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Review

Review of Wood Modification and Wood Functionalization Technologies

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Abstract: Wood modifications are becoming popular as a way to enhance the performance of wood, either to make it more durable, improve the performance of wood, or give it new functionality as a multifunctional or smart material. While wood modifications have been examined since the early 1900s, the topic has become a dominant area of study in wood science over the past decade. This review summarizes recent advances and provides future perspective on a selection of wood modifications, i.e., the methods that are currently commercialized (acetylation, furfurylation, and thermal modification), a rediscovered ancient practice (charring), a family of polymerization modifications that have so far made it to the pilot scale, and examples of novel wood-based functional materials explored at laboratory scale.

Keywords: wood protection; acetylation; chemical modification; furfurylation; thermal modification; wood decay; biodeterioration; wood-based functional materials

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1. Introduction: Wood as a Renewable Building Material

Wood is one of the oldest building materials. Evidence of the use of wood by ancient cultures dates back at least 1.5 million years [1]. Similarly, wood has been recognized in some of the earliest building codes; fire regulations for wood buildings were established as early as the 13th century in London [2,3]. As a material, wood has a high strength-to-weight ratio, can easily be machined, and comes from renewable resources. In the United States, approximately 70% of the lumber produced is used in the construction of buildings and 44% of the construction material is used in the construction of new, single family homes [4].

While wood has a long history as a construction material and with numerous environmental benefits [5], the use of wood as a building material is made difficult by its interaction with water. One of the biggest challenges of using wood is that water changes the dimensions of wood. Wood freely absorbs moisture from the environment. This absorption causes swelling and subsequent desorption causes shrinkage. As a result, special precautions need to be taken when connecting wood components to dimensionally stable parts of buildings (such as plumbing stacks) or connecting wood to materials with different hygric properties such as concrete. Repeated moisture cycling results in the formation of splits and checks within the wood surface, especially if the wood is constrained on one or more dimensions during moisture cycling. On top of all these dimensional stability issues during the service life of wood, it cannot be overstated how important the initial drying from the "green" (living) state to lumber is. Typically lumber must be kiln dried to protect it from warping, cupping, splitting, checking, and other defects that ultimately arise as a result of its dimensional instability. The kiln drying process is a major consumer of energy in the production of lumber and negates some of the carbon benefits of using wood as a building material [6].

Beyond dimensional instability with moisture fluctuations, an abundance of moisture within the wood can lead to a host of wood damage mechanisms, especially at high moisture contents. When wood is wet, it is susceptible to biodeterioration from decay fungi. Wood decay fungi can cause rapid strength loss, leading to failure of wood structures if these members are not replaced [7,8]. In damp environments, the surface of wood may also be colonized by mold fungi. While mold fungi do not affect the strength of wood [9], and molds may grow on many surfaces in addition to wood, molds discolor wood and may present a health hazard in the indoor environment [10]. Finally, at high moisture contents, metal fasteners embedded in wood are subject to corrosion from organic acids and other chemicals [11].

Despite these limitations, wood has successfully been utilized by humans for millennia. Wooden artifacts that have been kept dry such as the sarcophagus of Tutankhamun and the Shigir Idol have remained intact for thousands of years [12–14]. In fact, designing buildings to keep wood components dry is one of the best strategies for helping wood structures have a long service life [15]. These strategies were well known in ancient building practices and exceptional examples such as the Horyu-Ji temple in Japan, the Urnes Stave Church in Norway, and the Greensted church in England have all lasted more than 1200 years [16–18].

In some situations, such as railroad ties, it is not possible to keep wood dry during its service life. The 1800s marks the beginning of the modern wood preservation industry with the development of creosote impregnation to protect wood from decay (and insect attack) in wet and outdoor environments [19]. Wood preservatives are fungistatic or fungitoxic chemicals that are placed into the wood and are typically applied in a pressure treatment process where the wood is submerged in a treatment solution and put through pressure/vacuum cycles to drive the treatment solution into the wood [20]. Oilborne wood preservatives such as creosote and pentachlorophenol are still used for industrial applications where the wood does not need to be painted and there will be minimal contact with humans. In contrast, most dimension lumber is treated with waterborne wood preservatives. Nearly all waterborne wood preservatives contain copper as a biocide. Since some fungi are copper tolerant, a co-biocide is typically added as well. Both US and European standardization organizations have standardized use category systems so that the amount of wood preservatives used can be tailored to the exposure [21,22].

Wood preservatives are widely used and have enabled wood to be used in extremely challenging environments such as tropical climates and marine pilings. Despite their utility in protecting wood from decay, there are some drawbacks to preservative treated wood. Preservative treatments do not alter wood properties such as dimensional instability; they can only protect wood from decay and insects. Wood preservatives are registered pesticides. Consequently, their continued relevance depends on development within restrictions of use driven by environmental concerns, which will vary in different countries throughout the world. Furthermore, disposal of treated wood is a concern. Most treated wood must be disposed of in a landfill or combusted in special incineration facilities.

In contrast to wood preservatives, wood modifications alter the polymeric constituents of wood to achieve a desired property (typically enhanced durability). Modified wood is typically defined as any wood that has undergone a chemical, physical, or thermal process to improve its properties. Although many wood modification strategies are aimed at increasing the decay resistance of the wood, modifications may also improve the dimensional stability, decrease the hydrophilicity of wood and impact on some mechanical properties (e.g., hardness) at the same time. Although modern wood modifications were studied as early as the beginning of the 20th century [23], it has become an active area of research with over seven thousand papers published on the topic since 2000 according to Google Scholar.

These recent investments in wood modification technologies have resulted in several types of modified wood becoming commercially available. Thermally modified wood has been commercially available since the 1990s with the market growing from 20,000 m^3 per year in 2001 to currently over 500,000 m^3 [24,25]. Acetylated wood has been commercially available since the early 2000s, although pilot plants were developed as early as the 1990s. Roughly 60,000 m^3 of acetylated wood was produced in 2021 [26]. Similarly, full scale production of furfurylated wood began in 2009 and nearly 23,000 m^3 of treated wood was produced in 2018 [27]. Overall, the commercial volume of modified wood (approximately 600,000 m^3 per year) is still dwarfed by that of preservative treated wood (over 21 million m^3 per year in the United States alone [28] and 6.5 million m^3 in Europe annually [29]).

While wood is a commercially important construction material, its potential uses extend beyond lumber [30]. Wood has been used as a bioinspiring smart material with shape memory properties [31]. As these unique material properties are studied and discovered, they can be further enhanced by wood modifications turning wood into a fully functionalized material with many more potential uses.

In this paper we review different wood modification technologies with the goals of explaining how they enhance the properties of wood and highlighting unanswered research questions that will advance the field for further development. With the growing body of literature on wood modifications over the past 20 years, it is logical that many review papers on wood modification have also been written. One of the most cited works on wood modification is the seminal book on the topic written by Dr. Hill [24]. However, this book is now 15 years old and more current reviews have been published in the literature [25,27,32–36]. These reviews provide a valuable overview of the literature on wood modifications. Nevertheless, we see a need for new critical reviews of the most important existing methods, and an overview of current trends. Through these critical reviews of each modification we hope to summarize what is known and highlight the unknowns on each modification technology so that the next generation of researchers have a base from where to identify research needs and can continue to make important contributions to this field.

2. Nomenclature

Changing the wood chemistry by modification often leads to changes in wood–water interactions. Therefore, characterization of these is an important part of understanding the properties of the modified material. However, modification is nearly always accompanied by changes in mass and/or volume of the dry material. These two quantities are used in the calculation of the gravimetric moisture content and the swelling, respectively.

In order to evaluate how much the modification affects the moisture content of the wood and the dimensional changes, it is necessary to adjust these parameters to account for the changes in the dry material. Otherwise, a modification that just adds mass, e.g., by lumen filling, would automatically have a lower calculated moisture content even if the amount of water within the wood cell walls does not change. Similarly, a modification that decreases the volume, e.g., by densification, would automatically have a higher calculated swelling even if the volumetric changes of the modified and untreated materials are equal.

The change in mass from modification is often described in literature by either the "weight percent gain" (WPG) if the dry mass of the material increases or by the "mass loss" (ML) if the dry mass decreases. A more general term to describe the mass change is by the modification ratio, R_{mod} (g g^{-1})

$$R_{mod} = \frac{m_{m,d} - m_{0,d}}{m_{0,d}}$$

where $m_{m,d}$ (g) is the dry mass after modification and $m_{0,d}$ (g) is the dry mass prior to modification. Similarly, the change in volume from modification can be described by the bulking coefficient, R_{bulk} ($m^3\ m^{-3}$)

$$R_{bulk} = \frac{V_{m,d} - V_{0,d}}{V_{0,d}}$$

where $V_{m,d}$ (m^3) is the dry bulk volume after modification and $V_{0,d}$ (m^3) is the dry bulk volume prior to modification.

The modification ratio and bulking coefficient can be used to correct the calculated moisture content and swelling for the change in mass and volume, respectively, as shown in Table 1. The efficiency of the modification to lower the moisture content is known as the "moisture exclusion efficiency" (MEE) in literature, see Table 1. It is calculated from the moisture contents obtained after conditioning untreated and modified wood to equilibrium under the same environmental conditions. However, for those modifications with $R_{mod} < 0$, i.e., where the dry mass of the wood is decreased, no correction is needed. The efficiency of the modification to create a more dimensionally stable material, i.e., decrease the swelling, is known as the "anti-swelling efficiency" (ASE) in literature, see Table 1. It is calculated from the swelling determined after conditioning untreated and modified wood to equilibrium under the same environmental conditions, often using the water-saturated state.

Table 1. Parameters describing the change in wood–water interactions by modification. m_w (g) is the mass of water, m_d (g) is the dry mass of the wood (modified or not), u_m ($g\ g^{-1}$) and u_0 ($g\ g^{-1}$) are moisture contents of modified and untreated wood, respectively, V_u (m^3) is the bulk volume in a given moisture state, V_d (m^3) is the dry bulk volume, and $S_{sw,m}$ ($m^3\ m^{-3}$) and $S_{sw,0}$ ($m^3\ m^{-3}$) are the swelling of modified and untreated wood, respectively. * The correction is only needed for modifications with $R_{mod} > 0$.

Parameter	Original	Corrected
Moisture content, u ($g\ g^{-1}$)	$u = \frac{m_\mathrm{w}}{m_\mathrm{d}}$	$u_R = u(1 + R_{mod})$ *
Moisture exclusion efficiency, η_u (-)	$\eta_u = 1 - \frac{u_m}{u_0}$	$\eta_{u,R} = 1 - \frac{u_m}{u_0}(1 + R_{mod})$ *
Swelling, S_{sw} ($m^3\ m^{-3}$)	$S_{sw} = \frac{V_u - V_d}{V_d}$	$S_{sw,R} = S_{sw}(1 + R_{bulk})$
Anti-swelling efficiency, η_{sw} (-)	$\eta_{sw} = 1 - \frac{S_{sw,m}}{S_{sw,0}}$	$\eta_{u,R} = 1 - \frac{S_{sw,m}}{S_{sw,0}}(1 + R_{bulk})$

3. Acetylation

3.1. Process for Producing Acetylated Wood

Acetylated wood is produced by reacting wood with acetic anhydride. In this reaction, some hydroxyl groups in the wood cell wall are replaced with acetyl groups (Figure 1). The reaction between acetic anhydride and wood is a single displacement reaction; that is there is a 1:1 substitution of acetyl groups for hydroxyl groups and no further reactions or polymerizations occur [35].

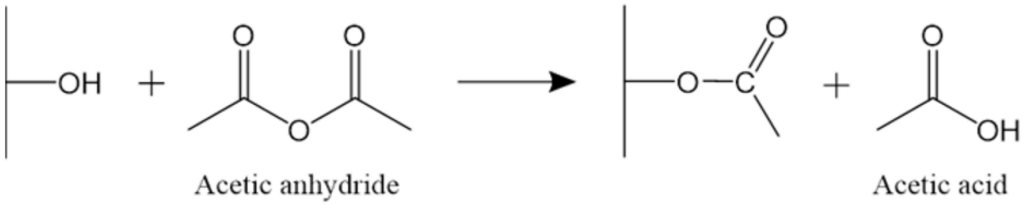

Figure 1. Schematic of the acetylation reaction.

The reaction of wood with acetic anhydride was first carried out by Fuchs in 1928 [37], however, Stamm and Tarkow were the first researchers to explore acetylation as a method of enhancing the dimensional stability and decay resistance of wood [38–40]. Commercialization of acetylated wood was attempted as early as the 1960s [41], however, full commercialization was not realized until the early 2000s in the Netherlands by Accsys Chemicals [24]. Accsys technologies now produces over 60,000 m^3 of acetylated wood per year [26].

Practically speaking, the acetylation process involves submerging wood in acetic anhydride at elevated temperature followed by a cleaning to remove excess acetic anhydride and acetic acid. Gas phase reactions with ketene gas or acetic anhydride vapor have also been used but are less common [42]. The amount of permanent uptake of acetic groups depends upon the reaction time, temperature, and the presence of initiators or swelling agents. Several reviews examine how the acetylation reaction can be tuned by changing the reaction parameters [24,41]. Readers interested in the production processes for acetylation are referred to these excellent publications.

3.2. How Acetylatation Affects the Wood Cell Wall

As stated previously, acetylation results in the replacement of a single hydroxyl group with an acetyl group. In the most basic sense, this substitution results in two changes. The first is a bulking effect since the acetyl group is larger than the hydroxyl group it replaces. Secondly, the acetyl group is less polar than the hydroxyl group and this affects the hydrophilicity of the wood cell wall.

Of these two factors, bulking has the largest effect on the reduction of moisture absorption [43]. Moisture absorption is an important metric for acetylated wood as preventing moisture absorption improves dimensional stability and resistance to wood decay fungi. Bulking was found to be the primary method by which acetylation affects moisture absorption in experiments where different sized carboxylic acid groups were substituted on hydroxyl groups; larger substituted groups reduced water vapor absorption with less chemical than smaller groups [44,45]. However, the reduced water absorption could not be entirely explained by the amount of bulking and the polarity of the side groups also affected the magnitude of absorption [43–45].

