* 123(5):1843–88.
- Eronen, Paula, Monika Österberg, and Anna-Stiina Jääskeläinen. 2009. "Effect of Alkaline Treatment on Cellulose Supramolecular Structure Studied with Combined Confocal Raman Spectroscopy and Atomic Force Microscopy." *Cellulose* 16(2):167–78.

- Faix, Oskar. 1991. "Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy."
- Fang, Yatong, Kexuan Chen, Lulu Xu, Yan Zhang, Yi Xiao, Yao Yuan, and Wei Wang. 2025. "Advances in Wood Processing, Flame-Retardant Functionalization, and Multifunctional Applications." *Polymers* 17(19):2677.
- French, Alfred D. 2014. "Idealized Powder Diffraction Patterns for Cellulose Polymorphs." *Cellulose* 21(2):885–96.
- Gullo, Francesca, Andrea Marangon, Alessandro Croce, Giorgio Gatti, and Maurizio Aceto. 2023. "From Natural Woods to High Density Materials: An Ecofriendly Approach." *Sustainability* 15(3):2055.
- Gullo, Francesca, Massimo Messori, and Paola Palmero. 2026. "Preservation of Wood Structure Using Stabilized Alkaline Bleaching Agents: A Novel and Mild Approach to Enhance Whitening for Lignin-Rich Wood Template." *Wood Science and Technology* 60(1):12.
- Hofstetter, Karin, Barbara Hinterstoisser, and Lennart Salmén. 2006. "Moisture Uptake in Native Cellulose—the Roles of Different Hydrogen Bonds: A Dynamic FT-IR Study Using Deuterium Exchange." *Cellulose* 13(2):131–45.
- Huo, Qisheng. 2011. "Synthetic Chemistry of the Inorganic Ordered Porous Materials." Pp. 339–73 in *Modern inorganic synthetic chemistry*. Elsevier.
- Ishikura, Y., and T. Nakano. 2005. "Adsorption Properties and Structural Features of Alkali Treated Wood." *Journal of the Japan Wood Research Society (Japan)* 51(6).
- Ji, Zhe, Jianfeng Ma, and Feng Xu. 2014. "Multi-Scale Visualization of Dynamic Changes in Poplar Cell Walls during Alkali Pretreatment." *Microscopy and Microanalysis* 20(2):566–76.
- Kang, Xue, Alex Kirui, Malitha C. Dickwella Widanage, Frederic Mentink-Vigier, Daniel J. Cosgrove, and Tuo Wang. 2019. "Lignin-Polysaccharide Interactions in Plant Secondary Cell Walls Revealed by Solid-State NMR." *Nature Communications* 10(1):347.
- Kirui, Alex, Wancheng Zhao, Fabien Deligey, Hui Yang, Xue Kang, Frederic Mentink-Vigier, and Tuo Wang. 2022. "Carbohydrate-Aromatic Interface and Molecular Architecture of Lignocellulose." *Nature Communications* 13(1):538.
- Kondo, Tetsuo. 2005. "Hydrogen Bonds in Cellulose and Cellulose Derivatives." *Polysaccharides: Structural Diversity and Functional Versatility* 69–98.
- Kostryukov, S. G., N. A. Malov, B. Matyakubov Kh, and I. A. Konushkin. 2022. "Quantitative Determination of Lignin in Plant Materials Using IR Spectroscopy." *Bulletin of Perm University//Chemistry* 12(1):5–16.
- Li, Yuanyuan, Qiliang Fu, Ramiro Rojas, Min Yan, Martin Lawoko, and Lars Berglund. 2017. "Lignin-retaining Transparent Wood." *ChemSusChem* 10(17):3445–51.

- Li, Yuanyuan, Qiliang Fu, Shun Yu, Min Yan, and Lars Berglund. 2016. "Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance." *Biomacromolecules* 17(4):1358–64.
- Li, Yuanyuan, Xuan Yang, Qiliang Fu, Ramiro Rojas, Min Yan, and Lars Berglund. 2018. "Towards Centimeter Thick Transparent Wood through Interface Manipulation." *Journal of Materials Chemistry A* 6(3):1094–1101.
- Liang, C. Y., and R. H. Marchessault. 1959. "Infrared Spectra of Crystalline Polysaccharides. I. Hydrogen Bonds in Native Celluloses." *Journal of Polymer Science* 37(132):385–95. doi:10.1002/pol.1959.1203713209.
- Lionetto, Francesca, Roberta Del Sole, Donato Cannoletta, Giuseppe Vasapollo, and Alfonso Maffezzoli. 2012. "Monitoring Wood Degradation during Weathering by Cellulose Crystallinity." *Materials* 5(10):1910–22.
- Lourençon, Tainise, Michael Altgen, Timo Paakkonen, Valentina Guccini, Paavo Penttilä, Eero Kontturi, and Lauri Rautkari. 2022. "Effect of Moisture on Polymer Deconstruction in HCl Gas Hydrolysis of Wood." *ACS Omega* 7(8):7074–83.
- Mann, J., and H. J. Marrinan. 1956. "The Reaction between Cellulose and Heavy Water. Part 1. A Qualitative Study by Infra-Red Spectroscopy." *Transactions of the Faraday Society* 52:481–87.
- Maréchal, Yves. 1997. "Interaction Configurations of H₂O Molecules in a Protein (Stratum Corneum) by Infrared Spectrometry." *Journal of Molecular Structure* 416(1–3):133–43.
- Montanari, Céline, Hui Chen, Matilda Lidfeldt, Josefin Gunnarsson, Peter Olsén, and Lars A. Berglund. 2023. "Sustainable Thermal Energy Batteries from Fully Bio-based Transparent Wood." *Small* 19(28):2301262.
- Montanari, Céline, Peter Olsén, and Lars A. Berglund. 2020. "Interface Tailoring by a Versatile Functionalization Platform for Nanostructured Wood Biocomposites." *Green Chemistry* 22(22):8012–23. doi:10.1039/D0GC02768E.
- Murby, E. John, and A. D. E. Pullin. 1979. "The Infrared Matrix Isolation Spectra of Water Species in a Deuterium Matrix." *Australian Journal of Chemistry* 32(6):1167–76.
- Nagy, Edwin. 2010. *A Lattice Model for the Prediction of the Mechanical Properties of Certain Softwoods*. The University of Maine.
- Nakamoto, Kazuo. 2009. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*. John Wiley & Sons.
- Olsen, Peter, Natalia Herrera, and Lars A. Berglund. 2019. "Polymer Grafting inside Wood Cellulose Fibers by Improved Hydroxyl Accessibility from Fiber Swelling." *Biomacromolecules* 21(2):597–603.

- Paulsson, Magnus, and Jim Parkås. 2012. "REVIEW: LIGHT-INDUCED YELLOWING OF LIGNOCELLULOSIC PULPS – MECHANISMS AND PREVENTIVE METHODS." *BioResources* 7(4):5995–6040. doi:10.15376/biores.7.4.5995-6040.
- Pönni, Raili. 2014. "Changes in Accessibility of Cellulose for Kraft Pulps Measured by Deuterium Exchange."
- Popescu, Carmen-Mihaela, Maria-Cristina Popescu, Ghita Singurel, Cornelia Vasile, Dimitris S. Argyropoulos, and Stefan Willfor. 2007. "Spectral Characterization of Eucalyptus Wood." *Applied Spectroscopy* 61(11):1168–77.
- Qin, Jiankun, Xiaowan Li, Yali Shao, Kaixin Shi, Xin Zhao, Tianshi Feng, and Yingcheng Hu. 2018. "Optimization of Delignification Process for Efficient Preparation of Transparent Wood with High Strength and High Transmittance." *Vacuum* 158:158–65.
- Rundlöf, Eva Svensson, Eric Zhang, Liming Zhang, and Göran Gellerstedt. 2006. "The Behavior of Chromophoric Structures in Softwood Mechanical Pulp on Bleaching with Alkaline Hydrogen Peroxide." *Nordic Pulp & Paper Research Journal* 21(3):359–64.
- Salmén, Lennart. 2015. "Wood Morphology and Properties from Molecular Perspectives." *Annals of Forest Science* 72(6):679–84.
- Schoemaker, H. E., U. Tuor, A. Muheim, H. W. H. Schmidt, and M. S. A. Leisola. 1991. "The Chemistry of Lignin Biodegradation Catabolism of Veratryl Alcohol and Its Methyl Ether." Pp. 69–86 in *Bioorganic Chemistry in Healthcare and Technology*. Springer.
- Sun, Zhaohui, Amin Ibrahim, Philip B. Oldham, Tor P. Schultz, and Terrance E. Connors. 1997. "Rapid Lignin Measurement in Hardwood Pulp Samples by Near-Infrared Fourier Transform Raman Spectroscopy." *Journal of Agricultural and Food Chemistry* 45(8):3088–91.
- Taniguchi, T., H. Harada, and K. Nakato. 1978. "Determination of Water Adsorption Sites in Wood by a Hydrogen–Deuterium Exchange." *Nature* 272(5650):230–31.
- Tarmian, Asghar, Ingo Burgert, and Emil Englund Thybring. 2017. "Hydroxyl Accessibility in Wood by Deuterium Exchange and ATR-FTIR Spectroscopy: Methodological Uncertainties." *Wood Science and Technology* 51(4):845–53.
- Teacă, Carmen-Alice, and Ruxanda Bodîrlău. 2016. "Photochemical Behavior of Wood Based Materials." Pp. 91–107 in *Photochemical behavior of multicomponent polymeric-based materials*. Springer.
- Tryjarski, Paweł, Jakub Gawron, Bogusław Andres, Agnieszka Obiedzińska, and Aleksander Lisowski. 2022. "FTIR Analysis of Changes in Chipboard Properties after Pretreatment with *Pleurotus Ostreatus* (Jacq.) P. Kumm." *Energies* 15(23):9101.

- Walker, John CF. 1993. "Basic Wood Chemistry and Cell Wall Ultrastructure." Pp. 23–67 in *Primary wood processing: principles and practice*. Springer.
- Wang, Shuliang, Changyu Liu, Guochao Liu, Ming Zhang, Jian Li, and Chengyu Wang. 2011. "Fabrication of Superhydrophobic Wood Surface by a Sol–Gel Process." *Applied Surface Science* 258(2):806–10.
- Winandy, Jerrold E., and Patricia K. Lebow. 2001. "Modeling Strength Loss in Wood by Chemical Composition. Part I. An Individual Component Model for Southern Pine." *Wood and Fiber Science* 239–54.
- Xia, Qinqin, Chaoji Chen, Tian Li, Shuaiming He, Jinlong Gao, Xizheng Wang, and Liangbing Hu. 2021. "Solar-Assisted Fabrication of Large-Scale, Patternable Transparent Wood." *Science Advances* 7(5):eabd7342.
- Xia, Qinqin, Chaoji Chen, Yonggang Yao, Shuaiming He, Xizheng Wang, Jianguo Li, Jinlong Gao, Wentao Gan, Bo Jiang, and Mingjin Cui. 2021. "In Situ Lignin Modification toward Photonic Wood." *Advanced Materials* 33(8):2001588.
- Xu, Xiaoying, Jonas Garemark, Farsa Ram, Zhen Wang, and Yuanyuan Li. 2024. "Metallic Wood through Deep-Cell-Wall Metallization: Synthesis and Applications." *ACS Applied Materials & Interfaces* 16(17):22433–42.
- Zhang, Jun, Yongling Ying, Xiaoyang Yi, Wenbo Han, Lu Yin, Yongjun Zheng, and Rongbo Zheng. 2023. "H₂O₂ Solution Steaming Combined Method to Cellulose Skeleton for Transparent Wood Infiltrated with Cellulose Acetate." *Polymers* 15(7):1733.
- Zhu, Mingwei, Jianwei Song, Tian Li, Amy Gong, Yanbin Wang, Jiaqi Dai, Yonggang Yao, Wei Luo, Doug Henderson, and Liangbing Hu. 2016. "Highly Anisotropic, Highly Transparent Wood Composites." *Advanced Materials (Deerfield Beach, Fla.)* 28(26):5181–87.

Chapter III

3.1. Process standardization and scalability of resin infiltration

In Chapter II, the first critical step for the production of transparent wood was introduced and studied. The work focused on preparing a bleached wood template that is resistant, easily workable, and integrated with existing technologies. In fact, 30% v/v H_2O_2 is already used for surface bleaching in the production of thin veneers that require attenuated coloring. (Bulian and Graystone 2009; Eul, Moeller, and Steiner 2000) The integration of a basifying agent that penetrates the bulk of the material at room temperature, accelerating and making the bright white color permanent, is readily feasible for both the production of new transparent laminated products and for translucent plywood.

However, to make the process fully adoptable by industry, it is also necessary to standardize and engineer the next phase, which involves impregnating the template with resins with a compatible refractive index. In this perspective, important parameters such as the volume of resin used, defined as the H/L ratio (height of the resin/thickness of the wooden template) and the pressure applied during infiltration, were considered to lower the resin consumption and study the synergistic effect of both parameters considered on the optical properties of the final composite.

A further element to consider concerns the choice of polymer matrices. Therefore, two epoxy resins with the same chemical composition were selected: one fully synthetic with a UV filter and one partially bio-based in the absence of a UV filter, both of which can be polymerized at room temperature. This is to reduce energy consumption and avoid disrupting existing production lines, i.e., to minimize economic impact on the development of the process at an industrial scale. Cold cross-linking also reduces the wood-polymer stresses that occur as the temperature increases and maintains a planar geometry of the resulting composite. (Pascault and Williams 2009; Plecnik et al. 1986) Although these are important aspects for large-scale production, the time variable,

generally longer for cold curing of resins, remains to be considered. (Oadian 2004; Prime 2005) Finally, optical durability was evaluated by exposure to the entire solar spectrum, using accelerated aging tests.

Chapter III therefore studies: i) the impregnation phase by means of a DoE approach to evaluate the effect of some variables on the optical properties of TWs, correlating the variation of transmittance and haze to the variation of microstructure; iii) the reinforcing effect of the wood template compared to the mechanical properties of the resin alone; ii) the effect of long-term UV-Vis light exposure on the optical yield of the sample; iii) the depth of aging recorded through the study of the surface and bulk structure of resins and TWs derived by IR spectroscopy in ATR and transmission. The publication derived from the study conducted is presented in the next paragraph.

3.2. Unpublished Paper: DoE-guided fabrication of transparent wood with tunable haze: linking infiltration parameters, microstructure, and long-term durability

DoE-guided fabrication of transparent wood with tunable haze: linking infiltration parameters, microstructure, and long-term durability

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Abstract

Transparent wood (TW) composites have attracted significant interest due to their bio-based nature and potential applications in areas such as architecture, photovoltaic systems and optical devices, where light transmittance and diffusion are crucial. Haze, often considered an intrinsic property of wood, can be an adjustable parameter in an engineered TW design. In this study, a Design of Experiments (DoE) was used to fabricate TWs from 1 mm-thick bleached balsa wood, which were subsequently vacuum-infiltrated with two commercial epoxy resins: a synthetic resin containing a UV filter and a partially bio-based resin (40%) without UV absorber. Two parameters were varied: the residual pressure and the amount of resin, calculated as the ratio between the height of the resin level in the impregnation container and the thickness of the wood, and their effects on optical transmittance and haze were studied. The response surfaces obtained provided information on the explored working window, showing how haze can be optimised by tuning these two parameters. Although DoE was not fully predictive due to the complexity of the infiltration step, it allowed identification of regions to both maximize and minimize haze, depending on the application considered. By correlating optical responses with scanning field-emission electron microscopy (FE-SEM), it was possible to associate haze with microstructural characteristics, thereby linking high haze to incomplete infiltration and low haze to continuous wood-polymer interfaces. Mechanical tensile tests and long-term aging confirmed, respectively, the structural reinforcement of TW compared to neat

epoxy resin and the good optical stability of the samples, in particular for TW composites infiltrated with commercial resin containing a UV filter, as expected. This work presents a quantitative framework for the controlled fabrication of TW and an experimental design to control optical performance.

1. Introduction

The growing demand for sustainable materials is directing research towards renewable solutions and low environmental impact consistent with the principles of the circular economy. (Abad-Segura et al. 2020; Choudhury and Hashmi 2020; Kandpal et al. 2024; Mohanty et al. 2018; Pandit et al. 2025) In this context, materials are no longer evaluated exclusively as a function of mechanical or functional performance, but also in relation to the origin of raw materials, the efficiency of production processes, energy consumption, the reduction or reuse of chemical waste, and the possibility of reuse or biodegradability of materials at the end of their life. (Schubert, Panzarasa, and Burgert 2023; Starzyk et al. 2025) In addition to the sustainability of feedstock, Life Cycle Analysis (LCA) and carbon footprint quantification play an important role in the actual industrial scale-up of new materials. (Alamandi 2025; Jang et al. 2025)

Wood, a renewable material used since ancient times, with a hierarchical structure and capable of sequestering CO₂ from the environment, represents an ideal platform for the development of advanced engineered bio-based composite materials. (He et al. 2023; Li et al. 2016; Montanari et al. 2021; Panzarasa and Burgert 2022; Song et al. 2018) Among the most promising innovations involving this resource is transparent wood (TW), obtained by modifying the chemical-physical properties of the wood template and subsequently infiltrating it with polymers having a refractive index compatible with that of the cell walls. (F. Gullo, M. Messori and P. Palmero 2026; Li et al. 2016; Zhu, Song, et al. 2016; Zhu et al. 2023) The TWs obtained have a good mechanical strength, with high light transmission and modulable diffusion, and are potentially usable in a wide range of applications, including architecture and construction, in photovoltaic devices, and in light management systems. (Jacucci et al. 2021; Wang et al. 2023; Wang and Zhu 2021; Wu et al. 2023; Wu, Meng, et al. 2024; Zhu, Li, et al. 2016)

Despite the bio-based origin of the wood substrate, most of the TWs reported in the literature use polymeric materials of fossil origin, such as poly(methyl methacrylate) (PMMA) or bisphenol-A-based epoxy resins. (Ding et al. 2022; Li et al. 2016; Martinka

et al. 2023; Wang et al. 2018; Zhu, Song, et al. 2016) Only a few studies have focused on the use of totally or partially bio-based resins, and the evaluation of the impact of resin formulation on the performance and overall sustainability of the material is poorly evaluated in the literature. (Bolognesi et al. 2026; Montanari et al. 2021; Muthoka et al. 2021; Wachter, Rantuch, and Štefko 2023) Since, to date, the polymer phase is the most significant fraction of the final mass of the composite, the choice of the polymeric fraction plays a key role both in terms of durability and environmental footprint. (Jiang et al. 2018; Wu, Ye, et al. 2024)

The fabrication of the TW is divided into two main phases: i) modification of the wood template, by delignification or selective bleaching, and ii) polymeric infiltration to reduce scattering due to the refractive index mismatch between the cell wall and the air trapped in the lumens. (Fink 1992; Hu et al. 2017) Conventional delignification processes, often derived from the paper industry, remove high levels of lignin by aggressive treatments, resulting in loss of structural integrity and a greater environmental impact. (Li et al. 2016; Wu et al. 2020; Zhu, Song, et al. 2016) Recent selective bleaching approaches, conducted in milder conditions and at room temperature, allow the deconjugation of lignin chromophores while maintaining a large part of the lignin in the central lamella and preserving the wood hierarchy, with benefits in terms of mechanical stability and sustainability of the process. (Gullo, Messori, and Palmero 2026; Xia, Chen, Li, et al. 2021; Xia, Chen, Yao, et al. 2021)

In addition to the preparation of the template, the infiltration step represents a crucial aspect that is still not very standardized. In the literature, fundamental parameters such as the resin feeding ratio relative to the thickness of the wood and the control of the residual pressure during vacuum infiltration are rarely reported or analyzed in a systematic way. (Mi et al. 2020; Zhang et al. 2023; Zhu, Li, et al. 2016) These parameters directly influence hydrostatic pressure, residual solvent removal, air evacuation from lumens, and microbubble formation, with effects that could be decisive for both transmittance and haze. (Cheng and Lu 2014; Gavrilovic-Grmusica et al. 2012; Li et al. 2016; de Meijer, Thurich, and Militz 2001; Terzopoulou, Achilias, and Vouvoudi 2025; Wu et al. 2025) Moreover, in the transition towards a possible industrialization of TW, standardization gaps emerge. In particular, mechanical tests do not always follow the same standards; optical properties are often reported without specifying the sample thickness, reference wavelength, and standard used; finally, LCA studies are still limited and not homogeneous. (F. Gullo, M. Messori and P. Palmero 2026)

A further critical aspect concerns the durability of composites when exposed to UV rays, which is crucial for outdoor applications. Although TW is proposed for façade or photovoltaic applications, systematic studies on UV aging are still few. (Bisht, Barshilia, and Pandey 2024; Bisht, Pandey, and Barshilia 2021; Katunský, Kanócz, and Karl'a 2018; Wachter et al. 2021) In the literature, Bisht et al. (2021) exposed TW to UVA for 250 h, and analyzed the formation of degradation products via IR. At the same time, Wachter et al. (2021) conducted UV-C exposure for 35 days under highly aggressive conditions to evaluate the effect of TW surface disinfection. Finally, another study of Bisht et al. (2024) was conducted by naturally exposing for 150 days and monitoring the photooxidation. However, such approaches predominantly focus on transmittance as a key parameter, while haze variation, which is critical for applications requiring light scattering control, is never analyzed. In addition, UV-C exposures favor the evaluation of accelerated photolysis and the direct breaking of C–C and C–O bonds, resulting in less representative of progressive degradation in real solar conditions. (Wachter et al. 2021)

This work addresses two main aspects that remain unexplored. Firstly, a Design of Experiments (DoE) approach based on Central Composite Design (CCD) is applied for the first time to control infiltration parameters, specifically the dimensionless volumetric feeding ratio between the resin level and the wood thickness (defined as a H/T ratio) and residual pressure, in order to evaluate their applicability to a complex and heterogeneous system such as the TW. Secondly, a UV aging study is conducted in a solarbox with a xenon lamp (290–800 nm), with a spectrum that remains constant and comparable to that of the sun, for a duration equivalent to 9 months of natural exposure, monitoring transmittance and haze weekly.

Two commercial epoxy resins with the same chemical base (bisphenol-A) were selected: a synthetic one containing a UV filter (ER) and a 40% bio-based one without UV stabilizers (PBER), together with their respective composites (TW-ER and TW-PBER). The wood used as a template is balsa wood, referred to as NW in its natural state and BW after bleaching. The materials were characterized by morphological analysis in Field Emission Scanning Electron Microscopy (FE-SEM) for the study of the microstructure, UV-Visible spectroscopy for the evaluation of optical properties (transmittance and haze) both in DoE and in aging, and mechanical tensile tests for the determination of ultimate strength, Young's modulus, and elongation at break.

The present study, therefore provides a quantitative and engineering framework for the fabrication and evaluation of the durability of transparent wood, highlighting that optical

stability over time is strongly influenced by resin and that the increase in haze, more than just the reduction in transmittance, is a crucial parameter to be controlled for the use of TW in outdoor applications.

2. Materials and Methods

2.1. Materials: wood templates and chemicals

Raw balsa wood panels (thickness: 1 mm) were purchased from Specialized Balsa Wood, LLC (USA). The density of the balsa wood ranged between 0.15 and 0.17 g·cm⁻³. Specimens were cut into 20 × 20 × 1 mm³ samples prior to chemical treatment.

For the bleaching process, a 30% v/v hydrogen peroxide (H₂O₂) solution (Sigma-Aldrich), potassium hydroxide (KOH) granules (Sigma-Aldrich, ≥85% purity), and sodium bicarbonate (NaHCO₃) powder (Solvay S.p.A., 99% purity) were used.

In the impregnation step, two bisphenol A-based epoxy resins were used. The commercial epoxy resin (Resin Pro) containing a UV stabilizer, purchased from Resina Pro, Italy, is composed of two components: A) 2,2-bis-[4-(2,3-epoxypropoxy)phenyl]propane; B) 3-aminomethyl-3,5,5-trimethylcyclohexylamine. This resin will be labelled as ER later on. The second epoxy resin (Art Pro Green), labelled as PBER, supplied by Resin Pro, Italy, was partially bio-based (~40% plant content) and contained the same components A and B as the previous epoxy resin. Both resins were used as received.

2.2. Alkaline H₂O₂ bleaching

Bleaching of balsa wood templates was performed according to the alkaline H₂O₂ protocol previously reported by the authors. (Gullo et al. 2026) Briefly, samples were treated with a 30% v/v hydrogen peroxide solution activated with KOH (2 M final concentration) at room temperature until complete bleaching was achieved. After stabilization in NaHCO₃ solution and extensive rinsing with deionized water, the samples were prepared for impregnation.

Samples were exchanged with organic solvents before the impregnation in order to remove residual water. In particular, the samples were soaked under vacuum 3 times in ethanol and 3 times in acetone. For each solvent, three vacuum cycles were applied to promote full solvent penetration and effective displacement of entrapped water. The

templates were finally stored in acetone until the impregnation step. The obtained bleached samples were named WB.

2.3. Resin impregnation

Prior to use, component A and component B of each epoxy system were mixed according to the manufacturer's recommended mass ratios (5:3 for Resin Pro and 2:1 for Art Pro Green). The resin mixtures were mechanically stirred for 2 min to ensure homogeneous blending. Two epoxy resins were employed: a synthetic resin containing an organic UV filter (ER) and a 40% bio-based resin without UV stabilizers (PBER). The bleached wood templates, previously stored in acetone, were immersed in each resin system. The amount of resin was controlled to achieve specific volumetric feeding ratios, defined as the H/T ratio (where H represents the height of the resin level within the container and T the wood template thickness). Three levels were investigated: H/T ratios of 5, 10, and 15 representing low, intermediate, and high resin availability, respectively. For all DoE experiments, the same geometry of the potting vessel, the same size of the acetone-preserved wood template, and the same two selected commercial resins were retained. As a result, the chemistry of the resin, its initial viscosity, and the geometry of the bleached wood sample were kept constant during the experiments. Vacuum impregnation was carried out at controlled residual pressures of 40, 70, and 100 mbar, each applied for 20 min. This duration was selected as sufficient to promote acetone removal from the wood template and to facilitate its replacement with epoxy resin. Upon the end of infiltration, excess resin was carefully scraped off from the sample surfaces using a laboratory spatula and the specimens were placed between two glass slides to maintain planar geometry and uniform thickness during curing. Polymerization was conducted at room temperature (23 ± 2 °C) for 24 h until complete hardening was achieved.

2.4. Experimental Design

The composite central design was generated using CAT (Composite Design Tool), while regression modelling, leverage analysis, and influence diagnostics were performed in Python (version 3.11.6) using the NumPy, SciPy, scikit-learn, and Statsmodels libraries. A total of 12 experimental runs were designed and reported in Table 1, following a Response Surface Methodology (RSM) approach. A Central Composite Design (CCD)

was selected to investigate how the two independent variables, resin amount (expressed as the H/T ratio, calculated relative to wood thickness) and residual pressure (mbar), influence the system response, namely the optical properties of TWs expressed in terms of transmittance and haze. The experimental design space consisted of an H/T ratio ranging from 5 to 15 and a residual pressure of 40-100 mbar. Optical properties were determined as described in Section 2.5.

2.5. Characterization

The transmittance and haze measurements were collected using a Cary 5000 UV–vis-NIR (Agilent, CA, USA) from 200 to 800 nm.

Transmittance measurements were conducted using an integrating sphere, with the sample positioned at the input port of the incident beam and the transmitted light collected through a secondary port coupled to an optical fiber. Haze values were determined according to ASTM D1003 (“Standard Method for Haze and Luminous Transmittance of Transparent Plastics”).

The microstructure of the samples was characterized using Scanning Field Electron Microscopy (FE-SEM) with a Hitachi S-4000 (Tokyo, Japan) in order to examine the hierarchical structure of wood in natural, bleached, and transparent balsa samples.

The tensile test was carried out using a Zwick-Line Z050 single-column machine (Genova, Italy). A total of 18 samples with dimensions of $5 \times 60 \times 1 \text{ mm}^3$ (tangential $\times$ longitudinal $\times$ radial directions) were analyzed. To ensure statistical reliability three replicates of each of the following samples were measured: ER, TW-ER, PBER and TW-PBER. The tests and sample preparation were carried out according to ISO 13061-6. The crosshead displacement rate was set to 2 mm/min, with a grip separation (gauge length between grips) of 42 mm. A 1 kN load cell was used to measure force. Strain was calculated as the ratio between crosshead displacement and the initial distance between grips. Engineering stress was calculated as the ratio between the applied force and the initial cross-sectional area of the specimen.

The accelerated aging tests were carried out in accordance with ISO 4892-2 ("Plastics - Methods of exposure to laboratory light sources - xenonic arc lamps"), using Cycle n.6 (Table 4). Accelerated aging was performed using a solarbox equipped with a 2500 W xenon arc lamp. The samples were positioned 20 cm from the lamp and exposed under continuous, dry conditions at a controlled temperature of 60 °C, 24 h per day, for a total

of 42 days of real exposure. The xenon lamp, characterized by a spectral distribution comparable to the solar spectrum in the 290–800 nm range, with a total irradiance of $550 \text{ W}\cdot\text{m}^{-2}$ and a spectral irradiance of $1.1 \text{ W}\cdot\text{m}^{-2}\cdot\text{nm}^{-1}$ at 420 nm, was consistent with the selected exposure cycle according to the ISO standard previously cited. Three replicates were exposed for each TW composite to ensure reproducibility of the subsequent analyses. The dose of Total Radiant Energy (TRE) to which transparent composites were exposed during accelerated aging was calculated as reported in Equation 1:

$$\text{TRE} = E_{\text{tot}} \cdot t \quad (1)$$

where:

E_{tot} is the total irradiance in the range of 290–800 nm, and t is the exposure time measured in seconds. Under operating conditions, the total radiating energy stored was approximately $2.85 \times 10^9 \text{ J/m}^2$ ($\sim 792 \text{ kW/m}^2$). To obtain a precise estimate of the exposure time, this value was compared with annual average solar irradiation data for Italy. Considering that about 52–55% of solar energy falls within the 290–800 nm range, the accelerated test corresponds to a representative average of 9 months of natural sunlight. As a result, one week of accelerated aging is equivalent to about 1.5 months of real sun exposure.

The optical properties of the TW specimens were monitored weekly during aging. The optical properties, in terms of transmittance and haze, have been measured in accordance with the standard described earlier in the same paragraph.

The FTIR spectra in transmission and ATR were recorded following the same procedure already described in the published article (p. 47). To improve spectral quality, the number of scans was doubled from 32 to 64.

3. Results and discussion

3.1. Design of experiments and response surface analysis for resin impregnation of bleached wood templates

In this work, a methodological approach of the response surface (RSM) based on a composite central design (CCD-type structure) was adopted to evaluate whether a statistically structured framework could be applied to a physically governed and

heterogeneous system, such as TW. The experimental design was designed to isolate the purely physical effects associated with infiltration and microbubble formation. To avoid confounding variables, the same bleached balsa wood pattern (thickness = 1 mm) and the same commercial bisphenol-A-based epoxy resin were used during the study. In this way, resin viscosity, wood-resin chemical reactivity, and inherent variation in hierarchical structure, including availability and arrangement of substrate porosity, were kept constant. The properties of the resulting wood-based composite, TW, are mainly due to phenomena of a physical nature, such as: i) hydrostatic pressure; ii) filling of the lumen by capillarity; iii) efficiency of the process in removing air and solvent from porosity; iv) kinetic velocity during degassing, and iv) possible formation of inter-structure microbubbles during vacuum release. (Jelee et al. 2023; H. Li et al. 2019; Park et al. 2022; Yang et al. 2024) One of the objectives of this DoE was therefore not only to explore the applicability of statistical modelling to heterogeneous systems, but also to identify processing conditions that can minimise resin consumption without compromising optical performance. The complete dataset is shown in Table 1.

