Functional Treatments for Modified Wood

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Wood modification has been defined by Hill as a process that "involves the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of the modified wood. The modified wood should itself be nontoxic under service conditions, and furthermore, there should be no release of any toxic substances during service, or at end of life, following disposal or recycling of the modified wood. If the modification is intended for improved resistance to biological attack, then the mode of action should be non-biocidal."

Keywords: modified wood ; functional wood ; multifunctional wood ; functional treatments ; UV stability ; weathering ; transparent wood ; dimensional stability ; durability

1. Introduction

Wood modification is a group of technologies that have shown steady growth in the past two decades. While timber is a ubiquitous material that has been known to humankind for millennia, and used in a wide range of forms, including structures, furniture and many household objects; it has also been applied in high technology industries such as engineered components for automotive, energy and aerospace industries $\frac{[1][2]}{2}$. Wood modification is a relatively new field, which has contributed to this development, and is likely to allow continued growth. Some of the limitations of wood, including its dimensional change in changing moisture environments, and susceptibility to insect attack or decay, have traditionally been addressed through good design, chemical treatments and strategic choice of wood species for the intended applications. However, wood modification has offered an alternative approach. The majority of dominant wood modification systems (chemical modification, thermal modification and polymer or resin impregnation) have sought to alter the relationship between wood and moisture, and as a result restrict dimensional change, and reduce susceptibility to decay. These attributes are well reported by Hill ^[2] and many recent reviews of the technology ^{[4][5][6]}.

However, if we cast the net slightly wider, some wood modifications offer benefits over and above the primary gains in dimensional stability and durability. Some seek specifically to enhance hardness or wear-resistance, while others seek to further gain UV weathering resistance. Other novel treatments seek to utilise the stability of the modified wood substrate to develop new technologies or ideas, for example as printable surfaces for electrical circuits or sensors and new bio-based electronics. These diverse options introduce multi-functionality to modified wood, so it is worth considering, do they themselves count as emerging multi-functional wood modification systems, or are they simply post-modification treatment options? This paper will firstly review some of the options for creating (multi)functional wood using modified wood as a substrate, then newer options for creating multifunctional wood using emerging systems and then consider and discuss this question further.

2. The Main Modification Systems

Wood modification has been defined by Hill ^[3] as a process that "involves the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of the modified wood." This is frequently considered to be a separate technology to the established wood preservative treatments using biocides ^{[Z][8]}. Several systems are well developed and commercially available, including:

- Acetylation—the process of esterifying wood using acetic anhydride, including Accoya[®] [9][10]
- Thermal modification—the process of altering hygroscopicity through use of elevated temperatures (160 °C to approx.
 230 °C) in an inert atmosphere, steam or vacuum, including Thermowood[®], VacWood[®], LunaWood[®], VAP Holzsystemr[®] [11]
- Resin or polymer modification—the process of impregnating wood with thermosetting resins, monomers or oligomers capable of cross-linking in situ in the wood cell wall and/or cell lumena to form a non-leachable polymeric system, including furfurylation (Kebony[®], NobelWood[®] ^[10]), resin modification (Impreg[™], Indurite[™], Lignia[®] ^[12]) and polymer impregnations (Permagrain, Permali[®], Jabroc[®]).

It will be assumed that readers can refer to detailed reviews elsewhere ^{[9][10][11][12]} for the principles and properties of each of these modifications, or gain specific details from product technical information via the relevant companies. The main modifications and estimated commercial volumes per year by region are presented in <u>Table 1</u>, based on data from Jones and Sandberg ^[6].

Table 1. Estimated global production of modified wood (Source: [6]).

Modification	Estimated Volumes (m ³)						
	Europe China		N America	Oceania/Japan	Other		
Thermally modified timber	695,000	250,000	140,000	15,000	10,000		
Densified wood	2000	<1000	-	<1000	-		
Acetylation	120,000	-	-	-	-		
Furfurylation	45,000	-	-	-	-		
Other methods	35,000	290,000 *	-	5000	TBD		

* Figures are a combination of furfurylation processes other than Kebony[®] and NobelWood[®] as well as DMDHEU and other resin treatments. Empty fields indicate that no data is available or that no modified wood of this type is known in this region to the authors of reference ^[6].

