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Review

# Review of Functional Treatments for Modified Wood

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**Abstract:** Wood modification is now widely recognized as offering enhanced properties of wood and overcoming issues such as dimensional instability and biodegradability which affect natural wood. Typical wood modification systems use chemical modification, impregnation modification or thermal modification, and these vary in the properties achieved. As control and understanding of the wood modification systems has progressed, further opportunities have arisen to add extra functionalities to the modified wood. These include UV stabilisation, fire retardancy, or enhanced suitability for paints and coatings. Thus, wood may become a multi-functional material through a series of modifications, treatments or reactions, to create a high-performance material with previously impossible properties. In this paper we review systems that combine the well-established wood modification procedures with secondary techniques or modifications to deliver emerging technologies with multi-functionality. The new applications targeted using this additional functionality are diverse and range from increased electrical conductivity, creation of sensors or responsive materials, improvement of wellbeing in the built environment, and enhanced fire and flame protection. We identified two parallel and connected themes: (1) the functionalisation of modified timber and (2) the modification of timber to provide (multi)-functionality. A wide range of nanotechnology concepts have been harnessed by this new generation of wood modifications and wood treatments. As this field is rapidly expanding, we also include within the review trends from current research in order to gauge the state of the art, and likely direction of travel of the industry.

**Keywords:** modified wood; functional wood; multifunctional wood; nanotechnology; transparent wood; durability; weathering; fire performance



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## 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 [1,2]. 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 [3] and many recent reviews of the technology [4–6].

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 [7,8]. 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 lumina to form a non-leachable polymeric system, including furfurylation (Kebony®, NobelWood® [10]), resin modification (Impreg™, Indurite™, Lignia® [12]) and polymer impregnations (Permagrain, Permalit®, Jabroc®).

It will be assumed that readers can refer to detailed reviews elsewhere [9–12] 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 Table 1, based on data from Jones and Sandberg [6].

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

Modification	Estimated Volumes (m <sup>3</sup> )				
	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 Table 2, with a note of the main technical limitations, such as corrosiveness to metal fixings, or loss of strength or toughness [6].

**Table 2.** Commonly achieved properties of modified wood from various systems (based on [6]).

Process	Typical Species Used Commercially	Dimensional stability	Durability	Hardness	Electrical Resistance	High Density	Low Mould Resistance	Corrosive to Fasteners	Reduced Mechanical Properties	Oil Exudation	Notes
Accoya®	Radiata pine	yes	yes	-	-	-	yes	yes	-	-	-
Thermal modification	Norway spruce, Scots pine, various hardwoods	yes	mod.	-	-	-	-	-	yes	-	mod. = moderate
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	-	-	-	-	-	-	-	Stable silver grey surface
Linotech (Linseed oil derivatives)	Scots pine, (Norway spruce)	-	yes	-	-	-	-	-	-	yes	-

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 [13–15]. 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 Table 2. 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 interchangeability 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. TiO<sub>2</sub> for Weathering Resistance

To improve weathering performance of thermally modified wood, the titania sol (TiO<sub>2</sub>) 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 [17]. 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 TiO<sub>2</sub> and ZnO nanoparticles were considered by Miklečić 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 TiO<sub>2</sub>/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 TiO<sub>2</sub>/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 TiO<sub>2</sub> nanoparticle coatings, and thermally modified timber with polydimethylsiloxane (PDMS) treatment, or combined TiO<sub>2</sub> and PDMS treatments. The TiO<sub>2</sub> treatment greatly reduced the development of lightness over weathering exposure period, whereas PDMS allowed bleaching to occur. The combined TiO<sub>2</sub> and PDMS treatments both gave low total colour change ( $\Delta E$ ) 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<sub>2</sub> treatments with PDMS second step further increased the contact angle to 125–135°. Both the PDMS, and the TiO<sub>2</sub>/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 bicine 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 vinyl 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 [7,39]. 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. The colour change of SA modified wood was reduced compared to the untreated wood, while the ESO grafted SA modified 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 [43] 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: Permalite, 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- $\epsilon$ -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 addition-fragmentation 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 bromoisobutryl 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 lumina 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 [57–60]. 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 [58,59,61–64]. 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 [57,58,62,65,66], 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,  $Cs_xWO_3$ ) [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 ( $Fe_2O_3@YVO_4:Eu^{3+}$ ) [76], luminescence [69], magnetic properties by incorporating  $Fe_3O_4$  nanoparticles [77].