Nº exp	H/T	P[mBar]	Coded Value (H/T)	Coded Value (P)	[%T]	[%Haze]
1	15	100	1	1	76.8	57.6
2	5	100	-1	1	68.6	73.2
3	15	40	1	-1	87.5	50.6
4	5	40	-1	-1	91.6	42.1
5	10	70	0	0	90.7	32.7
6	10	70	0	0	90.5	32.5
7	10	70	0	0	91.2	33.2
8	10	70	0	0	90.8	31.8
9	10	100	0	1	92.2	51.1
10	10	40	0	-1	90.5	56.4
11	5	70	-1	0	92	51.7
12	15	70	1	0	92.3	57.5
13	12.5	55	0.5	-0.5	90.1	47.2
14	7.5	85	-0.5	0.5	89.3	54.3
Validation Experiments						
15	9.6	61			91.2	26.3
16	9.6	61			90.7	24.3

Table 1. Real, coded values of the experimental points (H/T ratio and residual pressure (P)) for the composite central design (CCD) and their respective optical properties measured in terms of transmittance and haze (% at 550 nm). Additional internal points

(exp. 13-14) and model validation experiments at the predicted minimum haze point were included.

Two independent process parameters were selected: i) the height of the resin relative to the thickness of the wood, defined as a dimensionless H/T ratio and controlled by the volume of resin applied; ii) the residual pressure during impregnation in a vacuum. The H/T ratio was varied at three levels (5, 10, and 15), corresponding to low, medium, and high resin availability relative to the model thickness. In particular, the highest level (H/T=15) corresponds to the amount of resin commonly used in the literature for impregnation, when reported, or to solutions containing polymers dissolved in evaporable solvents during the impregnation process to obtain TW, and has therefore been included as a reference condition representative of conventional processing routes. (Mi et al. 2020; Zhang et al. 2023; Zhu, Li, et al. 2016) The H/T ratio was introduced as a parameter that describes the amount of resin available on top of the model during vacuum impregnation. Because the same resin, sample geometry, and potting vessel were used throughout the DoE, the observed differences cannot be attributed to changes in resin chemistry or inherent viscosity. Considering the low initial viscosity of the epoxy resin, the reduced sample thickness (1 mm) and the 20-minute vacuum treatment, a complete lumen filling is expected even at the lowest H/T values, if only the capillary infiltration mechanisms are considered. However, during vacuum impregnation, a vigorous release of acetone vapors and trapped gases was experimentally observed. Although these phenomena have not been quantitatively monitored, they suggest that the amount of resin available on top of the model may affect bubble evacuation and the stability of the wood–resin interface during pressure release. In addition, the removal of acetone progressively changes the local composition of the system and coincides with the beginning of epoxy curing. Therefore, lower H/T ratios may be subject to local increases in viscosity during impregnation, affecting resin redistribution and elimination of interfacial defects. The SEM observations discussed in Section 3.2, which show different microstructures showing resin detachment and interfacial discontinuity in some cases, support the hypothesis that H/T influences the final microstructure through transient phenomena of fluid dynamics, gas evacuation efficiency, and local viscosity changes that occur during infiltration, rather than through limitations in resin availability. As a result, the investigation of H/T aimed not only to understand its influence on optical properties, but also to identify the minimum resin consumption compatible with the production of TW.

The residual pressure was varied between 40 and 100 mbar. At 100 mbar, a condition of slight vacuum is reached, which limits the efficiency of degassing and can leave residual air in the lumen network, increasing optical scattering (more scattering). At 40 mbar, a lower vacuum pressure improves air removal, but can cause premature boiling of the resin and solvent (acetone) used to make the white wood template completely water-free, or violent outgassing, increasing the likelihood of microbubbles during pressure release. Therefore, both extremes of the pressure domain can generate optical defects for different physical mechanisms. (Chen et al. 2020; Li et al. 2016)

A CCD was implemented by including four factorial corner points, axial points along the pressure axis, and a center point ($H/T = 10$, $P = 70$ mbar). The center point was replicated four times via genuine replications to estimate the intrinsic experimental error. The standard deviation of replicated measurements ranged from 0.3% to 0.6%, indicating high process repeatability and negligible measurement noise relative to total response variability. In addition to the canonical composite design structure, two other internal experiments were subsequently introduced ($H/T = 12.5$ at 55 mbar and $H/T = 7.5$ at 85 mbar). These points were not intended to alter the geometric structure of the CCD; they were added to increase the number of residual degrees of freedom, improve regression strength, and better capture curvature effects within the design space.

The optical responses, namely total transmittance (%T) and haze (%), were modeled using a second-order polynomial equation expressed in real units:

$$\%T = 71.48 + 2.206A + 0.4480P - 0.1781A^2 + 0.02040AP - 0.005837P^2$$

$$\%Haze = 96.12 - 5.975A - 0.9946P + 0.4536A^2 - 0.04515AP + 0.01166P^2$$

where A represents the H/T ratio and P the residual pressure in mbar. The quadratic model explains 64.4% of the variance in transmittance ($R^2 = 0.644$, $R^2_{adj} = 0.422$) and 70.1% of the variance in haze ($R^2 = 0.701$, $R^2_{adj} = 0.513$). Although the quadratic model exhibits a moderate descriptive capacity ($R^2 \sim 0.64\text{--}0.70$), it effectively maps the experimental domain and highlights the fundamental physical trends. The residual variance not captured by the second-order polynomial is likely due to the inherent stochastic nature of the wood's hierarchical porosity rather than measurement noise.

Indeed, both the response surfaces and the contour plot of transmittance (Fig. 1a-b) and haze (Fig. 1c-d) show, respectively, a domed trend for transmittance and a convex

parabolic tendency for haze. In addition, both responses exhibit maxima near the model's central region. From a physical standpoint, this result is consistent with optimal infiltration conditions, in which resin availability is sufficient without excessive hydrostatic pressure, and a moderate residual vacuum facilitates effective removal of the storage solvent (acetone) without inducing a violent solvent–resin substitution process. Under the selected conditions, the central region represents the most controlled physical domain with respect to the balance between solvent expulsion and the progressive replacement of the solvent by the infiltrating resin.

It is also important to note that, while haze exhibits a distinct optimum within the investigated processing range, transmittance does not display a single optimal point but rather a broader operational window that can be considered optimal within the tested domain. In this case, however, there is a large region of the optimum in which the expected transmittance is $\geq 91\%$. This region was capped, accounting for the maximum optical response of the epoxy matrix (93%). The maximum transmittance limit of TW has been set at 93%. This value has been considered the maximum limit, excluding the possibility that the composite in TW has a transmittance higher than that of the resin alone. As a result, the transmittance-related response surface shown in Fig. 1b has an extended region. In this portion of the response surface, the parameters do not significantly affect transmittance because the composite's transmittance is limited by the resin's maximum transmittance. Thus, the optimal transmittance region should be viewed as a physically constrained performance window rather than a single stationary point as predicted by the polynomial model.

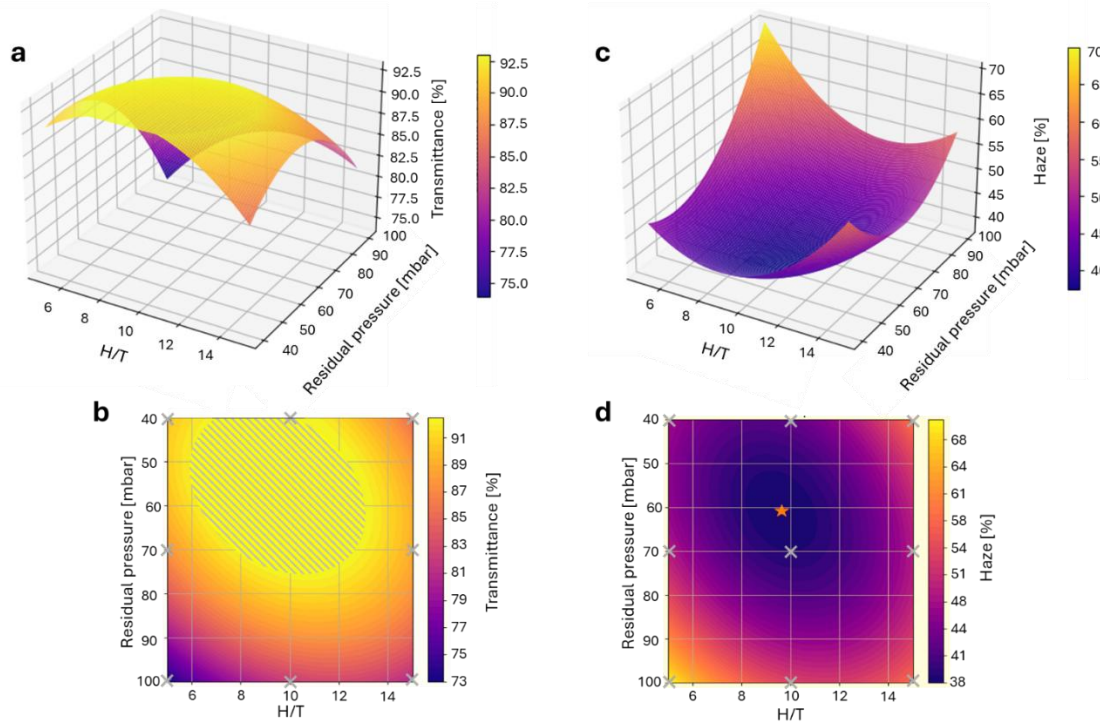


Fig. 1 Quadratic RSM surfaces and contour maps describing the effect of H/T ratio and residual pressure on the optical properties of TW (550 nm). (a) 3D response surface of total transmittance (%T). (b) Contour map of transmittance showing the plateau region (%T $\geq$ 91%; hatched area) approaching the intrinsic transparency limit of the resin. (c) 3D response surface of haze (%). (d) Contour map of haze with the predicted minimum region (star); crosses indicate experimental design points.

Leverage analysis and influence diagnostics (Fig. S1-S4, Supporting Information) confirm that the higher leverage values correspond to the edges of the model, as expected for CCDs. (Baddeley, CHANG, and Song 2013; Plummer 2025) However, the studentized residuals and Cook's distance indicate deviations, particularly at extreme pressures. These results indicate that the residual variance is not due to measurement uncertainty, as the pure error, calculated from the midpoint over 4 replicates (see Table 1), is limited to 0.3–0.6% and instead is driven by systematic model deficiencies. The optical response of TW is, in fact, governed by non-linear phenomena between the infiltration process and vacuum that are not fully described by the second-order polynomial surface. To validate the model at the expected optimum point (approximately 9.6 and 61 mbar), a further experiment (n. 15) was carried out. Under these conditions, the measured optical properties were 91.2% transmittance and 26.3% haze (Table 1), confirming the model-predicted trend in the response surface.

The same operating parameters were subsequently applied to PBER, a biobased epoxy resin (also based on bisphenol A), which exhibited a transmittance of 90.7% and a haze of 24.3% (Table 1, experimental n. 16). The consistency of these results indicates that the identified optimal region is primarily governed by expected physical infiltration mechanisms rather than by specific chemical-physical and rheological properties of the resin, and that the findings could be extended to other epoxy resins. Although the quadratic model exhibits moderate descriptive capacity ($R^2 \sim 0.64\text{--}0.70$) due to the inherent stochastic nature of the wood's hierarchical porosity, it effectively maps the working interval and highlights how the chosen physical parameters affect resin infiltration. The RSM confirms, in fact, that both the residual pressure and the H/T ratio are tunable parameters for controlling the optical properties of TW composites. By modulating both the residual pressure and the amount of resin available, the scattering of the composite can be modulated by acting on the continuity or discontinuity of the wood-resin interface. As a result, DoE demonstrates that haze can be adjusted within a defined range by using the same resin and engineering the material to either enhance light diffusion or reduce it to improve optical properties. In particular, for applications requiring high visual transparency and image definition, such as transparent glass in energy-saving buildings (Jia et al. 2019; Mi et al. 2020) or electronic screens, (Tang et al. 2018) operating conditions should be chosen in the region near the midpoint, where haze is low (<30%) and transmittance is high. Conversely, for applications that prefer more diffuse light management, such as photovoltaic devices, (Y. Li et al. 2019; Zhu, Li, et al. 2016) privacy panels (Zhou et al. 2026) and smart windows, (Montanari et al. 2023; Samanta et al. 2021) TWs can be designed following high haze levels (far from the DoE center).

For complex systems such as TWs, DoE should not be understood or structured to provide an absolute mathematical answer that explains the entire domain, but rather as a process engineering tool to minimize, as in this case, resin consumption while keeping optical performance within application-relevant ranges. As mentioned before, studies have qualitatively described the impregnation phase for producing TW, but systematic optimization strategies based on the Design of Experiments (DoE) to achieve this material are not reported. Most studies focus on the optical performance or chemistry of materials, whereas the process-property relationship governing resin infiltration in bleached wood patterns remains underdeveloped. (F. Gullo, M. Messori and P. Palmero 2026; Hu et al. 2023; Li, Vasileva, et al. 2018; Li, Yang, et al. 2018; Montanari et al. 2021) Compared

with the conventional process conditions reported in literature, where $H/T=15$, this DoE shows that the optimal region for infiltration is shifted towards the use of a lower amount of resin. Furthermore, considering the optical properties measured within the domain, diffusion can be controlled by optimizing the microstructure with respect to lumen infiltration, detachment at the wood-polymer interface, and the formation of internal microbubbles.

To deepen this aspect, the statistical analysis was integrated with morphological investigation using FE-SEM microscopy, as discussed in detail in the next section, in which TW samples exhibiting extreme optical responses were compared to correlate microstructural characteristics with optical properties.

Because clear wood is intended for a wide range of applications, including structural and functional, as well as optical, optimisation alone is insufficient. The influence of infiltration conditions on mechanical integrity and long-term durability is then addressed in subsequent sections through mechanical testing and UV aging experiments, including a comparison of synthetic resin and biobased epoxy systems with and without UV stabilizing additives, respectively.

3.2. Microstructural Investigation and Scattering Mechanism Assessment

To investigate the scattering mechanisms, DoE experiments with opposite optical trends were selected and subsequently correlated with microstructural analyses. In particular, experiments n. 2 and 7 in Table 1 have been chosen as representative, whose optical properties in the range 400 – 800 nm are presented in Fig. 2a and 2b, respectively. These samples, at 550 nm, showed opposite transmittance values of 68.6 and 91.2% and significantly different haze levels of 73.2% for sample n. 2 and 33.2% for sample n. 7.

The divergence of the results is also evident in the photos shown in Fig.2. When sample n. 7 is in direct contact with the paper (higher transmittance value and lower haze, Fig. 2b) it shows the underlying text sharp, indicating that light propagation is more dominated by direct transmission and forward scattering. (Chen et al. 2022; Vasileva et al. 2018) In addition, diffusion is limited and predominantly anisotropic, in good agreement with the literature for TWs. (Linder and Löfqvist 2012; Vasileva et al. 2018)

In contrast, under the same conditions, sample n. 2 with low transmittance and high haze (Fig. 2a) has text blur. This is an indication of an increase in isotropic scattering in the

material, which significantly reduces the definition of the image even in the presence of partial transmission (68.8%). (Popoff et al. 2010)

When both samples are placed 1 cm from the bottom, the differences are more evident. Sample n. 2 with high haze has a milky appearance, characteristic of a scattering of light due to the presence of a large number of scattering centers. (Zhu, Song, et al. 2016) In contrast, sample n. 7 shows better image definition.

The optical properties quantified by UV-Vis spectroscopy in the range of 400-800 nm (Fig. 2a and b) in terms of transmittance and haze were correlated with the images obtained by FE-SEM (Fig 3e-h).

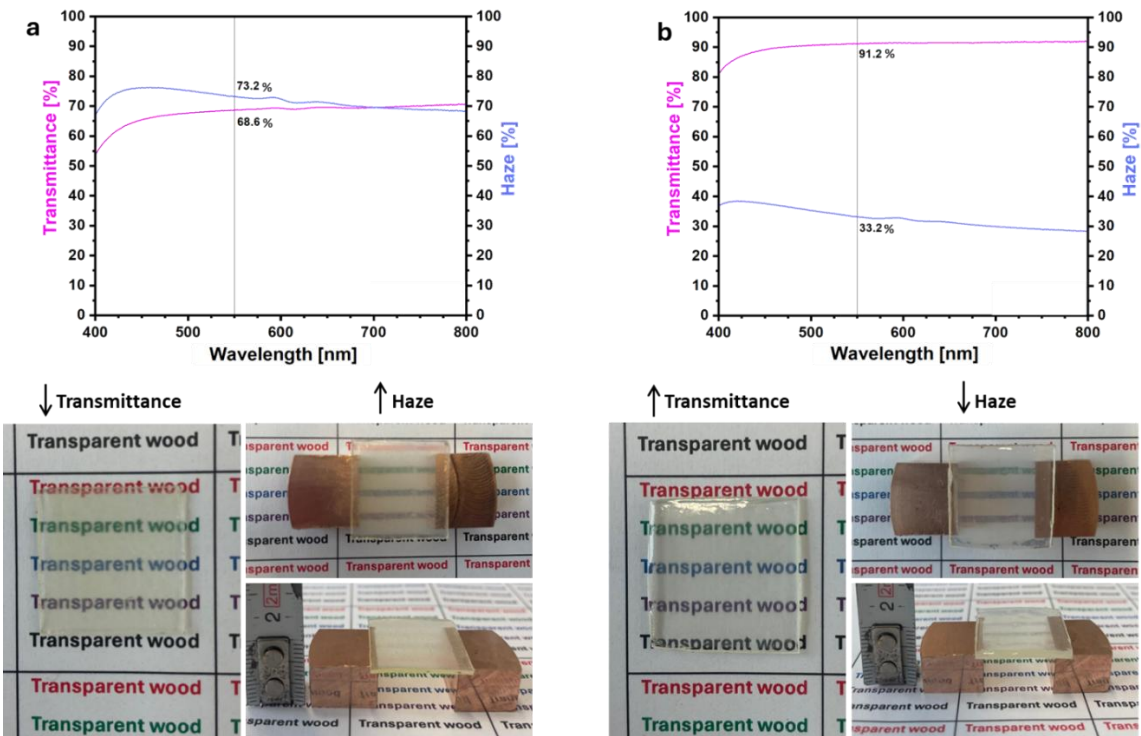


Fig. 2 Transmittance and haze measurements of representative DoE samples exhibiting opposite trends. a) Sample 2 (Table 1) characterized by high haze (—) and low transmittance (—) with corresponding photographic images; b) sample 7 (Table 1) characterized by low haze (—) and high transmittance (—) with corresponding photographic images.

The change in the pre (Fig. 3a-b) and post-bleaching (Fig. 3c-d) microstructure and the infiltration of the selected samples n.2 (Fig. 3e-f) and n.7 (Fig. 3g-h) was evaluated by FE-SEM analysis. For this study, balsa wood was selected as a model wood, widely studied in the literature, which has a low density and a high availability of porous volume,

characteristics that make it suitable for the manufacture of TW. (F. Gullo, M. Messori and P. Palmero 2026; Gullo et al. 2026; Li, Yang, et al. 2018; Long et al. 2025; Yin, Zhang, and Xu 2023)

With reference to Fig. 3 a-c at low magnification, at the microscopic level, the samples of natural wood (NW) and bleached wood (BW) present the typical structure of balsa wood, with numerous hexagonal-shaped macroporosities, ordered fibrils oriented along the longitudinal direction, which dominate the hierarchy of balsa wood. (Borrega et al. 2015; Fritz-Popovski et al. 2013) The pore diameters of pre- and post-treatment samples vary between 10 and 60 μm . As a result, no significant microstructural changes are observed post-bleaching, as highlighted in our previous work. (Gullo et al. 2026) This result is confirmed by high-magnification images (Fig. 3b and d), in which, post-bleaching, lignin is maintained in the central lamella, the area where it is anatomically most present. Furthermore, there is no evidence of microporosity formation in that area, unlike what happens with conventionally used delignification methods. (Li et al. 2016; Zhu, Song, et al. 2016)

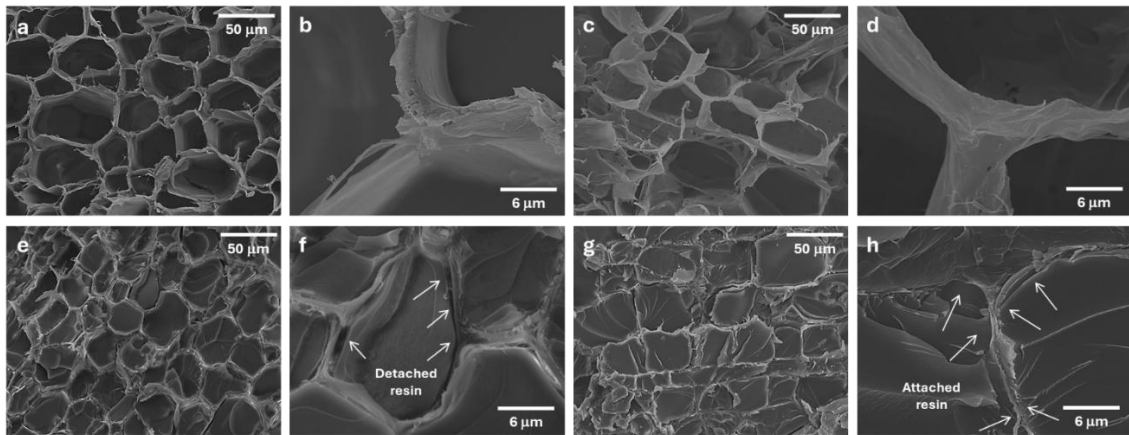


Fig. 3 FE-SEM images at high magnification (2000 $\times$ for TW samples and 4000 $\times$ for NW and BW) and low magnification (500 $\times$) of NW (a–b), BW (c–d), TW-ER (e–f), and TW-PBER (g–h).

Although the images of the TW samples (Fig. 3e–h) show, in general, good wood-polymer adhesion, important differences are observable, correlated with the optical properties discussed above. In particular, sample n. 2 (Fig. 3e–f), which showed high haze and low transmittance, at low magnification, shows an inhomogeneous infiltrated microstructure. Several areas of resin detachment from the cell wall can be observed, making the filling discontinuous. (Höglund et al. 2020) These discontinuities weaken the polymer-wood

interface and form potential scattering centers, as evidenced by the haze measured for this sample. At high magnifications (Fig. 3f), this phenomenon is even more evident: regions are observed in which the resin appears completely separated from the cell wall (see arrows in Fig. 3f).

On the contrary, sample n. 7 (Fig. 3g-h), with low haze and high transmittance, exhibits a more homogeneous, continuous wood-resin network. (Li et al. 2016; Zhu, Song, et al. 2016) At low magnifications (Fig. 3g), a more uniform filling of the porosity (lumens) is observed with the absence of macroscopic discontinuities. At high magnification (Fig. 3h), the resin appears completely adhered to the cell wall. This structural continuity reduces the number and size of scattering centers, favoring light propagation in forward scattering and a consequent reduction in haze, as evidenced by optical property analysis. From a direct comparison of the two TW complementary samples, it can be observed that the resin-cell wall interface and lumen-filling quality are controllable parameters that affect light diffusion. The observed differences confirm that the conditions examined by the DOE influence both the optical properties and the microstructural organization of the resulting composite, highlighting a strong link between the process and the internal structure.

3.3. Mechanical properties

The mechanical properties of the pristine samples and composites were evaluated by tensile testing (results shown in Fig. 4). As can be observed in the graph comparing the net resins, we can observe an enhancement of mechanical properties concerning both the Young's modulus (E) and the tensile strength from ER ($E = 105$ MPa, $\sigma_{\max} = 6$ MPa) to PBER ($E = 500$ MPa, $\sigma_{\max} = 18$ MPa). This is a highly promising result, especially considering that the optimal performance was achieved with a resin containing 40% green monomer.

If we compare the composite mechanical properties with those of pristine bleached balsa wood (WB), reported in Fig. 4 -gray color, we observe that both composites exhibit enhanced tensile strength with respect to WB, which can be attributed to good matrix-wood interaction. (Li, Vasileva, et al. 2018)

Moreover, we can also observe that TW-PBER ($E = 2.2$ GPa and $\sigma_{\max} = 37$ MPa) showed higher mechanical properties than TW-ER ($E = 1.0$ GPa and $\sigma_{\max} = 25$ MPa), in line with pristine resins behaviour.

In TW, the load-bearing capability primarily relies on the structural integrity of the cell walls and the mechanical properties of the infiltrated polymer. This interplay is crucial, as the interfacial bonding between the wood substrate and the resin significantly influences the overall mechanical performance of the composite. Strong bonding enhances stress transfer efficiency, making the composite more resilient to applied loads. (Montanari et al. 2021)

The superior mechanical performance of TW-PBER composites with respect to ER ones, can be attributed to several key factors. Firstly, the pristine PBER resin has been shown to possess inherently better mechanical properties than the synthetic epoxy resin (ER). Secondly, while SEM analyses confirm a high level of infiltration and a compact microstructure for both composites, the enhanced performance of TW-PBER suggests a superior chemical affinity between the PBER matrix and the wood cell walls. This advantage is likely rooted in the plant-based nature of the PBER monomer (40% v/v); as reported in the literature for other bio-based systems, such as the bio-acrylates investigated by Montanari et al. 2021 matrices derived from renewable resources often exhibit enhanced compatibility with the lignocellulosic structure of wood. (Montanari et al. 2021) Specifically, the presence of polar functional groups in the bio-based component may promote a denser network of hydrogen bonds at the interface, mimicking the natural interactions within the cell wall. This chemical synergy ensures a more efficient stress transfer from the matrix to the cellulose fibrils, effectively preventing micro-scale debonding and ensuring structural integrity. Consequently, the higher stiffness and tensile strength of TW-PBER are a direct result of this optimized interfacial adhesion and the intrinsic mechanical superiority of the bio-based resin. Furthermore, the values obtained for the mechanical properties of TW composites align closely with previously reported data for TW composites, confirming their reliability and potential applicability in the sector. (Li, Fu, et al. 2018; Li, Vasileva, et al. 2018; Story 2020; Zhu, Song, et al. 2016) Additionally, the transition from neat resins to composites results in an increase in stiffness. This phenomenon may be explained by the reinforcement provided by the wood fibers and the effective interfacial bonding with the resin, which enhances the overall rigidity of the composite structure. Notably, despite the two composites having different stiffness levels, both exhibit a similar elongation at break of approximately 4%. This consistent elongation may be related to the intrinsic strain limit of the interfacial bond between the resin and wood.

As illustrated in Figure 4.d, the toughness of the composites exceeds that of the white balsa (WB), indicating that the impregnated resin effectively enhances the ductility of the composite and increases the energy required for fracture. These results may be explained by considering the hierarchical structure of wood, comprising microfibrils, fibers, and lumen spaces, which could contribute to energy dissipation during deformation and fracture. When combined with the resin, this structure introduces multiple pathways for crack propagation, reinforcing the composite through toughening mechanisms such as crack deflection, bridging, and energy absorption. These mechanisms can significantly prolong the failure process, allowing the material to withstand impacts and dynamic loading more effectively than traditional monolithic materials. (Li, Vasileva, et al. 2018) These findings are particularly promising, suggesting that transparent wood composites could serve as viable alternatives to glass in structural applications, combining both strength and resilience in a lightweight material.

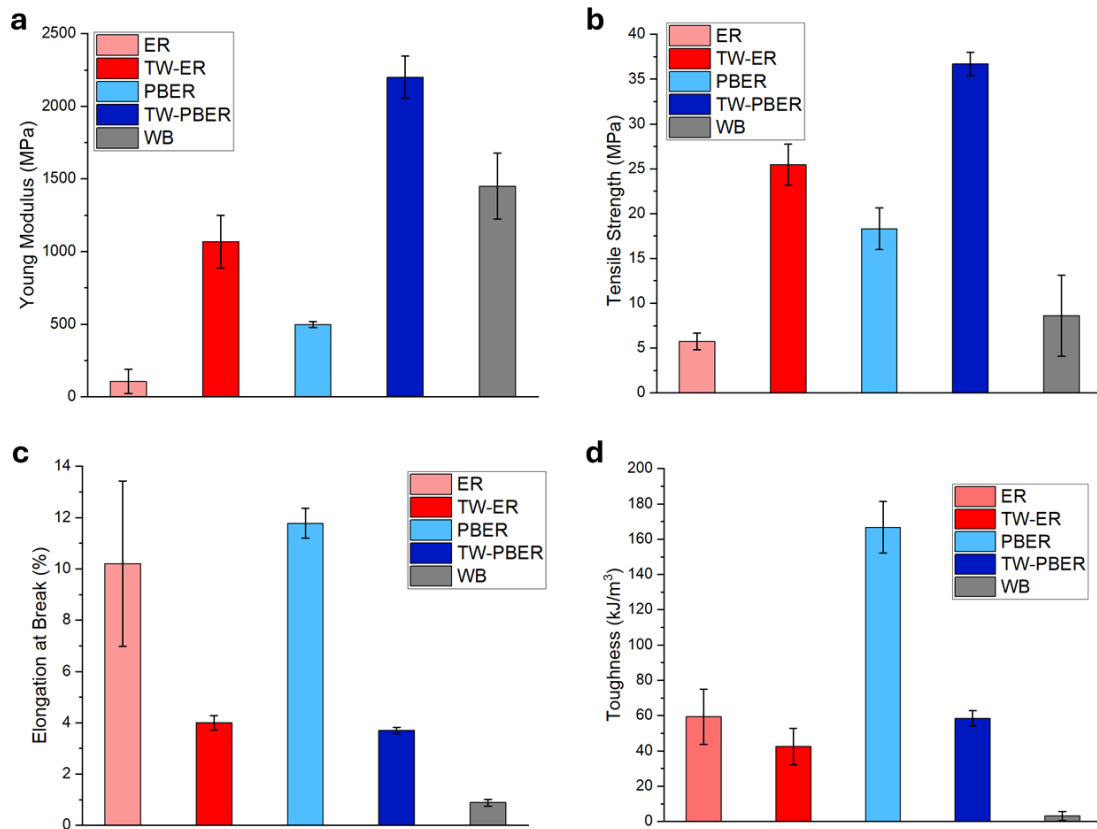


Fig. 4 Tensile properties of the pristine resins (ER and PBER) and the composites showing: a) Young's modulus; b) Tensile Strength, c) elongation at break, and d) toughness. Error bars indicate the standard deviation of the measurements.

3.4. TW UV-Aging

For the study of aging, the variation of optical properties through exposure to UV-Vis light in the solarbox between 290 and 800 nm was evaluated. Fig.4 shows the transmittance (Fig. 5a, c, e) and haze (Fig. 5b, d, f) spectra, respectively, at weeks 0, 4, and 5, which were the most significant.

To evaluate the effect of photochemical stabilization, the two epoxy resins were compared: the synthetic containing UV filter (ER), the 40% biobased without UV stabilizers (PBER), and the respective TW composites (TW-ER and TW-PBER).