3.3. Experimental Evidence on the Changes Caused by Acetylation

3.3.1. Hygroscopicity and Liquid Water Absorption

Acetylation reduces the number of sorption sites for water by replacing hydroxyls with acetyl groups. This has been shown by the decreasing hydroxyl accessibility for water, found by deuterium exchange, with increasing degree of acetylation [46–48]. The reduction in hydroxyl accessibility has been found to be around 24.1–28.8 mmol hydroxyls per gram mass gain [46–48] which is only slightly above the theoretical reduction from substitution of hydroxyls of 23.8 mmol hydroxyls per gram mass gain [47]. Besides this reduction, however, acetylation bulks the wood cell walls by adding molecular volume [45], which decreases the space for water within wood cell walls. Increasing the degree of acetylation will reduce the hygroscopicity of the wood approximately linearly up to MEE ~50% at $R_{mod} = 0.25$ g g^{-1} [43]. At higher mass gains the marginal change in hygroscopicity may decrease with an increasing degree of acetylation as seen from the slightly concave relationship between moisture exclusion efficiency and degree of acetylation [43].

Acetylation weakens the interaction between liquid water and wood as seen with low-field NMR spectroscopy [49,50] and from the decrease in contact angle with water [7–10]. For this reason, acetylation is expected to decrease the rate of liquid water uptake by capillary suction which has also been observed for acetylated alder [51].

3.3.2. Dimensional Stability

Since acetylation decreases the hygroscopicity and space for water within wood cell walls, the modification also affects the dimensional changes accompanying moisture changes. Firstly, the bulking from acetylation results in larger dimensions in the dry state of the wood [52–54]. This pre-swelling should be considered when evaluating the dimensional changes of acetylated wood, (see Section 2), although this is rarely done in literature [43]. Acetylation decreases the dimensional changes of wood approximately linearly up to ASE ~60% at R_{mod} = 0.2 g g^{-1} [43] without taking pre-swelling by bulking into account. At higher mass gains the marginal change in ASE decreases with increasing degree of acetylation, again without correcting for pre-swelling [43]. However, the total volume in the water-saturated state is similar between untreated and acetylated samples with initial similar volumes. While less water is taken up by acetylated cell walls, the pre-swelling of the modification and the additional swelling from water-saturating the cell walls add up to the same total volume as that of water-saturated untreated wood [52–54]. Therefore, the primary effect of acetylation on dimensional changes appears to relate to the smaller changes in moisture content in acetylated wood than untreated wood under similar climatic conditions.

3.4. Theoretical Basis for Wood Protection by Acetylation

The basis by which acetylation protects wood from decay has been debated since the development of the technology and a consensus remains elusive. Recent reviews on the mechanism of wood protection in acetylated wood by Ringman et al. [55–57] have summarized five major competing theories: (1) acetylation renders the wood polymers unrecognizable to fungal enzymes, (2) acetylation blocks the availability of nutrients to the fungus, (3) micropores in the wood cell walls are blocked, preventing degradation, (4) hydroxyl groups in the cell wall modified, preventing hydrolysis, and (5) the reduced moisture content of acetylated wood impedes diffusion.

The first hypotheses, that the acetylation makes the wood polymers unrecognizable to enzymes produced by the decay fungus or unavailable as fungal nutrients have been mentioned in reviews by Rowell [58,59] and Hill [60]. However, these reviews present this hypothesis in the passive voice and without citations. Therefore, it is impossible to know when the hypothesis was developed, or whether there was strong evidence to support the hypothesis. Although several of the sources are unclear about how the acetylation renders the wood polymers unrecognizable to the enzymes, Rowell et al. [59] state that acetylation may block the degradation of hemicelluloses by changing the conformation of the arabinose sugar. However, many researchers have shown that acetylation also retards the chelator-mediated-Fenton (CMF) reaction chemistry that precedes enzymatic degradation in brown rot decay [55–57,61–63]. Furthermore, there is evidence from chemically labeled measurements that enzymes cannot penetrate the intact cell wall, and therefore enzyme non-recognition cannot be responsible for inhibiting decay [60]. Finally, Beck et al. [64] have measured the acetyl content of modified wood during decay and found that the acetyl content of the wood dropped as the wood was decayed. In other words, fungi have been shown to either remove highly acetylated wood polymers or cleave acetyl groups from polymers. In a thorough review, Ringman et al. [57] concluded that, “the fungal metabolites and enzymes involved in wood degradation are still functional in at least some modified wood material”. Therefore, it is clear that these hypotheses must be rejected.

It is apparent from gene expression studies that wood decay fungi attempt to break down modified wood [57,62,63,65]. Clearly, this demonstrates that acetylation is not fungitoxic. Ringman et al. concluded that the fungi appear to make radicals needed for the primary stages of non-enzymatic degradation but “the fungal molecules needed for the formation of radicals are not able to penetrate the wood cell wall” [65]. In some experiments multiple levels of acetylation were examined. The time course of the gene expressions showed that the fungi cycled through the same progression of upregulating genes, however, the fungi spent much more time generating pre-enzymatic decay precursors with higher levels of acetylation [62,63]. These gene expression studies have shown that the fungal decay mechanisms are still functional in acetylated wood, however, the fungi are unable to rapidly break down the cell wall material [57].

Although it is often claimed that acetylated wood with a high mass gain (above R_{mod} ~0.15–0.20 g g^{-1}) is decay resistant [66–74], many recent papers have shown that acetylation does not prevent decay but rather greatly reduces the decay kinetics [57,60,62,63]. Beck et al. [63] stated that one reason for this discrepancy in the literature may be a result of the relatively short timeframes used in laboratory decay testing. While these tests are long enough for untreated controls to completely decay, highly acetylated wood exhibits a long initiation phase before decay can be observed [62,63]. Alfredsen et al. [62] examined different levels of acetylation for 36 weeks in a soil bottle tests and concluded, "there is no absolute decay threshold at high acetylation levels, but instead a significant delay of decay initiation and a slower decay rate". Similarly, Hill et al. [60] examined the porosity of acetylated wood and concluded that, "there is no evidence to suggest that cell wall decay is being prevented by anhydride modification, rather that the rate at which decay occurs is dramatically reduced".

Both the gene expression studies and corresponding observations that acetylation delays rather than prevents decay suggest that acetylation protects wood by altering the decay kinetics. Reaction kinetics depend upon diffusion, and often diffusion can be the rate limiting step in a kinetic process. Furthermore, Jakes et al. have shown diffusion is strongly dependent on the moisture content of the wood [75]. Therefore, the evidence suggests that unique wood moisture relations of acetylated wood may be a key to understanding its mechanism of wood protection.

The Role of Moisture in the Decay of Acetylated Wood

Of the five hypotheses for how acetylation protects wood presented by Ringman [55,57], it is clear that the reduced moisture content in the wood cell wall appears to be the primary method by which acetylation protects wood from decay. However, the mechanisms by which the lower wood moisture content leads to decay protection are still unclear.

Zelinka et al. [56] presented three potential hypotheses that might explain how acetylation disrupts diffusion of CMF reagents at the beginning of the decay process. Several of these hypotheses were based upon the observation that ionic conduction can be explained by percolation theory [76]. Therefore, there exists a threshold below which ionic conduction does not occur (the percolation threshold). Jakes et al. [77,78] built upon this observation and suggested that the percolation threshold could be explained by an interconnected region of softened hemicelluloses and this may explain the onset of wood damage mechanisms that occur above 0.16 g g^{-1} moisture content but below 0.3 g g^{-1}. In terms of acetylation, Zelinka et al. [56] hypothesized that acetylation may (1) inhibit the softening of hemicelluloses and thus block a percolating network for diffusion, (2) stop a percolating network from forming without affecting hemicellulose softening, or (3) greatly reduce the diffusion kinetics of CMF reagents without altering the percolation threshold.

Recent evidence suggests that the third hypothesis of Zelinka et al. [56] shows the most promise. Hunt et al. [79] used X-ray fluorescence microscopy to examine the threshold for diffusion in acetylated wood. They observed that diffusion occurred at high relative humidity (RH) in acetylated wood; however, it occurred at a higher RH than untreated controls. Jakes et al. [80] measured the diffusion constant for ions through the cell walls of unmodified wood and found that they decreased by four orders of magnitude from the water saturated state to in-equilibrium with 70% RH. Since acetylation lowers the wood equilibrium moisture content (EMC), it may also affect the moisture dependent diffusion rates. Such a decrease in diffusion could easily make it seem like acetylated wood does not decay. However, attempts to measure the diffusion rate of relevant ions or ion transport entities (such as for example iron oxalate) in water saturated cell walls of acetylated wood were inconclusive [81]; no differences were found between untreated and acetylated wood but the diffusion constants measured were many orders of magnitude smaller than those measured by Jakes et al. [80]. Clearly, more work needs to be conducted to understand how diffusion may be related to decay in acetylated wood. The polymer science models for diffusion in wood developed by Jakes [75,82] give important clues to how acetylation may greatly reduce the diffusion kinetics, and thus retard fungal growth in acetylated wood. Such a retardation in the diffusion rate may make acetylated wood appear "decay resistant" for practical purposes and this may explain why acetylation appears to completely inhibit decay in some experiments whereas in others it merely delays or slows decay.

If decay in acetylated wood were inhibited by diffusion, and diffusion through the cell wall depends upon the wood moisture content, we would expect to see relationships between the level of acetylation, wood moisture content, and amount of decay. Zelinka et al. [83] altered the soil water holding capacity and weight percent gain of acetylated samples to test decay as a function of acetylation at a fixed moisture content. They found that the wood moisture content and mass loss were strongly correlated, however, the analysis was incomplete because moisture generation from the fungus and passive moisture transport between the air, soil, and wood complicated the analysis.

Thybring [84] reviewed the literature and developed a model for correlating the moisture content at the end of a decay test to the amount of mass loss for modified and unmodified wood. The model was based upon the amount of moisture produced by fungal respiration. However, this model ignores the fact that fungi actively regulate the moisture of their surroundings. For example, Peterson and Cowling [85] found that *P. versicolor* actively manipulated the moisture content of Sitka spruce wafers even though the fungus did not cause any decay in the wafers. Similarly, Zelinka et al. [83] noted that Thybring's model could not fit their data and attributed these differences to active moisture transport. While moisture reduction is clearly part of the mechanism by which acetylation protects wood, designing experiments to explicitly test this variable are extremely difficult since moisture is freely exchanged (and in some cases actively transported) between the wood, soil, air, and fungus in typical soil bottle tests.

3.5. Future Perspectives for Acetylation

Acetylation has been widely studied and is commercially available. Despite the depth of study on this modification, there are still unanswered questions regarding how it protects wood. Better understanding these questions could perhaps improve the commercial process and make it more economical. One exciting development on this front was recently presented by Digaitis et al. [86] who developed a method for targeting acetylation so that it only modified areas of the cell wall near the cell lumina. Acetylating only part of the cell wall could allow many more experiments on how to test how acetylation leads to wood protection. Furthermore, if targeted acetylation shows a similar level of protection, it could greatly improve the economics of acetylation by using less reagents in the commercial process.

Another avenue that appears promising for further study is better understanding diffusion in acetylated wood. Jakes [82] used nanoindentation to measure the mechanical damping as a function of moisture content. He showed that these changes in the damping coefficient were related to rubbery regions in the wood cell wall that allowed diffusion and these changes were strongly correlated with ionic conduction changes. Repeating these experiments with acetylated wood could test whether acetylated wood is protected by changes in reagent diffusion.

4. Furfurylation

4.1. Furfuryl Alcohol and Its Cationic Polymerization

Furfurylation is a wood modification process based on impregnation with furfuryl alcohol (FA) and subsequent polymerization within the wood structure via heat curing. We start this part of the review by taking a look at how FA is produced, and how it polymerizes.

Plant biomass contains different constitutive sugars that can be valorized into building blocks, thus offering sustainable alternatives to oil-based feedstocks. Non-edible biomass residues that do not compete with food production are particularly interesting. Among them, hemicellulosic residues containing high proportions of xylose are the most relevant in this context, as xylose can be dehydrated into furfural, which is a central starting platform chemical in the hemicellulose value chain. This furanic compound enjoys industrial production worldwide and should reach a growing market share of €634 M in 2024 [87]. In the furfural value chain, furfuryl alcohol is one of the most promising derivatives, especially for the preparation of bio-based thermoset resins.

The cationic polymerization of FA is promoted by Brønsted or Lewis acidic initiators and thermal curing is necessary to fully polymerize FA. The word "initiators" is employed herein instead of "catalysts" as these latter are *stricto sensu* recycled while the acidic initiators are not recycled, but remain in the system. However, the purpose of these initiators is to accelerate the polymerization of FA, i.e., they have a catalyst-like role.

The initial autocatalytic stage consists in the formation of furyl carbenium centers that condense on the free C5 position of another furan ring. Accordingly, linear oligomers will be formed (Figure 2). However, it is important to notice that polyfurfuryl alcohol (PFA) is not at all a linear polymer whose chains could entangle or even crystallize with each other. Indeed, fully polymerized PFA is a rigid, black-colored cross-linked thermoset system not in line with the expectations from linear polymers. Choura et al. [88] explained the darkening by the internal formation of dihydrofuranic cycles allowing higher conjugation over the oligomers. These larger double bond delocalizations explain why PFA absorb UV and visible light. The dihydrofuranic rings and the furanic ring are prone to branch via Diels–Alder cycloadditions, which on the other hand break the conjugations. Branching occurs readily after the formation of the first oligomers. However, the retro Diels–Alder reactions that would revert back to the initial compounds (i.e., the furanic and the dihydrofuranic rings) are not observed for PFA, even at high temperature. This suggests that PFA degradation occurs before the potential retro Diels–Alder reactions. Finally, it is important to notice that FA is a liquid monomer (with a viscosity around 10^{-2} Pa s) leading to a cross-linked PFA, whose viscosity increases up to 10^{7} Pa s. The kinetics of FA polymerization are therefore rather complex and changes during the process. In the early stage of polymerization, it is controlled by the autocatalytic mechanisms (i.e., formation of carbocation under acidic catalysis) or chemical reactions, while it becomes controlled by diffusion of polymer chains in the late stage of the reaction [89]. It is rather difficult to ensure that in vitro PFA is completely cured as residual reactions can occur after devitrification (i.e., the process where a polymer is heated over its glass transition temperature). Falco et al. [90] showed that despite the absence of signal in calorimetry or in thermogravimetry, some residual branching reactions could be identified by dynamic mechanical analyses when PFA was heated above its final curing temperature. These reactions that still occur at high temperature in the rubbery state led to higher cross-linked PFA systems. To summarize, good control of the curing reaction and reaching complete curing is important to avoid leaching of small unreacted species (e.g., monomers and dimers) to the environment from the final product, but on the other hand extensive heat curing is detrimental in the case of furfurylation as it will impact the final properties of the furfurylated wood.