Other chemical modification systems exist, and some have been commercially available for intervals of time, e.g., the modification using DMDHEU (known as Belmadur[®], or its new name HartHolz[®]), or have been well investigated but currently left at a medium level of advancement, not yet developed through the scale-up and commercialisation process stages towards market availability. Such options include reaction of wood with other acid anhydrides including succinic or maleic anhydride; reaction of wood with citric acid and various polyols (glycerol, sorbitol, etc.); reaction of wood with silanes; reaction of wood with chitosan; impregnation and/or reaction of wood with natural oils, waxes or paraffins, impregnation and/or reaction of wood with silicates or water glass. Some of these systems may be already in use for specific small applications, such as conservation of archaeological woods, and others are still in active process of investment or development to the commodity market. Densification of wood, through the use of steam, heat or reagents under pressure has also been investigated, and a small quantity of densified or surface densified wood is reportedly available in Europe ^[6].

The main enhanced properties advertised for the wood modification systems are summarised in <u>Table 2</u>, with a note of the main technical limitations, such as corrosiveness to metal fixings, or loss of strength or toughness [6].

Process	Typical Species Used Commercially	Dimensional stability	Durability	Hardness	Electrical Resistance	High Density	Low Mould Resistance	Corrosive to Fasteners	Reduced Mechanical Properties	Oil Exudati
Accoya®	Radiata pine	yes	yes	-	-	-	yes	yes	-	-
Thermal modification	Norway spruce, Scots pine, various hardwoods	yes	mod.	-	-	-	-	-	yes	-
Kebony [®] NobelWood [®]	Radiata pine, Scots pine	yes	yes	yes	-	-	-	yes	yes	-
Compreg™	European beech veneer	-	yes	yes	yes	yes	-	-	-	-
Impreg™	European beech, Scots pine	yes	yes	-	-	-	-	-	yes	-
Lignia [®]	Radiata pine	yes	yes	-	-	-	-	-	-	-
HartHolz [®] (DMDHEU)	European beech, Scots pine	-	yes	-	-	-	-	-	-	-
Organowood [®] (Silicate modification)	Norway spruce, Scots pine	-	yes	-	-	-	-	-	-	-
Linotech (Linseed oil derrivatives)	Scots pine, (Norway spruce)	-	yes	-	-		-	-	-	yes

Table 2. Commonly	/ achieved r	properties of	modified	wood from	various s	vstems	hased	on [6	h
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Empty fields indicate that no benefit is claimed by the manufacturers, to the best of the authors' knowledge.

There are differences between modification systems in which mechanical properties are affected, for example a reduction of bending strength, hardness and toughness is reported for thermally modified wood, depending on the level of modification applied. For the furfurylated products, the loss of mechanical properties relates only to toughness, and for

Indurite the reported losses are for hardness and toughness. An interesting challenge is the poor mould resistance of thermally modified wood, and several of the investigations to add functionality to thermally modified wood relate to this issue—as we will discover in this review.

In his definition, Hill ^[3] indicates that wood modification is distinct from the more general band of wood treatments, such as traditional preservatives or fire retardants, which are frequently applied as aqueous solutions of emulsions, without any chemical grafting or reaction in situ ^[8]. However, the limitations of some modifications provide the impetus for adding functionality through secondary processes. This gives rise to combination treatments, with partial modification and partially traditional methods. For example, a commonly identified trait of thermally modified wood is its colour change on weathering. The thermally modified timber is generally a darker colour than the original untreated timber, however exposure to sunlight and rainfall leads to a relatively rapid change of colour towards a silver-grey form ^{[13][14][15]}. This has led to many research teams seeking to add a second treatment, either painted on, or impregnated into the wood, or using more innovative approaches, that would increase UV stability of the thermally modified timber ^{[16][17]}.