The transmittance and haze trends, plotted using the data at 550 nm, are shown in Fig.5 a and b. The properties of natural wood (NW) and bleached wood (BW) were also investigated, in order to evaluate the contribution of the wood template to that of the polymer matrix. The overall data are reported in Table S1 (supporting information)

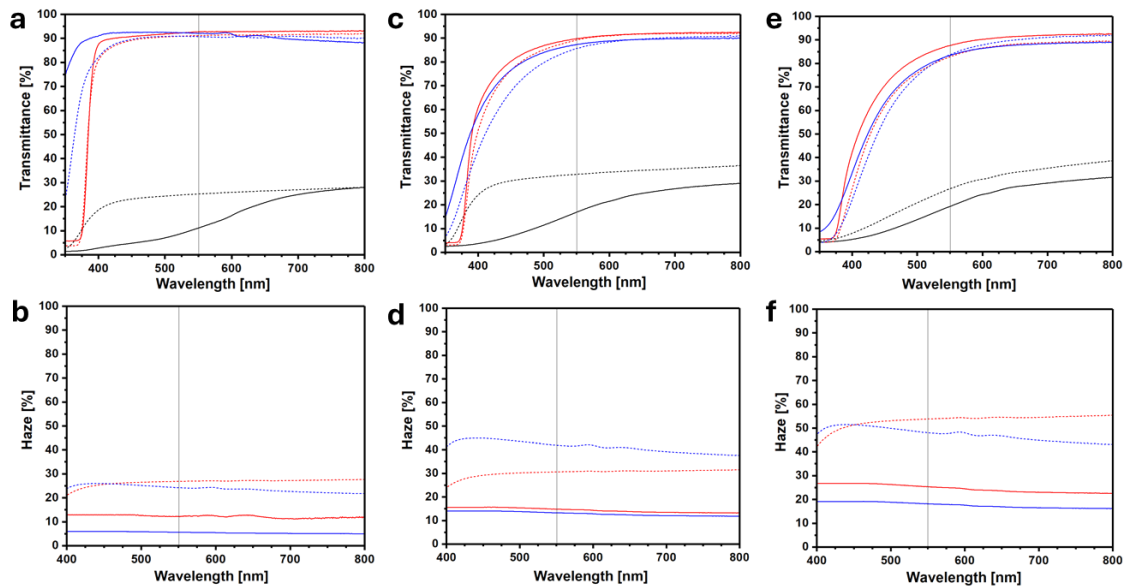


Fig. 5 Optical properties of NW (—), BW (---), ER (—), TW-ER (---), PBER (—), and TW-PBER (---) during UV aging; (a, c, e) Transmittance spectra measured at Week 0, Week 4, and Week 5, respectively. (b, d, f) Corresponding haze values at Week 0, Week 4, and Week 5.

In Fig. 5a it is observed that, at week 0, ER and TW-ER show very low transmittance in the UV region, indicative of the efficacy of the integrated UV filter, while the PBER and TW-PBER samples show an extended transmittance towards the lower wavelengths, suggesting a lower initial potential protection. (Bisht et al. 2024, 2021) At week 4 (Fig.

5c), ER and TW-ER maintain effective shielding of the UV region shown (300-350 nm), with moderate variations in the visible range (400-800 nm). In particular, transmittance, at the reference wavelength of 550 nm (vertical grey line in the figures) decreases from 92.8% to 89.9% for ER and from 91.2% to 86.2% for TW-ER between week 0 and week 4. In contrast, PBER and TW-PBER already show a widening of the absorption band, in the 300-400 nm region. Although the absolute transmittance values remain high, the relative reduction at week 4 is more pronounced for the non-stabilized composite: TW-PBER loses 5.8% of its initial transmittance (from 90.7% to 85.4%), compared to 5.4% for TW-ER, marking the onset of a faster degradation kinetic in the absence of filters (see Fig. 6a and b). At week 5 (Fig. 5e), the differences between the two resins and their respective TWs are less noticeable. Transmittance values converge to 87.6% for ER, 82.8% for TW-ER, 83.6% for PBER, and 83.4% for TW-PBER. At this stage, the increase in haze becomes significant for both the corresponding epoxy and TW, as deepened in the following, indicating that, in addition to the formation of chromophores, the resin aging contribution becomes significant for light scattering.

When looking at the behaviors of wood templates, reported in Table S1 (supporting information) however, NW is stable during the exposure period, while BW shows slight repigmentation after the fourth week. This phenomenon is consistent with the literature, which reports that lignin, due to its phenolic nature, efficiently absorbs UV radiation, generating free radicals that trigger photooxidation processes and the formation of secondary carbonyl groups, such as quinones, aromatic ketones, and aldehydes, responsible for the yellowing of the surface. (Bisht et al. 2021; F. Gullo, M. Messori and P. Palmero 2026; Paulsson and Parkås 2012) This can influence the aging of TWs, in which light can pass through the epoxy matrix and act on the residual or deconjugated lignin in the underlying BW, favoring its degradation. To confirm this, similar phenomena have been observed on woods coated with transparent coatings, in which the substrate continues to degrade under the protective layer. (Teacă and Bodîrlău 2016) However, in the case of TWs, the increase in haze observed after the fourth week suggests that degradation of the epoxy matrix is a major contributor to the loss of optical performance. (Bisht et al. 2021)

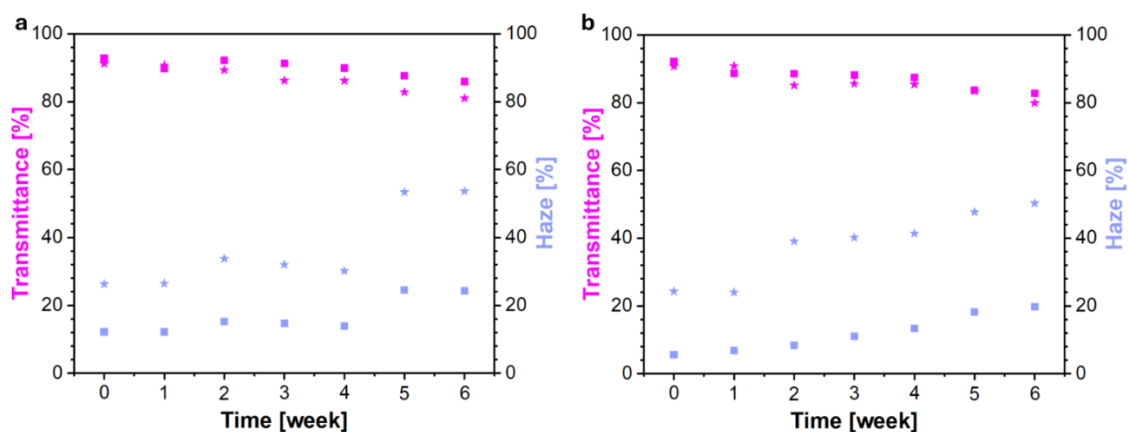


Fig. 6 Optical properties variation at 550 nm during the aging process (week 0 to week 6); a) synthetic epoxy resin (ER) materials, and b) bio-based resin (PBER) materials. The pink and red squares indicate the transmittance and haze (%) of the neat resins, respectively. The green and blue stars indicate the transmittance and haze (%) of the respective TWs.

Regarding the haze, in Fig. 5b (week 0), it can be observed that, while the initial transmittance values (Fig. 5a) between the resins and the TW were very close, the haze allows us to observe a first distinction. Focusing on the trend related to PBER (Fig. 6b), it is characterized by a lower starting haze (5.6%) compared to ER (12.2%), a difference that is significantly attenuated in the respective composites (24.3% for TW-PBER vs. 26.3% for TW-ER). This suggests that at week 0, the total haze of the TW is dominated by refractive-index mismatch and light scattering at the wood-matrix interface, which effectively equalizes the optical performance of the two resins. Haze values for NW and BW were not reported as they were close to 100% and therefore not very significant for comparative purposes. At week 4 (Fig. 5d), the haze of the resin without UV filter (PBER, 13.3%) is superimposable to that of the resin with UV absorber (ER, 13.9%), indicating that the isotropy of light in the visible zone increases more in the PBER sample, while for the resin with UV filter (ER) the increase is minimal. In composites, an even more marked difference is observed. In fact, TW-PBER has a higher haze than TW-ER (41.4% vs. 30.2%), suggesting a greater development of interfacial discontinuities in the system without stabilizers. At week 5 (Fig. 5f), after progressive degradation of the UV filter, both ER and TW-ER show a significant increase in haze. This behavior could be attributed to the degradation of the resin, which, by increasing its local stiffness, could favor the formation of micro-detachments at the interface between the cell wall and the polymer,

amplifying light scattering. At this stage, the differences between the two resins tend to decrease, suggesting that the matrix photooxidation process is the dominant factor.

The data presented in Fig. 6 a and b confirm the trend shown by the spectra; if we compare the transmittance and haze values of weeks 4 and 6 with the starting values of week 0, for ER, the transmittance decreases by 2.9% at week 4 and by 6.9% at week 6 (−4.0% between the fourth and sixth weeks), while haze increased by 1.7% at week 4 and +12.1% at week 6 (+10.4% in the last two weeks). The trend of TW-ER is more marked: −5.0% transmittance at week 4 and −10.2% at week 6, with an increase in haze that goes from +3.9% to +27.3% (+23.4% between weeks 4 and 6). The UV-free formulation (PBER) shows a reduction in transmittance of 4.7% at week 4 and 9.3% at week 6 (−4.6% in the last two weeks), while haze increases from 7.7% at week 4 to 14.2% at week 6. The behavior of TW-PBER follows the same trend, but with an even more evident increase in diffusion (+17.1% at week 4 and +26.0% at week 6). This two-stage degradation kinetic for the stabilized system is clearly supported by the trend shown in Fig. 6: between week 0 and week 4, the haze of TW-ER increases by only 3.9 percentage points (from 26.3% to 30.2%), demonstrating the effectiveness of the UV filter. However, between week 4 and week 5, a sharp 23.1% increase is observed (from 30.2% to 53.3%), indicating a functional failure of the stabilizer. In contrast, the TW-PBER system exhibits more progressive, linear growth, with an increase of 17.1 points already within the first 4 weeks, confirming a steady degradation process without a latency period. On the contrary, for PBER and TW-PBER there is a progressive degradation of both transmittance and haze from the initial week to the sixth week, indicating the progressive degradation of the epoxy resin, sensitive to UV exposure by nature, and the subsequent degradation of the deconjugated lignin still present in a high percentage within the white template. (Gullo et al. 2026)

The photographs shown in Fig. 7 support the experimental evidence obtained from the measurement of optical properties.

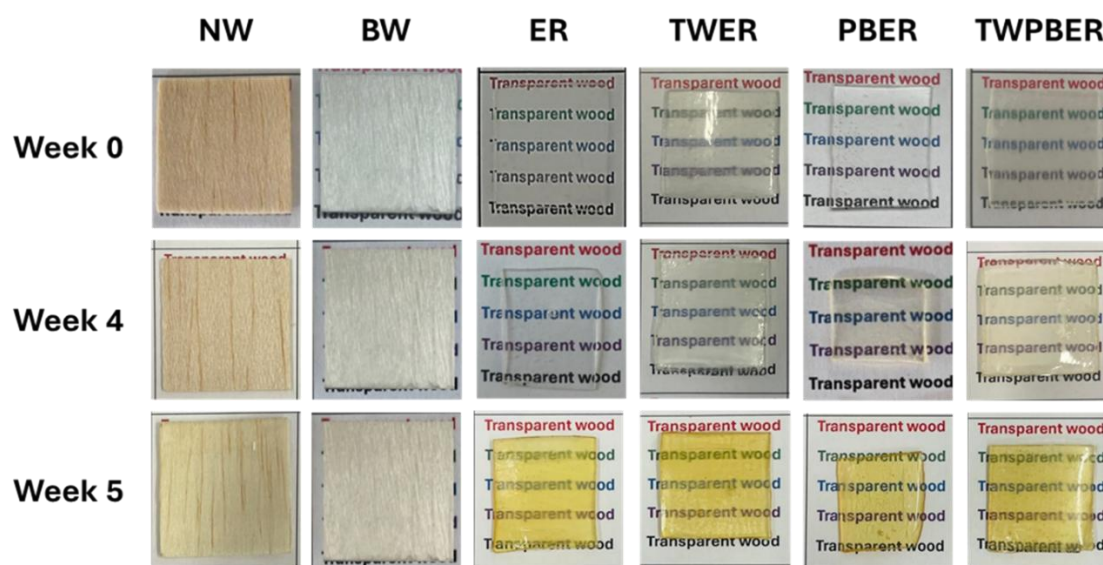


Fig. 7 Photographic images of NW, BW, ER, TW-ER, PBER, and TW-PBER samples during accelerated UV-Vis exposure. Images were recorded at the most representative time intervals: Week 0 (no exposure), Week 4 (onset of yellowing), and Week 5 (pronounced yellowing).

As shown in Fig. 7, at week 4, the ER and TW-ER samples show no evident yellowing, while PBER and TW-PBER show a slight yellowing. At week 5, all resin-based samples show a similar shade, indicating that once the effectiveness of the UV filter is reduced, ER also becomes susceptible to photooxidation. NW shows only a slight chromatic variation, while BW shows a light beige repigmentation consistent with the formation of secondary chromophores, as shown in Fig. 5e. The absence of drastic changes in BW transmittance compared to the significant increase in haze in TWs indicates that degradation is mainly attributable to the epoxy matrix and the influence of this degradation on the microstructure, with a low contribution of the lignocellulosic substrate.

3.5. Structural analysis of 6-week aging of epoxy resins and related composites

The samples presented in the previous paragraph (ER, TW-ER, PBER and TW-PBER) were analyzed by FTIR spectroscopy before (week 0) and after (week 6) exposure to UV aging. The FTIR spectra in transmission and ATR were recorded following the same procedure already described in the published article (p. 47). To improve spectral quality, the number of scans was doubled from 32 to 64.

The characterization carried out allowed to evaluate: i) the influence of the bleached wood template on the cross-linking kinetics of epoxy resins and ii) the post-aging structural transformations. In order to distinguish surface effects from bulk effects, two FTIR techniques were used:

- ATR spectroscopy for cortical layer analysis (sampling depth 10-15 μm) for the evaluation of surface photodegradation phenomena such as photooxidation and ablation of the outer layer of materials. (Nakamoto 2009) In addition, using the band at about 3400 cm^{-1} , which is linked to the presence of hydroxyl groups, it is possible to quantify the adsorption of moisture at the sample interface. (Fieldson and Barbari 1993)
- NIR spectroscopy in transmission in the $7500\text{--}4000\text{ cm}^{-1}$ region to investigate the bulk and, in particular, the internal propagation of degradation phenomena. (Alassali, Fiore, and Kuchta 2018; Neo et al. 2022) Furthermore, by exploiting the complete transmission of the radiation through the sample, the massive hygroscopic absorption was calculated, thereby evaluating the role of the wooden template in moisture absorption. (González, Cabanelas, and Baselga 2012)

3.5.1. ATR spectra at week 0: qualitative comparison of neat resins and TWs

Fig. 8 shows the ATR spectra of the four samples studied at time 0. In particular, Fig. 8 A shows the comparison between the ER and TW-ER samples, while Fig. 8 B shows the PBER and TW-PBER samples.

Looking at Fig. 8 we can see that the profile of the TWs does not show any variation compared to that of the starting resins, indicating that resin effectively recovered the template's surface in both composites shown. Furthermore, as expected, the two resins show no structural differences, since both systems share the same chemical nature based on bisphenol A. However, in composites, the intensity is modulated, and specific bands are widened, attributable to spectral overlap between the functional groups of the resins and those of the lignocellulosic template. These variations, particularly evident in the fingerprint region ($1200\text{--}1000\text{ cm}^{-1}$) in Fig. 8, arise from the sum of vibrational contributions and optical effects intrinsic to the ATR technique, such as variations in optical density and the quality of contact at the interface between the sample and the crystal. (Nakamoto 2009)

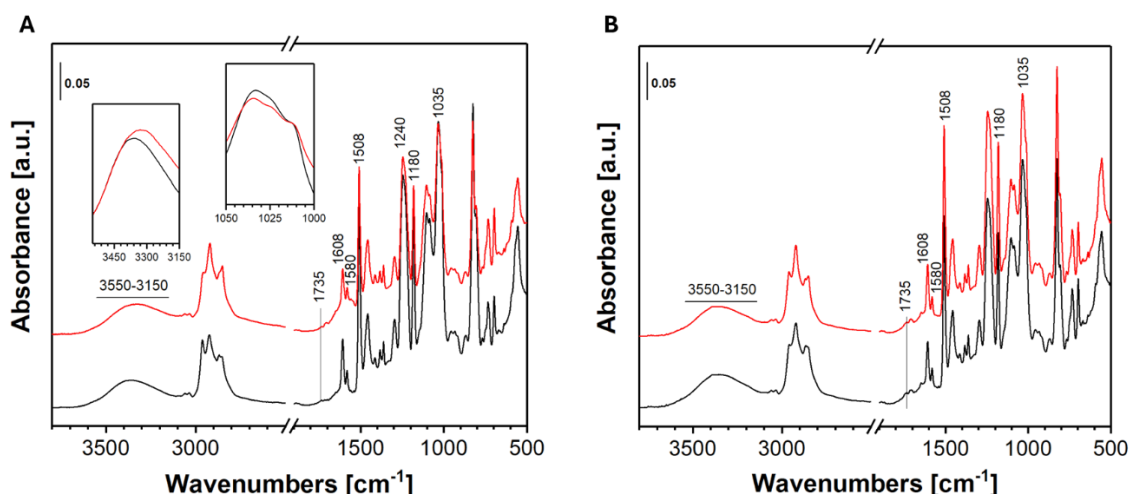


Fig. 8 ATR-FTIR analysis from 3800 to 500 cm^{-1} on resins and TWs at week 0. A) ER (black curve) vs TW-ER (red curve); B) PBER (black curve) vs TW-PBER (red curve)

The attributions of the main bands indicating the presence of resin with an aromatic structure in both resins and composites are summarized in Table 2. In particular: i) the broadband assigned between 3550-3150 cm^{-1} that is related to the stretching of -OH bonds increases in the composite (see the left inset in Fig. 8 A) due to the high density of both the hydroxyl groups of the cellulose and the residual lignin component that is preserved by the bleaching treatment; the intense and narrow bands related to the stretching of the aromatic ring at 1580, 1508 cm^{-1} confirm the presence of bisphenol A resin in addition to lignin and finally iii) the fingerprint region between 1050-1000 cm^{-1} , as can be seen in the right inset of Fig. 8 A, appears thickened in composites by overlapping between the C–O–C signals of the resin and the C–O bonds of the cellulose.

Wave Number [cm^{-1}]	Attribution of the bond / functional group	Differences and Notes	REF
3400 (broad)	ν OH (hydroxyls)	Increased intensity in composites due to cellulose - OH groups.	(Pandey 1999; Popescu et al. 2007)
2965 - 2870	ν C-H (aliphatic)	More marked peaks in the composite; overlap between the resin and cellulose groups.	(González, Cabanelas, and Baselga 2012; Pandey 1999; Popescu et al. 2007)
1608	ν C=C (aromatic ring)	Characteristic signal of the aromatic skeleton of bisphenol A.	(González et al. 2012)

1580, 1508	ν C=C (aromatic ring)	Characteristic signals of the aromatic skeleton of bisphenol A and lignin. In composites, they are well defined and very intense, confirming the massive presence of resin.	(González et al. 2012; Pandey 1999; Popescu et al. 2007)
1455	δ CH ₂ and CH ₃	Slight variation in shape due to the contribution of cellulose chains.	(González et al. 2012; Pandey 1999; Popescu et al. 2007)
1240	ν_{as} C-O-C (aromatic ether) ν C-O acetyl groups (hemicellulose)	Dominant epoxy resin band; in the composite, it overlaps the residual signals of lignin (methoxyl groups) and hemicelluloses (deacetylated residues after bleaching)	(Colom et al. 2003; González et al. 2012; Pandey 1999)
1180	ν C-O (phenolic/ethereal)	Combined resin/wood sign.	(González et al. 2012; Pandey 1999; Popescu et al. 2007)
1035 - 1050	ν_s C-O-C / C-O (alcoholic)	Very intense band in composites that adds to the signal of the resin and that of the bonds of the cellulose.	(González et al. 2012a; Pandey 1999; Popescu et al. 2007)
915	ν Oxiranic ring (epoxy)	Typical peak of bisphenol A used to assess the degree of cross-linking.	(González et al. 2012)
828	δ C-H out of plane (para-replaced ring)	Typical of bisphenol A. Very distinguishable in both samples.	(González et al. 2012)

Table 2. Assignment of FTIR-ATR bands for ER, TW-ER, PBER, and TW-PBER samples. The table shows the main bands, the functional groups associated with vibrations, and the interpretative notes on the contributions of the resin and the wood template to the observed variations in the composite.

Based on the attributions shown in the Table 2, the bands used for the quantitative analysis of aging after exposure to UV-Vis light have been identified. In particular, the intensity of the signal at 1608 cm^{-1} related to the aromatic C=C stretching of the resin alone was used as an internal reference for the normalization of the spectra, instead of the component at 1508 cm^{-1} , normally used in the literature, but in this case overlapping with the lignin band that absorbs in the same position. (Celina, Linde, and Martinez 2021; Masek et al. 2023) This normalization of intensities was used to calculate the Carbonyl Index ($I_{C=O}$ at

1735 cm^{-1}), which is normally used to quantify the degree of aging, and the hydroxyl index (I_{OH} at 3400 cm^{-1}), used to monitor moisture absorption. (Celina et al. 2021; González, Cabanelas, and Baselga 2012) The results obtained are presented in the following paragraph.

3.5.2. ATR spectra at week 6: study of aging and water absorption pre and post exposure to the solar spectrum

The analysis of the ATR spectra for the ER and TW-ER (Fig. 9 A) and PBER and TW-PBER (Fig. 9 B) samples after 6 weeks of exposure to accelerated aging shows radically different profiles in respect with the initial state (short-dashed curves). In particular, we can appreciate the surface degradation, already highlighted both at the macroscopic level (Fig. 7, unpublished paper p. 114) and through the monitoring of optical properties (Fig. 6, unpublished paper p. 112).

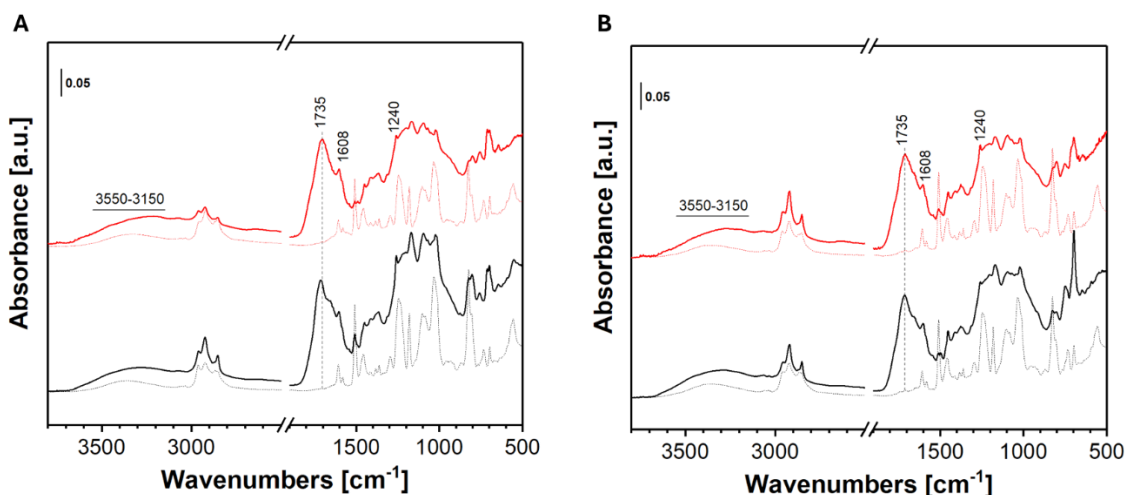


Fig. 9 ATR-FTIR analysis of resins and TWs at week 6 (solid lines) compared to week 0 (short-dashed lines) from 3800 to 500 cm^{-1} . A) ER (black) vs TW-ER (red); B) PBER (black) vs TW-PBER (red)

In fact, from the qualitative comparison between the pre-exposure and post-exposure (Fig. 9) spectra, a significant structural variation is observed, confirming the photooxidation of the resins and the composites derived from them, as deepened in the following. Furthermore, the absence of the characteristic peaks of inorganic species in Fig. 9, for the samples derived from the ER resin, suggests that the UV-absorber used is of purely organic origin and that, after 6 weeks of exposure, it is completely degraded,

exposing the wood template and the filler resin to the action of light. This is also confirmed by the simple chromatic variation observed (Fig. 6, unpublished paper p. 114). (Rivaton, Moreau, and Gardette 1997a, 1997b; Teacă et al. 2013)

The phenomena were quantified by normalizing the signals to the 1608 cm^{-1} band (aromatic C=C stretching), which was identified as the most intense and stable band attributable to pure resins. Table 3 shows the data relating to water uptake (column 3), calculated by means of the hydroxyl index, degradation by means of the carbonyl index (column 4), and the monitoring of the ether band (column 5).

Sample	Time [Week]	OH / H ₂ O 3400 cm^{-1}	Carbonyl 1735 cm^{-1}	Ether 1240 cm^{-1}
ER	0	0.551	Absent	3.703
	6	0.576	1.976	1.658
	Δ [%]	+4.5%	New	-55,20%
TW-ER	0	0.657	Absent	2.801
	6	0.844	2.059	1.464
	Δ [%]	+28.5%	New	-47.80%
PBER	0	0.758	0.091	3.547
	6	0.826	2.112	1.458
	Δ [%]	+8.9%	+2218.5%	-58.90%
TW-PBER	0	0.585	0.086	3.443
	6	1.070	2.361	1.540
	Δ [%]	+82.8%	+2644.1%	-55.30%

Table 3 Comparison between ER, TW-ER, PBER, and TW-PBER samples before and after exposure, for the quantification of degradation phenomena and water uptake, on the surface, expressed as Δ [%].

From the comparison between ER and TW-ER, considering the water uptake, it can be observed that pure resin has a low initial content, with a slight increase after 6 weeks (+4.5%). However, for TW-ER, moving from week 0 of exposure to week 6, there is a sharper increase in surface hygroscopic susceptibility (+28.5%). This fact suggests that the wood template, as expected, is more hydrophilic and that it hydrates as the organic filter degrades, probably assisted by the formation of surface microcracks induced by

photodegradation (observed at week 6). This process is confirmed by the appearance of the carbonyl-bound band at 1735 cm^{-1} , which goes from virtually 0 to about 2.0 for ER and 2.1 for TW-ER, indicating the formation of new groups, such as ketones and aldehydes, deriving mainly from the breaking of the bonds of the epoxy system rather than from the lignocellulosic system induced by photons. (Rivaton et al. 1997b; Teacă et al. 2013)

If, on the other hand, one compares the water uptake calculated for the PBER resin and the TW-PBER composite, it is possible to observe a higher initial water absorption than for ER (about double), probably related to the matrix nature (partially biobased). However, it is the composite that shows the most critical data in week 6, with an increase in the hydroxyl index of +82.8%. This result suggests that the absence of a UV filter exposes the bio-based matrix to accelerated degradation, also generating a greater exposure of a significant portion of the polar groups contained in the wooden template. This is confirmed by the calculated values for the carbonyl index at 1735 cm^{-1} , which go from a value close to 0 to 2.1 and 2.4 for pure resin and derived TW, respectively. This larger variation between PBER and TW-PBER compared to ER and TW-ER confirms faster degradation of the resin (see Fig. 5, unpublished paper, p. 112), which could expose not only the hydroxyls, but also the carbonyls of the lignocellulose matrix.

Finally, the reduction for all samples at week 6, relative to the band at 1240 cm^{-1} , with decreases between 48 and 59%, suggests a significant cleavage of the ethereal bonds in the wood-resin network. However, it is important to note that, in this case, the loss of intensity is less marked in both TWs than in pure resins. This result could suggest a structural scaffolding effect by the lignocellulosic component, through a mechanism of retention of degraded polymeric fragments within the cell lumen, limiting the complete ablation of the cortical layer. (Peng et al. 2020; Stark and Matuana 2006) In conclusion, from the results of the ATR surface analysis, one can confirm that the long-term durability of TWs biocomposites strictly depends on the type of resin used for infiltration. The use of epoxy resins without UV filters could lead to very marked photooxidation and water absorption processes, compromising the mechanical, optical, and chemical properties of the composite.

3.5.3. Spectra in transmission (NIR) week 0: qualitative comparison of neat resins and TWs

Fig. 10 shows the transmission spectra of the four samples studied at time 0 in the region between 7500–3800 cm^{-1} . In particular, Fig. 10 A shows the comparison between the ER and TW-ER samples, while Fig. 10 B shows the comparison between the PBER and TW-PBER samples. All NIR spectra of the analyzed samples show clearly distinguishable bands without saturation. This region, as described in Table 4, is dominated by combination bands and overtones of the fundamental vibrations of the C-H and O-H bonds, which allows for monitoring both the degree of internal cross-linking and the post-exposure degradation in the bulk.

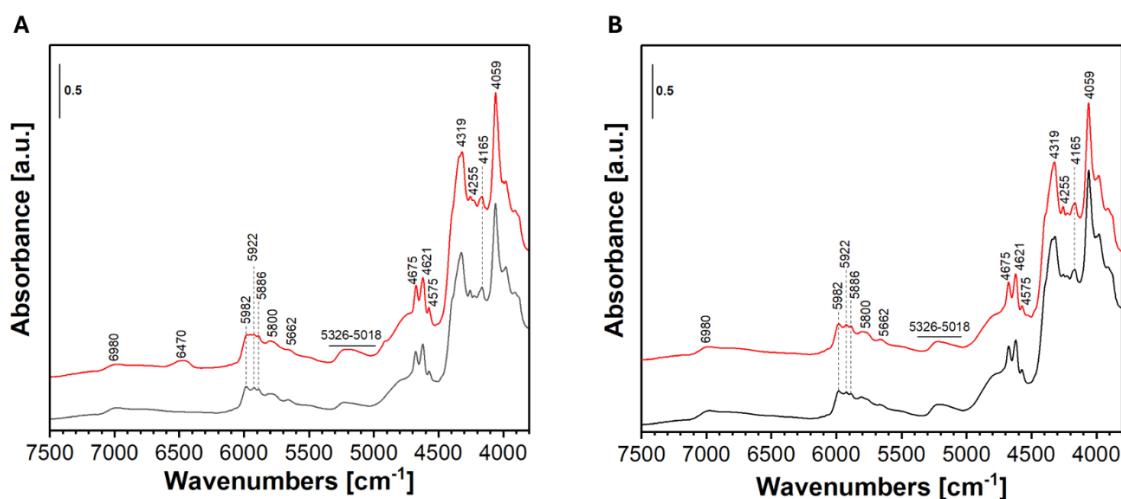


Fig. 10 FTIR analysis in transmission in the region between 7500 and 3800 cm^{-1} on resins and TWs at week 0. A) ER (black curve) vs TW-ER (red curve); B) PBER (black curve) vs TW-PBER (red curve).

The assignment of bands according to diagnostic significance is shown in Table 4.

The 4530 cm^{-1} band is linked to the presence of the oxiranic ring; its absence in the spectra indicates the complete polymerization of the two resins in all samples.

The 4621 cm^{-1} band is linked to the C=C and C-H combination motions of the aromatic rings and has been used as an internal normalization band for the considered bands. In particular, for the band linked to the hydroxyl and hydroperoxide overtones, in the area between 7000 and 6700 cm^{-1} , and for the water combination band, which falls in the region 5200–5100 cm^{-1} , the latter were used as markers for the evaluation of the presence of physisorbed water and the degree of oxidation (aging) of the bulk.

Region (cm ⁻¹)	Vibration Type	Functional Group	Origin (Resin/Wood)	Diagnostic Significance	REF
4530*	Combination	Epoxy Ring	Residual oxiranic groups	Calculation of the final conversion in bulk.	(González et al. 2012)
4760 – 4620	Combination	C=C Aromatic + C-H	Resin (Bisphenol A)	Normalization band of spectra.	(González et al. 2012; Workman Jr 2000)
7000 – 6700	Harmonica (Overtone)	-OH stretching	Cellulose / Hydroperoxides	Monitoring internal humidity and bulk oxidative degradation.	(Schwanninger et al. 2011; Tsuchikawa et al. 2003)
5200 – 5100	Combination (v+δ)	Water	Moisture Absorbed	Monitoring of the amount of water penetrated into the composite.	(Tsuchikawa et al. 2003)
6000 – 5700	Harmonica (Overtone)	-CH stretching	Epoxy / Wood Matrix	Polymer density and cellulose structure.	(Schwanninger et al. 2011; Tsuchikawa et al. 2003)
4400 – 4250	Combination	-CH/-CH ₂	Aliphatic chains	Integrity of the hydrocarbon chains of the resin.	(Workman Jr 2000)
4050 – 4000	Combination	C-H + C-C	Polymer skeleton	Deep structural degradation.	(Workman Jr 2000)

* *absent in all spectra*

Table 4. Assignment of NIR bands for ER, TW-ER, PBER and TW-PBER samples. The table shows the main bands (overtone and combination) and the functional groups associated with them, the interpretative notes relating to the contributions of the resin and the wood template, the variations observed in the composite and the diagnostic importance.