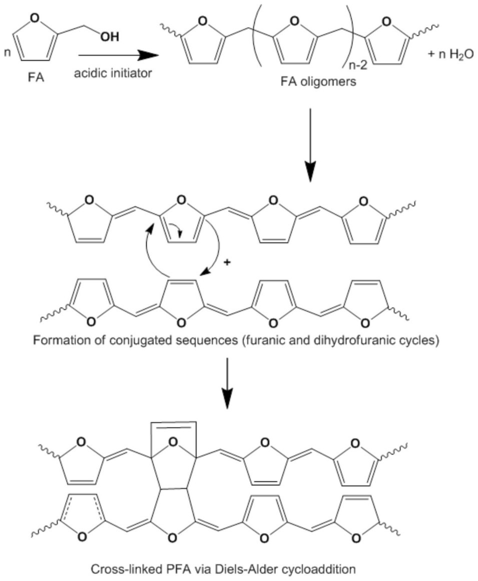

Figure 2. Schematic for polymerization of furfuryl alcohol.

4.2. Process for Producing Furfurylated Wood

Furfurylation of wood is comprised of two steps [91]. First, the wood is impregnated with a solvent containing FA and one or more acidic initiators, and afterwards the wood is heat cured. The impregnation typically takes place by first subjecting the wood to vacuum, then adding the impregnation mixture and applying pressure. A final vacuum drying step may be used to remove surplus solvent. The FA polymerization occurs during curing. In contrast to acetylation, which only affects the primary and secondary wood cell walls, the middle lamella and the cell corners (together, all these compartment are in this section on furfurylation henceforth denoted "cell wall"), furfurylation may also result in the filling of (part of the) cell lumina with a furan polymer [92] (Figure 3).

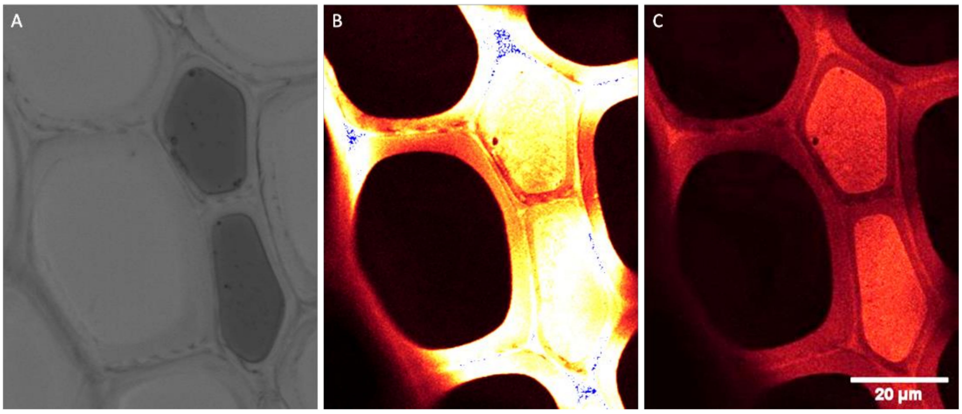

Figure 3. Cross section of furfurylated *Pinus radiata* as seen in transmitted light (**A**) and in CLSM using two different excitation wavelengths ((**B**) 488 nm and (**C**) 633 nm). CLSM images are color coded according to emission intensity, going from black over brown/red to yellow and white, while blue shows detector overflow. The CLSM images show presence of conjugated furan molecules both within the lumina (where a redshift is seen), and in cell walls, middle lamella, and cell corners, where the strongest fluorescence is seen from lignin-rich regions.

According to Lande et al. [91], furfurylation of wood was first described in the 1950s as a way of providing better resistance towards acid and base [93]. In this and other early work zinc chloride was used as a catalyst. This gave rise to two problems [91]: (1) zinc chloride degraded cellulose, thus resulting in strength loss and (2) zinc chloride had poor penetration into the wood, resulting in treatment gradients. During the 1990s two researchers, Schneider and Westin with coworkers, independently of each other suggested the same replacement catalyst: maleic anhydride [94,95], which alleviated both these problems. In later laboratory-scale furfurylation studies, citric acid or other weak acids have also been used as sole or additional initiators [91,92,96,97]. Apart from the type and amount of initiator(s) used, the furfurylation result is known to depend on the solvent. In addition to the trivial finding that dilution of FA in a solvent will result in a lower uptake (mass gain, modification ratio) than if neat FA is used [98], the identity of the solvent has also been found to affect the polymerization process during curing as well as the properties of the modified wood, but so far, results appear somewhat ambiguous. For example, one study found that if FA was diluted in isopropanol instead of water, FA polymerization began at a higher temperature during the curing step, resulting in a less complete polymerization [90], while another study comparing the same two solvents did not identify any differences in the FA polymer, neither when comparing the polymer present in lumina, or the polymer within cell walls [99]. The latter study did however find that use of isopropanol as solvent resulted in more earlywood lumina being filled with a FA polymer compared to the set-up where FA was diluted in water. A tentative explanation to these seemingly contradictory results might be that the more complete polymerization presents in the lumina dominated the macroscale results recorded in the former study.

4.3. How Furfurylation Affects the Wood Cell Wall

During the curing step of the wood furfurylation process, the added initiators help the FA polymerize with itself [92]. An experimentally based suggestion for the polymerization process of pure FA was published 25 years ago [88]. As mentioned in Section 4.1 above, according to this suggestion, linear chains of furans connected by a carbon molecule and with conjugated double bonds are formed. These stiff, flat linear molecules are fluorescent. During the continued polymerization, Diels–Alder crosslinking are believed to take place between these chains. During the curing step of wood furfurylation, FA most likely not only binds to other FA molecules to form a furan homopolymer in lumina and entangled within cell walls, but also cross-links to lignin [100–102]. The existence of such bonds has however never been proven in situ, only in vitro for lignin model compounds. It seems that FA binding to the C1 carbon of the propan tail situated in the para position compared to the phenoxyl in lignin monomers is at least just as likely as binding to the ring [100], explaining why infrared spectroscopy does generally not show any peak shift of aromatic lignin signals upon furfurylation. For thermodynamic reasons, binding to hydroxyl groups in lignin is unlikely to take place [100]. Recently, in vitro studies showed that no binding to hydroxyl groups within cellulose or hemicellulose takes place either [102]. This implies that furfurylation does not consume hydroxyl groups within the cell wall like acetylation would do. Rather, it blocks access to these groups by bulking the cell wall, presumably with a mixture of entangled, pure furan oligomers and a modified, furan-enriched lignin.

4.4. Experimental Evidence on Changes Caused by Furfurylation

4.4.1. Dimensional Stability

A number of studies have documented that furfurylation leads to increased dimensional stability in situations with fluctuating relative humidity levels [91,103–109]. The effect is linked to the mass gain and the RH range tested. For example, Lande et al. [91] found that ASE was close to 50% at R_{mod} = 0.32 g g^{-1}, and around 70% at R_{mod} = 0.47 g g^{-1}, both for an RH change from 30 to 90%. For a furfurylation mass gain of around 0.38 g g^{-1}, Esteves et al. [109] obtained ASE values in the range from 29–45% depending on the RH interval tested.

4.4.2. Hygroscopicity/Liquid Water Absorption

Furfurylation decreases the EMC of wood in the hygroscopic range [109] to roughly a little more than half the moisture content of untreated wood at R_{mod} = 0.38 g g^{-1}. The study just cited does not report whether the EMC was found after desorption or absorption. In a desorption study carried out for the upper part of the hygroscopic range [110], the reduction compared to untreated wood was more modest than these values, most likely because the EMC calculation was based on the dry weight of the unmodified wood, not the modified wood. For RH above 99%, furfurylated wood was found to contain more moisture than untreated wood. The authors speculated that this was an effect of the high mass gain (R_{mod} = 0.63 g g^{-1}), i.e., moisture in microcracks formed in the cell walls due to swelling during treatment. Yang et al. [111] show both absorption and desorption isotherms of furfurylated wood with R_{mod} = 0.21 g g^{-1}, which remain well below the isotherms of the untreated control throughout the hygroscopic range (dry weight of the modified wood assumingly used as base for EMC calculation). The uptake of liquid water has been less well investigated. A single study using the Wilhelmy plate technique found that furfurylated wood (R_{mod} = 0.32 g g^{-1} or 0.22 g g^{-1}) had a reduction in uptake by more than 70% compared to untreated wood [112].

4.4.3. Biodeterioration

That furfurylation protects wood against fungal degradation has been shown using different species of wood and fungi as well as different furfurylation procedures [91,113]. However, a recent study found that fungal wood decomposition can take place if small thin-walled earlywood samples are subjected to an aggressive brown rot strain favored by continuous access to water. Even under these circumstances was the mass loss limited to 10–15% [114]. The degradation happened within the first few weeks of the experiment, and then degradation stopped.

Regarding termites, several studies have shown that furfurylated wood can withstand these [91,115–118]. However, for these studies nothing is mentioned about possible leaching of the wood samples prior to the termite feeding trials. In another study it was found that the protective effect of the furfurylation was markedly reduced if the furfurylated wood was leached before the feeding trial [119]. This result confirms earlier results that leaching from furfurylated wood due to insufficient curing takes place [120,121], and that proper curing is of paramount importance to obtain a meaningful and fair evaluation of furfurylated wood products, both in industry and in research work.

Furfurylation has been found to postpone biodeterioration in the sea, both regarding shipworm and gribble [91,122,123]. An effect of the solvent during impregnation on the durability has been found. In one study, wood furfurylated in alcohol and with R_{mod} = 0.29 g g^{-1} was still sound or only slightly attacked after 16 years of exposure in the sea, while samples with R_{mod} = 0.64 g g^{-1} furfurylated in water failed within 8 years [124].

4.4.4. Hardness and Brittleness

A cured homopolymer of FA can obtain almost glassy properties. Indeed, the glass transition temperature (T_g) of in vitro PFA varies between 70 °C and 130 °C depending on how it has been cured (time, temperature, initiator, postcuring, presence of filler, etc.) [89,125,126]. This implies that at room temperature (or the usage temperature of wood), the PFA is in its glassy state. Moreover, the damping factor is very low and the cross-link density of PFA is high [127], which means that PFA is very rigid and brittle with a very dense network. The molecular mobility of PFA chains is thus quite restricted. In accordance with this, furfurylation has been found to make the wood harder and more brittle. Hardness increase has been documented both on the macroscale [91], and at cell wall level [96].

4.5. Theoretical Basis for Wood Protection by Furfurylation

The mode-of-action regarding moisture exclusion of furfurylation has not been debated as intensively as for acetylation. Even though the polymerization process is complex, the wood cell wall modification mode-of-action is, actually, simpler than for acetylation, as furfurylation is known not to involve condensation reactions with wood hydroxyl groups. That is: furfurylation is known to bulk cell walls without consuming hydroxyl groups, in contrast to acetylation, which does both, thus giving rise to discussions on which aspect is the most decisive for the resulting wood protection. In other words, furfurylation reduces the space available for water within the cell wall, which in itself is known to slow down or even hinder fungal decomposition [43,128], as discussed above regarding acetylation.

However, this is likely not the whole explanation as to how furfurylation protects wood against fungi. As mentioned above, recent research [114] has shown that in a situation where abundant moisture was present, a brown rot fungus was nevertheless able to initially remove 10%–15% of the dry mass of furfurylated wood with R_{mod} = 0.36 g g^{-1}. The degradation happened during the first weeks of the experiment, but then stopped, even though conditions were not changed. This implies that reduced moisture content in the wood is not the only mechanism explaining why furfurylated wood with a sufficiently high mass gain is not degraded. Brown rot fungi are believed to degrade wood using a two-step approach, with an oxidative phase followed by a hydrolytic phase [129,130]. Mapping of gene expression of the system just mentioned showed that the oxidative phase was maintained or extended for furfurylated wood [62,113]. It may be that furfurylation renders part of the lignin of the cell wall more resistant towards the oxidative tools of brown root fungi while unmodified, accessible parts of the cell wall are initially degraded if enough moisture is present.

When it comes to preventing degradation by termites and marine crustaceans such as gribble and shipworm, furfurylation has given positive results, albeit depending on the solvent used, as mentioned above. The exact mechanisms have not been fully elucidated [99]. An increase in material hardness most likely plays a role [131], as it makes the material more difficult to ingest for the animals, but enzyme non-recognition during digestion might also be involved [122].

4.6. Gaps in Our Understanding of Furfurylation

Many central questions have not yet been answered regarding furfurylation of wood. The three main knowledge gaps lie within (1) the furfurylation process and the resulting molecular structure, (2) the mechanisms by which furfurylation reduces biodeterioration, and (3) how to furfurylate more refractory tree species.

4.6.1. Furan Polymerization and Molecular Structure

As mentioned above, not even homopolymerization of FA is fully understood. For the more complicated wood furfurylation process, experimentally documented insights on the polymerization processes are likewise scarce. Cross-linking to lignin has been shown to take place in vitro [101,102], but never inside wood. It has been shown that fluorescent furan chains are longer in lumina than within cell walls [92], but their actual lengths remain unknown as well as their distribution within and between cell wall compartments. More fluorescence is seen from lignin-rich regions of furfurylated wood, but if quenching takes place, there is not necessarily a linear relationship between the intensity of the fluorescence detected and the amount of fluorophores present. Further, Diels–Alder cross-links would reduce fluorescence, i.e., fluorescence shows the early steps of the polymerization only. Finally, the effects of changing the furfurylation process in one way or another remain unknown beyond some qualitative indications.