Other combined wood treatments are developed using the initial chemical modification as a starting reaction, which then permits a second new chemical reaction, e.g., using functional groups introduced during step 1, or capitalising on changes achieved in step 1 (e.g., delignification). Many of these combined modification methods achieve stunning additional functionality in the wood, e.g., photoluminescence, electrical conductivity, sensors, transparency, etc. However, this may be at the expense of original material properties. In many cases the dimensional stabilisation that is achieved by the wood modification contributes to a more uniform and predictable starting material for the application of nanotechnology approaches. These systems will be introduced and discussed in greater detail to highlight future possibilities and limitations.

The sections which follow will consider each of the main modification systems, and the ways in which secondary treatments have been used to add functionality or overcome challenges identified in <u>Table 2</u>. We will also consider methods where wood modification methods have been used innovatively as part of a several step process. In some cases hybrid systems emerge, for example where a pre-treatment rather than post-treatment is used, but a wood modification technique remains as the central enabling step to permit new properties to be gained. The fields of application vary widely, as will be seen, and a large amount of potential exists for ongoing exploration and development in this field. Thirdly, we have included in the second part of the text a number of examples where the same active ingredients for functionalisation of wood have been used without modification, but where we see that there is significant potential for them to be included in modification approaches within the near future. This is true for many of the nanotechnology approaches, where a rapid growth of activity is showing interchangability between modified and unmodified wood substrates and combinations of active ingredients. We return to this consideration in the discussion section.

3. Adding Functionality to Modified Wood

3.1. Thermally Modified Wood with Functionality

3.1.1. TiO₂ for Weathering Resistance

To improve weathering performance of thermally modified wood, the titania sol (TiO₂) in paraffin was impregnated into pine wood that had been previously thermally treated at 212 °C. The paraffin assisted in retaining the titania on the wood surface (water stability), and UV resistance of the treated impregnated wood was observed ^[1,7]. Others have considered titanium dioxide or other oxides such as zinc or cerium in acrylic binders, as is common for UV protection of unmodified wood ^{[18][19]}. Both TiO₂ and ZnO nanoparticles were considered by Miklecic et al. ^[16] in a polyacrylate system, as a coating for thermally modified beech wood. Both nanoparticle types improved colour stability of the thermally modified beech, but the zinc oxide system was prone to more crack formation in the surface, and peeling of the coating. A TiO₂/Ce xerogel system was demonstrated for protecting wood by Guo et al. ^[20], which could also contribute to future development in this area for modified woods. The TiO₂/Ce xerogel blocked virtually all light with wavelength below 370 nm in their study. When dip coated onto wood a microsheet film was formed with thickness 7 µm (five dip cycles). Colour change during UV weathering test was greatly reduced for spruce wood treated with the xerogel.

Shen et al. ^[21] measured colour and water contact angle during an ASTM 154 weathering test on thermally modified timber, and thermally modified timber with TiO₂ nanoparticle coatings, and thermally modified timber with polydimethyoxysiloxane (PDMS) treatment, or combined TiO₂ and PDMS treatments. The TiO₂ treatment greatly reduced the development of lightness over weathering exposure period, whereas PDMS allowed bleaching to occur. The combined TiO₂ and PDMS treatments both gave low total colour change (ΔE) values compared to the control samples and the treatments when applied as stand-alone.

The water contact angle of thermally modified timber was initially high (over 100°) but rapidly decreased ^[21]. The PDMS treatment increased the initial contact angle to approx. 110°, and the TiO_2 treatments with PDMS second step further increased the contact angle to 125–135°. Both the PDMS, and the $TiO_2/PDMS$ systems retained their contact angles during the weathering exposure, whereas the untreated thermally modified timber lost hydrophobicity by the 168 h measurement time, and contact angle continued to decrease as weathering time increased up to 1176 h exposure.