3.5.4. Week 6 transmission spectra: study of aging and water absorption pre and post exposure to the solar spectrum in bulk

The analysis of the ATR spectra of the ER and TW-ER samples (Fig. 11 A) and of PBER and TW-PBER (Fig. 11 B) after 6 weeks of exposure to accelerated aging shows overlapping profiles compared to those shown in Fig. 10.

Unlike infrared analyses in ATR mode, which analyse only 10-15 μm of thickness with respect to the surface (cortical layer) and where the analyses show a high degree of degradation, analyses in transmission mode analyse the entire thickness of the sample (1 mm), highlighting the stability of the bulk after ageing.

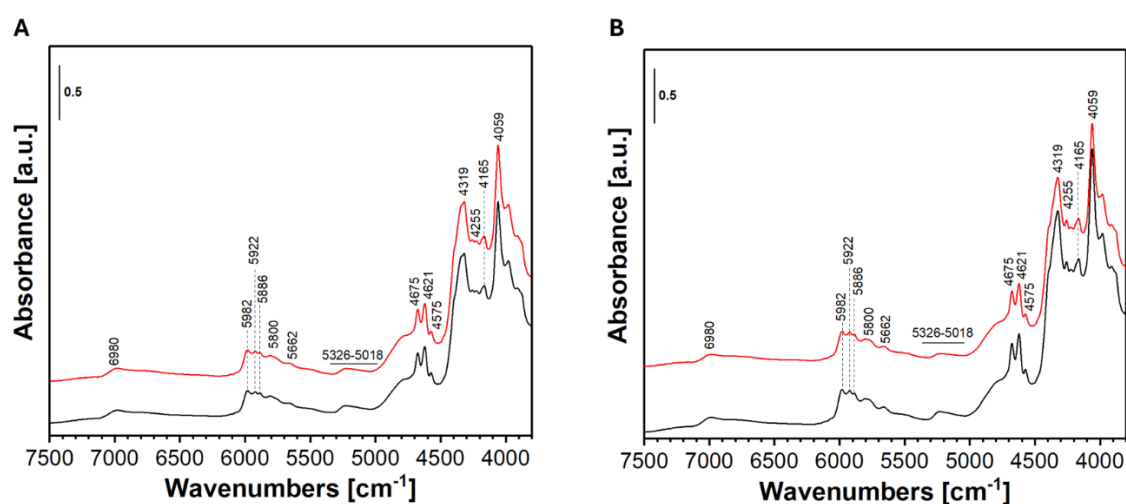


Fig. 11 FTIR analysis in transmission from 7500 to 3800 cm^{-1} on resins and TWs at week 6. A) ER (black curve) vs TW-ER (red curve); B) PBER (black curve) vs TW-PBER (red curve)

Quantitative data and percentage changes ($\Delta\%$) are shown in Table 5.

Sample	Time [Week]	Free Water (5200 cm^{-1})	-OH/Hydroperoxides (7000 cm^{-1})
ER	0	0.128	0.164

TW-ER	6	0.132	0.204
	Δ [%]	+2.9%	+24.4%
	0	0.209	0.133
	6	0.088	0.213
	Δ [%]	-58.0%	+59.7%
PBER	0	0.212	0.203
	6	0.112	0.166
	Δ [%]	-46.9%	-18.4%
TW-PBER	0	0.167	0.174
	6	0.047	0.168
	Δ [%]	-71.7%	-3.7%

Table 5 Comparison between ER, TW-ER, PBER and TW-PBER samples before and after exposure, for the quantification of degradation phenomena and water uptake in the bulk, expressed as Δ [%].

ER resin exhibits higher volumetric stability than that observed for the surface. In fact, in bulk, the variation of free water is negligible (+2.9%), compared to 4.5% measured in the surface area (see Table 3). If, on the other hand, one looks at the values calculated from the band intensity at 7000 cm^{-1} , an increase of 24.4% is observed, indicating not only superficial oxidation but also internal oxidation, probably due to the complete degradation of the UV filter. The TW-ER, on the other hand, shows a progressive reduction of physisorbed water in the bulk (-58.0%). This suggests that the thermal and radiative energy accumulated in the bulk favors post-curing and, therefore, the elimination of moisture initially present in the composite (effect of the resin and the wood template). If, on the other hand, the percentage calculated on the intensity of the hydroperoxide/hydroxyl signal is observed, there is an increase of 60%, suggesting that the degradation observed on the surface is also present in the bulk, although to a lesser extent.

Looking at the results obtained for samples obtained from partially bio-based resin, the situation is markedly different. PBER pure resin shows a decrease in both signals (-46.9% for physisorbed water and 18.4% for hydroperoxides/OH). This is even more evident in

the TW-PBER sample, where the free water decreases by 71.7%, while the signal at 7000 cm^{-1} linked to physisorbed water remains almost stable (-3.7%).

This behavior suggests that the bio-based system has greater structural stability in bulk than the fully synthetic resin and the derived TW. This result could be explained by the faster photooxidation of PBER compared to ER, due to the lack of UV filters, which could create a degraded, opaque, and yellowed cortical layer rich in chromophores that could act as a UV shield. (Gijsman, Meijers, and Vitarelli 1999; Rivaton et al. 1997b)

In addition, the high stiffness and hardness observed in the PBER matrix (Fig. 4, unpublished paper, p. 109) could reduce both the mobility of radicals and the diffusion of oxygen inwards. This would result in oxidative degradation confined to the first superficial layers (a few μm), both pure resin and PBER-based composite. (Audouin et al. 1994)

The clear distinction between surface degradation and bulk preservation is supported by the variation in the optical properties recorded for both sets of materials during the weeks of exposure (see Fig. 6, unpublished paper p. 112) In particular, although transmittance remains almost unchanged when comparing TW-PBER to TW-ER (79.9% vs 81.0% at week six), it is the variation in Haze that is more informative. PBER and TW-PBER show a more evident increase in haze, which doubles already in the first two weeks, while for ER and TW-ER the increase is more gradual, due to the presence of the UV filter. The sharp increase in haze values in bio-based samples could therefore be attributed to the formation of a degraded cortical layer that acts as a shield for the bulk while at the same time dulling its surface. In conclusion, the two types of resin exhibit different degrees of degradation. On the one hand, ER undergoes a slower degradation, propagated to the entire bulk of the sample, while on the other hand, PBER shows a faster aging, but localized at the first surface layers, where the rigidity of the network and the degraded surface shield the bulk of the material, preserving it.

4. Conclusions

In this work, a new approach for the controlled fabrication of TW composites was investigated, integrating a DoE-based approach to microstructural analysis, mechanical characterization and the study of long-term optical durability.

The application of a CCD, used for the first time on this type of material, enabled evaluation of the influence of infiltration parameters, such as the H/T ratio and residual pressure, on the optical properties of the TW. Although the applied model was not predictive across the domain, response surfaces enabled the identification of operating windows to minimize or maximize haze. This result showed that haze can be modulated by controlling process conditions.

FE-SEM analysis identified a direct correlation between the microstructure and the optical response. In particular, high haze values were associated with discontinuities at the wood-resin interface, i.e. incomplete lumen filling, while low haze values correspond to continuous and homogeneous interfaces. These results are important for confirming that the optical properties of TWs do not depend solely on the anisotropy of the wood but are also influenced by the quality of infiltration.

Mechanical tensile tests showed a significant increase in the elastic modulus and tensile strength of TWs compared to pure bleached white balsa, demonstrating the reinforcing contribution of the impregnated resins. Furthermore, TWs derived from partially bio-based epoxy resins demonstrated superior mechanical properties compared to fully petroleum-based resin. This finding confirms the feasibility of integrating greener matrices without significantly compromising the overall performance of the composite.

Through the study of accelerated aging in solarbox (290–800 nm), it was possible to observe how optical stability over time is strongly influenced by the resin formulation. In particular, the increase in haze, not yet considered in the literature for TW aging tests, has proved to be a critical parameter for evaluating durability in outdoor applications. The observed degradation is mainly attributable to the aging of both epoxy matrices, while the contribution of the lignocellulosic template is secondary.

The analysis of aging by FTIR-ATR and NIR transmittance has shown a surface structural modification of the TWs due to the degradation of the polymer directly exposed to UV-Vis radiation, while the bulk structure remains preserved. In addition, exposure to accelerated aging affected the material's opacity to a greater extent than previously considered in the literature, and should therefore be considered when assessing TW durability and subsequent integration into building components for outdoor applications (e.g., translucent panels or smart windows). Finally, the standardization of an impregnation protocol and the control of some infiltration parameters are fundamental for the possible transfer of the TW platform from the laboratory to industry. To overcome the durability limitations and improve the long-term durability of TWs, future approaches

could investigate optimizing UV absorber concentration or using systems that combine UV stabilizers with Hindered Amine Light Stabilizers (HALS) to achieve synergistic action. This would make it possible to obtain both physical shielding against radiation and the neutralization of the free radicals responsible for polymer chain breakdown. In addition, the development of multilayer structures that include a protective UV coating could shield the composite bulk from solar radiation, preserving both the polymer matrix and the wood-resin interface in the long term.

The methodology developed and studied through the DoE approach has, in fact, shown that it is possible to obtain materials with customizable optical properties by approaching methods compatible with current industrial woodworking technologies, paving the way for advanced applications, e.g., in the photovoltaic field, which will be conceptually explored in the next chapter.

The work represents the first step towards the engineering of haze through the design of experiments.

Future studies will focus on the integration of fully bio-based matrices and the optimization of infiltration parameters on a larger scale, including resin viscosity, cell wall pretreatment, air-vacuum infiltration cycles, and refractive index, to provide a complete picture of the effects on optical properties. In addition, durability analysis could be extended to real-world application conditions through large-scale TW to facilitate a concrete transition of TW into broad-spectrum industrial applications.

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5. References

Abad-Segura, Emilio, Ana Batlles de la Fuente, Mariana-Daniela González-Zamar, and Luis Jesús Belmonte-Ureña. 2020. “Effects of Circular Economy Policies on the Environment and Sustainable Growth: Worldwide Research.” *Sustainability* 12(14):5792.

- Alamandi, Morgan. 2025. "From Fossil to Function: Designing Next Generation Materials for a Low Carbon Economy." *Sustainability* 17(22):10254. doi:10.3390/su172210254.
- Alassali, Ayah, Silvia Fiore, and Kerstin Kuchta. 2018. "Assessment of Plastic Waste Materials Degradation through near Infrared Spectroscopy." *Waste Management* 82:71–81.
- Baddeley, Adrian, YA-MEI CHANG, and Yong Song. 2013. "Leverage and Influence Diagnostics for Spatial Point Processes." *Scandinavian Journal of Statistics* 40(1):86–104.
- Bisht, Priya, Harish C. Barshilia, and Krishna K. Pandey. 2024. "Effect of Natural Weathering on Optical Properties of Transparent Wood Composite." *Polymer Degradation and Stability* 221:110674.
- Bisht, Priya, Krishna K. Pandey, and Harish C. Barshilia. 2021. "Photostable Transparent Wood Composite Functionalized with an UV-Absorber." *Polymer Degradation and Stability* 189:109600.
- Bolognesi, Francesco, Emanuele Galvanetto, Leonardo Duranti, Andrea Bianco, Marco Togni, and Alessandra Bianco. 2026. "Toward Sustainable Aesthetic Transparent Wood from a Fast-Growing Hardwood Species: Paulownia Wood Templates Infused with Epoxy Bioresin." *ACS Omega*.
- Borrega, Marc, Patrik Ahvenainen, Ritva Serimaa, and Lorna Gibson. 2015. "Composition and Structure of Balsa (*Ochroma Pyramidale*) Wood." *Wood Science and Technology* 49(2):403–20.
- Bulian, Franco, and Jon Graystone. 2009. *Wood Coatings: Theory and Practice*. Elsevier.
- Celina, Mathew C., Erik Linde, and Estevan Martinez. 2021. "Carbonyl Identification and Quantification Uncertainties for Oxidative Polymer Degradation." *Polymer Degradation and Stability* 188:109550.
- Chen, Chaoji, Yudi Kuang, Shuze Zhu, Ingo Burgert, Tobias Keplinger, Amy Gong, Teng Li, Lars Berglund, Stephen J. Eichhorn, and Liangbing Hu. 2020. "Structure–Property–Function Relationships of Natural and Engineered Wood." *Nature Reviews Materials* 5(9):642–66.
- Chen, Hui, Céline Montanari, Ravi Shanker, Saulius Marcinkevicius, Lars A. Berglund, and Ilya Sychugov. 2022. "Photon Walk in Transparent Wood: Scattering and Absorption in Hierarchically Structured Materials." *Advanced Optical Materials* 10(8):2102732.
- Cheng, Hao-Bin, and Yen-Wen Lu. 2014. "Applications of Textured Surfaces on Bubble Trapping and Degassing for Microfluidic Devices." *Microfluidics and Nanofluidics* 17(5):855–62.

- Choudhury, Imtiaz Ahmed, and Mohamad SJ Hashmi. 2020. *Encyclopedia of Renewable and Sustainable Materials*. Elsevier.
- Colom, X., F. Carrillo, F. Nogués, and P. Garriga. 2003. "Structural Analysis of Photodegraded Wood by Means of FTIR Spectroscopy." *Polymer Degradation and Stability* 80(3):543–49.
- Ding, Linhu, Xiaoshuai Han, Lian Chen, and Shaohua Jiang. 2022. "Preparation and Properties of Hydrophobic and Transparent Wood." *Journal of Bioresources and Bioproducts* 7(4):295–305.
- Eul, W., A. Moeller, and N. Steiner. 2000. "Hydrogen Peroxide." *Kirk-Othmer Encyclopedia of Chemical Technology*.
- F. Gullo, M. Messori and P. Palmero. 2026. "Transparent Wood for a Bio-Based Future: A Critical Review." *Applied Materials Today*, February 23.
- Fink, Siegfried. 1992. "Transparent Wood—a New Approach in the Functional Study of Wood Structure."
- Fritz-Popovski, Gerhard, Daniel Van Opdenbosch, Cordt Zollfrank, Barbara Aichmayer, and Oskar Paris. 2013. "Development of the Fibrillar and Microfibrillar Structure during Biomimetic Mineralization of Wood." *Advanced Functional Materials* 23(10):1265–72.
- Gavrilovic-Grmusa, Ivana, Manfred Dunky, Jovan Miljkovic, and Milanka Djiporovic-Momicilovic. 2012. "Influence of the Viscosity of UF Resins on the Radial and Tangential Penetration into Poplar Wood and on the Shear Strength of Adhesive Joints." *Holzforschung* 66(7):849.
- Gijsman, Pieter, Guido Meijers, and Giacomo Vitarelli. 1999. "Comparison of the UV-Degradation Chemistry of Polypropylene, Polyethylene, Polyamide 6 and Polybutylene Terephthalate." *Polymer Degradation and Stability* 65(3):433–41.
- González, María González, Juan Carlos Cabanelas, and Juan Baselga. 2012a. "Applications of FTIR on Epoxy Resins-Identification, Monitoring the Curing Process, Phase Separation and Water Uptake." *Infrared Spectroscopy-Materials Science, Engineering and Technology* 2:261–84.
- González, María González, Juan Carlos Cabanelas, and Juan Baselga. 2012b. "Applications of FTIR on Epoxy Resins-Identification, Monitoring the Curing Process, Phase Separation and Water Uptake." *Infrared Spectroscopy-Materials Science, Engineering and Technology* 2:261–84.
- Fieldson, G. T., and T. A. Barbari. 1993. "The Use of FTIR-ATR Spectroscopy to Characterize Penetrant Diffusion in Polymers." *Polymer* 34(6):1146–53.
- Gullo, Francesca, Massimo Messori, and Paola Palmero. 2026. "Preservation of Wood Structure Using Stabilized Alkaline Bleaching Agents: A Novel and Mild

- Approach to Enhance Whitening for Lignin-Rich Wood Template.” *Wood Science and Technology* 60(1):12.
- He, Shuaiming, Xinpeng Zhao, Emily Q. Wang, Grace S. Chen, Po-Yen Chen, and Liangbing Hu. 2023. “Engineered Wood: Sustainable Technologies and Applications.” *Annual Review of Materials Research* 53(1):195–223. doi:10.1146/annurev-matsci-010622-105440.
- Höglund, Martin, Mats Johansson, Ilya Sychugov, and Lars A. Berglund. 2020. “Transparent Wood Biocomposites by Fast UV-Curing for Reduced Light-Scattering through Wood/Thiol–Ene Interface Design.” *ACS Applied Materials & Interfaces* 12(41):46914–22.
- Hu, Liangbing, Mingwei Zhu, Tian Li, Amy Gong, and Jianwei Song. 2017. “Transparent Wood Composite, Systems and Method of Fabrication.”
- Hu, Xin, Rujun Yu, Faming Wang, Zunfeng Liu, Hongyu Yang, Chaoji Chen, Yangling Li, Nuruzzaman Noor, and Bin Fei. 2023. “Fabrication, Functionalities and Applications of Transparent Wood: A Review.” *Advanced Functional Materials* 33(37):2303278.
- Jacucci, Gianni, Lukas Schertel, Yating Zhang, Han Yang, and Silvia Vignolini. 2021. “Light Management with Natural Materials: From Whiteness to Transparency.” *Advanced Materials* 33(28):2001215.
- Jang, Eun-Kyung, Min-Ji Kim, Sae-Min Yoon, Chang-Deuk Eom, and Yeo-Chang Youn. 2025. “Climate Change Mitigation Potential of Cascading Utilization of Wood Resources.” *Frontiers in Built Environment* 11:1490984. doi:10.3389/fbuil.2025.1490984.
- Jele, Thabisile Brightwell, Jerome Andrew, Maya John, and Bruce Sithole. 2023. “Engineered Transparent Wood Composites: A Review.” *Cellulose* 30(9):5447–71.
- Jia, Chao, Chaoji Chen, Ruiyu Mi, Tian Li, Jiaqi Dai, Zhi Yang, Yong Pei, Shuaiming He, Huiyang Bian, and Soo-Hwan Jang. 2019. “Clear Wood toward High-Performance Building Materials.” *ACS Nano* 13(9):9993–10001.
- Jiang, Feng, Tian Li, Yiju Li, Ying Zhang, Amy Gong, Jiaqi Dai, Emily Hitz, Wei Luo, and Liangbing Hu. 2018. “Wood-based Nanotechnologies toward Sustainability.” *Advanced Materials* 30(1):1703453.
- Kandpal, Vinay, Anshuman Jaswal, Ernesto DR Santibanez Gonzalez, and Naveen Agarwal. 2024. “Circular Economy Principles: Shifting towards Sustainable Prosperity.” Pp. 125–65 in *Sustainable energy transition: Circular economy and sustainable financing for environmental, social and governance (ESG) practices*. Springer.

- Katunský, D., J. Kanócz, and V. Karl'a. 2018. "Structural Elements with Transparent Wood in Architecture." *International Review of Applied Sciences and Engineering* 9(2):101–6. doi:10.1556/1848.2018.9.2.4.
- Li, Huayang, Xuelian Guo, Yuming He, and Rongbo Zheng. 2019. "A Green Steam-Modified Delignification Method to Prepare Low-Lignin Delignified Wood for Thick, Large Highly Transparent Wood Composites." *Journal of Materials Research* 34(6):932–40.
- Li, Yuanyuan, Ming Cheng, Erik Jungstedt, Bo Xu, Licheng Sun, and Lars Berglund. 2019. "Optically Transparent Wood Substrate for Perovskite Solar Cells." *ACS Sustainable Chemistry & Engineering* 7(6):6061–67.
- Li, Yuanyuan, Qiliang Fu, Xuan Yang, and Lars Berglund. 2018. "Transparent Wood for Functional and Structural Applications." *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 376(2112):20170182.
- Li, Yuanyuan, Qiliang Fu, Shun Yu, Min Yan, and Lars Berglund. 2016. "Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance." *Biomacromolecules* 17(4):1358–64.
- Li, Yuanyuan, Elena Vasileva, Ilya Sychugov, Sergei Popov, and Lars Berglund. 2018. "Optically Transparent Wood: Recent Progress, Opportunities, and Challenges." *Advanced Optical Materials* 6(14):1800059.
- Li, Yuanyuan, Xuan Yang, Qiliang Fu, Ramiro Rojas, Min Yan, and Lars Berglund. 2018. "Towards Centimeter Thick Transparent Wood through Interface Manipulation." *Journal of Materials Chemistry A* 6(3):1094–1101.
- Linder, Tomas, and Torbjörn Löfqvist. 2012. "Anisotropic Light Propagation in Paper." *Nordic Pulp & Paper Research Journal* 27(2):500–506.
- Long, Shoufu, Dingqiang Zheng, Ming Zhang, Wangchun Gou, Zhenghui Li, and Dongsheng Song. 2025. "Preparation of Photoluminescent Transparent Balsa Wood with Densifying Structure for Light-Scattering Windows Based on Cross-Linking of Lignocellulose and Poly (Vinyl Alcohol)." *International Journal of Biological Macromolecules* 311:143639.
- Martinka, Jozef, Jozef Mitterpach, Tomáš Štefko, Igor Wachter, and Peter Rantuch. 2023. "Fire Hazard of Epoxy-Based Transparent Wood." *Journal of Thermal Analysis and Calorimetry* 148(19):9893–9907.
- de Meijer, Mari, Katharina Thurich, and Holger Militz. 2001. "Quantitative Measurements of Capillary Coating Penetration in Relation to Wood and Coating Properties." *Holz Als Roh Und Werkstoff* 59(1):35–45.
- Mi, Ruiyu, Tian Li, Daniel Dalgo, Chaoji Chen, Yudi Kuang, Shuaiming He, Xinpeng Zhao, Weiqi Xie, Wentao Gan, and Junyong Zhu. 2020. "A Clear, Strong, and

- Thermally Insulated Transparent Wood for Energy Efficient Windows.” *Advanced Functional Materials* 30(1):1907511.
- Mohanty, Amar K., Singaravelu Vivekanandhan, Jean-Mathieu Pin, and Manjusri Misra. 2018. “Composites from Renewable and Sustainable Resources: Challenges and Innovations.” *Science* 362(6414):536–42.
- Montanari, Céline, Hui Chen, Matilda Lidfeldt, Josefin Gunnarsson, Peter Olsén, and Lars A. Berglund. 2023. “Sustainable Thermal Energy Batteries from Fully Bio-based Transparent Wood.” *Small* 19(28):2301262.
- Montanari, Céline, Yu Ogawa, Peter Olsén, and Lars A. Berglund. 2021. “High Performance, Fully Bio-based, and Optically Transparent Wood Biocomposites.” *Advanced Science* 8(12):2100559.
- Muthoka, Ruth M., Pooja S. Panicker, Dickens O. Agumba, Hoa D. Pham, and Jaehwan Kim. 2021. “All-Biobased Transparent-Wood: A New Approach and Its Environmental-Friendly Packaging Application.” *Carbohydrate Polymers* 264:118012.
- Nakamoto, Kazuo. 2009. "Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry." John Wiley & Sons.
- Neo, Edward Ren Kai, Zhiquan Yeo, Jonathan Sze Choong Low, Vannessa Goodship, and Kurt Debattista. 2022. "A Review on Chemometric Techniques with Infrared, Raman and Laser-Induced Breakdown Spectroscopy for Sorting Plastic Waste in the Recycling Industry." *Resources, Conservation and Recycling* 180:106217.
- Odian, George. 2004. *Principles of Polymerization*. John Wiley & Sons.
- Pandey, K. K. 1999. "A Study of Chemical Structure of Soft and Hardwood and Wood Polymers by FTIR Spectroscopy." *Journal of Applied Polymer Science* 71(12):1969–75.
- Pandit, Krutarth H., Abhijeet D. Goswami, Chandrakant R. Holkar, and Dipak V. Pinjari. 2025. “A Review on Recent Developments in Transparent Wood: Sustainable Alternative to Glass.” *Biomass Conversion and Biorefinery* 15(4):6331–43.
- Panzarasa, Guido, and Ingo Burgert. 2022. “Designing Functional Wood Materials for Novel Engineering Applications.” *Holzforschung* 76(2):211–22. doi:10.1515/hf-2021-0125.
- Pascault, Jean-Pierre, and Roberto JJ Williams. 2009. *Epoxy Polymers: New Materials and Innovations*. John Wiley & Sons.
- Park, Kyoung-Chan, Byeongho Kim, Hanna Park, Yesun Kim, and Se-Yeong Park. 2022. “Characterization of a Translucent Material Produced from *Paulownia tomentosa*

- Using Peracetic Acid Delignification and Resin Infiltration.” *Polymers* 14(20):4380.
- Paulsson, Magnus, and Jim Parkås. 2012. “Light-Induced Yellowing of Lignocellulosic Pulps-Mechanisms and Preventive Methods.” *BioResources* 7(4).
- Peng, Yao, Yujiao Wang, Pingan Chen, Wen Wang, and Jinzhen Cao. 2020. "Enhancing Weathering Resistance of Wood by Using Bark Extractives as Natural Photostabilizers in Polyurethane-Acrylate Coating." *Progress in Organic Coatings* 145:105665.
- Plecnik, Joseph M., John M. Plecnik, John H. Fogarty, and John R. Kurfees. 1986. “Behavior of Epoxy Repaired Beams under Fire.” *Journal of Structural Engineering* 112(4):906–22. doi:10.1061/(ASCE)0733-9445(1986)112:4(906).
- Plummer, Martyn. 2025. “Bayesian Measures of Leverage and Influence.” arXiv Preprint arXiv:2503.19996.
- Popescu, Carmen-Mihaela, Maria-Cristina Popescu, Ghita Singurel, Cornelia Vasile, Dimitris S. Argyropoulos, and Stefan Willfor. 2007. "Spectral Characterization of Eucalyptus Wood." *Applied Spectroscopy* 61(11):1168–77.
- Popoff, Sébastien, Geoffroy Lerosey, Mathias Fink, Albert Claude Boccara, and Sylvain Gigan. 2010. “Image Transmission through an Opaque Material.” *Nature Communications* 1(1):81.
- Prime, R. Bruce. 2005. “Thermal Analysis in Thermoset Characterization.”
- Rivaton, Agnès, Laurent Moreau, and Jean-Luc Gardette. 1997a. "Photo-Oxidation of Phenoxy Resins at Long and Short Wavelengths—I. Identification of the Photoproducts." *Polymer Degradation and Stability* 58(3):321–32.
- Rivaton, Agnès, Laurent Moreau, and Jean-Luc Gardette. 1997b. "Photo-Oxidation of Phenoxy Resins at Long and Short Wavelengths—II. Mechanisms of Formation of Photoproducts." *Polymer Degradation and Stability* 58(3):333–39.
- Samanta, Archana, Hui Chen, Pratick Samanta, Sergei Popov, Ilya Sychugov, and Lars A. Berglund. 2021. “Reversible Dual-Stimuli-Responsive Chromic Transparent Wood Biocomposites for Smart Window Applications.” *ACS Applied Materials & Interfaces* 13(2):3270–77.
- Schubert, Mark, Guido Panzarasa, and Ingo Burgert. 2023. “Sustainability in Wood Products: A New Perspective for Handling Natural Diversity.” *Chemical Reviews* 123(5):1889–1924. doi:10.1021/acs.chemrev.2c00360.
- Schwanninger, Manfred, José Carlos Rodrigues, and Karin Fackler. 2011. "A Review of Band Assignments in near Infrared Spectra of Wood and Wood Components." *Journal of Near Infrared Spectroscopy* 19(5):287–308.

- Song, Jianwei, Chaoji Chen, Shuze Zhu, Mingwei Zhu, Jiaqi Dai, Upamanyu Ray, Yiju Li, Yudi Kuang, Yongfeng Li, Nelson Quispe, Yonggang Yao, Amy Gong, Ulrich H. Leiste, Hugh A. Bruck, J. Y. Zhu, Azhar Vellore, Heng Li, Marilyn L. Minus, Zheng Jia, Ashlie Martini, Teng Li, and Liangbing Hu. 2018. "Processing Bulk Natural Wood into a High-Performance Structural Material." *Nature* 554(7691):224–28. doi:10.1038/nature25476.
- Stark, Nicole M., and Laurent M. Matuana. 2006. "Influence of Photostabilizers on Wood Flour–HDPE Composites Exposed to Xenon-Arc Radiation with and without Water Spray." *Polymer Degradation and Stability* 91(12):3048–56.
- Starzyk, Agnieszka, Nuno D. Cortiços, Carlos C. Duarte, and Przemysław Łacek. 2025. "Timber Architecture for Sustainable Futures: A Critical Review of Design and Research Challenges in the Era of Environmental and Social Transition." *Buildings* 15(15):2774. doi:10.3390/buildings15152774.
- Story, Natasha Claire. 2020. Investigating the Curing Process of Epoxy Thermosets by Near-Infrared (nIR) Spectroscopy. LA-UR--20-27087. Los Alamos National Laboratory (LANL), Los Alamos, NM (United States). doi:10.2172/1660573.
- Tang, Qiheng, Lu Fang, YunFei Wang, Miao Zou, and Wenjing Guo. 2018. "Anisotropic Flexible Transparent Films from Remaining Wood Microstructures for Screen Protection and AgNW Conductive Substrate." *Nanoscale* 10(9):4344–53.
- Teacă, Carmen-Alice, Dan Roşu, Ruxanda Bodîrlău, and Liliana Roşu. 2013. "Structural Changes in Wood under Artificial UV Light Irradiation Determined by FTIR Spectroscopy and Color Measurements--A Brief Review." *BioResources* 8(1).
- Teacă, Carmen-Alice, and Ruxanda Bodîrlău. 2016. "Photochemical Behavior of Wood Based Materials." Pp. 91–107 in *Photochemical behavior of multicomponent polymeric-based materials*. Springer.
- Terzopoulou, Paschalina, Dimitris S. Achilias, and Evangelia C. Vouvoudi. 2025. "Advancements in Wood Processing Utilizing Polymers for 'Transparent' Wood Composites: A Technical Review and Meta-Analysis." *Wood Science and Technology* 59(5):90.
- Tsuchikawa, Satoru, Kinuyo Inoue, Junichi Noma, and Kazuo Hayashi. 2003. "Application of Near-Infrared Spectroscopy to Wood Discrimination." *Journal of Wood Science* 49(1):0029–0035.
- Vasileva, Elena, Hui Chen, Yuanyuan Li, Ilya Sychugov, Max Yan, Lars Berglund, and Sergei Popov. 2018. "Light Scattering by Structurally Anisotropic Media: A Benchmark with Transparent Wood." *Advanced Optical Materials* 6(23):1800999.
- Wachter, Igor, Peter Rantuch, and Tomáš Štefko. 2023. "Fully Bio-Based Transparent Wood." Pp. 23–33 in *Transparent Wood Materials: Properties, Applications, and Fire Behaviour*. Springer.