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. [57] 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. [57], 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.

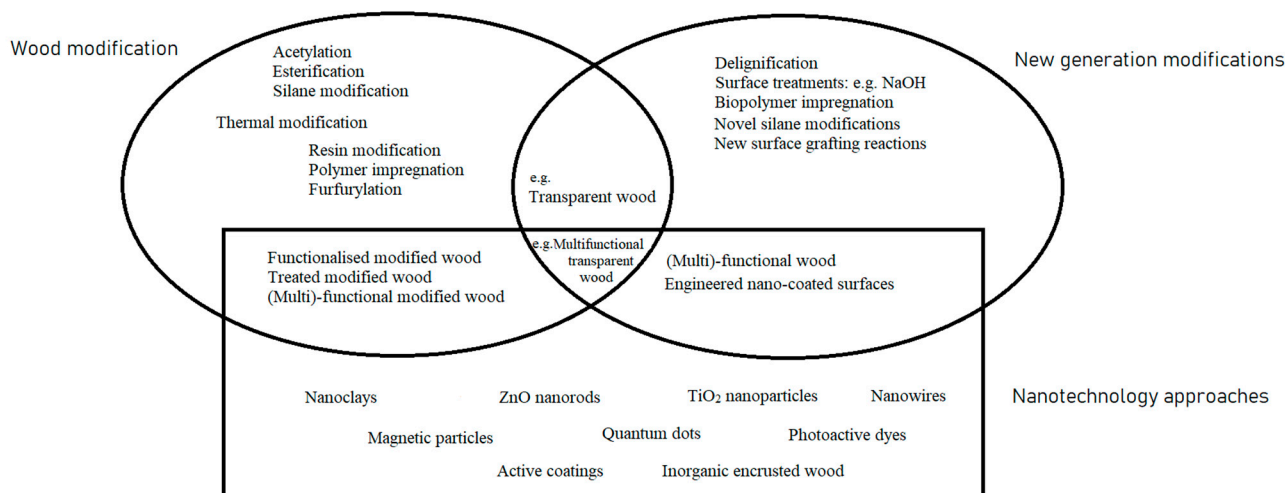
In a further development of the transparent wood concept, an intermediate step has been demonstrated by Montanari et al. [79]. Following delignification, the wood substrate was grafted with either maleic, itaconic or succinic anhydride from renewable sources. The esterification reaction onto the wood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

#### 4. Functionality and Multi-Functionality through Other Wood Modifications

##### 4.1. New Approaches for Functionality

Looking outside the literature relating to the primary, or fully commercialised wood modification systems, we find reviews which consider how wood can be given multi-functionality through any combination of cell wall modification, cell lumen surface modifications, and lumen filling. These can be considered to be 'new generation wood modifications', although there is some overlap with existing wood modifications mentioned in Section 2, as shown in Figure 1. Li et al. [59] comment that this can use "chemical reactions, physical adsorption or absorption, thermal treatment for phase separation effects, inorganic or metal particle precipitation from salt solution, and combined approaches." Many of these have been reviewed and compared in Burgert et al. [80], whose review also extended beyond wood modification to also consider using the hierarchical porous structure of the wood as a template for inorganic non-metallic materials, and applying biomimicry to cell wall structures, i.e., reassembling cellulose nanofibers to design new structures. These elements extend far outside the realms of wood modification, however many interesting principles can be considered based on the modification elements of Burgert et al.'s review [80]. The first insight is that the well-established wood modifications typically

focus on making wood more inert (e.g., blocking or removing hydroxyl groups), whereas many of the nanotechnology wood modifications have focused on increasing functionality, or chemical reactivity. A second insight is that the commercialised wood modifications are typically carried out with relatively little nanostructural control, i.e., they applied to the bulk of the wood. They also highlighted the emerging field of wood nanotechnology, which includes advanced wood functionalisation, where molecular features of the wood, and pore spaces within the wood cell wall are targeted specifically [80]. The pore spaces at specific length scales can be deliberately utilised to fine-tune the synthesis processes or to facilitate novel properties.