3.1.2. Silica Nanosols

Nanosol treatments are stable dispersions of inorganic nanoparticles, such as silica, that can be painted or sprayed onto a surface ^[22]. A number of studies have looked at using this technology with wood, and differing nanoparticles affect wood in different ways, e.g., silica- alkoxysilane sols can provide water repellence ^{[23][24]}, silicon oxide/boron oxide complexes can give flame retardancy, and silica oxide or boric acid sols can be used for biocidal properties ^[23]. With modified wood, and in particular thermally treated wood, iron salt sols and silica/iron oxide have been applied to improve weathering stability and water resistance Incorporation of pigments such as iron oxide red with the sol not only enhanced weathering protection and increased hydrophobicity but also enhanced aesthetic qualities ^{[23][25]}.

3.1.3. Suppressing Mould Growth

Another aspect of exterior use of thermally modified wood can be mould growth. A few different approaches have been tried to improve upon this. Kwaśniewska-Sip et al. ^[26] used caffeine, impregnated into wood prior to thermal modification, to alter the susceptibility to mould growth. Others have used methacrylate as a secondary treatment on thermally modified wood ^{[27][28]}. The methacrylate suppressed mould growth; however, it did not reduce the colour change due to UV.

3.1.4. Other Improvements through Concurrent Treatments

Other approaches for altering the properties of thermally modified timber include addition of reagents to the wood prior to heat treatment. One example is the use of a zwitterionic buffer during thermal modification to alter the reactions which occur. In a study by Duarte et al. ^[29], two zwitterionic buffers were used (bicine and tricine) alone or in combination with thermal modification of wood. It is proposed that the amine component of these zwitterionic buffers is able to contribute to Maillard-type reaction with the polysaccharide components of the wood at elevated temperatures ^[30] and influence the characteristics of the thermally modified wood. In the study by Duarte et al. ^[29] the presence of bicene and tricene had an effect on termite survival, but further investigations of the interactions of these molecules with wood during thermal modification was recommended.

Another attempt to modify the properties of thermally modified wood used vinylic monomers, impregnated into the wood before thermal treatment, the monomer solution also contained boron derivatives, to alter the termite resistance of the wood ^[31]. The polyglycerolmethacrylate and maleic anhydride-polyglycerol adducts improved the boron fixation, even after leaching. In addition, samples without boron treated at 220 °C showed benefit in termite resistance, indicating a synergistic effect between the thermal modification and reaction with monomers.

3.2. Resin Modified Wood with Functionality

UV Resistance Promotion for Resin Modified Timber

The UV stability of resin modified timbers was investigated by Kielmann and Mai ^[32]. Two types of resin modified timber were studied—based on N-methylol melamine (NMM) and phenol formaldehyde resin (PF), in addition, both resins were also studied when a dye had been incorporated into the resin during wood treatment. The timbers were coated with a translucent waterborne acrylic binder, with and without UV protective agents. The UV protective system (Tinuvin 533-DW) was a light stabilizer blend containing UV absorbers and hindered amine light stabiliser (HALS). While this acrylic treatment is a typical paint or varnish-type treatment, not a surface functionalisation or modification study, it is included in this review to reflect the interest in achieving UV stability enhancement for modified wood. The NMM modified wood, and NMM wood with dye both became whitish during weathering, relating to loss of polyphenolics from lignin, and leaching of the dye if present. The PF modified woods became a darker brown colour, while the PF wood with dye only became a slightly lighter shade of black, but with some lightish regions on the sample face. The darkening of PF modified woods has been previously reported in other studies ^{[33][34]} and is related to formation of new chromophores within the PF resin during UV exposure, which offsets the degradation of lignin and loss of polyphenolics from the wood itself.

In the coating study by Kielmann and Mai ^[32] the NMM, PF and PF with dye samples that had been coated with acrylic without UV agents gained a darker colour after weathering, which was attributed to the lack of removal of polyphenolic fragments, due to the coating inhibiting the action of water to mobilise these fragments. The samples with acrylic binder and light stabiliser blend turned only somewhat darker on UV weathering exposure, relating to the action of the UV stabilisers. The greatest benefit from the light stabiliser formation was seen for the NMM samples containing the dye.