4.6.2. Mechanisms behind Prevention of Biodeterioration

As mentioned above, there are still uncertainties when it comes to understanding the mechanisms behind the prevention of biodeterioration that furfurylation has been found to give, as it is clear that it is not only a question of moisture exclusion, albeit this for certain plays a role as in any type of wood modification. For fungi, it is yet unknown under which conditions (partial) decomposition of a furfurylated wood cell wall can take place, and which parts remain vulnerable. Furthermore, it is unknown how changes to the furfurylation process affect wood recalcitrance. When it comes to termites and marine wood borers, even less is known, and the situation is more complicated, as presence of a FA polymer in (part of) the lumina seems to play a role in addition to modifications within the cell wall [99,122].

4.6.3. Role of Wood Properties for Furfurylation Success

It is well known that tree species, moisture content and history as well as cell and pit types, state (open/closed) and sizes all play important roles in any type of impregnation process. Regarding impregnation of *P. sylvestris* sapwood with an aqueous solution of FA and initiators, it has been found that in general sapwood from fast grown individuals is easier to impregnate [132]. That is, the general rule-of-thumb that coniferous wood with a high proportion of latewood is easier to impregnate does not seem to apply. (The rule of thumb exists because the bordered pits connecting tracheids in the latewood xylem do not as easily close during drying as those between tracheids in the earlywood [133]). Rather, it seems large rays and wide tracheids are important for FA impregnation success, as exploited when fast-grown *P. radiata* is readily furfurylated. If future utilization of wood resources implies increased use of a range of less suited species, then ways to FA impregnate more refractory wood need to be obtained.

4.7. Future Perspectives for Furfurylation

At present, furfurylated wood is a niche product for façades and decking, bought by those who like its look and its environmentally friendly image and can afford to pay for these features. To perhaps produce similar modified wood by valorizing a side-stream product, it was recently suggested to use humins instead of furfuryl alcohol [134]. Humins are furan oligomers originating for example from biorefining of plant biomass. The conversion of sugars into platform chemicals such as furfural or hydroxymethylfurfural is impacted by the formation of humins issued from internal condensation between targeted furanic compounds and the residual sugars thus impacting the economical and environmental aspects of this value chain. The polyfuranic structure of humins is slightly less well-defined and less branched than PFA and more heterogeneous. Nevertheless, like FA or FA resins, they can be further cross-linked upon thermal heating [135]. Industrial humins from biorefining could thus be considered as "furanic lignins" if we make the parallel with the lignin issues in the pulp and paper industry. Similar to lignin valorization, extensive research and development are still needed on humins before competitive processes can emerge. In a seminal approach [134], the water soluble fraction (~35% of the humins) was separated out to prove the concept that this fraction could replace FA for wood impregnation. Impregnation with this subset of humins throughout the cell walls within veneer was found to take place in a laboratory set-up. As humins are more branched than monomeric FA, the curing conditions were less demanding (lower temperature and shorter time). This so-called "humination of wood" might have potential to be developed into a less costly parallel approach to the classical furfurylation.

A process relying on gas phase furfurylation [136] is another recent suggestion that could cut costs by reducing the consumption of furfuryl alcohol. In this process, any deposition of FA polymer in lumina is avoided, i.e., all furfuryl alcohol left in the wood will be positioned within the cell walls. Additionally, to remove excess impregnation solvent (typically water) via drying will be redundant.

Another possible future perspective for furfurylation is to reduce the brittleness of the product, as this would open up new application areas for furfurylated wood, including some that can better accommodate the relatively high price of the process. Along these lines, it seems the use of furfurylated wood as an alternative to endangered tropical wood species for high-end furniture or even musical instruments could be within reach. A recent study [137] tested impregnation of wood with a mixture of furfuryl alcohol and epoxidized soybean oil, followed by heat curing. The addition of the oil as a plasticizer gave a less brittle product that could potentially be machined. Machining was however not tested in the study. In another study it was found that when FA polymerization takes place in a protic polar solvent (such as water or aliphatic alcohols), it can to some extent lead to opening of the furan rings, which leads to a less rigid polymer being formed [127]. The consequence is that the PFA chains cured with these solvents have a lower cross-link density, which macroscopically lead to lower elastic modulus and lower glass transition temperature. However, the thermal stability seems not dramatically affected by this furan ring opening. One can speculate that enhancement of this aspect of the furfurylation process could have similar advantages as the addition of a plasticizer.

5. Thermal Modification

5.1. Process for Producing Thermally Modified Wood

Thermal modification causes a permanent change of wood properties by heating at elevated temperatures—a phenomenon that was first observed over 100 years ago [138]. After early attempts at a commercialization in the USA [139] and in Germany [140,141], the industrial production of thermally modified wood began in earnest in the 1990s in Finland, France, Germany, and the Netherlands. Today, more than one hundred manufacturers of thermally modified wood exist worldwide, most of them being located in Europe, and the annual production of thermally modified wood has increased to more than 500,000 m^3 [27,142].

The production of thermally modified wood usually takes place between 160 and 240 °C; hence the temperatures are higher than during the conventional kiln-drying of wood, but still low enough to keep the thermal conversion at a manageable rate. Furthermore, commercial processes avoid spontaneous wood combustion by excluding oxygen from the surrounding atmosphere. This is realized differently, for example by heating wood in partial vacuum, in a steam atmosphere, in hot oil, or in an inert gas atmosphere such a nitrogen. Besides the treatment atmosphere, commercial processes also differ in treatment temperature and duration (also during the heating-up and cooling-down stages), wood species, initial and final wood moisture contents, or the use of open or closed systems. Most thermally modified wood is produced according to the ThermoWood® (Lahti, Finland) process, which uses superheated steam in an open system. However, there is a great variety of commercial processes with a broad range of annual production capacities. Technical details of some commercial processes are discussed by Esteves and Pereira [143], Militz and Altgen [144], and Sandberg and Kutnar [145].

5.2. How Thermal Modification Affects the Wood Cell Wall

Thermal modification relies on the effect of heat and does not require any chemical additives. Hence, the process is also applicable to refractory wood species that are difficult to impregnate, and the wood is affected through its entire cross-section. The treatment in an environment with low oxygen content at 160–240 °C partially degrades the wood, which causes changes in the chemical composition and the ultrastructure of the cell wall. Thermal degradation leads to a loss in wood mass, mainly due to the emission of water, carbon dioxide, methanol, acetic acid and formic acid from degraded cell wall polysaccharides [146]. A higher mass loss is observed with increased treatment temperatures and/or longer durations.

Mass loss is primarily caused by the degradation of amorphous polysaccharides, i.e., hemicelluloses. Hemicelluloses are the most thermally labile wood cell wall polymers. Their degradation typically starts with the cleavage of acetyl groups from the side groups of hemicelluloses, i.e., xylans, which results in the formation of acetic acid that catalyzes further degradation [147]. Hemicellulose degradation involves the rupture of the β-(1-4) linkage between the sugar units and the dehydration of the monomeric sugars. Furfural and hydroxymethylfurfural are the dehydration products of pentoses and hexoses, respectively, and they can undergo further degradation or react with lignin and other degradation products [148–150]. The degradation of hemicelluloses is dependent on their composition and hemicelluloses in hardwoods (e.g., arabinoxylan) degrade faster than hemicelluloses in softwoods (e.g., galactoglucomannan) [151,152]. Furthermore, side-chain sugars (e.g., arabinose and galactose) are more labile than the sugars that comprise the main chain (e.g., xylose, mannose, and glucose) [153].

The degradation of cellulose is limited to the amorphous regions; hence, the proportion of crystalline cellulose increases in thermally modified wood [154]. Crystalline cellulose is presumably unaffected by temperatures below 300 °C [155]. The preferential degradation of amorphous polysaccharides also results in a proportional increase in lignin. However, although the lignin content increases, lignin still undergoes chemical changes during thermal modification involving both depolymerization and repolymerization [154,156]. Some hemicellulose degradation products, such as furfural or hydroxymethylfurfural, can also react with the lignin and they may contribute to the increased lignin content that is determined by sulfuric acid digestion [156–158].

Overall, degradation reactions in wood during thermal modification are complex and depend on the wood species and the process conditions applied. For more detailed information on chemical changes in thermally modified wood, the reader may refer to the recent review by Hill et al. [25].

5.3. Experimental Evidence of Changes Caused by Thermal Modification

5.3.1. Hygroscopicity and Liquid Water Absorption

Thermal modification reduces the affinity of wood to take up moisture. The water vapor sorption decreases with increasing treatment intensity (i.e., temperature and duration of the process). The reduction in EMC typically reaches a maximum at a mass loss ($R_{mod} < 0$) of 0.06–0.08 g g^{-1} and remains nearly constant for higher mass losses [159,160]. However, the EMC reduction that is determined immediately after the modification process is not completely permanent. Water soaking or exposure of the modified wood to elevated humidity partially cancel the initial EMC reduction [161–165]. This phenomenon does not occur when the wood is heated in saturated water vapor but is particularly observed when the thermal modification process involves wood drying at elevated temperatures [163]. Hence, the reversible EMC reduction is presumably related to drying stresses remaining in the amorphous cell wall regions after the process, which are relaxed by subsequent moistening of the wood [162,163].

Thermal modification also reduces the wettability by water, which is observed by increased water contact angles at the wood surfaces [166–168]. This reduced wettability also limits the capillary water uptake. The water absorption coefficients of wood mostly decrease after thermal modification, particularly in radial and tangential direction [169–171]. An exception is Scots pine (*Pinus sylvestris* L.) sapwood, which shows an increased liquid water absorption after mild thermal modifications, presumably due to an increased permeability of the wood [170,171]. The latter may be related to damages to the membranes in the fenestriform crossfield pits in Scots pine that have been observed after thermal modification [172].

5.3.2. Dimensional Stability

In line with the reduced affinity of thermally modified wood to take up moisture, thermal modification improves the dimensional stability of wood. The effect of thermal modification on the dimensional stability depends on the wood species and the process conditions. Thermal modifications at temperatures of 200 °C or more can result in an average ASE during water-soaking cycles of ca. 40%–55% [141,173,174]. In drying and re-wetting cycles, thermally modified wood not only shows a reduced water-saturated wood volume [175,176], but the removal of cell wall constituents also reduces the dry wood volume compared to untreated wood [177]. A dimensional stabilization by thermal modification is only achieved when the reduction in water-saturated volume exceeds the reduction in dry volume [175,176]. Thermally modified wood retains its dimensional stability even after several drying and re-wetting cycles. In some cases, however, soluble degradation products remain in the wood after the modification process and occupy cell wall space. Leaching of such soluble degradation products during wetting and re-drying cycles causes a further decrease in wood dry volume, which reduces the ASE [161,178].

5.3.3. Biodeterioration

After thermal modification, the wood becomes more resistant against decay fungi. In laboratory tests with basidiomycetes on an agar malt-medium, an improved resistance has been found for a number of wood decaying basidiomycetes, including white- and brown-rot fungi [179–182]. Although the wood can still be degraded by fungi, thermal modification prolongs the time until decay starts and decreases the rate at which mass loss proceeds during the incubation with decay fungi [183,184]. Similar to the reduction in hygroscopicity, the effect on the decay resistance is dependent on the process conditions; hence, higher temperatures and longer treatment durations cause an increase in the decay resistance [180,181].

The enhanced resistance against basidiomycetes in laboratory tests has been confirmed by field tests in above-ground conditions [182,185,186]. After a nine-year lap-joint test, untreated softwood samples were severely decayed, while thermally modified samples showed only small areas of incipient decay [185]. However, thermal modification is less effective in improving the biological durability in ground-contact, which has been shown under laboratory conditions [181,187] and in field tests [182]. Consequently, Welzbacher and Rapp [182] considered thermally modified wood as unsuitable for in-ground contact applications.

5.3.4. Mechanical Properties

The above-described improvements of wood properties by thermal modification are accompanied by a loss in strength and ductility. The strength loss is dependent on the direction of load [188]. For example, the tensile strength parallel to the grain decreases strongly after thermal modification [188,189], while the compression strength shows a moderate decrease [190] or even increases [188]. The impact of thermal modification is often evaluated in static bending tests, which show only a small impact on the stiffness, a loss in strength, but most significantly, a brittle behavior with little plastic deformation and a strong reduction in toughness [157,191,192]. In contrast to small and clear test samples, full-sized boards also suffer from growth-related and processing defects. Thermal modification increases the checking in knots compared to kiln-dried wood and fractures during bending often propagate from such checks [193]. Overall, these effects typically limit the use of thermally modified wood to non-load bearing applications.

5.4. Theoretical Basis for Wood Protection by Thermal Modification

It is commonly accepted that the preferential degradation of hemicelluloses plays a dominant role in changing the properties of wood by thermal modification. Hemicellulose degradation interferes with the load-sharing capabilities of the cell wall to decrease the strength and toughness of the wood [153,194], reduces the number of sorption sites for water [175,195] and removes easily accessible nutrients for decay fungi [180]. Consequently, wood property changes often correlate with the wood mass loss during the thermal modification, which is primarily caused by hemicellulose degradation [159,196].

However, the removal of hemicelluloses is not the only cause for the wood protection effect. Hakkou et al. [167,197] showed that an exposure of wood to elevated temperatures reduces its wettability by water before mass loss and hemicellulose degradation take place. Based on results from differential scanning calorimetry and chemical composition analyses, Repellin and Guyonnet [198] concluded that the reduction in swelling and fiber saturation point of thermally modified wood cannot be attributed to hemicellulose degradation. Furthermore, elevated wood moisture contents during the thermal modification facilitate the removal of hemicelluloses, but do not result in a further reduction of the EMC or swelling of the final product [199–201]. As reviewed by Hill et al. [25] several explanations for the behavior of thermally modified wood other than the removal of hemicelluloses have been provided in the literature, such as the formation of covalent cross-links, permanently aggregated structures after drying at elevated temperatures, or hydrophobic and resin-like compounds in the cell wall. However, none of the explanations is fully consistent with the observed behavior of thermally modified wood.