**Figure 1.** Interaction of wood modification and nanotechnology to create functional and multi-functional wood.

Through these impregnation or mineralisation approaches we find examples of fire-retardant wood [81], magnetic wood [76,77,82,83], UV stabilised wood [76,82,84], and conductive wood [55,56]. However, some references for conductive wood refer to systems where the wood is so highly carbonised that it should no longer be called modified wood, for example many studies have used carbonised wood as a substrate for lithium or other conductive materials for battery anodes [85]. Other studies [56] have used conductive polymers to impregnate the wood without causing this severe degradation, permitting the conducting or super-conducting behaviour. In some of the above studies, the functionalising agent was incorporated within the polymer during impregnation, while for others a pre-treatment with dye or functionalising agent was completed prior to polymer impregnation which sealed the treatment agent in situ [59]. Thus, not only is wood modification occurring, but in some systems nanoparticles are being utilised to extend the types of functionality given to the wood. These nanoparticle-based modifications will be considered in following sections, but are represented by the rectangular field in Figure 1, intersecting with both the traditional and new generation modifications.

#### 4.2. Delignified Wood with Functionality

In the section on polymer modified woods (above), we identified the use of delignified wood with a polymer impregnation process to form transparent wood. Other work has considered the use of delignified wood without polymer, as a scaffold for further modifications. One example is the luminescent wood films proposed by Fu et al. [86], where the delignified wood also had a reduced hemicellulose content, enhancing hydrophobicity, and was infused with quantum dots before densification. Light scattering by the delignified wood was supplemented by the presence of quantum dots to generate different colours of light. After densification, the wood film was protected by a further modification using hexadecyl trimethoxy silane, so we observe a three-step modification, combining well known techniques to generate the desired functionality. The use of a silane to protect the

wood film was selected to avoid debonding of a more rigid polymer such as the PMMA or epoxy that are often used in transparent wood systems. As a result, a high level of flexibility was formed in this product.

Frey et al. [87] used delignification followed by densification to produce a bulk composite with specific fibre folding patterns that had excellent elastic (circa 35 GPa) and tensile (270 MPa) properties and could be easily shaped. They also reported the potential for further functionalisation of the material. Delignification of wood followed by freeze drying and compression has been used [88] to create highly compressible aerogels with very low thermal conductivity values (0.028 W/mK) that could have other applications such as noise adsorption or soaking up pollution like a sponge. Extreme modification has been performed using delignified wood as a template for precision casting with a nanosol of cerium zirconium oxide to form a non-structural ceramic like material with potential applications in fuel cells or catalyst systems [89].

#### 4.3. Sodium Hydroxide Treatment

A less intense chemical pre-treatment has been used for creation of wood scaffolds for metal organic frameworks (MOFs) by Tu et al. [90]. Sodium hydroxide pretreatment does not substantially delignify wood when conducted at room temperature, but does open up the wood structure to facilitate the necessary rough fibrillar structure for MOF formation. The sodium hydroxide solution also leads to substitution of sodium cations into the wood structure replacing carboxyl groups, and these sodium ions are believed to act as nucleation sites for the MOF deposition process [90]. Two MOFs were formed, including a zeolitic imidazole framework (ZIF-8) derived from zinc nitrate and 2-methyl imidazole, demonstrated in beech, spruce and basswood; and a demonstration of MOF-199 in beech only. The tensile and compressive strength of the beech timber was greatly increased by formation of the ZIF-8 composite, and the porous MOF deposited within the cell lumina showed good adsorption of gases, with potential suitability for environmental or energy applications.