Evans et al. ^[33] used hindered amine light stabilisers (HALS) in the PF resin formulation that they used to resin modify wood veneers. Resin at 10, 20 and 30% resin solids content were tested, and the presence of 1% or 2% HALS additives. The PF resin and the HALS additive had a beneficial effect, reducing strength loss resulting from natural weathering. SEM images of the UV exposed PF treated wood containing HALS (150 h exposure) revealed that middle lamellae (ML) were intact, and very limited damage to cell walls, whereas the untreated wood tracheids had clearly separated due to loss of lignin from the ML. The PF treated wood without HALS showed an intermediate state of damage, with some small fissures beginning to develop between cells along the line of ML. After 1070 h of UV exposure clear differences remained between the samples, and macro scale observations indicated greater structural integrity of the PF modified wood with the HALS.

Resin modification has been used as a second step on succinic anhydride modified wood by Wang et al. ^[35], with the claim that this led to enhanced dimensional stability, water repellency (determined by contact angle) and flame retardancy (determined by LOI, limiting oxygen index). The combination of treatments showed ASE values than the individual succinylation or melamine formaldehyde impregnation treatments. Both the resin impregnation and the succinylation are known to have a beneficial effect on dimensional stability, however it was suggested that the succinic anhydride promoted cross linking between the resin and the wood.

3.3. Acetylation and Esterification of Wood with Added Functionality

3.3.1. Chemical Modification with UV Stability

Esterification is a popular method for reducing the colour change of wood when exposed to weathering conditions. For example, acetylated timber shows only minor changes on weathering, if sufficient weight percent gain (WPG) has been achieved ^{[36][37]}. Acetylation shows good colour stability, while succinic and maleic anhydride performed acceptably, but phthalic anhydride modified wood tended to gain more chromophores during UV exposure test. Esterification of fir with benzoyl chloride was also shown to reduce colour change, in tests by Pandey and Chandrashekar ^[38]. For untreated wood bleaching is common as lignin is degraded by UV light, and water removes fragments of polyphenol decomposition products from the wood surface ^{[Z][39]}. Rosu et al. ^[40] investigated further enhancement of UV stability of esterified wood (prepared with succinic acid anhydride modification) by an epoxidized soybean oil (ESO) treatment. The ring opening of the succinic anhydride during the wood modification step presented carboxylic acid functional groups on the wood surface for further grafting of the ESO, thus this is a two-step modification process, with the ESO being grafted on the surface of the wood had very low colour change, which on the first observation interval (20 h) was below the threshold for detection by the human eye. An ESO treatment for unmodified wood was previously reported by Olsson et al. ^[41], in an experiment with additional UV absorbing agent, 2-hydroxy-4(2,3-epoxy propoxy)-benzophenone (HEPBP), where it showed reduction in colour change on artificial and natural weathering.

3.3.2. Esterification as a Pre-Treatment for Other Purposes

Esterification with maleic anhydride was used by Li et al. ^[42] to pre-swell wood prior to a second step—grafting of a mix of glycidyl methacrylate and methyl methacrylate monomers. They reported better interfacial compatibility between the phases of wood and polymer, and a high level of dimensional stability was reported. Pre-treatment of wood with succinic anhydride (another cyclic anhydride molecule) was reported by Wang et al. ^[35] for resin modifications, as noted above.

3.4. Polymer Impregnation with Functionality

Polymer impregnation of wood has been recognised for many years. Initial interest in impregnating the cellular structure of wood with monomers or polymers such as methyl methacrylate or epoxy or microscopy led to advances in larger scale pieces of polymer impregnated wood for high performance applications. Schneider and Phillips ^[4:3] reported investigations on methyl methacrylate impregnated timber giving it the term wood polymer composite (which has since been assigned to other composites with a wood flour filler in any polymer matrix). Several commercial systems were developed in the UK, North America and elsewhere, and found niche applications such as neutron shielding, or machinable wood blanks for manufacturing high wear components for motorsport and engineering, or hardwearing flooring. These included products which are still available today: Permali, Jabroc and Insulam. Work in this area continues today, considering polystyrene ^[44], polymerised glycidyl methacrylate ^[45] and polymethylmethacrylate (PMMA) ^[46].