- Wachter, Igor, Tomáš Štefko, Peter Rantuch, Jozef Martinka, and Alica Pastierová. 2021. "Effect of UV Radiation on Optical Properties and Hardness of Transparent Wood." *Polymers* 13(13):2067.
- Wang, Jing, and Jian'gang Zhu. 2021. "Prospects and Applications of Biomass-Based Transparent Wood: An Architectural Glass Perspective." *Frontiers in Chemistry* 9:747385.
- Wang, Ming, Hongchen Liu, Xiao Feng, Xijun Wang, Kaiyuan Shen, Haisong Qi, and Orlando J. Rojas. 2023. "State-of-the-Art Luminescent Materials Based on Wood Veneer with Superior Strength, Transparency, and Water Resistance." *Chemical Engineering Journal* 454:140225.
- Wang, Xuan, Tianyi Zhan, Yan Liu, Jiangtao Shi, Biao Pan, Yaoli Zhang, Liping Cai, and Sheldon Q. Shi. 2018. "Large-size Transparent Wood for Energy-saving Building Applications." *ChemSusChem* 11(23):4086–93.
- Workman Jr, Jerry. 2000. *The Handbook of Organic Compounds, Three-Volume Set: NIR, IR, R, and Uv-Vis Spectra Featuring Polymers and Surfactants*. Elsevier.
- Wu, Jiamin, Xiangzhen Meng, Anran Dong, Wenchao Zhao, Liping Cai, and Changlei Xia. 2024. "Advancing Sustainable Construction through Innovative Transparent Wood Composite Structures with Enhanced Functionalities." *Industrial Crops and Products* 218:118902.
- Wu, Jiamin, Tianhao Shen, Suiyi Li, Yingji Wu, Liping Cai, and Changlei Xia. 2025. "Sustainable Transparent Wood Focusing on Lignin Decolorization Methods, Polymer Impregnation Techniques and Applications in Functional Buildings: A Review." *International Journal of Biological Macromolecules* 302:140554.
- Wu, Jiamin, Haoran Ye, Suiyi Li, Zeli Que, Yucheng Peng, Liping Cai, and Changlei Xia. 2024. "Life Cycle Assessment of Transparent Wood in Building Industry: A Sustainable Solution for Global Warming Mitigation." *Construction and Building Materials* 438:137303.
- Wu, Xinyu, Zhangqian Kong, Xingzhou Yao, Jian Gan, Xianxu Zhan, and Yan Wu. 2023. "Transparent Wood with Self-Cleaning Properties for next-Generation Smart Photovoltaic Panels." *Applied Surface Science* 613:155927.
- Wu, Yan, Jichun Zhou, Qiongtao Huang, Feng Yang, Yajing Wang, and Jing Wang. 2020. "Study on the Properties of Partially Transparent Wood under Different Delignification Processes." *Polymers* 12(3):661.
- Xia, Qinqin, Chaoji Chen, Tian Li, Shuaiming He, Jinlong Gao, Xizheng Wang, and Liangbing Hu. 2021. "Solar-Assisted Fabrication of Large-Scale, Patternable Transparent Wood." *Science Advances* 7(5):eabd7342.
- Xia, Qinqin, Chaoji Chen, Yonggang Yao, Shuaiming He, Xizheng Wang, Jianguo Li, Jinlong Gao, Wentao Gan, Bo Jiang, Mingjin Cui, and Liangbing Hu. 2021. "In

- Situ Lignin Modification toward Photonic Wood.” *Advanced Materials* 33(8):2001588. doi:10.1002/adma.202001588.
- Yang, Yadong, Xinyi Liu, Caichao Wan, Sulai Liu, Xingong Li, Yuan Zhu, Zhenxu Yang, Liangli Li, Zhe Zhang, and Zaiyang Zhou. 2024. “Powering the Future Green Buildings: Multifunctional Ultraviolet-Shielding Transparent Wood.” *ACS Nano* 18(32):21288–301.
- Yin, Xuefeng, Yaqian Zhang, and Yongjian Xu. 2023. “Luminescent Transparent Wood from Balsa Wood Loaded by Graphite Carbon Nitride for Application in Photoelectric Device.” *Wood Science and Technology* 57(2):467–81.
- Zhang, Jun, Yongling Ying, Xiaoyang Yi, Wenbo Han, Lu Yin, Yongjun Zheng, and Rongbo Zheng. 2023. “H₂O₂ Solution Steaming Combined Method to Cellulose Skeleton for Transparent Wood Infiltrated with Cellulose Acetate.” *Polymers* 15(7):1733.
- Zhou, Xingbei, Nian Zhang, Shiyan Yin, Xuan Wang, Hang Su, Yaoli Zhang, Liping Cai, and Jianxiong Lv. 2026. “Investigation of Surface Construction of Porous and Superhydrophobic Transparent Wood With High Haze.” *Polymer Composites*.
- Zhu, Mingwei, Tian Li, Chelsea S. Davis, Yonggang Yao, Jiaqi Dai, Yanbin Wang, Feras AlQatari, Jeffrey W. Gilman, and Liangbing Hu. 2016. “Transparent and Haze Wood Composites for Highly Efficient Broadband Light Management in Solar Cells.” *Nano Energy* 26:332–39.
- Zhu, Mingwei, Jianwei Song, Tian Li, Amy Gong, Yanbin Wang, Jiaqi Dai, Yonggang Yao, Wei Luo, Doug Henderson, and Liangbing Hu. 2016. “Highly Anisotropic, Highly Transparent Wood Composites.” *Advanced Materials (Deerfield Beach, Fla.)* 28(26):5181–87.
- Zhu, Sailing, Subir Kumar Biswas, Zhe Qiu, Yiyang Yue, Qiliang Fu, Feng Jiang, and Jingquan Han. 2023. “Transparent Wood-Based Functional Materials via a Top-down Approach.” *Progress in Materials Science* 132:101025.

Chapter IV

This part of the work was developed during the research period at the WWSC department of the Royal Institute of Technology (KTH) in Stockholm, under the supervision of the group of L. Berglund and Y. Li, who in 2016 published one of the works considered pioneering in the field of TW. (Li et al. 2016) In the following years, in the KTH group, different approaches were developed for obtaining transparent composites, ranging from the use of PMMA loaded with active fluorescent materials, (Li, Yu, et al. 2017) to the use of wood-resin compatibilization (Li et al. 2018) processes or swelling of the nanostructure with a green process, (Chen et al. 2025) up to the use of a biobased acrylate polymer alternative to PMMA. (Montanari et al. 2023; Montanari, Ogawa, et al. 2021)

In the previous chapters, two fundamental aspects for the fabrication of TWs have been discussed, focusing on the enhancing of the current laboratory preparation steps. In particular, Chapter II dealt with the development of a new rapid and sustainable bleaching process, capable of retaining lignin to obtain white wood templates at room temperature. Chapter III, on the other hand, focused on optimizing the impregnation phase with resins using DOE to tune the optical properties of the composite and reduce resin consumption. In those Chapters, two bisphenol A-based crosslinkable epoxy resins were used, one synthetic and one partially biobased. These resins are widely used for the small-scale production of TW, but their large-scale use could compromise the overall sustainability of the final composite. In particular, the presence of fossil components, whether total or partial, and the RT cross-linking of excess resin not incorporated into the template (waste), reduces its renewability.

For this reason, during the research period at KTH, the focus was on using a fully biobased matrix, compatible with wood cell walls, with optical properties suitable for obtaining composites such as TW for energy applications. One of the acrylic resins, already investigated by the Stockholm group for TWs, is PLIMA, a resin derived from limonene, a cyclic terpene widely available as a by-product of the citrus industry.

(Montanari, Ogawa, et al. 2021; Montanari et al. 2023; Montanari, Olsén, and Berglund 2021)

4.1. The role of PLIMA as a filler for the preparation of fully biobased TW for potential energy applications

The use of PLIMA as a polymeric filler, as an alternative to both epoxy resins and PMMA, in lignin-rich wood templates, obtained through the patented process (Chapter II), offers several advantages in terms of optical behavior, interfacial interactions, processability, and sustainability, which will be explored below. In particular, the PLIMA has a refractive index of 1.52, which is similar to, but not the same as, that of the cell wall. (Montanari, Ogawa, et al. 2021) Unlike epoxy resins, which allow for minimizing optical mismatch thanks to a wide range of refractive indices (1.50-1.60) and therefore to maximize transparency, PLIMA introduces a controlled mismatch at the polymer-cell wall interface. (Tsuda and Urabe 2009) This promotes the diffusion of light, resulting in high haze values. For optoelectronic applications, such as photovoltaic devices, this optical property is advantageous because it increases the photon path length in the material, thereby promoting effective light capture. (Li et al. 2019; Montanari, Ogawa, et al. 2021) In addition, PLIMA is characterized by functional groups that interact with the hydroxyl-rich lignocellulosic template, leading to the formation of new physical and chemical bonds. These interactions improve adhesion to the interface, favoring a more effective integration between the polymer matrix and the wooden template. (Montanari, Ogawa, et al. 2021; Montanari et al. 2023) In addition, the use of PLIMA simplifies the fabrication of TWs when compared to acrylic resins of the same family, but of synthetic origin, such as PMMA. Unlike methyl methacrylate (MMA), which requires a prepolymerization step to achieve a viscosity suitable for infiltration, limonene acrylate (LIMA) already has a viscosity for direct diffusion into the wood's porous structure. (Montanari, Ogawa, et al. 2021; Montanari et al. 2023) This eliminates intermediate processing steps, reducing both time and energy and reagent consumption. In addition, the absence of a prepolymerization step avoids viscosity variations associated with process parameters such as temperature, initiator concentration, and reaction time, making the system more stable and controllable. Finally, the use of PLIMA is more sustainable and promotes material circularity. At the end of its life cycle, in fact, the polymer matrix can be removed and

replaced, recovering the wooden template. In addition, the monomer not used for curing, which would normally be discarded, can be used in multiple infiltration cycles, reducing waste. All these aspects make PLIMA a competitive, sustainable polymer compared to conventional thermoset matrices, such as epoxy resins and PMMA, which are generally difficult to recycle and use for subsequent infiltration cycles, contributing to the development of more eco-friendly, fully biobased composite systems. (Montanari, Olsén, et al. 2021)

Unlike TWs designed for building applications, which must have high transmittance and low haze, high haze values are advantageous for energy applications, as mentioned before. (Jia et al. 2019; Li et al. 2019; Mi et al. 2020; Zhu et al. 2016) The scattering of light within the composite, due to the anisotropy of the wooden template, potentially improving radiation absorption in thin-film devices, such as gallium arsenide and perovskite solar cells. This advantage in implementing TWs has been demonstrated by Zhu et al. (2016) and Li et al. (2019), who used TWs as structural substrates for gallium arsenide (GaAs) and perovskite solar cells, respectively. For assembly in perovskite solar cells, the delignified template was infiltrated with PMMA, achieving a transmittance of 86% and a haze of 70%. Despite the good results, the fossil-based filler does not reflect the sustainability purpose of industrializing a composite not only based on a natural aromatic skeleton, but also a biobased filler.

For this reason, the research activity has focused on the potential integration of PLIMA-TW in these optoelectronic devices to obtain a fully biobased and renewable TW, which has not yet been explored. The visual scheme of the research activity is illustrated in Fig. 8.

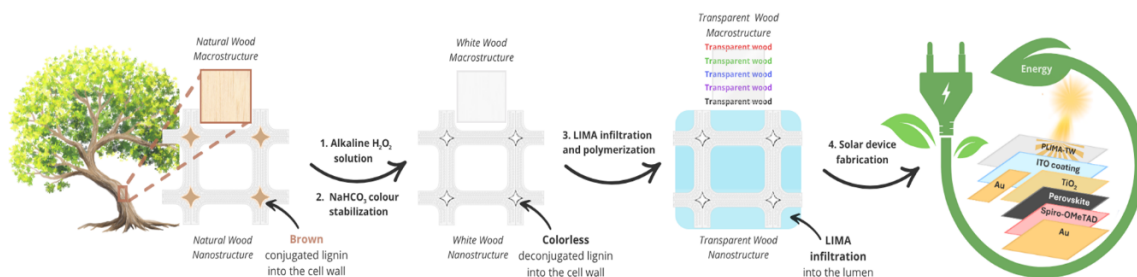


Fig. 8 A diagram illustrating the process of creating transparent wood using LIMA infiltration, along with the construction of a perovskite solar cell that utilises the transparent composite as a substrate for the diffusion of solar light.

The diagram in Fig. 8 shows the sequence of steps that start from the preparation of the white wood template, subsequently infiltrated with the limonene acrylate monomer (LIMA), and finally from the possible integration into the photovoltaic device by deposition of a conductive coating of indium tin oxide (ITO) on one of the two sides. This specific configuration was the subject of a preliminary study conducted in collaboration with Uppsala University to evaluate whether the TW prepared with PLIMA, starting from a lignin-rich wood template, could serve as a suitable active substrate for solar cells. Following the approach of Li et al. (2019), these solar cells are designed to be assembled at low temperature ($\sim 150^\circ\text{C}$), to preserve the integrity of both resin ($T_g = 130^\circ\text{C}$) and the substrate, avoiding thermal degradation of the entire composite. While a similar architecture was previously proposed by Li et al. (2019) using a fully delignified wood template infiltrated with PMMA, this work investigates employing the PLIMA bio-based matrix with a lignin-rich white wood template.

As mentioned above, the efficacy of TW depends on the matching between the refractive index of the cell wall and that of the polymer filler. While cellulose has an anisotropic index that varies from 1.53 to 1.59 depending on directionality (birefringence), standard epoxy resins based on bisphenol A provide a good match with an RI between 1.57 and 1.58. (Brandrup et al. 1999; Chen et al. 2019) The PLIMA is instead placed in an intermediate position, with a value of 1.52, which is advantageous for controlling scattering and bringing it towards higher haze values than those obtained in the last chapter using epoxy resins. (Montanari, Ogawa, et al. 2021)

From a chemical point of view, PLIMA is derived from the radical polymerization of the LIMA monomer, synthesized by the opening of the epoxy ring of limonene oxide with acrylic acid. This synthesis, described by Montanari et al. (2021), allows limonene (industrial by-product) to be reused, obtaining a monomer with three important functionalities: i) a reactive acrylic double bond for polymerization; ii) a terpene double bond that, for the most part, remains intact, contributing to the stability of the network, and iii) a group β -hydroxyl which favors interaction with the cell wall through the formation of a weak chemical bond. (Montanari, Ogawa, et al. 2021; Montanari et al. 2023)

The temperature polymerization process is the same as that used for PMMA and involves initiators such as 2,2'-azobis(2-methylpropionitrile) (AIBN), which is particularly suitable for hydrophilic materials because it is not very sensitive to residual moisture. As

evidenced by the spectroscopic analyses (ATR-FTIR) reported in Fig. 9, the reaction transforms the monomer (or the initial mixture of oligomers) (curve a) into a three-dimensional amorphous network, as demonstrated by Montanari et al. 2021 (curve b). (Montanari, Ogawa, et al. 2021)

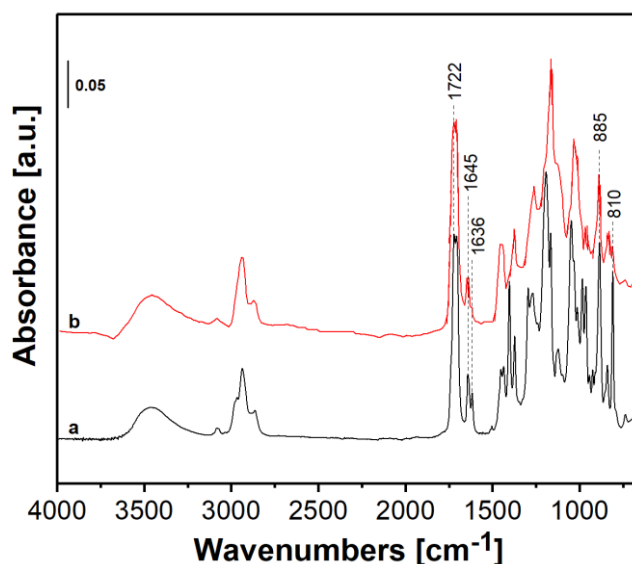


Fig. 9 ATR-FTIR analysis in the range 4000-650 cm^{-1} of the LIMA (a) and PLIMA (b) samples.

In particular, observing the spectrum related to the monomer/oligomer (a) and that relating to the PLIMA (b) is possible to see the partial reduction of the intensity of the band to about 1636 cm^{-1} , related to the stretching of the acrylic C=C double bond, which confirms the radical addition reaction that has taken place. (Montanari, Ogawa, et al. 2021) Furthermore, in curve (b), the disappearance of the peak at 810 cm^{-1} is observed, which is associated with the out-of-plane bending of the bonds of the =CH group in the acrylate, confirming the polymerization that has taken place. (Montanari, Ogawa, et al. 2021) Moving towards the region of the carbonyls 1720-1740 cm^{-1} , it is possible to observe variations between the profiles of curves (a) and (b). (Socrates 2004) Although both spectra show an absorption at 1722 cm^{-1} , the band in the polymer curve (B) is more defined and exhibits a shoulder at higher wavenumbers (1738 cm^{-1}). The observed phenomenon is consistent with the loss of conjugation between the C=O group and the adjacent acrylic double bond. This blue shift is expected in the presence of polymerization aeration, during which saturated C-C bonds are formed. (Montanari, Ogawa, et al. 2021; Socrates 2004)

Finally, we can see in both spectra the bands at 1645 and 885 cm^{-1} related to the vibration of the double bond of the limonene isopropenyl ring. (Montanari, Ogawa, et al. 2021) This result indicates that the polymerization selectively involved the acrylic groups, maintaining the cyclic structure of the original terpene. (Montanari, Ogawa, et al. 2021)

4.2. The infiltration process and the investigation of the microstructure

The microstructure, from natural balsa wood (NB) to transparent composite (PLIMA-TW), was investigated by FE-SEM microscopy to evaluate the effectiveness of the impregnation process and the integrity of the lignocellulosic template. As detailed in section 4.9, the infiltration process was conducted under mild, unregulated (departmental) vacuum, reaching the minimum residual pressure of the system. The process was carried out alternating vacuum-air cycles for a total time of 36 h. This strategy was adopted to promote the removal of air from the cell lumens and allow the homogeneous diffusion of the LIMA monomer within the cell wall. The viscosity of LIMA enables good cell wall wettability and a lower shrinkage volume during curing than PMMA, which does not require prepolymerization. (Montanari, Ogawa, et al. 2021; Montanari, Olsén, et al. 2021) Figure 14 presents images of samples of natural wood (NB), white wood (WB), and transparent wood (PLIMA-TW), analyzed both at the macro scale (optical photo) and at the micro scale.

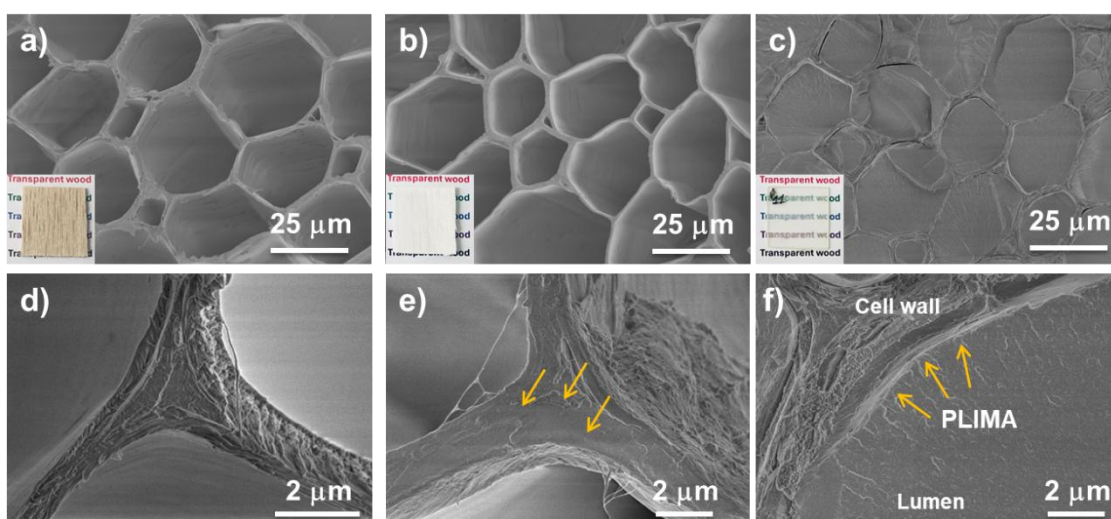


Fig. 10 SEM images displaying the microstructure of cross-sections of NB (a,d), WB (b,e), PLIMA-TW, with magnification increasing from top to bottom.

The images at high magnifications, relative to NB (Fig. 10a) and WB (Fig. 10 b) show the typical hierarchical structure of balsa wood, characterized by open cellular lumens with honeycomb morphology. The structure is preserved after the removal of the lignin chromophore groups at high magnifications, in which there are no WB microcracks (Fig. 10 e), and the deconjugated lignin is maintained within the middle lamella. (Borrega et al. 2015; Gullo, Messori, and Palmero 2026a) On the other hand, when looking at the post-infiltration balsa at high magnifications (Fig. 10c), a complete and uniform filling of the lumens is observed, with a reduced number of gaps at the wood-PLIMA interface. (Chen et al. 2022; Montanari, Ogawa, et al. 2021; Montanari et al. 2023) This result is confirmed by FE-SEM images at high magnifications (Fig. 10c), in which the PLIMA-TW shows a complete adhesion of the polymer to the cell wall. This is due to the formation of strong hydrogen bonds between the hydroxyl groups of the PLIMA and those of the lignocellulosic template, in which the matrix is not only trapped in the porosity of the wood on a physical level, but is chemically anchored, ensuring better adhesion between the components of the composite than purely hydrophobic acrylic resins such as PMMA.

4.3. The Optical Properties of Pure PLIMA vs TW-PLIMA

The optical properties of the pure PLIMA and the obtained PLIMA-TW were analyzed using transmittance and haze measurements, and the corresponding spectra are shown in Fig. 11. The optical properties will be commented on using the values measured at 550 nm, a value generally used in the literature as a reference wavelength for the TW. (Gullo, Messori, and Palmero 2026b)

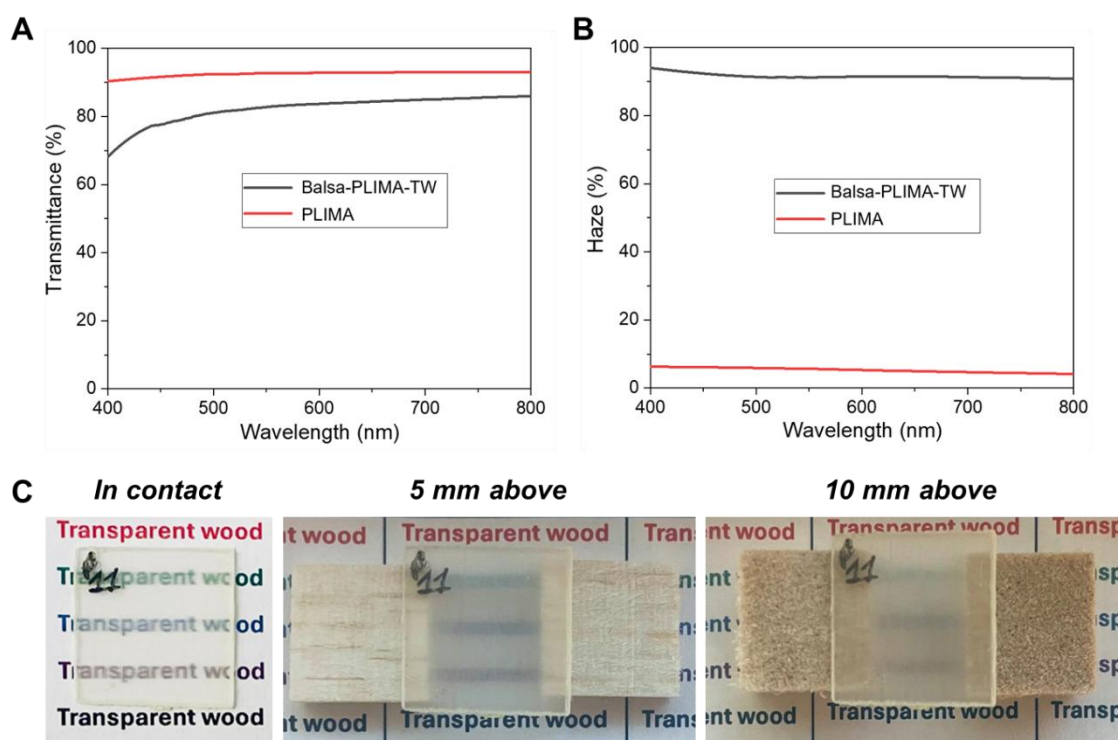


Fig. 11 Optical transmittance (A) and haze (B) spectra of PLIMA-TW and PLIMA. C) Photograph of PLIMA-TW in contact and 5, 10 mm above the printed paper.

As can be seen in Fig. 11 A and B, pure PLIMA has excellent optical properties, with a transmittance of 95% and a low haze value of 7%. This confirms the high transparency, already reported in the literature, of the biobased polymer used as a filler. (Montanari, Ogawa, et al. 2021) On the contrary, the PLIMA-TW composite, while maintaining a high transmittance of 85%, shows a strong increase in scattering, with a haze value of 92%. This is particularly interesting when compared with similar balsa-based TWs present in the literature. In the work of Montanari et al. 2021 using delignified balsa with the same density but low lignin content (2%), the haze value was 39%. (Montanari, Ogawa, et al. 2021) This marked difference is due to the white wood template used here, which showed a high residual lignin content (93%, see Chapter II, Fig. 4, p. 72). As explored by Chen et al. (2022), which considers the optical path of photons through various TWs, preserved lignin can act as a scattering center. (Chen et al. 2022) For this reason, the hierarchical structure of the wood, combined with the slight optical mismatch between the refractive index of the PLIMA and the anisotropic index of the lignin-rich cell wall, lengthens the optical path of photons within the material. This high diffusion rate is visually confirmed by the photographs shown in Figure 15C. In fact, looking at the PLIMA-TW sample in contact with the printed paper, it is possible to distinctly read the underlying text thanks

to the 85% transmittance, but when the distance between the sample and the sheet increases to 5 and 10 mm, respectively, a progressive and rapid blurring occurs, which explains the strong haze. This observed behavior confirms that the increase in optical path due to residual lignin and the greater optical mismatch between the wooden template and the PLIMA make this TW the ideal platform to improve light capture in the active layers of perovskite solar cells, a potential application developed at KTH.

4.4. PLIMA-TW vs NB and PLIMA Mechanical Properties

Table 3 shows the mechanical properties obtained from longitudinal tensile tests for natural wood (NB) and the PLIMA-TW biocomposite compared to those of pure PLIMA reported in the literature. (Montanari, Ogawa, et al. 2021) In this study, NB was used as a reference for the wood template to ensure a consistent comparison with the KTH literature benchmarks, in which natural balsa is often used as the standard of comparison with TWs. From the data shown in the table, it is possible to affirm the structural reinforcement of the composite obtained from NB and PLIMA. The synergistic reinforcement of natural wood and pure resin is evident in the maximum tensile strength, with a clear improvement compared to the two neat starting materials (+52% compared to NB and +66% compared to PLIMA).

Furthermore, the increase in the composite's final stiffness (2.9 GPa) compared to the two single materials (2.2 GPa) confirms the reinforcing role, similar to that of natural reinforcing fibers, of the cell walls of balsa wood, which act as a porous template, reinforcing the resin used as a filler. (Bledzki, Sperber, and Faruk 2002; Bradai et al. 2024; Haldar et al. 2011; Li et al. 2016) Finally, looking at the data on the material's ductility (% elongation at break), substantial maintenance is observed ($0.2 \pm 0.31\%$ and $0.1 \pm 0.076\%$ respectively for PLIMA and NB).

Sample	Maximum Tensile Strength [MPa]	Young Modulus [GPa]	Elongation at break [%]
PLIMA*	14.9±6.6	2.2±0.4	0.7±0.3
NB	16.3±0.03	2.2±0.2	0.8±0.03
PLIMA-TW	24.7±1.6	2.9±0.09	0.9±0.07

*data reported from Montanari et al. (2021)

Table 3 Mechanical properties of pure PLIMA, NB and PLIMA-TW.

If we compare the TW obtained with PLIMA-based acrylic resin with the results obtained on epoxy resins discussed in Chapter III (Fig. 4, p.109, unpublished paper) for pure matrices, the PLIMA demonstrates better mechanical properties than both the synthetic epoxy resin (ER, with $E = 105 \text{ MPa}$, $\sigma_{\max} = 6 \text{ MPa}$) and the plant-based epoxy resin (PBER, with $E = 500 \text{ MPa}$, $\sigma_{\max} = 18 \text{ MPa}$). This result is due to the glassy nature of PLIMA, arising from the stiffness of the limonene ring, which offers a more solid structure than epoxy resins but less than fossil-based acrylics (e.g., PMMA). (Fu et al. 2018; Li et al. 2016, 2018; Montanari, Ogawa, et al. 2021)

Although the maximum tensile strength of the PLIMA-TW (24.7 MPa) is lower than that recorded for the TW-PBER (36.7 MPa), this difference is due to the elastoplastic response of the two matrices.

In fact, the stiffer and more glassy nature of PLIMA-TW demonstrates a lower tolerance to the deformation generated during tensile stress than PBER resin (more ductile). As reported by Montanari et al., the presence of β -hydroxyl groups favors the formation of hydrogen bonds with the cell wall, thereby optimizing stress transfer at the nanoscale. However, the reduced elongation at break of the PLIMA-TW allows, as mentioned before, a lower redistribution of local stresses before failure, leading to a final value lower than TW-PBER and a higher elastic modulus.

The lower ductility of PLIMA-TW compared to epoxies (4% elongation) is designed to provide greater dimensional stability. The stiffness of the PLIMA-TW limits micro-deformations of the substrate under mechanical load. This structural rigidity, together with the low thermal expansion of the lignocellulosic skeleton, makes the composite a suitable support for the preservation of fragile functional layers, (e.g. ceramic thin films) used in perovskite solar cells, which could be affected by excessively deformable substrates. (Rolston et al. 2018; Zhang et al. 2023; Zhu et al. 2016)

4.5. Polishing procedure and study of surface roughness by Atomic Force Microscopy (AFM)

To prepare the PLIMA-TW interface for deposition of the functional ITO coating, the surface was manually polished to reduce post-infiltration and post-curing roughness. The effectiveness of the polishing procedure was verified by comparing topographies of as-fabricated PLIMA-TW samples and polished samples using AFM (Fig. 12).

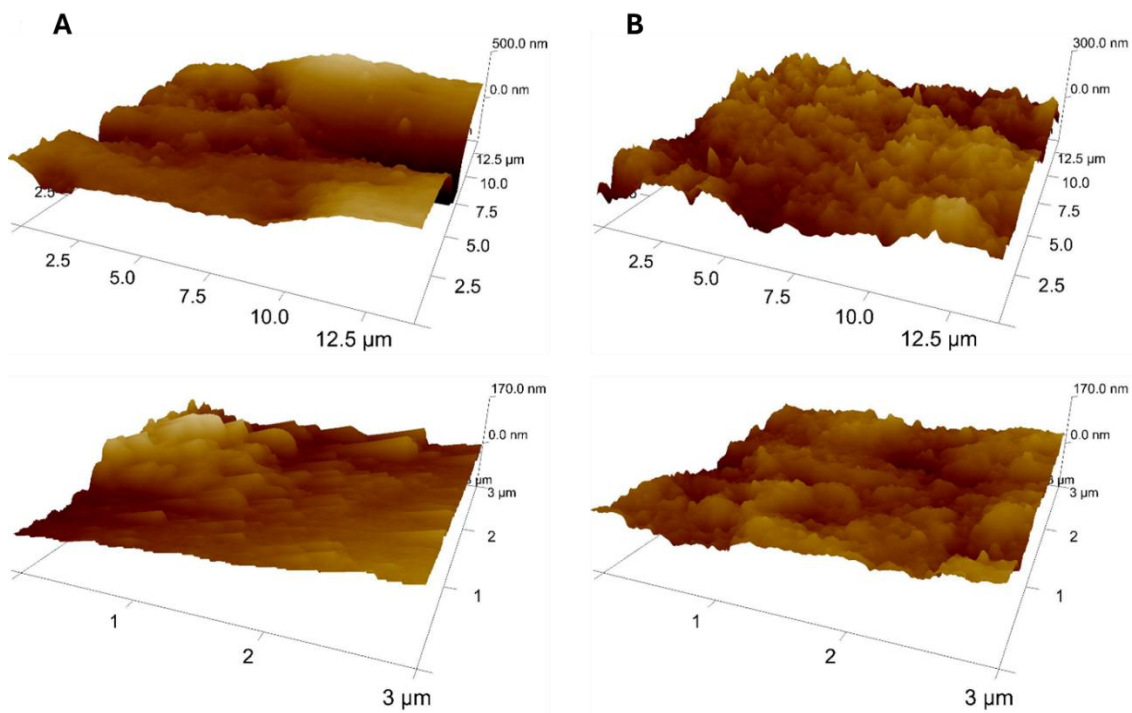


Fig. 12 AFM topographical images, showing surface texture and roughness of A) as-fabricated PLIMA-TW and B) polished PLIMA-TW surfaces at 2 different scales.