Moreover, the wood protection effect of thermal modification is not entirely permanent. In addition to the permanent reduction in EMC and swelling, there is a reversible reduction that can be restored by exposing the modified wood to elevated humidity or by soaking in water [161–163,200]. This reversible effect is not related to chemical changes or to changes in hydroxyl accessibility [202], but associated with the high-temperature drying of the wood during the modification process [162,163]. Endo et al. [163] explained this reversible effect by the annealing of amorphous polymers that is driven by high-temperature drying, and this may also affect the mechanical behavior of the modified wood [162].

5.5. Gaps in Our Understanding of Thermal Modification

Although the technical aspects of thermal modification and the properties of the final products are well known, we are still lacking in our understanding of the cell wall changes that are responsible for the wood protection effect. A better understanding may help us in further improving the properties of interest, while minimizing the undesired impacts of thermal wood modification. The main reason for our lack of understanding is the complexity of the chemical reactions in wood during its exposure to heat. Simplifying these complex cell wall changes by studying isolated cell wall polymers could be an option [203]. Unfortunately, the thermal behavior of isolated polysaccharides may be different from the behavior of polysaccharides within the cell wall in presence of lignin [204,205]. A more common approach is to investigate how the structure-property relationship of wood is affected by variation of the process conditions, such as the temperature and duration [196], the shielding atmosphere [206], the pressure and the relative humidity [163,206] or the wood moisture content during the process [201]. However, while correlations between chemical changes and resulting wood properties can be found easily, it is difficult to validate if they describe an actual causation. Extensive research during the past decades has already aimed at an understanding of the wood protection effect by thermal modification, and even with the help of modern analytical tools, this research will probably continue for some time.

5.6. Future Perspectives for Thermal Modification

The growing market for thermally modified wood is a positive trend in view of an increasing use of environmentally friendly products in the built environment. However, the large number of manufacturers has also resulted in a very broad range of thermally modified wood products that are available on the market, which presents a future challenge. Although all thermal modification processes follow the same basic principle, the properties and characteristics of the thermally modified wood vary greatly depending on the raw materials used or the process technologies and conditions applied. Quality assurance systems exist in different European countries as an effort to accomplish more transparency on the thermal modification market [144]. However, it seems impossible to define characteristic attributes to describe the entire range of thermally modified wood products [207]. Furthermore, the processes also vary in their environmental loads, such as the energy consumption, or the emissions and waste that they emit. Although thermal modification processes are considered as ecofriendly, data to support this is often missing. More information is needed on how different production steps and process factors contribute to the environmental impact of the products. Common calculation rules with defined system boundaries and assessment criteria are then required for a transparent comparison of the different process technologies. This will also set a basis for further process optimization with the aim of reducing the environmental impact required to prolong the service life of wood [145,208].

6. Surface Charring as a Wood Modification Method

6.1. Background: Process for Producing Charred Wood

As wood burns, it turns to char in a series of sequential and overlapping reactions. In the low temperature regime these reactions are similar to thermal modification (Section 5). Charring simply takes the pyrolysis further and the aim is to partially destroy the wood components, reducing them to a carbonaceous residue. Wood pyrolysis and combustion are complex processes, but the char formation itself is a quite well-known phenomenon. The wood components degrade within certain temperature ranges that to an extent depend on wood properties (e.g., species and density) as well as surrounding environmental factors (atmosphere).

Charring has been a historical method to modify wood to enhance durability. There are several examples from around the globe where structures such as fence posts were blackened in a fire prior to use to protect them from biological degradation [209]. The Japanese method of yaki sugi is what most people think of when discussing charring. It involves burning sugi (*Cryptomeria japonica*) exterior cladding or fencing boards to protect the wood from weathering, humidity and rot. Houses with yaki sugi claddings can be found especially in the Western regions of Japan. Lately, the technique has seen a new rise in popularity, partly due to prominent architectural designs (Figure 4). The often-seen term *shou sugi ban* was originally a mistranslation of the term *yaki sugi* (literally burned/charred sugi), but it has rooted itself in the market of surface charred cladding boards produced in the USA and Europe.

Figure 4. A detail of a sauna made from surface charred elements in Espoo, Finland; a restaurant in Helsinki with a flame charred exterior.

Surface charring can be implemented in several ways [210–212]. The traditional yaki sugi is made by tying boards in a triangle, setting fire from beneath and waiting while a chimney effect draws the flame upwards, spreading evenly on the boards. The ties are cut and the fire doused with water. The modern methods usually employ gas-fired ovens or chambers. The modification temperatures tend to be high and the treatment time short, producing a thin, heavily charred surface with a thin transition zone beneath. Several papers have been published on surface modification with a hot plate [213–216]. This type of method offers better reproducibility, as the temperature of the hot plate can be accurately maintained at a desired setting. Similar type of technique has also been used in Japan, mainly for decoration purposes [210].

6.2. How Charring Affects the Wood Structure

Because charring takes place essentially only on the surface, the rest of the wood remains intact. This is the fundamental difference between charring and other wood modification methods. It may be justified to compare the char layer to a coating, although no external products are applied but the "coating" is produced from the wood itself.

The depth of the charred layer depends on the temperature and the modification time. The temperature can be relatively low in contact heating, moderate in traditional fire charring and very high in gas-flame charring, and the modification time is shorter the higher the temperature to avoid excess consumption of wood. Beneath the char is a transition zone (a.k.a. pyrolysis zone or thermally modified layer), that, depending on temperature and modification time, may be anything from lightly dehydrated to extensively thermally modified.

The final properties of char depend on the starting material. Specimen morphology (species, pore characteristics, and size of specimen) exerts the major influence on reaction by controlling flows of reactants and products within the burning zone [217]. The chemical composition, namely lignin content, structure of hemicelluloses, and content and composition of extractives, play an important role.

The starting moisture content may influence the resulting charred surface in several different ways. Gray et al. [218] reported that increased MC improves the porosity, and char yield by about 5% ($0.16\ \mathrm{g\ g^{-1}}$ vs. $0\ \mathrm{g\ g^{-1}}$ moisture content), but in surface charring the quantitative relevance may not be crucial, considering the charred layer is relatively thin. Furthermore, in the same study, above 420 °C the samples released more tar at the expense of solid char formation. The initial moisture content is probably more important in the context of dimensional stability—warping and cupping—of boards during the charring process, as well as evaporative surface cracking and, thus, stability of the surface. However, moisture content may affect the final chemical composition of the char in a manner that can alter the surface properties in service. This kind of fine-tuning of properties is well known in activated carbon manufacturing, but not yet studied in the context of surface charred wood.

Density is one of the most important parameters in charring, as thermal conductivity increases with increasing density—in porous wood the air hinders heat transfer effectively. The other components in generally lighter softwoods, such as resin canals, may change thermal properties of a wood sample significantly. Final char depth tends to be lower for softwoods than hardwoods, partly because the resin spots increase fire spread rate, hence decreasing char yield [219]. The Eurocode 5 [220] gives charring rates of 0.5–0.65 mm per minute in a one-dimensional fire, depending on the type of wood (soft- or hardwood), and type of material (sawn wood, glued panels, or cladding boards). A one-dimensional fire simulates, for example, the burning of wall structures in a house fire and is therefore relatable to charring with fire. The Eurocode estimates are rather simplified and differences marginal and a wider range of 1 to 0.46 mm per minute for very light (200 kg m^{-3}) to very dense (1000 kg m^{-3}) woods has also been suggested [221]. Some authors, however, have found that density has no strong correlation with the burning (and, thus, charring) rate of wood. The present theory is that it might be more related to the wood type and species [222], but it is likely both parameters play an important role. The charring rate may also be presented as a function of wood moisture content [223], or not [224], further highlighting the complexity of the process. Naturally, the grain direction has an effect on thermal conduction, but the only peer-reviewed paper on the subject did not report significant differences between radial and tangential surfaces [215]. Machova et al. [216] studied radially sawn beech but did not measure thermal conductivity nor char layer depth.

In addition to the material properties, it is important to consider the preparation method (Figure 5). The charring rate, directly connected to char depth, depends strongly on the initial surface temperature [219]. In slow heating (as in contact charring) the decomposition proceeds stepwise and results in stable molecules [225]. In rapid heating (gas flame) the macromolecules are torn into volatiles and the arrangement of molecules is disordered. Therefore, the microstructure and surface chemical structure differ from char formed by slow heating [226,227]. Rapid heating produces much more volatiles than slow heating [225], thus reducing relative solid yield, and also increases the number of char fissures [228] that can significantly alter the pyrolysis result in the transition zone, namely by providing pathways for flow of reactants [217]. However, higher temperatures result in char with higher fixed carbon content than chars prepared at lower temperatures [212]. This "quality" is connected to the stability of the char surface during use.

Figure 5. From left: Surfaces formed by compressive contact heating of pine at 260 °C, contact heating of spruce at 320 °C, gas flame charring of spruce (M. Kymäläinen).

6.3. Dimensional Stability, Hygroscopicity, and Absorption of Surface Charred Wood

Charred surfaces may be used in several design applications both in- and outdoors. Relevant surface properties therefore include wear resistance, dimensional stability, and surface wettability. Because char is rather inert both chemically and biologically, it is presumed that the overall performance is determined by the thickness of the carbonized layer [211,214,229]. In general, char is porous and friable, and therefore is not very resistant to mechanical wear caused by handling, installation, use, and abrasion from rain and wind. However, certain wood species can form a compact char later with little cracking depending on the density and lignin content [230].

Dimensional stability of surface charred wood has not been thoroughly reported in literature but cupping towards the charred side is normal due to a strong temperature gradient [212]. Both dimensional stability and hygroscopicity correlate strongly with method of charring—namely peak temperature, but also modification time [213]. For example, regarding surface wettability, wood charred at moderate temperatures on a hot plate exhibits a high, steady contact angle, whereas high temperatures or flame charring increase the angle only momentarily because of increased porosity and cracking [213]. The surface is prone to liquid water absorption, but adsorption/absorption of water vapor is reduced due to compositional modifications, namely lignin cross-linking, increased crystallinity, and reduced number/accessibility of hydroxyl groups [214,231]. Char generally exhibits the same microstructure as the starting material, which facilitates liquid water movement within the tracheids, vessels, and pores. A flame charred surface tends to be highly cracked, but there has been indication that absorbed liquid water may also evaporate easily if the cracks do not penetrate the char layer—the surface “breathes” and therefore the water is also quickly evaporated [227,232]. If the cracks run through the modified layers it is possible that absorption of water molecules into cell wall of unmodified wood takes place. Cracking through the char layer may explain the contrasting results obtained by Okamura et al. [211], where desorption of charred sugi was reported slower than for unmodified wood.

Char cracking is a typical thermal shock process induced by unbalanced shrinkage [228]. Zicherman and Williamson [217] suggested that cracks are initiated at 200–270 °C because of mechanical stresses caused by uncontrolled drying in the transition zone and simultaneous degradation of the highly stressed surface, as well as uneven cooling after exposure. The transition zone coincides with areas of high stress development due to material property differences of char and whole wood and causes longitudinal cracking. Tangential surfaces tend to crack more, and as reported by Machova et al. [216], both cracking and surface roughness were reduced for radial samples compared to tangentially cut samples charred between 200 and 400 °C. It is likely that also tangentially cut defect-free wood that has been dried to 0 g g^{-1} moisture content would withstand charring without warping or cupping, and therefore also liquid water sorption without severe secondary cracking, but there have yet been no published studies on this.

Experimenting with several different modifications and wood species, Kymäläinen and Dömény [232] found that dimensional changes of flame charred samples associated with water sorption are reduced in comparison to contact charred and unmodified samples. Contact charring at low to moderate temperatures creates a hard, smooth surface that is easy to handle and does not stain but may crack more in use [227,232]. This was shown also in [213], where water floating of contact charred samples resulted in severe cupping and cracking that was likely caused by high internal stresses originating from the process. The samples had been charred with additional pressure to avoid cupping away from the heated plate during modification and, therefore, formation of an uneven surface. Some pressure is likely to be mandatory in contact charring of entire boards, as kiln dried boards are rarely defect free but exhibit varying degrees of warp, twist, and cup. To obtain an evenly charred surface, the boards need to be pressed against the heated surface. Finding the correct pressure is therefore vital in terms of adequate surface quality as well as minimal formation of compressive stresses.

6.4. Biodeterioration and Weathering

Surface charred boards were historically used outdoors as claddings or fencing. The exterior stresses include ultraviolet (UV) radiation induced photodegradation, rain, humidity and temperature fluctuations that cause dimensional strains, mechanical/abrasive stress from wind and wind-blown particles, as well as biological agents such as insects, mold, and decay fungi. As far as biological degradation is considered, the original yaki sugi is thought to withstand fungal decay very well. The same assumption is behind the traditional practice of burning the grounded ends of fence stakes. However, the experiments made by Okamura et al. [211] using *Pleurotus* sp. showed that the surface may still be colonized by fungi. Similar results were reported by Kymäläinen et al. [233] after torrefied wood and charcoal field storage experiments, where naturally occurring fungi were reported to colonize the material, despite soluble sugars mostly being depleted in the manufacturing process. Studies published on commercial [234] and contact heated samples [216] have been rather inconclusive, but wood species seems to affect the decay rate [234].

While limited data exist on the fungal degradation of charred wood, the material should likely not be used in ground contact. Sufficient distance from the ground also reduces mechanical wear from splashing water and allows the structure to ventilate properly, which is essential for practically all wooden structures. Everything considered, there are degrading organisms even for lignite and hard coal [235], so complete protection of wood may be impossible without biocides. In practical use the relevant organisms are at the very least greatly hindered by removal of soluble substances. Ebner et al. [212] noted an increase in pH after charring, which affects the growth of common decay fungi negatively. Given that char formation begins at above 300 °C, the degradation of wood components is already very far at this point. However, cracking through the surface and transition zone may create paths for spores and hyphae to colonize unmodified wood layers.