#### 4.4. Other Modifications with Functionality

Many of the emerging wood modifications for enhanced functionality rely on a set of additives that can be incorporated into the wood during polymer modification, or decorated onto the wood surface as a separate treatment step. Many are compiled in Table 3, although the list is far from exhaustive. Several of the inorganic or metallic particles listed are familiar ingredients for wood coatings, and indeed, there is some overlap between coatings and surface treatments for functionalised wood [91]. During the process of compiling this review the wide range of such additives has become apparent. It was also noted that there is considerable cross-over between the use of such treatments on or in modified wood, versus their use on unmodified wood to create similar functionalities. Therefore, some overlap between modified and unmodified woods is acknowledged, but as research continues, there is a high likelihood that treatments currently demonstrated on one substrate will be further developed on others, to generate modifications of the future. Other reviews which consider nanoparticles as treatments for wood or for surface coatings contain additional information [22,92–96].

**Table 3.** Typical or potential additives used to add functionality during or after a main wood modification step.

Additive	Used during Modification	Used after Modification	Properties Given or Enhanced	Refs.
Metal oxides nanoparticles: TiO <sub>2</sub> , ZnO, CeO <sub>2</sub>	-	Unmodified wood	Photocatalytic properties; UV-protection; Self-cleaning	[19]
Silicon nanoparticles; TiO <sub>2</sub> nanoparticles; ZnO nanorods	-	Unmodified wood	Superhydrophobic properties; Fire retardancy	[97,98]
TiO <sub>2</sub> (anatase form)	Polymer impregnated wood	Unmodified wood [99] Thermal mod. [17,21]	Hydrophobic surface treatment	[17,21,99,100]
TiO <sub>2</sub> (rutile form)	-	Unmodified wood [101]; Thermal mod. [16]	UV resistance	[16,101]
Nanoclay (layered aluminosilicates)	PF Resin modification, Polymer impregnation	-	Quicker reaction, Improved dimensional stability	[100,102]
Halloysite, Montmorillonite, Calcium carbonate, TiO <sub>2</sub> , silica nanoparticles	-	-	As a carrier for biocides	[103]
Montmorillonite clay	-	Delignified wood	Fire retardancy; Readily splits into multiple platelets	[84,98]
Fe <sub>3</sub> O <sub>4</sub> particles; MnFe <sub>2</sub> O <sub>4</sub> particles; CoFe <sub>2</sub> O <sub>4</sub> particles	-	-	Magnetic properties	[83]
Fe <sub>3</sub> O <sub>4</sub> nanoparticles	Before PMMA impregnation	-	Magnetic properties	[78]
CoFe <sub>2</sub> O <sub>4</sub> nanoparticles	Before silane treatment	-	Magnetic properties; hydrophobicity when combined with OTS	[77]
Metal organic frameworks (MOFs) ZIF-8 & MOF199	-	NaOH pretreated scaffold	Adsorption of gases	[89]
Metal oxides (atomic layer deposition)	-	Unmodified wood	Hygroscopicity and resistance to mould growth	[104]
MXene (transition metal carbides, carbonitrides and nitrides)	-	Unmodified wood	Electromagnetic shielding	[105]
Silver nanoparticles	Before thermal modification	Unmodified wood	Decay resistance; electrical conduction	[106–108]
Quantum dots (Si and CdSe) (CdSe and ZnS)	PMMA impregnation (transparent)	Delignified scaffold	Luminescence—red & green excitation caused by blue or UV light	[68,109]
Electrochromic polymers (ECPs)	PMMA impregnation (transparent)	-	Colour change on electrical current	[74]



Table 3. Cont.

Additive	Used during Modification	Used after Modification	Properties Given or Enhanced	Refs.
Rh6G dye (Rhodamine 6G)	PMMA impregnation (transparent)	-	Red colour of transparent wood; laser output (565 to 570 nm) from the wood perpendicular to input laser (532 nm)	[70,71]
Carnauba wax and organoclay	-	Thermal modification	Reduction in water uptake; increase in strength properties; improved photostability	[110]

One common treatment seen in many of the nanotechnology based systems is the reaction of wood with organosilanes. Several have already been mentioned in this review for their ability to assist in grafting of the treatment [17,80,109], or to protect the treatment once in situ [111–113]. Silanes are also used in the functionalisation of nanoclays, to enhance their compatibility with the intended polymer matrix, or to promote binding of active substances. For example, Devi et al. [100] used a functionalised nanoclay in preparing resin modified wood, the nanoclay had previously modified with octadecylamine and aminopropyl triethoxy silane.