The qualitative analysis of topographic images reveals a modification in surface morphology. While the comparison between the pre- and post-polishing images shown in Fig. 12, at both scan scales, shows a shift in roughness towards smaller (submicrometric) scales, the quantitative data presented in Table 4 shows that polishing effectively flattens the surface texture. As shown by the data presented in Table 4, the effect is particularly marked on the larger scan scale ($14 \mu\text{m} \times 14 \mu\text{m}$), where a reduction of all parameters is observed: the value of the arithmetic mean height of the deviations from the mean plane (S_a) decreases from 88.5 nm to 39.3 nm, while the maximum height of the surface (S_z) decreases from 1084.1 nm to 333.8 nm.

Sample	Sa (nm)	Sq (nm)	Sz(nm)
PLIMA-TW as fabricated (14 $\mu\text{m} \times 14 \mu\text{m}$)	88.5	127.4	1084.1
PLIMA-TW as fabricated (3 $\mu\text{m} \times 3 \mu\text{m}$)	22.3	28.8	180.5
Polished PLIMA-TW (14 $\mu\text{m} \times 14 \mu\text{m}$)	39.3	48.8	333.8
Polished PLIMA-TW (3 $\mu\text{m} \times 3 \mu\text{m}$)	19.5	24.8	181.5

Table 4 PLIMA-TW as fabricated and polished PLIMA-TW surfaces roughness parameters (ISO 251782) for AFM scans at two scales.

This significant decrease indicates that the mechanical polishing treatment removes long-range undulations and macroscopic roughness (peaks and deep valleys), standardizing the overall topography.

At the reduced scale of 3 $\mu\text{m} \times 3 \mu\text{m}$, roughness decreases, though less pronounced, with Sa decreasing from 22.3 nm to 19.5 nm. This suggests that while polishing effectively levels out mesoscopic features, some microscopic structures may remain, which may be intrinsic to the material or related to the size or pressure of the abrasive used.

The statistical analysis of the height distribution (Fig. 13) further confirms the achievement of a highly homogeneous post-polishing surface. The histograms show, in fact, a transition from a wide, asymmetrical distribution of the PLIMA-TW as fabricated to a narrow, centered distribution of the polished PLIMA-TW sample, confirming the suppression of morphological singularities and maximum deviation peaks.

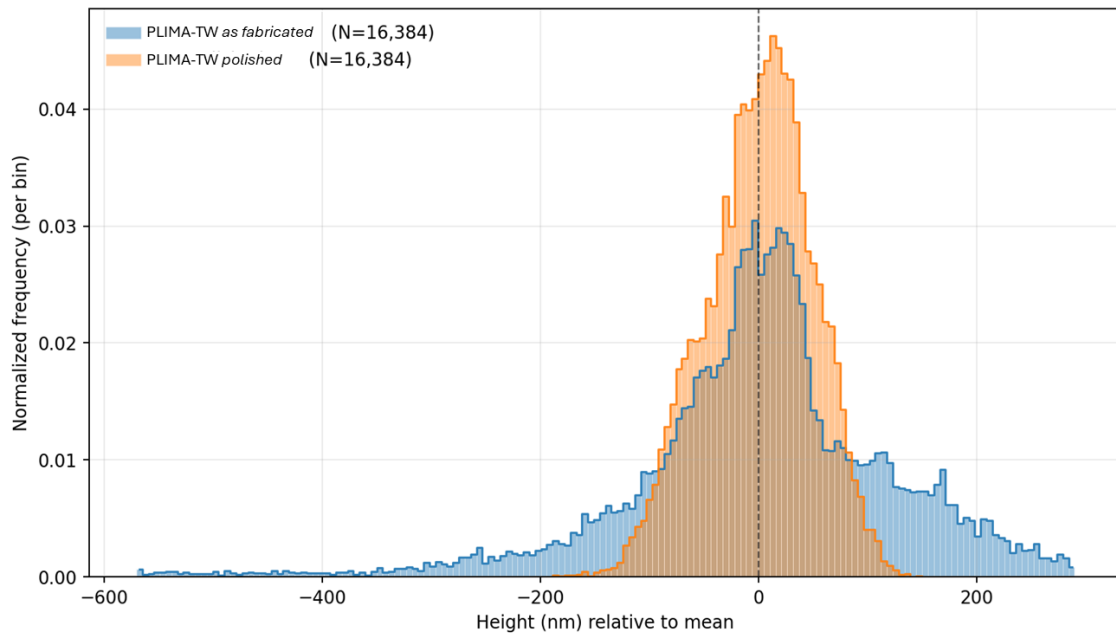


Fig. 13 Statistical analysis of surface topography. Histograms of the distribution of PLIMA-TW sample heights, as fabricated (blue) and after polishing (orange).

The significant reduction in areal roughness achieved minimizes reflection and surface scattering, providing a stable, planar substrate. (Chen et al. 2022; Chkhalo et al. 2024; Li et al. 2019) This optimization is necessary to prevent discontinuities and mechanical stresses during solar cell assembly, ensuring electrical continuity and structural integrity of the final device.

4.6. Humidity and Optical Properties Testing

To evaluate the response of PLIMA-TW composites to exposure under severe humidity conditions, exposure tests were conducted in an alternating dry/wet environment. The test was conducted on 5 replicas of the composite obtained from the same production batch. Fig. 14 A shows the percentages by weight measured over 21 days of exposure, calculated as the average water uptake [%] across the 5 samples tested.

Based on the reported trend, the PLIMA-TW samples remain stable for the first 5 days of exposure, corresponding to about 3 months of real exposure, highlighting an initial phase in which the acrylic resin effectively limits moisture penetration. Subsequently, the percentage of adsorbed water rises to a maximum of about 4%, a value consistent with literature data for similar materials exposed for prolonged periods under less severe

conditions. (Montanari et al. 2023) A plateau is observed from day 17 (about 9 months of simulated aging) to day 21 (1 year), indicating the system has reached hygroscopic equilibrium.

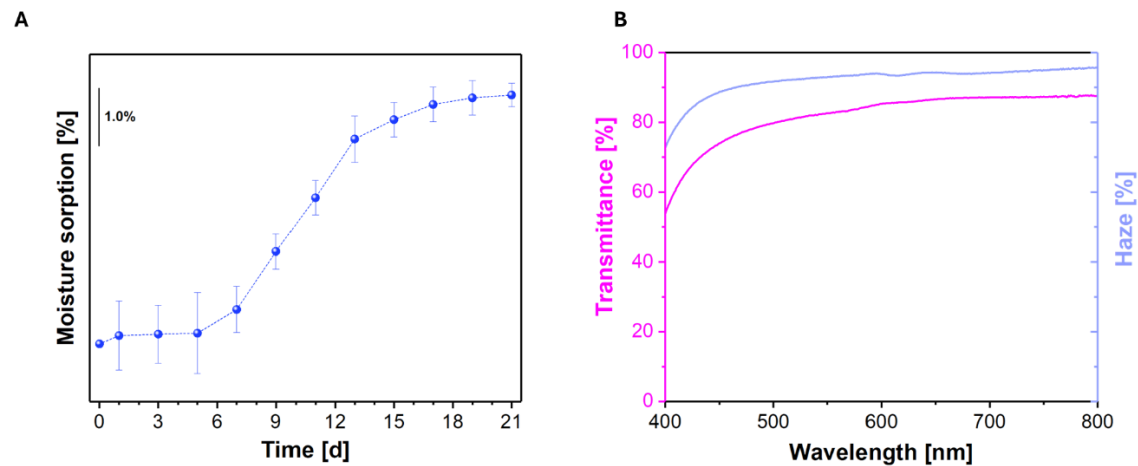


Fig. 14 A) Average of the moisture uptake of 5 samples of PLIMA-TW and relative standard deviation; B) Optical properties of PLIMA-TW after 21 days of moisture test.

In Fig. 14 B the optical properties in terms of transmittance and haze are presented. As shown by the curves, for both transmittance and haze, there are no appreciable differences between the composite before (see figures 15A and 15B) and after exposure to humid conditions. For direct comparison, the optical properties data at day zero and 21 are shown in Table 5.

Sample	Day	Transmittance [%]	Haze [%]
PLIMA-TW	0	82.7	91.2
	21	82.6	92.9

Table 5 Optical properties of PLIMA-TW before (day 0) and after moisture test (day 21).

This result shows that the moisture absorption (Fig. 14A) did not trigger interface degradation phenomena or wood-polymer detachment mechanisms, which would lead to a loss of optical performance. (Dhakal, Zhang, and Richardson 2007; Li, Fu, et al. 2017) On the contrary, the stability of the transmittance and haze curves (Fig. 14B) highlights the high chemical compatibility and structural integrity of the PLIMA-TW composite even in critical environmental conditions.

4.7. FTIR analysis in ATR and transmission before and after exposure to humidity for the determination of H₂O absorption

To investigate the structural mechanisms underlying the observed hygroscopic stability, a comparative spectroscopic analysis was conducted on pre- and post-moisture exposure PLIMA-TW samples. The objective of the characterization involves, on the one hand, the quantification of the % variation of the surface water content and bulk, in ATR and transmission modes, respectively; and, on the other hand, the verification of the ability of the biobased composite to preserve structural integrity after exposure to extreme environmental stresses.

4.7.1. ATR-FTIR surface analysis

Fig. 15 shows the ATR-FTIR spectra of the PLIMA-TW composite before and after moisture exposure. In the image, two diagnostic regions useful for the study have been assigned. In particular, the broadband centered at 3400 cm⁻¹, characteristic of the stretching of hydroxyl groups (-OH) involved in hydrogen bonds, and the more defined band at 2920 cm⁻¹, attributable to the asymmetric stretching of the -CH bonds of the hydrocarbon chains of the PLIMA and the white wood template. (Socrates 2004)

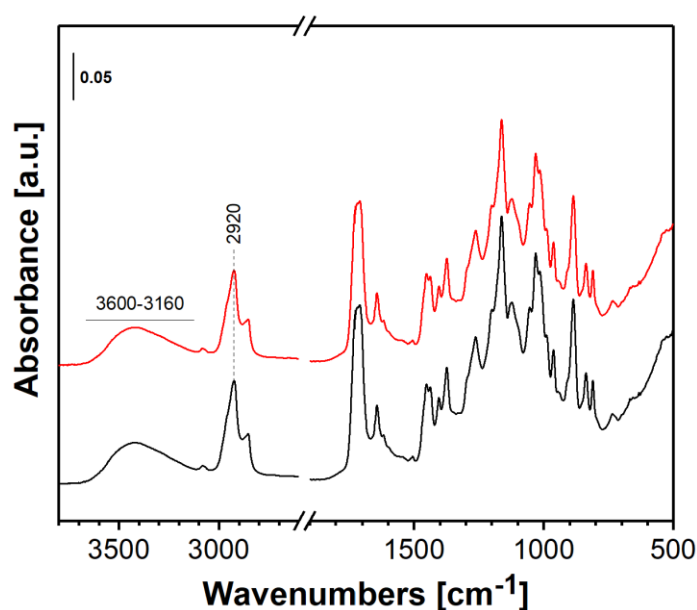


Fig. 15 ATR-FTIR analysis from 3800 to 500 cm^{-1} on PLIMA-TWs pre (black curve) and post (red curve) moisture exposure.

To quantify the change in surface humidity, the relative intensity of the -OH band was calculated by normalizing it to the peak intensity at 2920 cm^{-1} . The latter has been chosen as an internal reference because, as reported in the literature, signals related to -CH stretching are stable and do not participate in hydrogen-bond formation. (Socrates 2004) Data from pre-exposure (day 0) and post-exposure (day 21) TWs samples to humidity are shown in Table 6. It is worth noting that while day 0 samples were characterized in their as-prepared state, having reached an equilibrium with ambient laboratory humidity ($23 \pm 2^\circ\text{C}$, 40-50% RH), the day 21 samples were analyzed directly after the last “Phase B” cycle (50 $^\circ\text{C}$, 50% RH) described in Materials and Methods, p.156.

Sample	Time [d]	-OH/H ₂ O 3400 cm^{-1}	-CH (Reference) 2920 cm^{-1}	Normalized water signal (I_{3400}/I_{2920})	$\Delta\%$
PLIMA-TW	0	0.149	0.248	0.597	-32.3%
	21	0.044	0.109	0.404	

Table 6 Calculation of surface H₂O adsorption from ATR-FTIR analyses.

The results show a 32.3% decrease in the superficial -OH/H₂O index at the end of the 21 days of testing. This result contrasts with the uptake measured by gravimetry; however, the environmental conditions to which the 21-day sample was exposed differ. In the first, the weight of the capions was measured in phase A (*Cool/Humid* conditions, as described in Materials and methods section, p.156), while for structural characterization, the sample was measured in phase B (*Warm/Dry* conditions, see p.158). This distinction allowed highlighting the reversibility of water surface adsorption and the post-curing effect of the biobased polymer matrix that occurred under dry conditions (phase B). Specifically, the thermal treatment at 50 $^\circ\text{C}$ during the aging cycles effectively removed the intrinsic moisture originally present in the starting material at day. During this cycle, the polymer network is stabilized and compacted at temperature, maintaining the optical properties unaltered, as shown in Fig. 14 B and Table 5, and reducing the number of available surface sites for water binding.

4.7.2. FTIR bulk analysis in transmission

To evaluate moisture penetration into the bulk of the composite, NIR transmission spectroscopy was used (Fig. 16). The signals in the spectral region of interest are the 5200 cm^{-1} band, related to the combination of stretching and bending of water molecules, and the 5900 cm^{-1} band, corresponding to the first overtone of the -CH bond stretching. (Schwanninger, Rodrigues, and Fackler 2011) Also for this analysis, the signal at 5900 cm^{-1} was used as an internal normalization band to ensure statistical consistency with the ATR analysis. (Schwanninger et al. 2011)

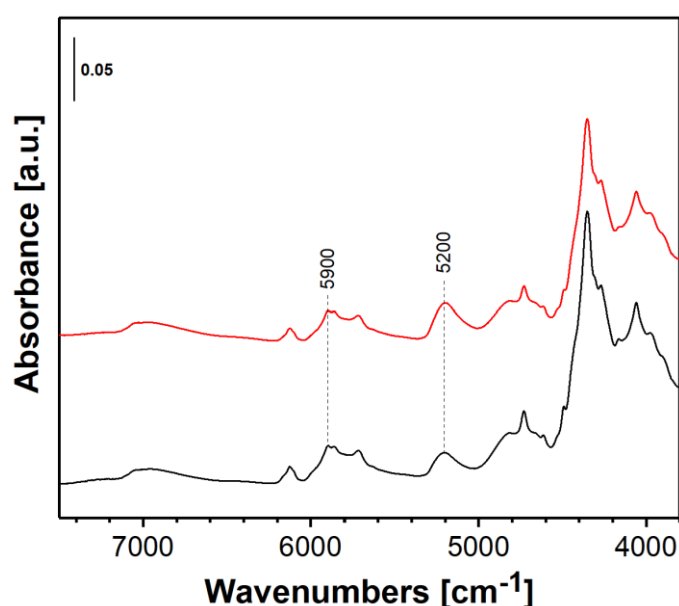


Fig. 16 FTIR analysis in transmission from 7800 to 3800 cm^{-1} on PLIMA-TWs at week pre (black curve) and post (red curve) water sorption.

The data relating to the PLIMA-TW samples are shown in Table 7

Sample	Time [d]	Free Water 5200 cm^{-1}	-CH (Reference) 5900 cm^{-1}	Normalized water signal (I_{3400}/I_{2920})	$\Delta\%$
PLIMA-TW	0	0.284	0.242	1.173	-27.8%
	21	0.188	0.222	0.847	

Table 7 Calculation of bulk H_2O adsorption from transmission FTIR analyses.

In line with the decrease observed by surface analysis, there was also a reduction in the -OH/ H_2O index of 27.8% in bulk. This trend confirms that the thermal conditions of

“Phase B” (50 °C) were sufficient to drive out not only the surface moisture but also a portion of the core-absorbed water originally present in the lab-stored samples. The percentage decrease calculated in bulk is less marked than in the superficial one. This difference suggests that, while the surface releases adsorbed molecules more quickly during the dry phase (B phase), eliminating moisture, the migration of water from the bulk to the outside is regulated by slower diffusive processes within the more complex porous cellular network of wood. However, the signal reduction recorded in the bulk also confirms that the PLIMA-TW composite is not subject to permanent free-water accumulation. This means maintaining a dimensionally stable interface that reduces water content when not exposed to humidity, which, combined with the preservation of optical properties, makes this TW particularly suitable for photovoltaic applications.

4.8. Conclusions

This chapter reports part of the research conducted at the KTH in Stockholm, in the WWSC department, aimed at studying the properties of a completely bio-based TW using PLIMA to replace fossil-based polymer matrices. The properties of the TW obtained were optimized and studied for the possible integration of TW into photovoltaic devices for energy storage. The analyses conducted by AFM confirmed the importance and effectiveness of the polishing process in reducing topographic discontinuities of the material. Surface roughness reduction was considered to ensure a planar interface suitable for integrating thin layers of TW (1 mm thick) into perovskite solar cells.

A particularly promising result was obtained by exploiting the optical mismatch between the PLIMA and the white lignin-rich template. In fact, PLIMA-TW showed high haze values, which could potentially be used to improve energy conversion efficiency. The maintenance of optical properties was confirmed through durability tests under wet/dry cyclic conditions to simulate high work stresses. FTIR monitoring of water release under dry conditions confirmed the strength and renewability of the TWs substrate, even under high humidity (RH 90%). The analyses conducted showed that the chemical structure of the bio-based matrix exerts an effective protective effect on the cellulosic template, allowing the material to maintain the haze value unchanged even after numerous environmental stress cycles (1 year of total exposure).

The results presented in this work provide a useful contribution to the discussion in the next chapter on the prospects for the future use of this versatile and innovative material in industry and on the impact of these composites within the framework of the global energy transition.

4.9. Materials and methods

Bleaching of the wood template:

Wood templates were treated with a 2 M H₂O₂/KOH solution at room temperature for 2 hours, in accordance with the previous protocol. (Gullo et al. 2026a)

LIMA synthesis:

LIMA was synthesized through the ring-opening acrylation of limonene oxide with acrylic acid, following the previous protocol. (Montanari, Ogawa, et al. 2021)

LIMA infiltration:

The infiltration of the WB template was carried out under vacuum after adding the monomer and 0.3% AIBN as the thermal initiator. (Li et al. 2016) To ensure complete wettability and to compensate for the evaporation of the LIMA monomer during prolonged degassing phases, the samples were immersed in an excess of monomer, ensuring complete coverage of the template throughout the process. This process consisted of 32 hours of effective vacuum, applying intermittent cycles (8 hours of vacuum alternating with 12-14 hours at atmospheric pressure) to promote capillary ascent and complete filling of porosity. During the vacuum phases, the system's minimum achievable residual pressure (uncontrolled vacuum) was applied.

Polishing:

The surfaces of the transparent wood samples were prepared using a multi-step manual polishing protocol. The samples were subjected to a gradual sanding phase (lapping) with deionized water, using P600, P1000 and P4000 abrasive papers in sequence. During this process, the movements were alternated between circular and orthogonal to minimize the formation of cross-scratches and ensure the flatness of the plane. Next, a pre-polishing was performed by suspending silica nanoparticles on a MicroCloth (Buehler) soft cloth. Finally, the polishing was completed with diamond paste (grain size 1 µm) on a TexMet C support. At the end of the treatment, any abrasive residue was removed by cleaning

with damp microfiber cloths and 70% ethanol, verifying the absence of opacity or surface defects in grazing light before atomic force microscopy (AFM) analysis.

Characterization:

The cross-sections of the wood samples were analyzed using a Field Emission Scanning Electron Microscope (Hitachi, S4800, Japan) at an acceleration voltage of 1 kV. To prepare the cross-sections, the samples were fractured after being cooled with liquid nitrogen, and then freeze-dried for 24 hours using a Hypercool 3110 (Gyrozen, Korea).

FTIR analyses in ATR and transmission were performed following the procedure described previously in the published article (Chapter II, published paper, p.47).

The optical properties were analyzed following the same procedure as previously reported in Chapter III (unpublished paper, p.97).

The surface morphology of the transparent wood samples, before and after polishing, was analyzed using atomic force microscopy (AFM) with a Multimode 8 (Bruker, Santa Barbara, CA, USA). The images were acquired in tapping mode with ScanAsyst-Air probes (TAP150). The analysis was conducted on samples of about 5 mm × 5 mm taken from the central section of the specimens, selecting over 10 regions to ensure representativeness.

The scans were carried out at two different areal scales (14 μm × 14 μm and 3 μm × 3 μm) to distinguish roughness contributions at the meso- and micro-scales. The parameters shown below in Table 4 have been measured in accordance with the ISO 251782 standard for the structure of areal surfaces, the following parameters have been calculated:

- *Sa (nm)*: Arithmetic mean height of the deviations from the mean plane calculated using Equation 1:

$$Sa = (1/A) \iint |z(x,y)| dA \quad (1)$$

- *Sq (nm)*: Square root of the mean squares of the deviations (RMS), calculated using Equation 2:

$$Sq = \sqrt{(1/A) \iint z(x,y)^2 dA} \quad (2)$$

- *Sz (nm)*: Maximum surface height, calculated as the distance between the highest peak and the deepest valley in the evaluation area.

The durability and stability in wet conditions of the PLIMA-TW composite were evaluated by exposing the samples to repeated thermal-hygroscopic expansion and

contraction cycles in a Memmert climatic chamber model ICO50med, Schwabach, Germany. The test was performed according to a protocol compliant with ASTM D3459-98. To make the survey closer to real operating conditions, more stringent conditions than ordinary standards were used, increasing both thermal deltas and wet saturation levels. 2 phases (A and B) were alternated for 24 hours, as shown below:

- *Phase A (Cool/Humid)*: 12 hours at a temperature of 20 °C and a relative humidity (RH) of 95%.
- *Phase B (Warm/Dry)*: 12 hours at a temperature of 50 °C and relative humidity (RH) of 50%.

The total exposure of the samples was 21 days to simulate accelerated aging equivalent to about one year of real exposure in environments subject to strong seasonal fluctuations. Samples were extracted from the chamber at regular intervals and weighed with a Sartorius ED224S Extend analytical balance (accuracy ± 0.1 mg). The percentage of water absorption W_a [%] was calculated according to the following equation:

$$W_a [\%] = \frac{m_{RH} - m_i}{m_i} * 100$$

Where m_i is the initial mass of the sample, and m_{RH} is the mass of the sample after exposure to moisture. To carry out the test, 5 genuine replicas of the same sample were used, and the reported trend was calculated as the average of the values obtained from each sample. The relative standard deviation was calculated to account, at the statistical level, for the natural morphological and dimensional variability of the composites used.

References

- Bledzki, Andrzej K., Volker E. Sperber, and Omar Faruk. 2002. *Natural and Wood Fibre Reinforcement in Polymers*. Vol. 152. iSmithers Rapra Publishing.
- Borrega, Marc, Patrik Ahvenainen, Ritva Serimaa, and Lorna Gibson. 2015. "Composition and Structure of Balsa (*Ochroma Pyramidale*) Wood." *Wood Science and Technology* 49(2):403–20.
- Bradai, Hamza, Ahmed Koubaa, Jingfa Zhang, and Nicole R. Demarquette. 2024. "Effect of Wood Species on Lignin-Retaining High-Transmittance Transparent Wood Biocomposites." *Polymers* 16(17):2493.
- Brandrup, Johannes, Edmund H. Immergut, Eric A. Grulke, Akihiro Abe, and Daniel R. Bloch. 1999. *Polymer Handbook*. Vol. 89. Wiley New York.
- Chen, Hui, Adil Baitenov, Yuanyuan Li, Elena Vasileva, Sergei Popov, Ilya Sychugov, Max Yan, and Lars Berglund. 2019. "Thickness Dependence of Optical Transmittance of Transparent Wood: Chemical Modification Effects." *ACS Applied Materials & Interfaces* 11(38):35451–57.
- Chen, Hui, Jonas Garemark, Lengwan Li, Mathias Nero, Maximilian Ritter, Ocean Cheung, Tom Willhammar, Ilya Sychugov, Yuanyuan Li, and Lars A. Berglund. 2025. "Green Nanotechnology of Cell Wall Swelling for Nanostructured Transparent Wood of High Optical Performance." *Small* 21(5):2406749. doi:10.1002/sml.202406749.
- Chen, Hui, Céline Montanari, Ravi Shanker, Saulius Marcinkevicius, Lars A. Berglund, and Ilya Sychugov. 2022. "Photon Walk in Transparent Wood: Scattering and Absorption in Hierarchically Structured Materials." *Advanced Optical Materials* 10(8):2102732.
- Chkhalo, N. I., A. A. Akhsakhalyan, M. V. Zorina, M. N. Toropov, and Yu M. Tokunov. 2024. "Method for Obtaining Atomically Smooth Substrates from Single-Crystal Silicon by Mechanical Lapping." *Technical Physics* 69(4):812–17.
- Dhakal, Hom N., ZY and Zhang, and Mel OW Richardson. 2007. "Effect of Water Absorption on the Mechanical Properties of Hemp Fibre Reinforced Unsaturated Polyester Composites." *Composites Science and Technology* 67(7–8):1674–83.
- Fu, Qiliang, Min Yan, Erik Jungstedt, Xuan Yang, Yuanyuan Li, and Lars A. Berglund. 2018. "Transparent Plywood as a Load-Bearing and Luminescent Biocomposite." *Composites Science and Technology* 164:296–303.
- Gullo, Francesca, Massimo Messori, and Paola Palmero. 2026a. "Preservation of Wood Structure Using Stabilized Alkaline Bleaching Agents: A Novel and Mild Approach to Enhance Whitening for Lignin-Rich Wood Template." *Wood Science and Technology* 60(1):12.

- Gullo, Francesca, Massimo Messori, and Paola Palmero. 2026b. "Transparent Wood for a Bio-Based Future: A Critical Review." *Applied Materials Today* 49:103168.
- Haldar, S., N. Gheewala, K. J. Grande-Allen, M. A. Sutton, and H. A. Bruck. 2011. "Multi-Scale Mechanical Characterization of Palmetto Wood Using Digital Image Correlation to Develop a Template for Biologically-Inspired Polymer Composites." *Experimental Mechanics* 51(4):575–89.
- Jia, Chao, Chaoji Chen, Ruiyu Mi, Tian Li, Jiaqi Dai, Zhi Yang, Yong Pei, Shuaiming He, Huiyang Bian, and Soo-Hwan Jang. 2019. "Clear Wood toward High-Performance Building Materials." *ACS Nano* 13(9):9993–10001.
- Li, Yuanyuan, Ming Cheng, Erik Jungstedt, Bo Xu, Licheng Sun, and Lars Berglund. 2019. "Optically Transparent Wood Substrate for Perovskite Solar Cells." *ACS Sustainable Chemistry & Engineering* 7(6):6061–67.
- Li, Yuanyuan, Qiliang Fu, Ramiro Rojas, Min Yan, Martin Lawoko, and Lars Berglund. 2017. "Lignin-retaining Transparent Wood." *ChemSusChem* 10(17):3445–51.
- Li, Yuanyuan, Qiliang Fu, Shun Yu, Min Yan, and Lars Berglund. 2016. "Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance." *Biomacromolecules* 17(4):1358–64.
- Li, Yuanyuan, Xuan Yang, Qiliang Fu, Ramiro Rojas, Min Yan, and Lars Berglund. 2018. "Towards Centimeter Thick Transparent Wood through Interface Manipulation." *Journal of Materials Chemistry A* 6(3):1094–1101.
- Li, Yuanyuan, Shun Yu, Jonathan GC Veinot, Jan Linnros, Lars Berglund, and Ilya Sychugov. 2017. "Luminescent Transparent Wood." *Advanced Optical Materials* 5(1).
- Mi, Ruiyu, Tian Li, Daniel Dalgo, Chaoji Chen, Yudi Kuang, Shuaiming He, Xinpeng Zhao, Weiqi Xie, Wentao Gan, and Junyong Zhu. 2020. "A Clear, Strong, and Thermally Insulated Transparent Wood for Energy Efficient Windows." *Advanced Functional Materials* 30(1):1907511.
- Montanari, Céline, Hui Chen, Matilda Lidfeldt, Josefin Gunnarsson, Peter Olsén, and Lars A. Berglund. 2023. "Sustainable Thermal Energy Batteries from Fully Bio-based Transparent Wood." *Small* 19(28):2301262.
- Montanari, Céline, Yu Ogawa, Peter Olsén, and Lars A. Berglund. 2021. "High Performance, Fully Bio-based, and Optically Transparent Wood Biocomposites." *Advanced Science* 8(12):2100559.
- Montanari, Céline, Peter Olsén, and Lars A. Berglund. 2021. "Sustainable Wood Nanotechnologies for Wood Composites Processed by In-Situ Polymerization." *Frontiers in Chemistry* 9:682883.
- Rolston, Nicholas, Kevin A. Bush, Adam D. Printz, Aryeh Gold-Parker, Yichuan Ding, Michael F. Toney, Michael D. McGehee, and Reinhold H. Dauskardt. 2018. "Engineering Stress in Perovskite Solar Cells to Improve Stability." *Advanced Energy Materials* 8(29):1802139.

- Schwanninger, Manfred, José Carlos Rodrigues, and Karin Fackler. 2011. "A Review of Band Assignments in near Infrared Spectra of Wood and Wood Components." *Journal of Near Infrared Spectroscopy* 19(5):287–308.
- Socrates, George. 2004. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. John Wiley & Sons.
- Tsuda, Hiroshi, and Kei Urabe. 2009. "Characterization of Long-Period Grating Refractive Index Sensors and Their Applications." *Sensors* 9(6):4559–71.
- Zhang, Meihe, Zhihao Li, Zheng Gong, Zhen Li, and Chao Zhang. 2023. "Perspectives on the Mechanical Robustness of Flexible Perovskite Solar Cells." *Energy Advances* 2(3):355–64.
- Zhu, Mingwei, Tian Li, Chelsea S. Davis, Yonggang Yao, Jiaqi Dai, Yanbin Wang, Feras AlQatari, Jeffrey W. Gilman, and Liangbing Hu. 2016. "Transparent and Haze Wood Composites for Highly Efficient Broadband Light Management in Solar Cells." *Nano Energy* 26:332–39. doi:10.1016/j.nanoen.2016.05.020.

Chapter V

5.1. General Conclusions and Future Perspectives

5.1.1. Summary of objectives and achieved results

The present PhD work has been carried out with the aim of improving the applicability of the processes currently used in the literature for obtaining TW and making them more sustainable from an environmental and energy point of view, as well as in terms of time spent, with a view to a faster transfer from the laboratory to the industrial scale-up. In fact, despite the excellent potential investigated in the literature and demonstrated on a small scale, TW is not yet suitable for large-scale regulated industrial production. The results presented in this thesis constitute a concrete contribution to the path towards real applications, serving as a further necessary step in defining production standards that will enable, in the near future, the transfer of technology from the laboratory to the market.