In addition to biodeterioration, wood is also susceptible to damage by UV radiation in outdoor applications. The most important component to consider in the context of weathering is lignin, which is the only structural polymer to absorb UV radiation [236–238]. In a coating, protection from UV may be achieved with stabilizers, UV-absorbers and antioxidants, but in char the thermally degraded components contribute. Lignin pyrolysis forms aromatic products and reduction and condensation of structural units occur [239]. Because of these changes, there has been speculation that the modified lignin would not absorb UV-light to the same extent as in unmodified wood. Kymäläinen et al. [240] analyzed contact charred spruce panels after two years of natural weathering and reported degradation of lignin by the use of FTIR. However, the panels in the experimental wall still maintained their original appearance without much visible weathering damage. Recently, Kymäläinen et al. [241] reported the presence of highly stable char structures in flame charred wood after one year of natural weathering by using Raman spectroscopy. Still, more research is needed to understand the UV stability of charred wood. Several factors contribute, but it is likely that the thickness of the char layer dictates the final stability towards weathering of the surface charred wood. Visible light only penetrates the surface down to about 200 µm [238] and degraded components take time to wash off. The thicker the char layer, the longer the underlying wood remains intact.

6.5. Current Knowledge on Charring as a Form of Wood Modification

Peer-reviewed studies on surface charring as wood modification method are scarce. This lack of scientific knowledge has been identified also in Japan, which may be considered the home of using fire to protect wooden surfaces. Okamura et al. [211] suggested that yaki sugi has been such a common technique that it did not need to be recorded in encyclopedias or researched in a scientific context. There are some studies related to fire-safety of buildings with traditional materials [242], but the descriptions on the manufacturing techniques, methodology and service life are practically non-existent. Recently, Ebner et al. [212] have delved into the subject of traditional manufacturing methods but utilizing Austrian wood species. The results have been very similar to those reported for sugi by Okamura et al. [211], regarding temperature, holding time and final char layer thickness.

As discussed previously, char layer thickness seems vital for the durability of a charred surface. Because charring proceeds at a known rate, what can be altered is the modification time, method, or environment. Tran and White [243] quote several studies placing the char formation temperature between 280 and 350 °C. However, for practical purposes the difference between these temperatures is not large since the thermal gradient before the char front is steep. The char line is therefore usually considered to be located at the 300 °C isotherm [221], and the carbonization is almost (80%) complete between 400 °C to 600 °C [244]. Charring with a flame is difficult to control, regardless of the technique. Using the traditional method, average surface temperatures are somewhere around 400–500 °C [211,212]. Using gas flame, the maximum can be well over 1000 °C. If the surface temperature continues to rise above 500 °C, secondary reactions (visible as glowing) within the char will create combustible products on the expense of the solid, and at above 1000 °C carbon is consumed as fast as the reaction zones penetrate into the wood [225]. Moreover, once charring reactions are completed, the residue will turn to ash, that further catalyzes secondary reactions on the surface where tar particles are decomposed into light organics and water instead of forming char [218].

Contact charring has been proposed [205–207,245] as a viable modification method to facilitate a longer modification time and a careful control of temperature. If the contact surface is sufficiently compressed against the heated plate, the vapors streaming from the wood exclude oxygen [225,243], therefore delaying combustion even above combustion temperature. Longer modification time also promotes the formation of the transition zone (Figure 6). It has been hypothesized that the thermally modified transition layer is of importance in the stability of the surface charred product [211,214]. In a flame charred wood, the transition zone is only a few cell layers thick because of the low thermal conductivity of wood [217]. It is to be noted that this zone appears to be critical in crack propagation and fissure formation [210] which directly affects the structural integrity of wood. Contact charred wood pieces may exhibit a transition zone with a thickness of several millimeters. The contribution of this zone to the severe cracking reported after sorption and weathering experiments requires further study. As mentioned, controlling initial moisture content may be crucial to eliminate the need for compression/weight, and therefore reduce at least some of the stresses, but the practicality of oven-drying is another matter. As charred wood is not meant for load-bearing applications, and therefore does not require maximal structural integrity, the transition zone mainly affects sorption, and may also have implications on fungal growth as mentioned in the previous section.

Figure 6. Transition zones of *Alnus glutinosa* contact charred at 320 °C (**up**) and flame charred (**bottom**), microscope image of transverse surface of spruce (*P. abies*) contact charred at 300 °C (bar 2 mm).

The effect of atmosphere could be important regarding consistency of the charred product. Oxidative reactions consume char especially at low heat flux levels [243]. At low temperatures (below 300 °C), increasing the oxygen concentration from 2 to 21% had no significance, but temperature was the main contributor [246]. In inert conditions, active pyrolysis is reached at temperatures above 300 °C, while in presence of air, the exothermic point may be reached already at about 240 °C [225]. Candelier et al. [205] concluded that under vacuum the degradation was slower than under nitrogen: a vacuum removes all volatile products, restricting secondary reactions, while a nitrogen atmosphere increases the lignin and carbon content of the residue. Kampe and Pfriem [229] published a short note on flame charred spruce, describing an experimental device utilizing gas flame under a flow of nitrogen to avoid ignition. Char depths were not reported, but other results seem comparable to published studies. Theoretically, the atmosphere could be interesting in the context of the before-mentioned fine-tuning of char properties. In practice the use of gases such as nitrogen may be less useful, especially when taking into account that flaming/sufficient surface pressure excludes air from the surface. This results in little or no oxidation in any case, thus preserving the formed char layer.

6.6. Gaps in Our Understanding of Charring as a Wood Modification and Future Perspectives

Although the practice of burning wood surfaces has existed for many years, there is still a great need for further research. Optimal methods for producing charred wood surfaces are yet to be published. As discussed, there are several factors that affect the charring process of wood. This makes it difficult to provide exact instructions on manufacturing, since different wood species may require different recipes—in terms of modification method, peak temperature, modification time, moisture content, etc. Furthermore, the natural durability of the starting wood material and how the charring process affects this durability may be an important factor that could describe discrepancies in the literature about the durability of the charred wood product.

In developing protocols, it is important to determine what is desired from the product. What is the required service life, and what sort of maintenance is needed to reach this? A traditional yaki sugi façade, for example, is not expected to stay the same throughout its lifetime. The much-quoted service life of up to 80 years without maintenance is indeed the service life of the façade, but after this time it will look very different. The surface will keep its black appearance for some time (depending on manufacturing method, purpose of use and exposure site), but as the surface weathers and washes off, the unmodified layers will be revealed. The result is a mix of washed out, greying, and black charred parts, especially in the latewood sections and knots, as well as in areas protected from direct sunlight/rain. This kind of natural aging is a part of the concept of *wabi sabi*, which celebrates the beauty of imperfection and transience. A structure made of natural materials is expected to wear, fade, and be true to its origin.

However, western consumers most often require consistency and therefore suppliers tend to deliver their products with a coating and instructions to recoat at even intervals (though exceptions exist). Coating also reduces sooting of flame charred surfaces, making them easier to handle and clean. On the other hand, coating with an inorganic layer negates some of the benefits of using charred wood as an organic, natural material. Additionally, the maintenance requirements become similar to non-charred products.

Research is needed to stabilize the surface in a manner that would eliminate maintenance needs, improve mechanical wear resistance, and reduce staining. This would promote the organic nature of the product and reduce the life cycle costs and environmental loads. Using wood that has been impregnated with organic resins, or otherwise modified may be an interesting subject, although cost effects and actual environmental benefits should be carefully considered. Additives, such as carbon black, could also be used, but the renewability of the source material should be considered; for example, carbon black was recently reported to have been produced from biomass pyrolysis oil [247].

The surface of flame charred wood may also be brushed to remove the most friable char, which makes it easy to handle, but this again changes the properties of the product. As mentioned, the char layer thickness is an important factor in durability. By brushing, however, it is possible to alter the appearance of the product by varying the brush (bristle, metal) and brushing depth, and, also, facilitates further surface treatments. For brushed surfaces, Kymäläinen [227] reported fading of color after weathering, that was similar to contact heated wood samples, but sorption behavior and dimensional stability was closer to flame charred samples [232]. Because of the fading color, exposure to sun and rain may not be recommendable, but there are several interesting uses indoors or in sheltered exterior locations.

Some manufacturers have recently begun marketing flame charred acetylated and thermally modified wood. The long-term durability is yet unknown, but it is likely the service life predictions given for the raw material hold true also for surface charred variants. As the surface slowly degrades during use, the original yet modified surface is revealed and most likely withstands as long as the non-charred counterparts.

7. Other Polymerization Methods for Wood Modification

7.1. Process for Producing Resin-Treated Wood

Treatments with water-soluble thermosetting resins have been intensively studied for both solid wood [248–251] and wood-based panel [252–255] applications during recent decades. First attempts to use thermosetting formaldehyde resins for wood modification purposes were recognized in the middle of the 20th century [256,257]. In particular, low molecular weight phenol formaldehyde (PF) and melamine formaldehyde resins (MF) or cyclic N-methylol compounds such as 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) were used to modify wood [258]. Since treatments with formaldehyde-based thermosetting resins may change the wood chemistry by polymerization reactions, they constitute an “active modification”, which comprises two steps: (1) full volume impregnation of wood with the chemical diluted in a solvent under vacuum and/or pressure and (2) reaction and fixation of the chemical compound in the wood structure.

Principally, PF, MF, or DMDHEU monomers and oligomers can be impregnated in any proportion with water as solvent, which swells the wood and by that enables resin molecules to diffuse into the cell wall along a concentration gradient [259–261]. The pH of the impregnation solutions varies depending on the resin and catalyst used and might be neutral to slightly acidic (DMDHEU [262]) or alkaline (MF, PF [255,263]). After impregnation, the polymerization and reaction to macromolecules are induced by heat curing, which removes the solvent (water) and creates methylene bridges or ether bonds between the resin molecules (Figure 7). Temperatures of 120–140 °C have been suggested to achieve an adequate fixation and complete reaction of the resins [248,260,264]. Depending on the pH level of the monomeric or oligomeric resin solution, the acidity of wood [264,265] and in some cases initiators [266] may accelerate the polymerization of the resin molecules during heat curing.

To obtain the best performance from the modified wood, a uniform distribution of fixated chemical is needed. For this, and to minimize undesired formaldehyde emissions from treated wood blocks, curing process conditions (temperature, duration), especially moisture conditions [251,261], appear crucial for the polymerization and fixation of resin molecules [248,262,267]. Since formaldehyde emissions may originate from free, non-reacted hydroxymethyl groups (-CH_2-OH) or non-reacted resin compartments in the wood-polymer matrix [255,264,268], they correlate positively with the applied resin concentration and negatively with the degree of curing [262,268]. Nevertheless, an increase in formaldehyde emissions compared to untreated wood blocks is an inevitable with PF, MF, or DMDHEU modifications [268].

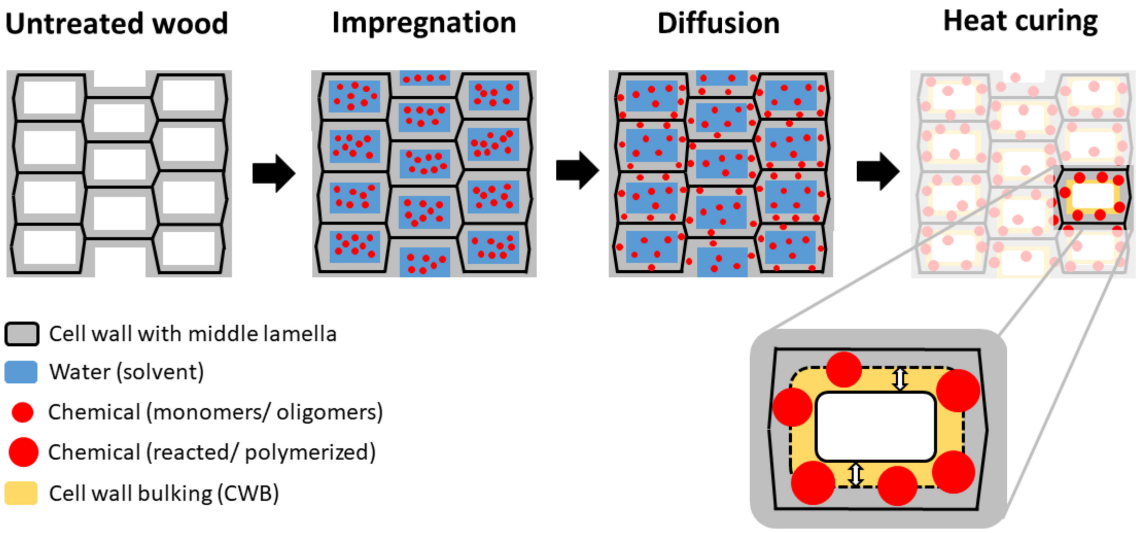

Figure 7. Schematic illustration showing the effects of chemical wood modification on cellular level from impregnation with a chemical diluted in a solvent (e.g., water) to drying and curing of the monomeric modification reagent causing a cell wall bulking (CWB).

For curing commercially sized wood, which is impregnated with aqueous solutions of thermosetting resins, a superheated steam atmosphere has been recommended [248,249,251]. Superheated steam creates a uniform distribution of well-fixated chemical, low prevalence of drying failures, and formaldehyde emissions that do not exceed legal limits (e.g., [248,262,268,269]). Currently, impregnation modifications with thermosetting resins have been successfully applied to permeable softwood species such as Scots pine (*Pinus sylvestris* L.) and Radiata pine (*Pinus radiata* D. Don) sapwood [248,270]. Recent research has focused on transferring these developments to a variety of hardwood species [255,260,268,271,272].

7.2. Chemical Reagents and Its Modes of Reaction

Thermosetting resins used for wood modification purposes are characterized by their molecular weight (size) and polarity, which allows to enter the macropores (cell lumen) but also the nanopores of the water-swollen wood cell wall [255,262,273–277]. Similar to other impregnation modification techniques, treatments with thermosetting resins create a bulking effect (CWB), as the cell wall is set in a permanent swollen state when resin molecules polymerize within the cell wall (Figure 8). Usually, the CWB is expressed by the percentage increase in dry dimensions after the resin treatments or by R_{bulk} in m^3/m^3. However, when utilizing impregnation solutions with an alkaline pH (e.g., MF), removal of cell wall constituents may occur which counterbalance the CWB effect of the resins. Thus, measuring macroscopic changes in wood dimensions may not reliably express cell wall diffusion of resin molecules [261].