3.4.1. Biodegradability in Impregnated Wood

Some of the new generation of modification systems have sought to address dimensional stability while retaining the biodegradability of wood. A good example is the polymer modification proposed by Ermeyden et al. ^[47], who generated poly-ε-caprolactone (PCL) in situ by ring opening polymerisation. PCL is a synthetic polymer with strongly biodegradable character, when subjected to the correct conditions. Depending on the solvent used during modification, the experiments indicated that good distribution of the PCL within the cell wall is possible, although toluene as a solvent gave a lumen-filling and cell wall coating, rather than bulking ^[47]. Consequently PCL synthesised in dimethyl formamide solution showed greater anti-swelling efficiency (ASE) than the toluene synthesised PCL modified wood.

Studies by Noel et al. ^{[48][49]} used four biopolymers, polylactic acid (PLA), polyglycolic acid (PGA), polybutylene adipate (PBA) and polybutylene succinate (PBS). A mixture of cell wall bulking and cell lumen filling properties were observed. The PLA and PBS showed very interesting affinity for the wood cell wall material, leading to migration into the cell wall structure during a heating stage, which enhanced dimensional stability ^{[50][51]}. Both PBS and PLA show biodegradability, however PLA requires careful control of conditions to facilitate degradation, and may result in a less biodegradable modified wood product.

3.4.2. Pretreatments and Grafting for Polymer Impregnation Modifications

Other systems from the new generation of polymer functionalisation reactions make use of wood modification, prior to full polymer impregnation This can be to control the location of the polymer within the wood, or to ensure maximum grafting between the wood cell wall and the polymer phase. Berglund and Burgert ^[52] summarised the pretreatments and

polymerisations, with typical applications, in their review. Atom transfer radical polymerisation (ATRP), reversible additionfragmentation chain transfer polymerisation (RAFT) and ring opening polymerisation (ROP) can be used to graft the intended functionality onto the wood surface for subsequent reactions. Various surface initiated polymerisations can also be used.

In one example a pH responsive wood system was created, using two different grafted polymers (PMMA and PDMAEMA, poly(2-dimethylamino)ethyl methacrylate) to favour water uptake under acidic or basic conditions by Cabane et al. ^[53]. In a later work by Cabane et al. ^[54] they used a bromoisobutyryl bromide (BiBB) initiator and ATRP to graft polystyrene and poly-N-(isopropyl acrylamide) (PNIPAM) into wood, demonstrating different functionalities. The polystyrene modified wood was intended as a hydrophobic treatment, while PNIPAM is known to change its hygroscopicity with temperature-induced change in microstructure, offering potential to give control over the hygroscopicity of PNIPAM modified wood. The contact angle at room temperature was low for PNIPAM wood, but after heating to above the critical temperature (32 °C) the contact angle significantly increased, demonstrating very low wettability ^[54]. A wealth of other grafting-based reactions are possible. For example, Trey et al. ^[55] polymerised aniline within the cell lumena of Southern yellow pine veneers, creating semi-electrically conductive wood, with potential application in anti-static or charge-dispersing materials ^[56].

3.4.3. Delignification Combined with Polymer Impregnation—Transparent Wood

Polymer impregnation is a key step in the manufacture of transparent wood, however this is done following a prior delignification step, so is a two-step, or hybrid, modification ^{[57][58][59][60]}. However, once the delignification has been accomplished, various options exist for the polymer impregnated wood, as well reviewed by ^{[59][60]}. Polymethyl methacrylate is a commonly chosen polymer for this ^[57], although other researchers have considered epoxy resins, PVA or other systems ^{[58][59][61][62][63][64]}. In order to make a two-component material (such as composite or impregnated wood) transparent, the difference between the refracted indices of the two phases must be minimised to reduce diffraction at interfaces between the two phases ^[57].