Within the PNRR NODES project, in line with the SDGs of the 2030 Agenda, the Thesis addressed as its main objectives: i) the increase of mechanical properties of bleached wood templates by exploring an innovative bleaching method; ii) the control of the infiltration process and the study of UV-Vis stability of TWs using commercial epoxy resins with and without UV filter and; iii) the use of totally biobased matrices for the use of TWs in engineering applications, such as photovoltaic devices.

The first step in the preparation of the white template, presented in Chapter II, ended with the development of a new selective bleaching process for lignin chromophore groups, as an alternative to traditional delignification and bleaching methods. The developed process, which uses alkaline H_2O_2 and subsequently stabilizes it with NaHCO_3 , allows the preservation of over 90% of the starting lignocellulosic mass.

The process developed in this Thesis differs significantly from the two main approaches (delignification and bleaching) reported in the literature to date for obtaining white templates. In particular, this process differs from conventional delignification methods,

which treat lignin as an undesirable component responsible for the brownish coloration of wood and remove it almost completely (80-90%). Through these approaches the structural integrity of the wood is difficult to maintain, with a significant decrease in mechanical performance compared to native wood.

In addition, the developed methodology addresses the limitations of previously documented bleaching processes. Although such approaches seek to preserve lignin, by selectively acting on chromophore groups, they often present critical issues: i) they require high temperatures or UV radiation, which generate toxic volatile by-products, and ii) they fail to penetrate the wood bulk for thicknesses greater than 2 mm. This limits the bleaching effect to the surface only, making such processes ineffective for thick samples. Unlike these processes, the proposed treatment acts in mild conditions at room temperature, ensuring high uniformity of the final color both on the surface and in the bulk, even for significant thicknesses (10 mm) of low-density hardwoods such as balsa. Through this approach, the white templates obtained in this first phase have demonstrated good potential for use in the fabrication of TWs rich in deconjugated lignin. The almost total conservation of this fraction (93%), as verified by sugar analysis, in addition to ensuring greater mechanical and dimensional stability compared to the deignified templates, allows the maintenance of a higher volumetric fraction, defined as the ratio between the lignocellulosic skeleton and the total volume. This makes it possible to produce TW with a higher wood/polymer ratio.

In addition, the lignin preserved and modified in the templates thus obtained becomes chemically exploitable. As already mentioned, the selective treatment that forms additional -OH groups during conjugation increases the accessibility and responsiveness of these groups compared to natural wood. This promotes stronger chemical interactions (hydrogen bonds) with the filler resin, as evidenced by the exchange with D₂O, resulting in a final composite with potentially high optical properties.

The second objective of the thesis, presented in Chapter III, addressed another important aspect to be controlled and standardized for the production of TWs: the optimization of the infiltration process and the determination of how some process parameters affected the yield of the final composite in terms of optical properties and their correlation with the continuous and discontinuous wood-polymer interface, determined through microstructure analysis. In the current literature, this step is often considered secondary to the optical index of the polymers used or to changes at the interface, leaving a gap in the control of polymer diffusion within the template. Through the adoption of a DOE

approach, this work establishes, for the first time, a correlation between the process parameters, microstructure, optical properties, and stability of TWs in outdoor applications.

The results show that TW composites cannot be considered systems solely guided by the choice of wood and the starting polymer, but also depend on the process of obtaining, in which the variation of parameters such as the H/T resin-polymer ratio (defined as the height of the resin level (H) relative to the thickness of the wood template (T)) determines wood-polymer interfaces (continuous or discontinuous) that influence light propagation and scattering phenomena. In particular, the study shows that haze, often considered an intrinsic property of wood and its interaction with resin (optical mismatch), can be adjusted by controlling the filling of the lumen and the presence of interfacial defects. This enables an active design of the material's optical properties, allowing the final composite to be customized for a wide spectrum of applications, ranging from low-haze windows to highly diffusive (high-haze) panels for photovoltaic systems. As mentioned above, microstructural analyses provided further confirmation, showing that variation in the selected process parameters results in significant differences in polymer phase distribution, microvoid formation, and, consequently, overall interface quality. The microvoids and discontinuities act as scattering centers, directly influencing the optical profile of the final composite. Identifying an optimal process window, where high transmittance is maintained, and haze can be controlled using the same polymer matrix, is an important step towards industrial scalability, as it allows resin consumption to be reduced without compromising performance.

The last objective of this research was presented in Chapter IV, where the properties of a completely bio-based and sustainable TW system were studied using a polymer matrix derived from limonene, PLIMA. This part of the work addressed one of the main challenges in the TW landscape, where the white wood template is often combined with fossil-based polymers, which limits its overall sustainability.

The integration of PLIMA into the bleached template resulted in TW with promising optical performance. In fact, thanks to the optical mismatch, close but not identical to that of the lignin-rich cell wall, PLIMA favored diffusive scattering of light, yielding high haze values (over 90%) while maintaining good transmittance (80%), an advantageous combination for optoelectronic applications. Regarding this potential application, it is important to note that the research activity, particularly on perovskite solar cell assembly,

is ongoing to evaluate the integration of PLIMA-TW as active substrates in photovoltaic applications.

Specifically, in collaboration with the KTH Institute and Uppsala University, both in Stockholm, the use of TW to enhance the light path in perovskite solar cells is under investigation. The methodology involves the use of the high-haze fully biobased TW substrate to increase the photon walk in the device's active layer, thereby improving light absorption without significant reflection losses, based on a previous study carried out in 2019 by the two above-mentioned universities. Preliminary results, as discussed in Chapter IV, suggest that the strong interfacial adhesion between the bio-based PLIMA and the lignin-rich template provides a stable platform for these multilayered devices, making TW not conceived as a transparent substitute for glass or transparent polymers, but as an active optical substrate capable of increasing photon path length and improving light accumulation in devices such as perovskite solar cells.

In addition, PLIMA, previously studied at KTH by Li Y. and Berglund L. research group but never applied to photovoltaics, has hydroxyl groups that favor strong interactions with the same groups present in the lignocellulosic template, thereby strengthening and improving interfacial adhesion and the effective transfer of mechanical stress, as demonstrated by FTIR, SEM, and mechanical analyses. Finally, the viscosity of the LIMA precursor enables direct infiltration without prepolymerization (unlike PMMA), simplifying the process and improving reproducibility. This is important when considering subsequent industrial scalability, where process stability and reduced variability are crucial.

The objectives achieved in this work, considered as a whole, show how transparent wood can be engineered through the integration of chemical processes, process design, and material design, to obtain a multifunctional platform with adjustable optical and mechanical properties.

5.1.2. Future perspectives: short-term developments

Several challenges remain open in the short term to fully exploit the industrial potential of TW. Among these, the long-term stability of polymer matrices to environmental exposure (solar and humidity) is critical. Although the materials developed in this work have shown promising resistance to accelerated aging, the phenomenon of photooxidative

degradation remains a limiting factor, particularly in outdoor applications. Future studies should focus on the use of resins with durable stabilizing systems added directly to the impregnating resins, or on integrating waterproofing and UV-resistant coatings. The matrices used should ideally derive from renewable sources capable of ensuring both the long-term durability of the TWs platform and the sustainability of the composite as a whole.

In addition, the infiltration process should adopt the DOE approach to control all process parameters that affect the interface, such as resin viscosity, cell wall pretreatment, air-vacuum infiltration cycles, and refractive index.

Finally, another important challenge concerns extending the bleaching process developed to even the densest woods of large dimensions. Although the present work has demonstrated the possibility of treating balsa and birch woods at different thicknesses (1 and 3 mm) for small sizes (2.5 x 2.5 L x W), the construction application of the TW requires materials with larger dimensions. The achievement of this goal is strictly dependent on the optimization of reagent diffusion within the hierarchical porous structure of wood.

5.1.3. Long-term vision and advanced scenarios

If the focus shifts to the long term, the TWs platform has the potential to evolve into a new class of multifunctional engineered capable i.e. of addressing the complex challenges of modern infrastructure. The potential of this platform lies in its ability to tailor the wood-polymer composite for specific macro-sectors, such as energy management, smart building construction, sustainable electronics, and advanced architectural design.

In the energy and thermal sectors, TW can act active component for energy efficiency. Beyond its high thermal insulation properties compared to glass, TW can be engineered as a thermal storage system. One of the most promising already presented in the literature exploits the intrinsic porosity of wood for the integration of phase-change polymers to store and release thermal energy for application in passive energy management systems. Furthermore, as demonstrated by the ongoing research, presented in Chapter IV, the ability of TW to manage the light path makes it an ideal substrate for solar cells, such as perovskite, where it serves as a light-harvesting platform to maximize photon capture.

In addition, the integration of conductive phases, such as small percentages of organic/inorganic nanocharges or active polymers within the wooden template, little investigated in the literature, could allow the development of sensitive and reactive TW. These materials could enable real-time monitoring of environmental parameters (e.g., humidity and temperature) or mechanical stresses within the building's structural components, feeding the data directly into management models. In this context, the development of smart windows and facades that incorporate thermo-reactive or photo-reactive molecules represents a key application. TWs could thus actively adjust their transparency or color in response to outdoor temperature or solar intensity, as shown in small-scale literature, adjusting their opacity in the presence of light and thus reducing energy demand.

In addition to structural and energy functions, the TW platform also opens up new applications in the fields of aesthetics, interior design and functional lighting. In fact, through the precise adjustment of the optical mismatch and process parameters, it is possible to obtain what in the literature is defined as aesthetic wood that preserves the natural grain and texture of the wood, while offering customizable colors and transparency. In addition, the integration of fluorescent or phosphorescent quantum dots or nanoparticles allows the fabrication of luminescent TWs that could be used both for ambient lighting and for emergency signage, through direct integration into structural panels.

Finally, the development of composites that can be separated and recovered at the end of their life cycle remains a challenge that has not yet been investigated. Future studies should therefore focus on exploring reversible or selectively degradable polymer matrices to enable the recovery of the polymer phase and the wood template from a circular economy perspective.

In conclusion, this thesis demonstrates that transparent wood could not remain confined to an experimental scale, but become a fully engineerable and scalable platform, with tunable properties through the control of microstructure and process parameters. By adopting this approach, it was possible to overcome the limitations of traditional methodologies and take some fundamental steps towards a new generation of TWs

Appendix A

List of abbreviations

AFM	Atomic Force Microscopy
AIBN	2,2'-azobis(2-methylpropionitrile)
ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared spectroscopy
BET	Brunauer-Emmett-Teller
BT	Ballistic Transmittance
CCD	Central Composite Design
CLT	Cross-Laminated Timber
C _I	Crystallinity Index
CTW	Compressed Transparent Wood
DMF	Dimethylformamide
DOE	Design Of Experiment
ER	Epoxy Resin
FE-SEM	Field-Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared spectroscopy
HALS	Hindered Amine Light Stabilizers
ITO	Indium Tin Oxide
LCA	Life Cycle Assessment
LIMA	Limonene Acrylate
LVL	Laminated Veneer Lumber
MMA	Methyl methacrylate
Na ₂ SO ₃	Sodium sulfite
NaClO	Sodium hypochlorite
NaClO ₂	Sodium chlorite
NaHCO ₃	Sodium bicarbonate
NaOH	Sodium hydroxide
NB	Natural Balsa
NIR	Near Infrared
NODES	Nord-Ovest Digitale e Sostenibile
PBER	Plant Based Epoxy Resin
PEG	Polyethylene glycol
PLIMA	Poly limonene acrylate
PMMA	Poly methyl methacrylate
PNNR	National Recovery and Resilience Plan
PVA	Polyvinyl alcohol
RH	Relative Humidity
RI	Refractive Index
RSM	Response Surface Methodology
RT	Room Temperature
SDG	Sustainable Development Goal

SEM	Scanning Electron Microscopy
SR	Specular Reflectance
SSA	Specific Surface Area
TEMPO	2,2,6, 6-tetramethylpiperidin-1-oxyl
TMFP	Transport Mean Free Path
TRE	Total Radiant Energy
TT	Total Transmittance
TW	Transparent Wood
TWF	Transparent Wood Film
UV	Ultraviolet
WB	Bleached Wood
WWSC	Wallenberg Wood Science Centre
XRD	X Ray Diffraction

List of reagents

D ₂ O	Deuterium Oxide
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric Acid
KOH	Potassium hydroxide
Na ₂ SO ₃	Sodium sulfite
NaClO	Sodium hypochlorite
NaClO ₂	Sodium chlorite
NaHCO ₃	Sodium bicarbonate
NaOH	Sodium hydroxide
TiO ₂	Titanium dioxide
ZnO	Zinc oxide
ZrO ₂	Zinc peroxide

Appendix B

Italian Patent (IT102024000023808) - Method for Bleaching Wood using Stabilized Activating Alkaline Agents

METHOD FOR BLEACHING WOOD USING STABILIZED ACTIVATING ALKALINE AGENTS

DESCRIPTION

Summary

5 The present invention relates to a method for
producing bleached wood from both softwood and
hardwood, in both block form and as chip form, by
modifying the lignin structure with a chemical reaction
at ambient temperature using hydrogen peroxide in an
10 alkaline environment stabilized with sodium
bicarbonate. This method preserves the lignin which,
being only deconjugated and not removed from the wood,
may act as a glue, providing a strong wood scaffold and
maintaining the porosity thereof.

15 Scope of the invention

Wood has been widely used as a renewable energy
source for the supply of primary energy. The complexity
of its hierarchical structure and the variability of
the biological structure, as well as the availability
20 of numerous technological advances allowing a more
efficient use of this resource, have expanded the
fields of application of this biomaterial.

The porous and fibrous trunk, mainly consisting of
cellulose, hemicellulose and lignin, gives wood a
25 variable hardness depending on the considered type,
making hardwoods suited to producing solid supporting
structures and softwoods to making solid structures for
functional applications.

In this regard, since 2016 with the work of Zhu et
30 Al. (Zhu, Mingwei, et al. Highly Anisotropic, Highly
Transparent Wood Composites. *Advanced Materials*

(*Deerfield Beach, Fla.*), 2016, 28.26: 5181-5187), wood has attracted interest in the scientific community for the creation of transparent wood composites, this being a new eco-compatible construction material with improved optical and mechanical properties compared to conventional wood. Furthermore, the final transparent composite is characterized by high energy efficiency compared to glass and could be used for substituting it in the construction of internal and external parts in green buildings. Transparent wood allows the passage of direct solar light, requiring, for example, a reduced use of coal-based electricity, with respect to glass, and playing a considerable role in the gradual replacement of fossil fuels with bio-based products.

The first step to obtain a transparent wood composite consists of removing or modifying the lignin present by means of aggressive chemical treatments which use heat sources (heaters, plates, microwaves, sonication, etc.) or UV rays to promote the activation of the reagents used. In the literature, numerous bleaching treatments based on chlorinated or sulfur-containing reducing/oxidizing agents are present, which produce polluting and toxic molecules as the reaction proceeds and as the temperature increases. The majority of the processes used are based on the almost complete removal (higher than 80%) of lignin (delignification). However, these processes are scarcely applicable to wood specimens thicker than 5 mm because they require the use of more concentrated solutions or higher temperatures to obtain a white coloration. However, an excessively severe delignification process leads to the

total removal of lignin, the disintegration of the hierarchical structure of the wood, and the obtaining of individual cellulose fibers.

In the literature, there are further lignin
5 modification treatments based on the use of hydrogen peroxide, which is capable of acting on the individual chromophoric units of lignin to remove them selectively or to modify them so as to render the lignin white. Although producing effluents with a lower environmental
10 impact, this treatment cannot penetrate into the bulk of wood specimens thicker than 5 mm.

Task of the invention

With the present invention, it is intended to modify or remove the chromophoric groups of lignin,
15 without completely removing it, so as to preserve its adhesive action and maintain the hierarchical structure of wood unchanged, to obtain bleached woods for different engineering applications, e.g., such as:

- i) bleached wood pulp for papermaking;
- 20 ii) highly densified bleached wood for structural applications;
- iii) transparent wood composites for functional applications with improved energy efficiency, thermal shielding and heat storage;
- 25 iv) transparent wood for electro- or photochromic devices;
- v) transparent composites for solar cells;
- vi) transparent woods for gas sensors.

The principal applications are:

A) the treatment of waste wood chips for producing bleached paper in replacement of the methods currently used in the paper industry (e.g., the Kraft method);

B) the impregnation of the bleached wood obtained
5 with different types of transparent polymers having specific properties, also maintained in the final composite, and a refractive index similar to that of cellulose. The presented solution is applicable to both hardwoods and softwoods. Usually, the dark coloration
10 of wood is due to the presence of lignin, while cellulose and hemicelluloses in the absence of lignin are colorless, but appear white due to light scattering phenomena within the porous structure. Lignin is different from the carbohydrate polymers of the
15 cellulose and of the hemicellulose, because it shows a complex aromatic structure consisting of three types of alcohols: p-coumaryl, coniferyl and sinapyl, mutually interconnected via ether bonds. In natural wood, lignin binds to hemicelluloses at the molecular scale and is
20 in contact with cellulose fibers at the nano- and micro-scale, as filler and adhesive, by virtue of its functional groups and amorphous network structure. Following the complete removal of lignin by means of delignification processes, or the modification/removal
25 of only the chromophoric units thereof by means of bleaching processes, bleached wood having improved optical properties may be obtained. However, only through the modification/removal process may the hierarchical structure of the wood be preserved or
30 improved. Indeed, with the suggested method, the post-treatment wood structure does not undergo degradation

from a morphological point of view. It may be assumed that the hierarchical structure is maintained or improved because the residual chemical reagents act on the porosities to improve the performance in the
5 infiltrating step.

Background art

Currently, two approaches are used to obtain bleached woods from natural wood materials: i) bottom-up and ii) top-down.

10 The first method, based on wood defibration processes for obtaining cellulose fibers which are subsequently reassembled by means of hot pressing, is scarcely used due to the high costs and the difficult scalability at the industrial level. Conversely, the
15 second method, to which the present invention also belongs, starts from specimens of formed wood and acts on the color of specimens of natural wood.

The latter is lightened using a delignification process for removing the majority of the lignin, or,
20 alternatively, a selective chemical bleaching process capable of acting on the chromophoric groups of lignin, such as benzene rings, quinonoids, vinyl, phenolic and carbonyl groups. These chromophoric units are selectively removed because they form complex
25 conjugated systems responsible for the dark color of the wood.

There are two strategies to remove the color and increase the degree of whiteness of the wood:

- i) lignin removal, and
- 30 ii) lignin bleaching.

In the lignin removal strategy, aggressive processes based on concentrated chlorine-containing chemicals (chlorine, hypochlorite, and chlorine dioxide) and oxidants (oxygen, ozone, and peroxide) are used to break down and completely solubilize the lignin.

In lignin bleaching methods, a moderate reductive action (hydrosulfite) or oxidative action (hydrogen peroxide) at temperature or by means of photodegradation are commonly used to alter or remove the chromophoric groups and lignin systems, selectively decolorizing it and keeping the macrostructure intact.

In (Zakzeski, Joseph, et al. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical reviews*, 2010, 110.6: 3552-3599) an example is given of chromophoric lignin groups with carbon-carbon conjugated double bonds with the aromatic rings and other aromatic extractives which contribute to the dark color of the wood.

The approaches mentioned in the literature for producing bleached wood are based almost exclusively on substrate delignification processes, and therefore complete removal of lignin. In the mentioned studies, delignification is crucial since lignin is responsible for 80-95% of the light absorption in wood.

For example, Fink (Fink, S., 1992. Transparent wood-a new approach in the functional study of wood structure, *Holzforschung*, vol. 46, no. 5, 1992, pp. 403-408) treated the wood with a 5% aqueous solution of sodium hypochlorite for 1-2 days to remove the colored

substances, including lignin. In the work by Li et al. (Li, Y., Fu, Q., Yu, S., Yan, M., & Berglund, L. (2016). Optically transparent wood from a nanoporous cellulosic template: combining functional and structural performance. *Biomacromolecules*, 17(4), 1358-1364),

a delignification process was carried out by the treating with sodium chlorite. The lignin content was significantly reduced from about 25% to less than 3%.

In the work by Zhu et al. (Zhu, M., Song, J., Li, T., Gong, A., Wang, Y., Dai, J., & Hu, L. (2016), *Highly Anisotropic, Highly Transparent Wood Composites. Advanced Materials* (Deerfield Beach, Fla.), 28 (26), 5181-5187) the lignin was removed by a wood cooking process in a solution of NaOH and Na₂SO₃, followed by a treatment with hydrogen peroxide (H₂O₂), obtaining a lignin content of less than 3%. Although the results obtained in the cited studies are considered critical, the delignification processes described above entail long process times and poor environmental compatibility. Sulfur-containing compounds, such as methyl mercaptan, dimethyl sulfide and hydrogen sulfide, are generated during industrial processes, such as production of Kraft pulp intended for papermaking (Antczak, Andrzej, et al. The comparison of acid and enzymatic hydrolysis of pulp obtained from poplar wood (*Populus* sp.) by the Kraft method. *Drewno: prace naukowe, doniesienia, komunikaty*, 2019, 62.203: 53--66.; Akgül, Mehmet; ÇÖPÜR, Yalçın; TEMİZ, Seyfettin, A. *Comparison of kraft and kraft-sodium borohydrate brutia pine pulps*, Building and

Environment, 2007, 42.7:2586-2590). Furthermore, the formation of toxic effluents, such as chlorinated dioxins during delignification suggests that processes totally free of chlorinated reagents are preferable.

5 Furthermore, lignin accounts for about 30% by weight of the wood and crosslinks with various polysaccharides present in the wood to confer structural support. For this reason, the complete removal of lignin damages and weakens the structure of the wood, making the

10 manufacture of substrates both thick and of large size difficult and not very manageable. This also limits the number of wood species that may be treated. Pine and balsa, for example, degrade into pieces containing condensed cellulose fibers after the delignification

15 step.

On the basis of the arguments above, the suggested technology makes it possible to achieve bleached wood without delignification. The modification of lignin by removing or modifying only the chromophoric structures

20 has the potential for the preparation of bleached wood on a large scale, independently of the wood species. It is known that hydrogen peroxide reduces light absorption in wood with a low degree of delignification

In literature, there are studies which employ

25 hydrogen peroxide as a base reagent for chemical modification processes.

For example, Li et al. (Li, Yuanyuan, et al. *Lignin-retaining transparent wood*. ChemSusChem, 2017, 10.17: 3445-3451) treated different softwood specimens

30 at 70°C with an alkaline hydrogen peroxide solution containing different reagents, including magnesium

sulfate, which in the reaction step produces sulfur-based toxic compounds. The obtained wood retained 80% of lignin with creation of specimens having a thickness of 1.5 mm with a structure similar to that of natural wood.

According to the present invention, instead, the hydrogen peroxide was combined with an alkaline activating substance (KOH) which allows a deeper penetration of the hydrogen peroxide into the structure of the specimen allowing not only the treating of different types of wood, but also different thicknesses (up to 15 mm) without requiring the aid of external heating sources. During the process, the chromophoric structures are removed or selectively reacted, preserving the lignin mass which is not involved in the process. Therefore, the hierarchical structure, as well as the main structural components of the wood, are preserved.

In delignification processes, which use sodium chlorite (NaClO_2), the complex aromatic structure of lignin undergoes oxidative ring-opening reactions to form acid carbonyl groups (a), which render lignin more soluble in water. Delignification processes constitute a well-established strategy widely used to prepare white wood specimens. Instead, the alkaline treatment uses hydrogen peroxide (H_2O_2) to remove or selectively react (modify) the chromophoric units present in the amorphous aromatic structure, while the lignin mass is preserved.

With the process described, after the alkaline treating with hydrogen peroxide, advantageously only

10-15% of lignin is removed, avoiding the breakage and the degradation of the bleached wood.

The present invention is part of the top-down approach and falls within the second type of process, i.e., bleaching, focusing on the use of hydrogen peroxide in the presence of diluted hydroxides for the bleaching both of wood chips with different granulometry and of preformed woods with thicknesses between 0.5 and 10 mm.

According to a specific feature of the invention, the bleaching process involves two steps:

the complete immersion of the specimens in an alkaline hydrogen peroxide solution at ambient temperature until complete bleaching; and

a subsequent step of washing by means of an aqueous sodium bicarbonate solution (NaHCO_3) to obtain pH stabilization and the final color, in order to avoid the chromogenic reaction between the base and the deconjugated lignin chromophoric groups upon depletion of hydrogen peroxide, in the reaction environment.

This latter step uses a sodium bicarbonate solution to arrest undesired side reactions, such as the recombination of chromophoric groups, previously deconjugated or solubilized from lignin. At the same time, the process also leads to stabilization of the final color, surpassing the process suggested in patent no. AU2018245016B2, which instead exploits the neutralization process of the basic pH with acids and removes the metals present in solution, in particular Na and Mg, to avoid the chromogenic reaction of lignin.

Further, unlike the washing processes reported in the literature which involve the use of organic solvents such as Ethanol, Methanol and Acetone (Zhang, J., Ying, Y., Yi, X., Han, W., Yin, L., Zheng, Y., & Zheng, R. (2023), *H₂O₂ Solution Steaming Combined Method to Cellulose Skeleton for Transparent Wood Infiltrated with Cellulose Acetate*, *Polymers*, 15(7), 1733; Wu, Y., Wu, J., Yang, F., Tang, C., & Huang, Q. (2019). *Effect of H₂O₂ bleaching treatment on the properties of finished transparent wood*, *Polymers*, 11(5), 776), the last reaction step of the present invention avoids the production of effluents based on organic solvents by using aqueous solutions in lieu thereof. Furthermore, with respect to existing processes, the following suggestion avoids the pairing of sulfur-containing reagents, such as sodium sulfite of the Kraft method (Antczak, Andrzej, et al. The comparison of acid and enzymatic hydrolysis of pulp obtained from poplar wood (*Populus* sp.) by the Kraft method (Drewno: prace naukowe, doniesienia, komunikaty, 2019, 62.203: 53-66.; Akgül, Mehmet; ÇÖPÜR, Yalçın; TEMİZ, Seyfettin. *A comparison of kraft and kraft-sodium borohydrate brutia pine pulps*, *Building and Environment*, 2007, 42.7: 2586-2590) or chlorinated compounds which would lead to the formation of undesired toxic and polluting by-products.

From the foregoing, the numerous advantages of the present process are evident. These include mild reaction conditions at ambient temperature, with minimization of reaction effluents and the obtaining of bleached woods while maintaining times of the same order of magnitude as the processes used in the

literature. Furthermore, the processes in the literature exclusively concern wood with a maximum thickness of 3 mm, while instead the process which is the object of the invention permits the bleaching of wood up to 15 mm in thickness. Furthermore, although in the literature it is stated that the reaction times and the concentrations of the reagents used increase as the thickness of the woods increases, the present invention instead makes it possible to obtain bleached woods both superficially and throughout the bulk, while maintaining the same reaction conditions, including timing. Consequently, the invention may be used for applications which go beyond the conventional use of wood, such as lightweight yet strong structural materials, energy storage, conversion and bioengineering.

From an economic point of view, the absence of heat and of apparatuses related to the development and the management thereof will allow applying the following invention using technologies of simple design consisting of tanks and pumping systems for the introduction and removal of the solutions. At the same time, the absence of toxic by-products, such as chlorinated compounds, simplifies and economizes the set-up of the process, without requiring control, treating, and disposal systems of such by-products. Therefore, the process is easily scalable and does not expose operators to organic solvents and concentrated chemicals.

To complete the overview of the background art, in light of the innovative solution suggested herein, the

inventors intend to provide a comparative analysis of the patents as well as of the most significant scientific publications obtained from an in-depth prior art search, highlighting the conceptual differences and the procedural steps, with the shortcomings and disadvantages resulting therefrom.

Patents:

US Patent 4,793,898 dated 27th October 1988: The cited patent discloses a process for obtaining white wood fibers starting from pine chips.

In one of the examples given, 50 g of pine chips (92% dry matter) were immersed in 250 ml of formic acid, 75 ml of water, and 60 ml of a 50% hydrogen peroxide solution (corresponding to 60% hydrogen peroxide on the dry weight of the chips). The chips were impregnated with the mixture under vacuum for 30 minutes, finally the temperature was brought to 70° C for 2.5 h.

The cooking liquor was removed by filtration, and the chips were defibrated.

The pulp dried at ambient temperature was treated with an alkaline hydrogen peroxide solution at 80° C for 2 hours at 10%, with the addition of NaOH at 5%. Subsequently, the 0.2 % of stabilizing agent DTPA (diethylenetriaminepentaacetic acid) was added. After the treatment, the pulp was washed, and acid was added to bring the pH back to neutrality.

Although using some of the reagents employed in the process described herein, this US patent exploits the bleaching solution at temperature to completely

destruct the wood and obtain individual cellulose fibers.

Instead, the process of the present invention employs oxidizing agents at moderate concentrations to
5 maintain the hierarchical structure of the wood unchanged, by acting on the removal or modification of only the chromophoric units constituting the lignin. Furthermore, in the washing procedure, it exploits the use of sodium bicarbonate in aqueous solution, both for
10 color stabilization and for neutralization of the residual hydroxide originating from the dissociation of the base used (KOH), thereby dispensing with both the use of DTPA and acid solutions, used in US Patent 4,793,898 instead.

15 **US Patent 2007/0256804 A1 dated 8th November 2007:**

The mentioned US patent is used for treating wood pulp, and therefore loose wood fibers.

In one of the examples present in the patent, the wood pulp is treated at 70°C in water and
20 ethylenediaminetetraacetic acid (DTPA).

After the addition of sodium percarbonate (source of H_2O_2), under the action of heat, the pulp was maintained at 70-75°C for 1 hour. Finally, sodium dithionite was added, at temperature, for a further 30
25 minutes.

White wood fibers were obtained with this process.

In the mentioned patent, a chelating agent (DTPA) combined with sodium percarbonate is used. In this case the chelating agent, by sequestering sodium from
30 the percarbonate, releases hydrogen peroxide and allows the bleaching at temperature of the wood pulp. The

patent is very different from the method suggested for bleaching solid wood, fibers, and powders, because it uses a hydrogen peroxide source and a chelating agent at temperature for treating only wood pulp. Instead, 5 the described process is applicable to both pulverulent and solid woods up to the thickness of 15 mm by means of the penetration of alkaline hydrogen peroxide at ambient temperature directly into the bulk of the specimen for persistent bleaching even in cross- 10 section. Finally, the treated specimen is stabilized with an aqueous solution of sodium bicarbonate, avoiding the use of chelating agents.

Patent AU 2018245016B2 dated 29th March 2018:

In one of the examples given, the bleaching 15 solution for cooking wood chips is prepared using deionized water, sodium silicate, sodium hydroxide solution, magnesium sulfate, diethylenetriamine pentaacetic acid (DTPA), as a chelating agent, and H₂O₂. The bleached wood substrates were obtained by 20 immersing 10 soft balsa wood chips with lower thickness in 200 mL (quantity in excess) of bleaching liquor at 70°C until the wood turned white, about 2 hours.

Although using some of the reagents employed in the described process, the cited patent makes use of a 25 temperature cooking process of wood chips only. The technology suggested here is not only capable of penetrating within the bulk of wood up to 15 mm thick, but exploits the stabilization of both color and pH effected with sodium bicarbonate, avoiding both the use 30 of organic or mineral acids for neutralizing the base and using chelating agents to remove excess metal to

avoid the chromogenic reaction due to the recondensation of the chromophoric groups of lignin.

Two documents were cited as relevant in the written opinion of the Italian Patent Application:

5 **D1: document CN 103 144 158 B** describes a method for decolorizing paulownia wood which first involves soaking the wood in an alkaline solution (sodium hydroxide) and then in a weakly alkaline solution containing hydrogen peroxide and sodium bicarbonate.
10 Additionally, reagents such as SDS, sodium sulfite, and borax in combination with the bleaching agents are used. These additives can enhance the penetration of the solution into the wood matrix and promote solubilization of lignin, thereby increasing
15 delignification. Such a sequence and combination favor a stronger lignin removal rather than a controlled bleaching.