Heat curing removes the solvent (water), and also results in polymerization of resin monomers and oligomers. The polymerization causes the resin to become insoluble in water and irreversibly fixed in the hierarchical wood structure. Besides self-condensation of adjacent resin molecules via methylene bridges or ether bonds, co-condensation between DMDHEU resin molecules and the polymeric cell wall constituents (i.e., hemicelluloses and amorphous cellulose) may occur [278,279]. Nevertheless, recent studies found indications but no evidence for covalent bonds between DMDHEU monomers and accessibly hydroxyl groups (co-condensation) of the cell wall polymers [265,266,280]. In contrast to acetylation, which is a single displacement reaction with a 1:1 substitution of acetyl groups for wood hydroxyl groups, the reaction mechanisms of thermosetting resin monomers in wood are manifold and even hard to predict and prove. For DMDHEU monomers, it remains unclear to which extent and proportion self-condensation and co-condensation of the resins occur in impregnated wood specimens [280]. On the other hand, MF and PF resins are supposedly fixated inside the wood structure primarily by mechanical mechanisms (i.e., entanglement) when forming macromolecules via self-condensation [255,261,263,281,282]. Basically, the morphology of polymerized resin and the curing reaction depend on distinct factors, including the reactive functional groups, molar ratios of the reactants, the temperature and moisture conditions during the reaction, and the pH [261,262,265,283–285].

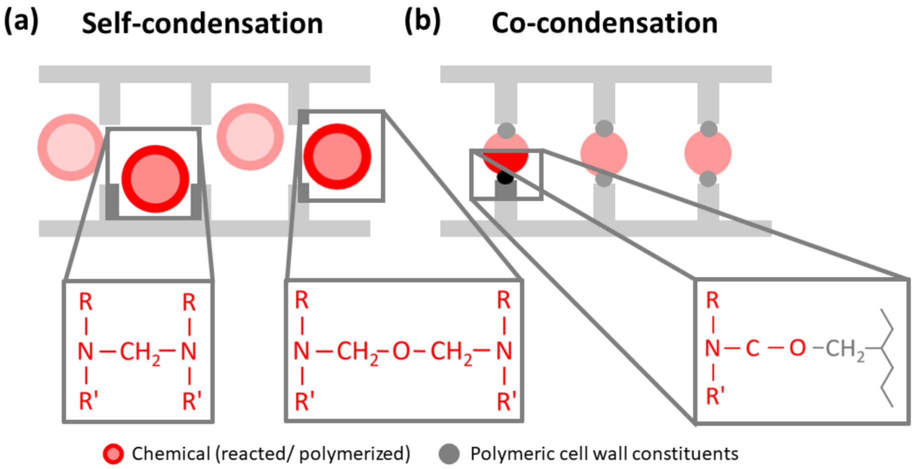

Figure 8. Potential reaction mechanisms of DMDHEU monomers on cell wall level derived from reaction mechanisms proved in cellulose-based fabrics (**a**) self-condensation (**b**) co-condensation [277].

When operating wood modification technologies with DMDHEU, MF, or PF resins, formaldehyde emissions appear to be inevitable. For this reason, ultra-low formaldehyde and formaldehyde-free chemistries have been considered for wood modification. Specifically, methylated and diethyleneglycolated DMDHEU (mDMDHEU) and zero-formaldehyde N,N′-dimethyl-4,5-dihydroxyethyleneurea (DMeDHEU) were studied for modifying wood [286,287]. Compared to DMDHEU, mDMDHEU molecules cause similar CWB but lower formaldehyde emissions during the polymerization reaction, which occur at a lower monomer reactivity. The latter is attributed to chemically bonded methyl groups or diethylene glycol groups (DEG), which must split off prior polymerization reactions can occur [288]. Utilizing DMeDHEU monomers resulted in significantly higher CWB compared to the N-methylol compounds (DMDHEU, mDMDHEU), whereas the fixation decreased due to steric hindrance and lower reactivity of the ring hydroxyl groups (-OH) in the 4,5 position, in comparison with the hydroxymethyl groups (-CH_2-OH) of the N-methylol compounds.

7.3. Experimental Evidence on the Changes in Material Properties by Resin Treatments

Since the late 1990s, investigations on the performance of resin treated wood have been subject of a number of scientific publications and theses [248,249,251,255,262,263,268,289–295]. Based on the extensive laboratory studies, it can be stated with certainty that treatments with low molecular PF, MF and DMDHEU improve the biological durability, dimensional stability, weathering performance and hardness of solid wood and wood-based panels. Principally, the property improvements correlate positively with the chemical loading, being expressed by the mass gain that originates from the added chemical [251,255,262,268,272].

In particular, a large number of laboratory studies analyzed the resistance to degradation by decay fungi and showed that treatments with thermosetting resins achieve resistance levels that correspond to the European durability class (DC) 1 (“very durable”) to 2 (“durable”) [248,255,268,296]. Nevertheless, only a few field test studies are available for resin treated wood [297], which validate the results of short-term laboratory decay tests [298]. Besides an increased resistance against decay fungi, resin treatments diminish even the attack by marine borers [299,300] and subterranean termites [301]. During accelerated, artificial and outdoor weathering, UV degradation of cell wall components, colonization and growth of blue stain and molds and moisture fluctuations were reduced by modifications with thermosetting resins but still apparent and not fully prevented [251,252,255,302,303]. As a key objective of chemical modification technologies, moisture-induced dimensional changes of the cell wall may be reduced up to 70% by resin treatments [34,251,255,262,268,304,305]. Similar to other impregnation modification techniques, the later was attributed to a CWB effect, which limits the moisture variability rather than restrain swelling directly [280]. Elasto-mechanical properties may be affected to different extents. While surface hardness [251,262,268,272] and compression strength [248,268,270] increase with increasing modification mass gain, bending strength and modulus of elasticity were almost unaffected by resin modifications [248,252,253]. Nevertheless, a remarkable loss in resistance towards mechanical, dynamic impacts appeared as an inevitable side effect of treatments with formaldehyde thermosetting resins [251,255,286]. More detailed information on the property profile of wood treated with MF, PF, or DMDHEU were recently summarized by Bicke [255], Emmerich et al. [34], and Behr [251], providing a valuable overview of these technologies.

7.4. Studying the Mode of Action of Thermosetting Resins

Recent work has focused on understanding how thermosetting resins affect wood properties. Similar to other impregnation modification techniques (e.g., acetylation), it is clear that an increased decay resistance is not related to any fungicidal effect. Ringman et al. [55] suggested for DMDHEU treated specimens that micropore blocking, a reduced number of accessible hydroxyl groups and a reduced cell wall moisture content respectively, were the key reasons for a reduced degradation rate of decay fungi. However, more in-depth studies on the mode of protective action against decay fungi for resin treated wood are needed. For instance, it remains unclear, whether the decay rate may change during prolonged incubation with decay fungi, thus if an improved decay resistance measured during standardized, short-term decay tests might just be a matter of delayed degradation processes.

In the past, decay resistance in resin treated wood was often attributed and correlated with the chemical loading expressed by the modification mass gain [262,268,306]. According to Emmerich et al. [287], it is the cell wall deposition of the resin molecules (CWB), i.e., the chemical location on cellular level, rather than the chemical loading of a piece of wood itself (e.g., modification mass gain) that determines the resistance against fungal decay. Hence, the CWB was suggested as the important parameter for the decay resistance in resin treated wood. This was clearly shown when comparing treatments with DMDHEU and DMeDHEU. During decay tests with basidiomycete monocultures, both resins increased the durability of Scots pine sapwood (*Pinus sylvestris* L.) from European durability class 5 (“not durable”) to durability class 1 (“very durable”), even though the modification mass gain of DMeDHEU treated specimens measured one third of DMDHEU treated specimens, but identical CWB levels [287]. Emmerich et al. [307] mimicked wood products with a homogeneously treated shell and an untreated core zone by a laboratory set-up. This study proved that hyphae of both white- and brown-rot fungi are able to grow through resin treated substrates without causing severe decay, but after that degrade the untreated core zone. This emphasized that a reliable protection against wood-destroying fungi by resin treatments requires a uniform distribution of fixated chemical throughout treated wood specimens. Necessarily, this fact limits the efficacy of treatments with thermosetting resins to permeable wood species.

Studies on the water vapor sorption, hydroxyl accessibility and swelling behavior of MF [308] and DMDHEU [280] treated wood gave indications on the reaction mechanisms of both types of resins. Potentially, these mechanisms might be self-condensation of adjacent resin molecules via methylene bridges or ether bonds, or co-condensation between resin molecules and polymeric cell wall constituents. Yet it appeared nearly impossible to identify and differentiate between these two types of chemical reactions when resin molecules react inside the wood structure. However, the type of reaction mechanism directly impacts water vapor sorption in resin-treated wood. On one hand, resin treatments may block accessible hydroxyl groups of the cell wall polymers by CWB effects or co-condensation reactions with resin molecules and decrease the water vapor sorption. Conversely, resin structures may deposit additional hydroxyl groups in the wood structure, which leads to an increase in water vapor sorption. For these reasons, it is difficult to differentiate whether sorption sites (hydroxyl groups) are provided by the polymeric cell wall constituents (e.g., cellulose) or polymerized resin structures. Finally, the extent of self-condensed resin molecules in case of DMDHEU treatments strongly depends on the location of the cured resin, thus, whether it is deposited in the cell lumen or the cell wall [280]. More studies are required to understand the cellular level chemical changes by resin treatments and their relevance for the performance of treated wood blocks.

Considering the chemical constitution, it is expected that the degree of co-condensation between resin molecules and cell wall polymers decreases in the order of DMDHEU, mDMDHEU, and DMeDHEU [279]. In reverse order, treatments with DMeDHEU caused much higher CWB compared to N-methylol compounds (DMDHEU, mDMDHEU) but less reductions in dynamic strength properties. From its chemical constitution, treatments with DMeDHEU expected much lower degrees of co-condensation compared to N-methylol compounds. Therefore, it was suggested that covalent bonds between resin molecules and polymeric cell wall constituents plus the flexibility of the cured resin were crucial factors for maintaining dynamic strength properties [286].

7.5. Future Perspectives for Resin Treated Wood

Treatments of wood with thermosetting resins such as PF, MF, and DMHEU have been intensively studied and processes developed up to pilot scale. However, only small amounts of wood treated with PF are available on the European market, while MF and DMDHEU technologies are near industrial production, with some level of commercial activities in Germany, New Zealand, and China (<1000 m^3 annually).

However, there are still unanswered questions relevant for an industrial implementation and questions regarding the mode of action of thermosetting resins in wood. This includes even the reaction mechanisms that lead to a fixation of resin molecules inside the hierarchical wood structure, which are complex rather than clear and defined.

Especially MF and PF resins tend to alter their morphology by self-condensation during storage, which may severely affect their shelf life and ability to diffuse into the wooden cell wall and generate a cell wall bulking effect [255]. Thus, research has been initiated on the reusability and ageing behavior of resin molecules.

Resin deposits inside the cell lumen were shown to not significantly improve the material performance, but rather involve adverse side effects such as an increased moisture uptake [280]. Hence, identifying the molecule concentration inside impregnation liquids at which resin molecules start to deposit in the cell lumen rather than the cell wall, would further contribute to make treatment processes more economically feasible.

Formaldehyde-free N-methyl compounds (DMeDHEU) showed promising perspectives to improve the decay resistance and wetting ability of wood. However, the latter were associated with a reduced fixation compared to formaldehyde containing resins. Even though wetting ability and resistance indicating factors from laboratory trials enabled a forecast of a high biological durability for respectively treated materials outdoors, further field test studies are required to prove the performance in real life situations, thus validate the suitability to substitute formaldehyde containing resins [280].

8. Wood-Based Functional Materials

In the past the main motivation for wood modifications was to tackle the intrinsic drawbacks of wood, including methods to increase the dimensional stability, enhance UV stability or to equip wood with improved fire retardancy. However, within the last ten years there has been a fascinating increase in projects, works, efforts and publications dealing with the development of novel wood-based functional materials [25,309].

The main driving forces for this development are twofold. Firstly, there is a general focus in materials science to develop functional high-performance materials based on renewable resources. Secondly, wood as a material itself has gained tremendous interest in materials science. Wood possesses a unique anisotropic hierarchical porous structure from the nano- to the macroscale that can be extremely valuable for the development of functional materials when equipped with materials including polymers, nanoparticles, metal-organic frameworks, or metals [310–312].

In principle, there are two main approaches for the development of wood-based functional materials. Wood can either be directly utilized for functionalization treatments or the wood-inherent cellulose scaffold is first obtained by structure-retaining delignification processes prior to the functionalization treatments. These top-down processes are fundamentally different from common bottom-up processes, for example 3D printing, where cellulosic materials (crystals, fibers) are used to build up 3D materials. The advantage of directly using wood is to avoid disassembly and reassembly processes. Of course, the tremendous progress in 3D printing offers an enormous range of operating conditions, providing excellent flexibility in accessible shaped structures. This could be partly compensated by recent developments of utilizing cellulose scaffolds, as these scaffolds are shapable in their wet state and allow the fabrication of complex geometries [313].

In materials science, the non-homogeneous nature of wood is sometimes classified as a disadvantage. For example, the native density of xylem tissue (wood) in trees can range from 100–1200 kg m^{-3}. However, this heterogeneity can be turned into an advantage by carefully choosing the wood species for the targeted application. For example, in the case of transparent wood, low density species are the wood of choice whereas for membrane application wood species with large vessels should be applied [310,314].

In this section we provide a brief overview of recent developments in the field of wood-based functional materials for novel applications. It is beyond the scope of this section to provide a complete overview of this vastly growing research field and the reader is referred to detailed recent reviews [310–313].