Uses for this wood include optically transparent or opaque materials to permit light to enter structures [57][58](52](55)[66], transparent materials and light diffusing layers for solar cells [67](68], and diffused luminescence wood structures [69]. Further functionality can be added by incorporating particles, dyes or other additives into the polymer during impregnation of the delignified wood. Examples of extended functionality include: wood based lasers (using a dye in the transparent wood to give laser activity) [70][71], heat-shielding transparent wood windows (incorporating nanoparticles, Cs_xWO₃) [72], thermo-reversible optical properties—using phase change materials [73], electrochromic properties [74], energy storage through encapsulation of phase change materials such as polyethylene glycol [75], luminescent properties by incorporating nanoparticles (Fe₂O₃@YVO₄:Eu³⁺) [76], luminescence [69], magnetic properties by incorporating Fe₃O₄ nanoparticles [72].

Materials can be produced with high optical transmittance (over 80%) and haze (over 70%) $^{[57]}$. It is also reported that thermal conductivity is low $^{[66]}$, and load bearing capacity is good—as reflected in tough, non-catastrophic failure behaviour, or the absence of a shattering behaviour $^{[57][69]}$. In some applications the optical haze is seen as beneficial, to create a uniform and consistent distribution of daylight without any glare effect $^{[66]}$, while in other applications a greater level of clarity is sought through adjustment of refractive indices of the wood and the polymer matrix $^{[64]}$. The process has now also been applied to bamboo $^{[64][78]}$.

The actual mechanical properties of the transparent wood have been tested and reported by Li et al. $^{[52]}$ and Zhu et al. $^{[58]}$ and show that the delignification has a large reduction in strength, which is then overcome by the polymer impregnation. This provides a stiffness of the transparent wood (MOE = 2.05 GPa) that is higher than the PMMA polymer used for impregnation (MOE = 1.8 GPa) $^{[54]}$. For an epoxy matrix based transparent wood studied by Zhu et al. $^{[58]}$, the MOE value was 1.22 GPa when loaded in the radial direction (i.e., higher than the unmodified Basswood in this test orientation (0.19 GPa). Meanwhile, in the longitudinal direction the transparent wood MOE was 2.37 GPa, which was approximately half the strength of the natural wood prior to delignification and polymer resin impregnation (5.78 GPa).

A compression step was added to the transparent wood preparation by Li et al. ^[52], which further increased the stiffness value to 3.59 GPa, the tensile stress for this compressed transparent wood was higher than PMMA (ca. 90 MPa and ca. 40 MPa, respectively) when the wood was loaded longitudinally, whereas the delignified wood had a maximum stress of below 5 MPa ^[57]. The level of delignification in the study was high, reducing lignin content of the balsa wood used from 24.9% to 2.9% ^[57]. However, there is also interest in development of a method for creating optically transparent wood which has not been subjected to such intense delignification, to reduce the loss of strength, and to reduce the time-consuming delignification step ^[61]. A method where 80% of lignin remains in the wood has been proposed and demonstrated, using a hydrogen peroxide system ^[61]. The method focused on bleaching by removal of the chromophoric structures, while leaving bulk lignin in situ within the wood cell wall, preserving the structure of the wood. Reaction time was significantly reduced for four species studied by Li et al. ^[61] and the wet strength of the wood parallel to the grain was significantly higher than the full delignification method.

In a further development of the transparent wood concept, an intermediate step has been demonstrated by Montanari et al. ^[79]. Following delignification, the wood substrate was grafted with either maleic, itaconic or succinic anhydride from renewable sources. The esterification reaction onto the wood substrate permits interface tailoring in subsequent reaction

with active agents and controls the wood-polymer interaction necessary for optical transparency. Additionally, the esterification reduces moisture sorption of the wood, as would be expected based on the well-known esterification family of chemical modification systems.

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