While D1 discloses the use of an alkaline activating substance such as sodium hydroxide to
20 increase wood permeability, prior to treatment with hydrogen peroxide and sodium bicarbonate, the present invention differs in the type of alkaline substance, the sequence and the technical effect. Indeed, the penetration of the solution and then the preservation
25 of lignin are carefully controlled by applying hydrogen peroxide and KOH within an optimized concentration range. This ensures that the oxidative decondensation of chromophoric groups occurs without excessive delignification, allowing for uniform bleaching while
30 maintaining the structural integrity of the lignin

throughout the wood matrix, as supported by experimental evidence.

Furthermore, the simultaneous presence of KOH and H₂O₂ in the claimed method contributes to controlled pH
5 conditions which favor chromophore deactivation without significant delignification, an effect neither suggested nor achievable in D1.

D2: Patent CN 113 334 515 B discloses a method for treating wood by soaking in a buffer solution
10 containing sodium bicarbonate and sodium carbonate and adding a toner, i.e., hydrogen peroxide, the pH of the resulting solution being 10.

A first fundamental difference concerns the type of treated wood: while D2 mentions wood veneer, the
15 claimed process is applicable to pre-formed wood, powders, and chips, and therefore addresses applications outside the scope of D2.

Moreover, D2 includes a preliminary delignification step, which removes a substantial
20 portion of lignin. Conversely, the present invention substantially preserves lignin and achieves bleaching through the deconjugation of chromophoric groups, thereby maintaining both the structural integrity and natural composition of the wood. Therefore, the
25 controlled bleaching process that preserves the lignin, which is only deconjugated and not removed from the wood, is entirely novel.

Another key distinction concerns the use of carbonate/bicarbonate solutions. In D2, these are
30 employed as an integral part of the bleaching process, whereas in the present invention, they are used only as

a washing step to rapidly neutralize residual base and prevent chromogenic reactions. Although the reagents are nominally similar, their function and effect in the process are fundamentally different.

5 Finally, D2 aims primarily at color adjustment while preserving the natural grain of the veneer, resulting in a lightening effect rather than true bleaching.

 The effect of D2 is similar to that observed in D1
10 producing only partial lightning. Conversely, the present invention achieves uniform white bleaching while preserving lignin and the original dimensions of the wood.

Publications:

15 1) Dai, J., Styles, G. N., Patti, A. F., & Saito, K. (2018). CuSO₄/H₂O₂-catalyzed lignin depolymerization under the irradiation of microwaves. ACS omega, 3(9), 10433-10441.

 In this publication, a process is presented for
20 the depolymerization of the lignin contained in wood powders with the aid of microwave radiation. In this process, the reagents used are copper sulfate (CuSO₄) and hydrogen peroxide (H₂O₂) in a solution brought to a temperature of 110°C for 7 min.

25 In the process of the present invention, lignin is not depolymerized by the use of heat, heat sources or concentrated chemical agents. This allows maintaining the lignin within the structure of the wood, while maintaining the architecture of the pores unchanged,
30 thus the hierarchical structure and the anisotropic properties. Lignin is selectively bleached by means of

deconjugation of chromophoric groups, both in pulverulent wood and in preformed wood having a thickness of up to 15 mm.

Furthermore, the suggested technology, by using a basic hydrogen peroxide solution at ambient temperature with the aid of KOH subsequently stabilized with sodium bicarbonate, avoids the use of sulfur-containing salts for obtaining highly bleached woods.

2) Wu, Y., Wu, J., Yang, F., Tang, C., & Huang, Q. (2019). Effect of H₂O₂ bleaching treatment on the properties of finished transparent wood. Polymers, 11(5), 776.

In this publication, the bleaching solution used on solid wood specimens was prepared by mixing H₂O₂, trisodium citrate dihydrate, NaOH and ultrapure water. The wood specimens with a thickness of 0.4 mm were treated at 60°C for 150 min.

The described process does not use trisodium citrate as a stabilizing agent, but uses sodium bicarbonate to have a dual action: pH stabilization and coloration obtained after the bleaching treatment. Furthermore, it preferably uses KOH as a source of hydroxide ions because it is capable of intercalating to a greater depth in the wood structure with respect to sodium hydroxide and results in the suggested process being applicable also to woods of thickness up to 15 mm, avoiding the use of heat employed instead in the cited publication.

3) Xia, Q., Chen, C., Li, T., He, S., Gao, J., Wang, X., & Hu, L. (2021). Solar-assisted fabrication of

large-scale, patternable transparent wood. Science
advances, 7(5), eabd7342.

In this publication, wood specimens having a
maximum thickness of 1 mm were first delignified with a
5 sodium hydroxide solution brushed on the surface,
subsequently with concentrated H₂O₂ also brushed on the
surface, and finally exposed to UV radiation for one
hour.

The technology of the present invention exploits a
10 greater penetration of potassium hydroxide in a
solution in which the specimen is completely immersed,
in contrast to the cited publication, which exploits
only superficial contact of the solution by means of
brushing. The technology of the present invention
15 exploits a greater penetration of potassium hydroxide
in a solution in which the specimen is completely
immersed, in contrast to the cited publication, which
exploits only superficial contact of the solution by
means of brushing.

20 Thereby, the suggested process is also applicable
to thick materials (up to 15 mm) without the use of
auxiliary reagents.

Instead, in the cited publication by Xia Q. et al., the
mechanism of action of the hydrogen peroxide present on
25 the surface is activated by means of UV radiation,
which is capable of penetrating only for a few hundred
microns within the bulk of the specimen and may
therefore be effectively used only for thin wood (up to
2 mm) and not for thick wood (e.g., 5-15 mm).

4) Ouyang, X., Huang, X., Ruan, T., & Qiu, X. (2015). Microwave-assisted oxidative digestion of lignin with hydrogen peroxide for TOC and color removal.

Water Science and Technology, 71(3), 390–396. In this publication, a lignin standard was used as a reference for lignin-containing specimens and not a real specimen.

Powdered lignin was bleached using an acidified or basified hydrogen peroxide solution (pH from 3 to 11) and placed in a Teflon container under the action of microwaves at 80–160°C for 15–150 minutes. The cited publication uses a lignin standard adapted to simulate the process of bleaching of materials containing lignin.

However, in real cases, lignin functions as a glue in a complex structure in which primarily two other compounds are present: cellulose and hemicellulose. The technology of the invention is instead applicable on a laboratory scale to real specimens, such as preformed wood specimens, wood chips, or wood powders (e.g., waste sawdust).

5) Zhang, J., Ying, Y., Yi, X., Han, W., Yin, L., Zheng, Y., & Zheng, R. (2023). H₂O₂ Solution Steaming Combined Method to Cellulose Skeleton for Transparent Wood Infiltrated with Cellulose Acetate. Polymers, 15(7), 1733.

In the cited publication, wood specimens having a thickness from 1 to 5 mm were bleached with a concentrated hydrogen peroxide solution at 95°C for 7.5 h. Subsequently, they were placed in a specific reactor under H₂O₂ vapor at 95°C for 2.5 h.

Instead, the process according to the present invention exploits the penetrating action of KOH to induce hydrogen peroxide to penetrate into the bulk of the thicker woods, avoiding the use of heat and hydrogen peroxide vapors. The bleaching action occurs at ambient temperature.

6) Wu, Y., Zhou, J., Huang, Q., Yang, F., Wang, Y., & Wang, J. (2020). Study on the properties of partially transparent wood under different delignification processes. Polymers, 12(3), 661.

In this publication, the wood specimens with a maximum thickness of 2 mm were bleached with a sodium chlorite solution acidified to pH 4.6 with acetic acid (standard method) and brought to 70–90 °C for 45–135 min. With this method, complete depolymerization of lignin is observed.

By means of the process described herein, the lignin is not depolymerized, but its chromophoric groups are selectively deconjugated or removed. Thereby, the original hierarchical structure of the wood is maintained, and the porosity is preserved for a possible infiltration of polymers adapted to make the specimen transparent (main object of the bleaching).

Further, the process described herein uses an alkaline hydrogen peroxide solution at ambient temperature to treat specimens with a thickness up to 15 mm, avoiding the use of chlorinated compounds.

DETAILED DESCRIPTION OF THE INVENTION

Further features and advantages of the invention will become apparent from the detailed description that follows, with reference to the accompanying figures

which show different embodiments and the results of tests performed on specific applications:

In the drawings:

figure 1 is the diagrammatic representation of the structure of lignin in softwoods and of the chromophoric units present with carbon-carbon conjugated double bonds with the aromatic rings, and other aromatic extractives which contribute to the dark color of the wood, according to the background art (see Zakzeski et al. (2010). Chemical Reviews, 110, 3552-3599;

figure 2 is the reaction diagram between the representative structures of the chromophores of lignin and the main products formed in the NaClO_2 -based delignification process and bleaching by means of alkaline H_2O_2 -based lignin modification (adapted from Li, Yuanyuan, et al. Lignin-retaining transparent wood. ChemSusChem, 2017, 10.17: 3445-3451;

figure 3 is a diagram exemplifying the bleaching process according to the present invention;

figure 4 is an example of bleaching carried out on soft balsa wood: at the top, a balsa specimen before treatment, and at the bottom, the bleached specimen by means of the process according to the present invention;

figure 5 shows, in comparison, a specimen of beech wood when treated according to the bleaching procedure shown in the article by Xia et Al. previously cited, with respect to the specimen as-is, which has not yet undergone said procedure: also visually, the bleaching of the wood is very limited;

figure 6a shows, at the top, a beech specimen bleached by means of the described process, and at the bottom, the specimen as-is; the treated specimens have size 10x50x5 mm (tangential x longitudinal x radial);

5 figures 6b and 6c show the specimens cut into 10x5x5 mm sections in order to appreciate the success of the treatment according to the present finding, not only on the surface but also in the bulk of the specimen;

10 figure 7 shows waste wood chips containing different types of hardwoods and softwoods, pre- and post-treatment;

figure 8 shows the structural analysis carried out by means of Attenuated Total Reflection Fourier
15 Transform Infrared Spectroscopy (FTIR-ATR) on the hardwood specimens shown in fig.5.

In the methods for the bleaching of wood by means of chemical modification of the lignin, the combined action of alkaline agents such as ammonia, chlorinated
20 compounds, and alkaline hydroxides may be exploited, of which, in the present invention, potassium hydroxide is preferred in combination with hydrogen peroxide.

The reaction diagram of the described process is shown in figure 3: the invention provides for the
25 treatment of a wood specimen completely immersed in a solution of H_2O_2 with a concentration comprised between 5 and 30 % v/v and KOH with a concentration comprised between 0.1 and 3 M, at ambient temperature, which may therefore vary in a range conventionally between 4 and
30 45°C for a time between 1 and 24 h, but without any additional thermal input with respect to such ambient

conditions. The process is repeated until complete bleaching of the specimen.

An essential part of the invention, subsequent to this treatment, and necessary to stabilize the color
5 obtained (white), is the immersion of the specimen in a sodium bicarbonate solution with a concentration between 0.01 and 1.1 M for a minimum time of one minute, adapted to re-establish a correct pH value and stabilize the produced specimen in terms of the color
10 obtained during the preceding treatment, through the neutralization of the effect of re-conjugation of the chromophores contained in the lignin, previously deconjugated during the bleaching process.

Hereafter, a detailed description of a series of
15 embodiment examples is given:

Example 1: The softwood specimen having dimensions 15x50x7 mm (tangential x longitudinal x radial) is completely immersed in 20 mL of a solution of H₂O₂ at 30% v/v, in which KOH granules have been dissolved
20 until reaching a concentration of 2 M. To promote complete immersion of the specimen in solution, a glass weight is applied. The specimen is left in immersion until complete bleaching (about 2 hours). Finally, it is washed with water and bicarbonate by means of
25 immersion in solution at a concentration of 0.5 M for 5 minutes. The bleached wood is dried in an oven at 65°C overnight.

Example 2: The hardwood specimen having dimensions 10x50x5 mm (tangential x longitudinal x radial) is
30 completely immersed in 20 mL of a solution of H₂O₂ at 30% v/v, wherein KOH granules have been dissolved until

reaching a concentration of 2 M. To promote complete immersion of the specimen in solution, a glass weight is applied.

Since the structure of lignin in hardwoods is different
5 than softer woods, both the penetration of the solution into the bulk and the modification of the lignin are more difficult. For this reason, the specimen is treated twice with the alkaline solution to obtain a complete bleaching, respectively for 4 and 2 h.
10 Finally, it is washed with water and bicarbonate by means of immersion in solution at a concentration of 0.5 M for 5 minutes. The bleached wood is dried in an oven at 65°C overnight.

Example 3: 1.5 g of mixed waste wood chips (containing
15 different types of softwoods and hardwoods) are immersed, under stirring, in 10 mL of a solution of H₂O₂ at 30% v/v, in which granular KOH has been dissolved to reach a concentration of 2 M. After complete bleaching is achieved, the specimen is
20 filtered, washed with water and bicarbonate by means of immersion in a solution at a concentration of 0.5 M for 5 minutes under stirring, and finally filtered again. The bleached specimen is dried in an oven at 65°C overnight.

25 Numerous tests were carried out by varying the concentrations both of the bleaching solution, using a concentration range of hydrogen peroxide of 5, 15, 30 % v/v and KOH at 0.1, 1, 1.5, 2, 3 M, and the solution employed in the washing procedure with concentrations
30 of sodium bicarbonate in water of 0.01, 0.1, 1.1 M. Each test was repeated on 5 different specimens of the

same type of wood, both in powder and solid, using 5 solutions prepared independently of each other (genuine replicates).

Figure 4 shows at the top a soft balsa specimen
5 as-is and at the bottom the same specimen bleached by means of the process of the invention.

The treated specimens shown in the example have a thickness of 7 mm. The specimens have size 15x50x7 mm (tangential x longitudinal x radial).

10 In figure 5, specimens of the same size again of beech hardwood are shown before and after the bleaching carried out according to the procedure shown in the article by Xia, Q., Chen, C., et al., which proves to be absolutely unsatisfactory.

15 In figure 6a, at the bottom, a beech hardwood specimen as-is is shown, and, at the top, the same specimen bleached by means of the process of the invention. The treated specimens shown in the example have size 10x50x5 mm (tangential x longitudinal x
20 radial).

In figures 6b and 6c, the specimens cut in 10x5x5 section are shown, now side by side, to appreciate the success of the bleaching treatment according to the present invention, not only on the surface (figure 6b),
25 but also in the bulk of the specimen (figure 6c).

Fig. 7 shows wood chips pre- and post-treatment. Being waste powders containing different types of hardwoods and softwoods, the size may vary on the order of microns.

30 In figure 8, the structural analysis carried out by means of Fourier Transform Infrared Spectroscopy in

Attenuated Total Reflection (FTIR-ATR) on the hardwood specimens shown in figure 6a, in particular for the raw beech specimen (a) and the bleached beech specimen (b), from 4000 cm^{-1} to 500 cm^{-1} , is shown.

5 From the comparison of the FTIR-ATR spectra of the specimens of natural beech wood and bleached beech wood shown in figure 8, the success of the suggested treatment may be appreciated by observing the two bands highlighted at 1735 and 1509 cm^{-1} . In particular, the
10 band at 1735 cm^{-1} , relating to the ester groups of both lignin and hemicellulose, is completely absent after the treatment. This indicates the removal of the groups of the carbonyl chromophoric groups of both the lignin and the hemicellulose due to the basic action of
15 KOH. Finally, the second band at 1509 cm^{-1} , relating to the presence of benzene rings of lignin, is moderately attenuated indicating that the process preserves the aromatic chain of lignin, confirming the selective deconjugation of chromophoric groups.

20 To corroborate the obtained results, many laboratory tests were carried out using solutions at a concentration comprised within the previously shown ranges. Such tests were repeated 5 times for each tested concentration, both on softwoods and on
25 hardwoods, so as to evaluate the repeatability of the suggested process for obtaining the sought degree of bleaching. For all tests, structural characterizations were performed by means of physical-chemical analyses, such as X-ray Diffractometry (XRD) and Attenuated Total
30 Reflectance Infrared Spectroscopy (FTIR-ATR), which confirmed the success of the treatment.

CLAIMS

1) A process for producing bleached wood from softwood or hardwood, in block or chip form, by modifying the lignin structure with a chemical reaction at ambient
5 temperature, characterized in that it uses hydrogen peroxide in an alkaline environment stabilized with sodium bicarbonate, to preserve the lignin, which, resulting only deconjugated and not removed from the wood, still continues to act as a glue by providing a
10 strong wood scaffold and maintaining its properties.

2) A process for producing bleached wood from softwood or hardwood, in block or chip form, by modifying the lignin structure with a chemical reaction at ambient temperature using hydrogen peroxide, according to claim
15 1, characterized in that said process takes place at ambient temperature, in two steps:

combining to the hydrogen peroxide in a hydrogen peroxide solution, into which the specimen is fully immersed, potassium hydroxide (KOH), an activating
20 alkaline substance that allows deeper penetration of hydrogen peroxide into the structure of said fully immersed specimen, thus selectively removing and/or reacting the chromophore structures of lignin while preserving the lignin mass, which does not take part in
25 the process, until the specimen is completely bleached, without delignification, and

immersing the specimen thus treated in a sodium bicarbonate solution to stabilize the color obtained by stopping undesirable side reactions, such as the
30 rejoining of chromophore groups contained in the lignin, which, being only deconjugated and not removed

from the wood, can act as a glue, providing a strong wood scaffold and maintaining its porosity.

3) A process for producing bleached wood according to claim 2, characterized in that in step a) the wood specimen is completely immersed in a solution of H₂O₂ with a concentration comprised between 5 and 30 % v/v and KOH with a concentration comprised between 0.1 and 3 M, at an ambient temperature, which can vary in a range typically comprised between 4 and 45°C for a time between 1 and 24 h, but without any additional heat contribution with respect to such ambient conditions.

4) A process for producing bleached wood according to claim 2, characterized in that in step b) to stabilize the color obtained (white), the specimen is immersed in a sodium bicarbonate solution with a concentration comprised between 0.01 and 1.1 M for a minimum time of one minute, adapted to reestablish a correct pH value and stabilize the specimen produced in terms of color obtained during the previous treatment by means of the neutralization of the reconfiguration effect of chromophores contained in the lignin previously deconjugated during the bleaching process.

5) A process for producing bleached wood according to any one of the claims 1-3, characterized in that the bleached wood exiting the washing step b) is dried in an oven at a temperature between 60 and 70°C, preferably 65°C, for the time required for complete dehydration.

6) A process for producing bleached wood according to any one of claims 1-5, characterized in that it is applicable to pulverulent woods up to the thickness of

15 mm by means of the penetration of alkaline hydrogen peroxide at ambient temperature directly into the bulk of the specimen for persistent bleaching even in cross-section, avoiding the use of heat.

5 **7)** A process for producing bleached wood according to any one of the preceding claims, characterized in that by maintaining the hierarchical structure of the wood, it allows bleached woods to be obtained for different engineering applications such as:

- 10 i) bleached wood pulp for papermaking;
 ii) highly densified bleached wood for structural applications;
 iii) transparent wood composites with improved energy efficiency, thermal shielding and heat storage;
15 iv) transparent wood for electro- or photochromic devices;
 v) transparent composites for solar cells; and
 vi) transparent woods for gas sensors.

8) A process for producing bleached wood according to
20 any one of the preceding claims, characterized in that by occurring in the absence of toxic byproducts, it does not require systems to control, treat, and dispose of such byproducts, it is easily scalable, and does not expose operators to organic solvents and concentrated
25 chemicals.

9) Bleached wood obtained by modification or partial removal of the chromophoric groups of lignin only, according to the process of claim 2, so as to preserve its adhesive action and keep the hierarchical structure
30 of the wood unchanged, for use in different engineering applications such as:

- i) bleached wood pulp for papermaking;
 - ii) highly densified bleached wood for structural applications;
 - iii) transparent wood composites with improved energy efficiency, thermal shielding and heat storage;
 - iv) transparent wood for electro- or photochromic devices;
 - v) transparent composites for solar cells; and
 - vi) transparent woods for gas sensors.
- 10 **10)** A bleached wood according to the preceding claim, characterized by having a thickness comprised between 0.5 mm and 15 mm, a uniform bleaching both superficially and throughout the bulk, and a lignin removal of 7-8%.
- 15 **11)** A bleached wood according to claim 9, characterized in that structural analysis performed by Fourier Transform Infrared Spectroscopy in Total Attenuated Reflection (FTIR-ATR) on hardwood specimens shows that: the band at 1735 cm^{-1} related to the ester groups of
- 20 both lignin and hemicellulose is completely absent, indicating that the removal of the carbonyl chromophore groups of both lignin and hemicellulose has occurred; while the second band at 1509 cm^{-1} , related to the presence of benzene rings of lignin, appears moderately
- 25 attenuated, indicating that the bleaching process undergone preserves the aromatic chain of lignin, despite the degradation of chromophore groups, preserving or improving the hierarchical structure of the wood and its optical properties.

METHOD FOR BLEACHING WOOD USING STABILIZED ACTIVATING ALKALINE AGENTS

ABSTRACT

A process for producing bleached wood from softwood or hardwood, in block or chip form, by modifying the lignin structure with a chemical reaction at ambient temperature uses hydrogen peroxide in an
5 alkaline environment stabilized with sodium bicarbonate, to preserve the lignin, which, resulting only deconjugated and not removed from the wood, still continues to act as a glue by providing a strong wood scaffold and maintaining its properties. Thus, bleached
10 woods suitable for various engineering applications can be obtained.

FIG. 1

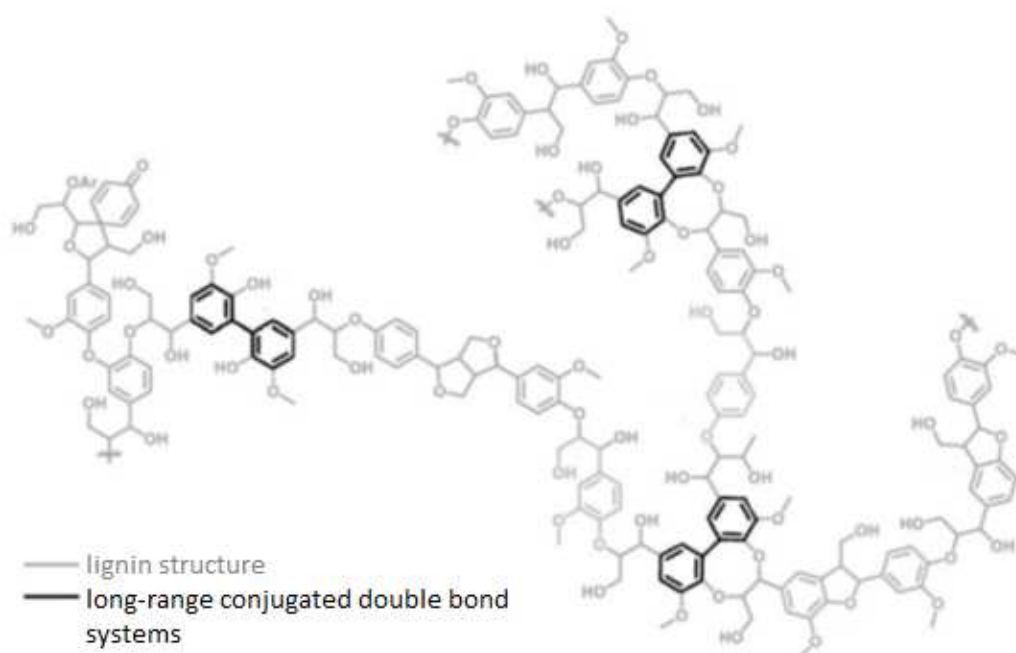


FIG. 2

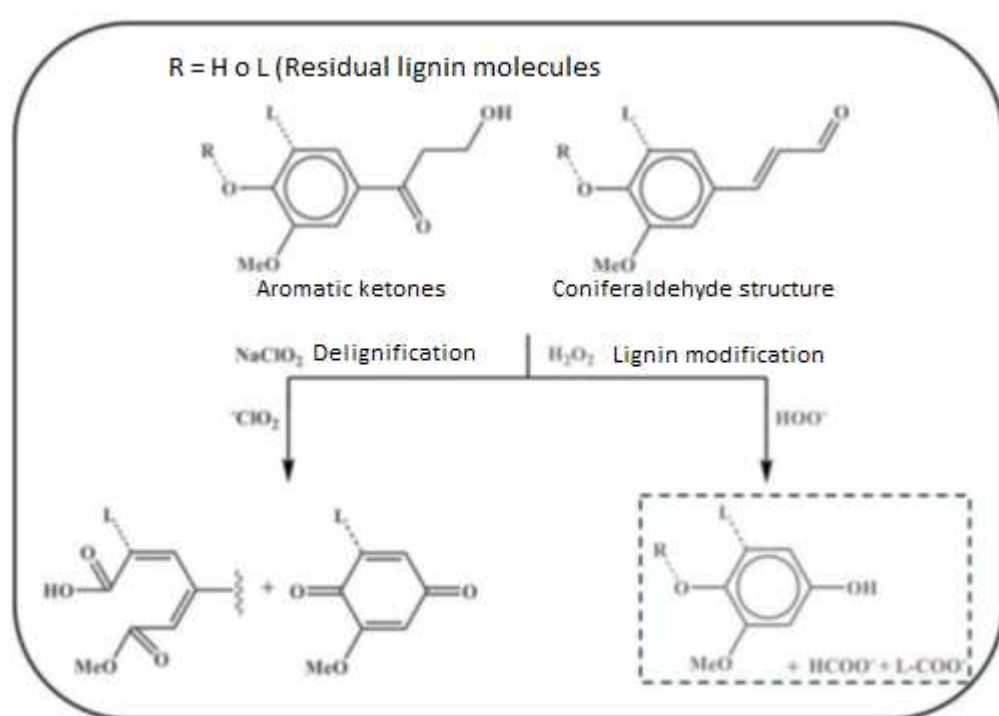


FIG. 3

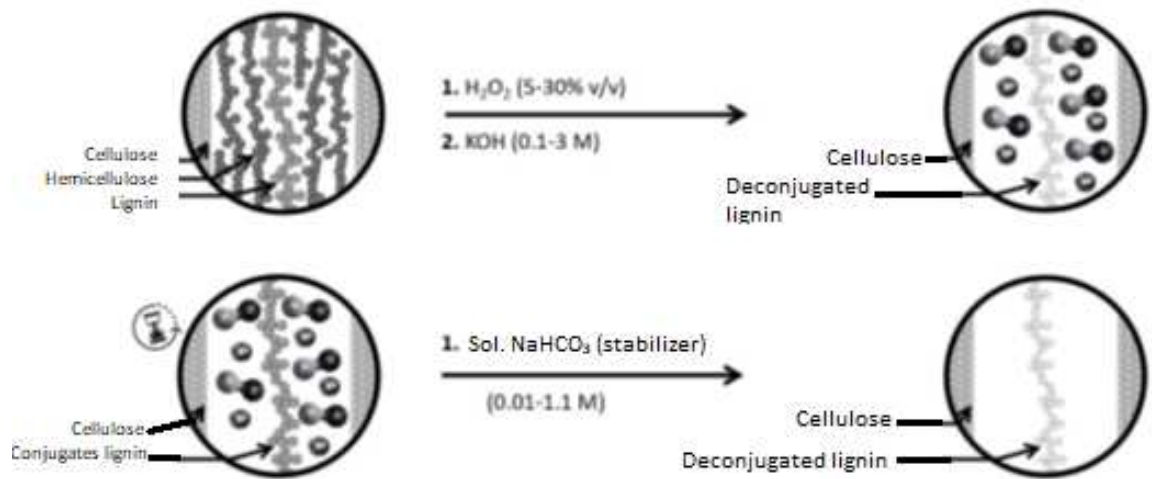


FIG. 4



FIG. 5
BACKGROUND ART



FIG. 6a

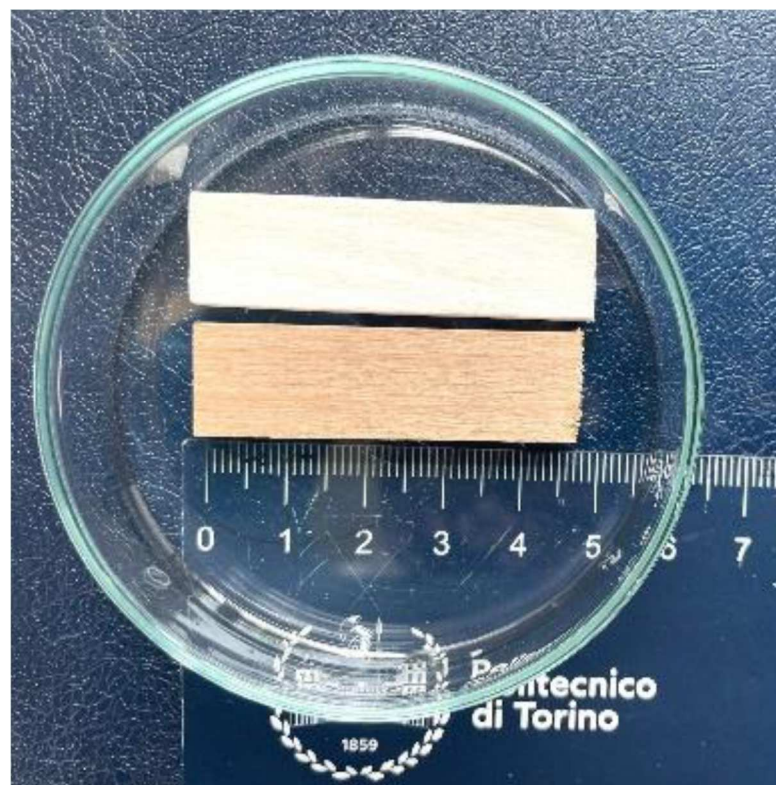


FIG. 6b



FIG. 6c

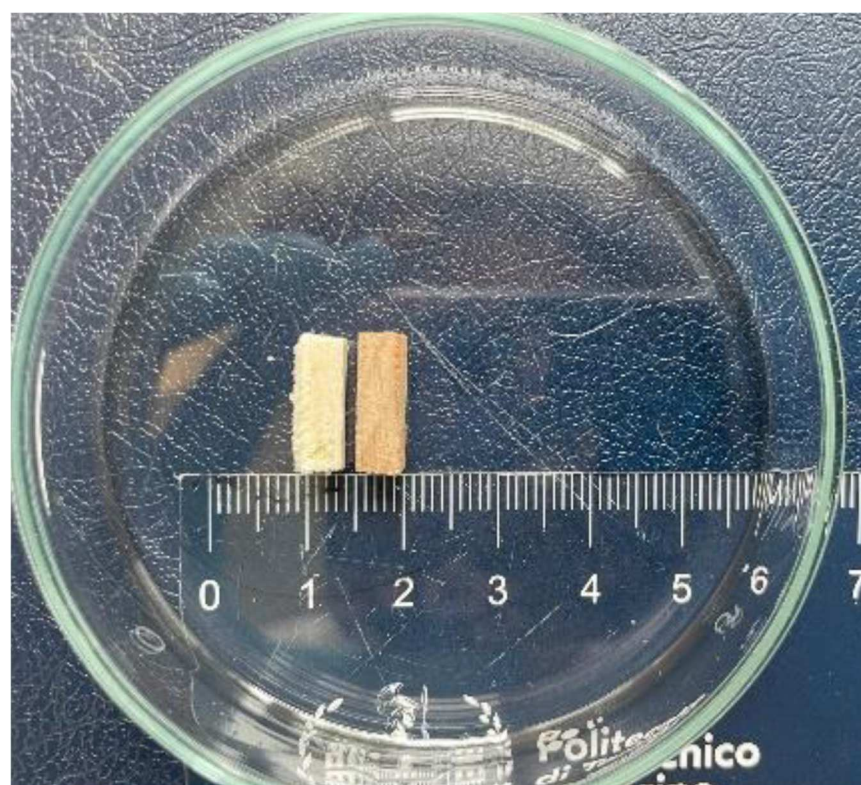


FIG. 7



FIG. 8