8.1. Transparent and Multifunctional Transparent Wood

Wood itself is not transparent due to its strong absorption and light scattering. Light absorption is heavily dependent on the chemical constituents, in the case of wood this involves lignin and other chromophores. Light scattering in wood is a result of the porous structure and the non-homogeneous distribution of wood constituents. Hence, to obtain transparent wood, the initial step comprises the removal of lignin or its decolorizing, which results in a white material that is opaque due to the different refractive index of carbohydrates and air. In a second step the wood scaffold is then impregnated with a refractive index matching polymer (Figure 9).

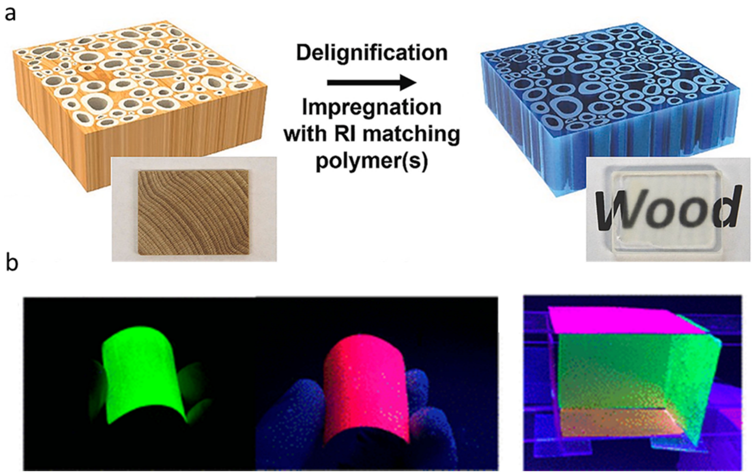

Figure 9. (**a**) Preparation of transparent wood, based on delignification of wood followed by filling

with index-matching polymers. Reprinted with permission from [315]. Copyright 2016 John Wiley and Sons. (**b**) Luminescent wood obtained by functionalization with quantum dots emitting red and green colors. Reprinted with permission from [316]. Copyright 2020 American Chemical Society.

The basic idea of transparent wood goes back to initial works by Fink et al. in 1992 [317]. Back then the goal was to utilize transparent wood for optical microscopy. Around 25 years later this approach was picked up again by two independent research groups to develop and fabricate novel wood-based transparent materials for engineering applications [315,318].

Since these reports by Bing and Berglund et al. [315,318] considerable progress has been made regarding the material. For example, lignin-retaining wood was developed, bio-based polymeric systems were introduced for refractive index matching and targeted interface modifications between cellulose matrix and the cellulose scaffold improved the overall transparency [319–321].

Of course, transparent wood does not possess an intrinsic optical advantage by itself, but in its inherent anisotropic structure. These attractive anisotropic optical properties result in a haze with broad scattering angles, which could be interesting in smart building applications for designing light transmittance and solar cells. In addition, transparent wood possesses lower thermal conductivity compared to glass, high impact strength, and low density [310,322,323].

Transparent wood can be further combined with other functionalizing agents, such as nanoparticles, quantum dots, lasing dyes to obtain for example luminescent wood. Potential application fields comprise lasers, electroluminescent devices and LED lighting (Figure 9b) [316].

8.2. Energy Harvesting Wood-Based Materials—Triboelectric Wood Nanogenerators

Another emerging research field of wood-based functional materials is the utilization of wood for energy-related applications, for example supercapacitors or batteries. Here we focus on a recent development in the field, namely the development of energy harvesting wood-based materials including wood nanogenerators [311].

The general effect of generating electrical charges when pressure/mechanical forces are applied or its adverse effect, the development of a mechanical strain upon application of electrical bias are well-known phenomena, which were discovered in 1880 by the Curie brothers for different crystals [NC1, NC2] {Curie, 1880 #2340;Curie, 1881 #2341}. Initial studies on "electromechanical coupling" of wood and wood materials dates to the 1940s and the reported piezoelectrical effects were small, around 1/20 of that of a quartz crystal [324].

Within the last couple of years research on electrochemical effects of wood and related biomaterials has gained interest due to the potential in manifold application scenarios including energy harvesting, sensors, or actuators. Utilizing wood or other wood-based materials in these scenarios instead of synthetic polymers or ceramics would have the advantage of sustainability, low density, excellent mechanical properties, and its relevance as building material. However, to be applicable, the achievable electromechanical coupling must be significantly increased. Recently, Sun et al. [325] tackled these shortcomings by simple delignification approaches to enhance the electrical output. Delignification of balsa wood, either by a chemical process or by a biotechnological treatment utilizing a fungus, resulted in a "wood sponge" equipped with a spring-like microstructure (Figure 10). The combination of multiple of these elements resulted in an electrical output that was sufficient for small electronic devices. Despite these results, it remains questionable if this type of materials will be competitive for energy harvesting applications in the future [325,326].

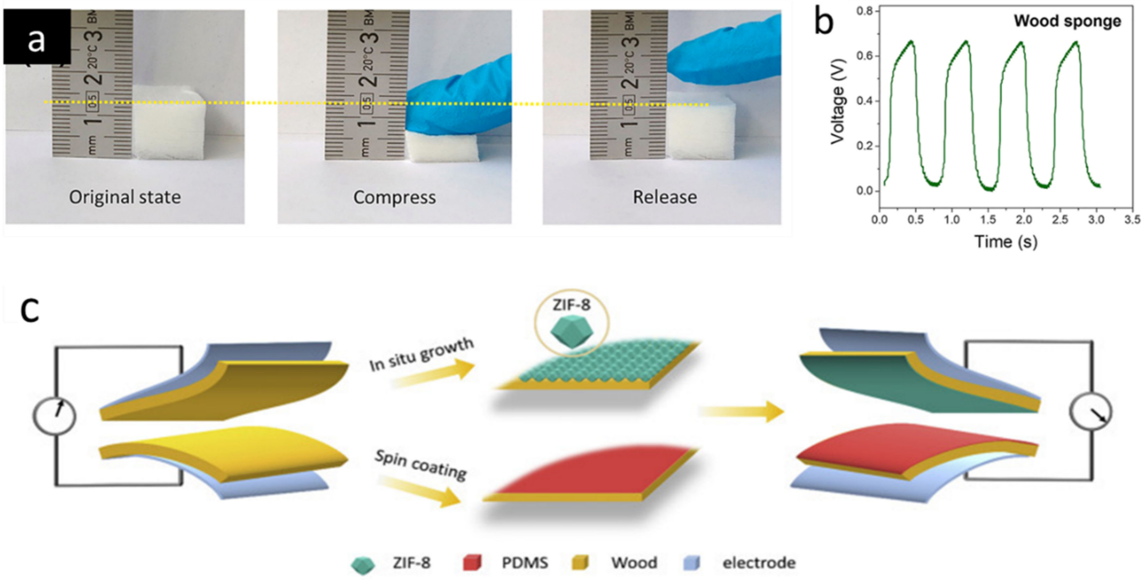

Figure 10. (**a**) Compressibility of wood sponges obtained by delignification of balsa wood and (**b**) the corresponding piezoelectrical output. Reprinted with permission from [325]. Copyright 2020 American Chemical Society. (**c**) Functionalization of a wood-based triboelectric nano-generator [327].

A potential alternative is the utilization of triboelectricity. To boost the required polarizability of the wood, different functionalization treatments have been developed. For example, wood was modified with metal organic frameworks and polydimethylsiloxane. This functionalized wood possess potential for the design of the next generation of sustainable power supplies in smart buildings [327].

8.3. *Wood as Filtration Membrane or Flow through Microreactor*

Considering the multi-hierarchical structure of wood based on aligned microchannels it is obvious that wood represents a promising material for different types of membrane- and flow through applications, such as filtration of catalytic processes [311].

Natural xylem itself possesses filtration properties for particles with a size cut-off ranging from a few nanometers to around 500 nm, depending on the tree species. Boutilier et al. [328,329] utilized pine sapwood membranes (thickness ca. 2.5 cm) to reduce turbidity and remove bacteria from wastewater by pressure-driven filtration. The limitation of this type of wood membrane is the drastic reduction of the flow after drying. Upon drying the pits close and the fluid pathways are blocked [328,329].

Regarding this topic, in 2021 Ramchander et al. [330] provided a thorough study of the relevant main parameters when using xylem for filtration, such as operation stability, fouling, thickness, and flow resistance. For retaining the flow in dried wood filters, a process based on swelling followed by dehydration with ethanol was described.

Wood can also function as a natural microreactor due to its natural microchannels along the growth direction, providing a high-efficiency liquid transportation corridor. Hence, it provides a unique scaffold material for biocatalysis or other catalytic applications. Tu et al. [331] recently reported the fabrication of a structured bimetallic silver-palladium catalytic native wood microreactor for continuous hydrogen generation (Figure 11). It was shown that wood microreactors possess excellent mechanical properties, and high mass transfer efficiency, which offer manifold applications in the energy-water nexus.

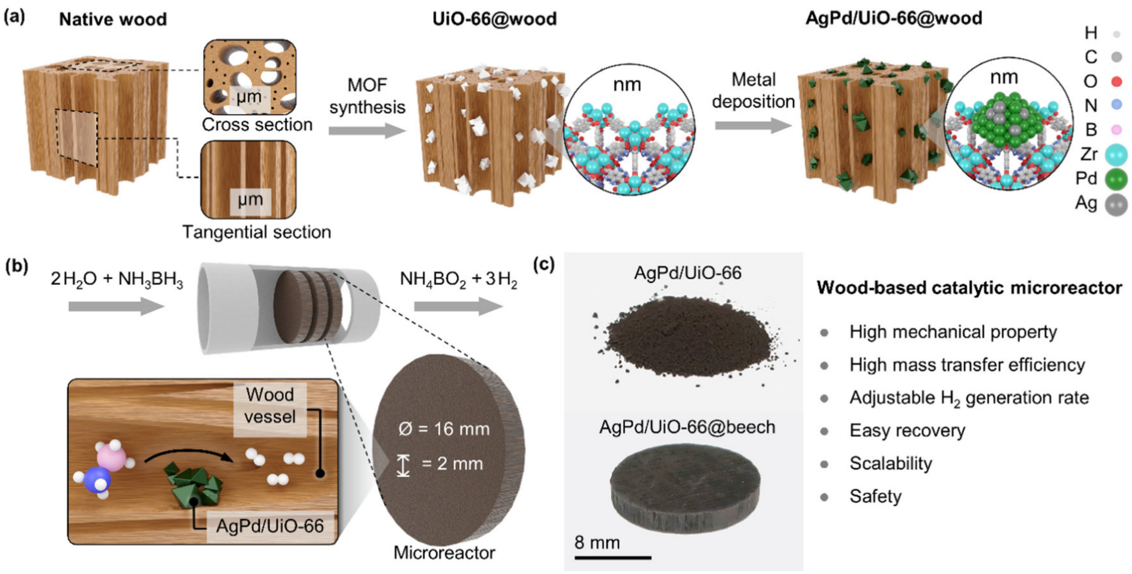

Figure 11. Schematic representation of the synthesis and catalytic application of a wood-based structured catalysts for hydrogen generation. Reprinted from [331]. (**a**) The preparation steps and (**b**) the modular use of structured catalytic reactors in series for the hydrogen generation from ammonia borane in flow. (**c**) The utilization of wood-based catalytic microreactor under pressure-driven flow-through system possesses many advantages compared to using powder catalysts in batch mode, including high mechanical property, high mass transfer efficiency, adjustable H2 generation rate, easy recovery, scalability, and safety.

8.4. Fire Protection of Wood by Modification

One of the disadvantageous properties of wood as a construction material is its reaction to fire. Wood is combustible and prone to ignition and fire propagation. Fire retardants are therefore sometimes used to improve the fire performance of wood-based construction materials, e.g., for façade claddings. Conventional halogen and boron-based fire retardants have potential health risks, may produce toxic gases, and accumulate in the environment because of their stability [332]. Instead, the last decade has seen attention shift to chemical modification for fire protection of wood and biobased materials. Today, research within this topic is rapidly developing and a wide range of treatments has been described in literature, with new modifications emerging every year [310]. Today, research within this topic is rapidly developing and a wide range of treatments has been described in literature. These include a variety of bio-inspired mineralization on the nano- and submicron scale [333–335], co-reaction with modifications for improving decay resistance [336], formation of zinc oxide nano-rods [337], and clay impregnation of cell walls [338].

8.5. Conclusion and Outlook Regarding Wood-Based Functional Materials

This section presents a brief overview of recent and ongoing development in the field of wood-based functional materials. It is impressive to see these developments because they represent a joint effort of different research fields such as chemistry, wood science, and materials science. The clear need for sustainable high-performance functional materials drives these efforts.

However, there are still open questions that need to be addressed. For example, there is the requirement to develop strategies for up-scaling the numerous functionalization approaches by creating new businesses through bundling know-how from existing ones or to use green chemistry for functionalization, accompanied by thorough life cycle analysis of the respective materials. The functional wood-based materials must be designed for recycling after the end-of-life cycle. The wood-based industry is falling behind compared to other industries and rapid action is needed.

Regarding the performance of the materials, it is important to note that it is not sufficient to simply state that the materials are more sustainable compared to others. They must possess a similar performance than comparable synthetic systems. In specific cases the lack of performance may be compensated by utilizing more of the material.

9. The Future of Wood Modification

In the broadest sense, humans have attempted to modify wood to improve its properties since their first uses of wood as tools or building materials. However, in face of the urgent need of drastically reducing the carbon footprint of the building industry, development of wood-based materials that can meet the increasing demand for sustainable and carbon neutral or negative materials is more important than ever before.

As we see it, this includes the need for increased focus on combined treatments, for example modification to both give fire retardancy and resistance to fungal decay. Moreover, as climate change allows termites to spread to new regions of the world, the need for modifications to protect against these insects becomes ever more relevant.

In addition to developments in new modification technologies, there is a need to establish more linkages to existing industries and processes. Once these niche technologies are incorporated more broadly into the industry, it may be possible that the cost of the technologies to decrease, or new potential uses could be developed.

As illustrated in this review, substantial research efforts have been dedicated in the past decades to advance our understanding of several different types of wood. However, many central questions about fundamental aspects of the various modifications persist. We hope this review will inspire more researchers to engage in this exciting field to help move research and knowledge at the pace required by the urgent need for sustainable and climate friendly building materials.

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