The grafting of different silanes onto wood to increase hydrophobicity were considered by Donath et al. [114] and depending on the pendant functional groups many different levels of effect may be achieved. Other organic silicon compounds can include chlorine or fluorine species, further altering the properties provided to the wood [115]. One frequent aim is to enhance hydrophobicity through alkyl or other low polarity functional groups. In performing these reactions, a sol-gel process is common, where a hydrolysis reaction of the silane creates silanols leading to sol formation, followed by gel formation through cross linking reactions. Some treatments utilise the moisture content of the wood to supply water for hydrolysis reactions to occur in situ, while other systems may generate the sol in a reactor prior to impregnation. Donath et al. [108] favoured the in situ reaction for good results in wood modification, with better distribution of the silane in the wood structure. The use of emulsions, plasma treatments and other methods for surface coating or for impregnation into the bulk of the wood were considered in the review by Mai and Militz [115].

## 5. Targeted Properties

### 5.1. Hydrophobicity

As introduced above, one issue for modified wood is the loss of hydrophobicity on weathering exposure, for example thermally modified wood has relatively high hydrophobicity immediately after treatment, but contact angle decreases with UV exposure [21]. Ways of improving the contact angle of unmodified wood have also been studied, using similar approaches, such as deposition of titanium dioxide on the wood surfaces to enhance hydrophobicity. Sun et al. [99] used a hydrothermal method to achieve the surface deposition of TiO<sub>2</sub>, with certain deposition conditions generating a micromorphology on the surface that demonstrated hydrophobic (contact angle of over 90°) or superhydrophobic (contact angle of over 150 °C) behaviour. Such micromorphologies can result in the 'lotus effect' with either Cassie-Baxter or Wenzel mode and are found in various plant leaves, giving rise to a well-investigated field of biomimetic surfaces [116,117]. For example, a water contact angle of 154 °C was demonstrated for hydrothermal growing process at 130 °C, whereas lower temperatures gave contact angles of 85° or above. This growth process followed an earlier deposition stage in a treatment solution of tetrabutyl orthotita (TBOT) in ethyl alcohol with sodium dodecyl sulphate (SDS), conducted at 70 °C for 4 h. The pH of the starting solution also had a significant influence on deposition of the



TiO<sub>2</sub> and contact angle achieved, with lower pH favouring higher hydrophobicity [100]. TiO<sub>2</sub> occurs in several crystalline forms, or polymorphs, and the anatase form (tetragonal) shows photoactivity [118], this form was also achieved during the deposition method of Sun et al. [99].

Similar techniques have since been used with modified wood. Titanium dioxide sols have been applied to thermally modified Scots pine to enhance weathering resistance [17]. They demonstrated that TiO<sub>2</sub> sol was not resistant to water, but the addition of paraffin emulsion helped the retention of the TiO<sub>2</sub> by the wood surface. The samples impregnated with the combined TiO<sub>2</sub> and paraffin emulsion showed improved resistance to the effects of ultraviolet light and water on the wood surface, and degradation of the wood components was slowed by the presence of the treatment. In a second study, using a two-step process, Shen et al. [21] applied titanium dioxide nanoparticles, followed by a silane coating. The titanium nanoparticles were grown from acidic solution of ammonium fluorotitanate and boric acid, into which wood samples were immersed for three days. The TiO<sub>2</sub> treated wood was then washed and dried before silane treatment with hydroxyl-terminated polydimethyl siloxane (PDMS) by brush application. A weathering test (ASTM 154) was used to evaluate UV resistance. Water contact angle was measured at intervals over the weathering experiment, and TiO<sub>2</sub> treatments, with and without the PDMS retained the high contact angle that indicates hydrophobicity (values between 110 to 145°). Colour change was also inhibited by the combined treatment.

Zinc oxide nanorods have also shown enhanced hydrophobicity when grown on the wood surface [83,97]. Control of the nanorod morphology and coating of the nanorod assembly with PTES (perfluorotriethoxy silane) led to contact angles of 130° (without PTES) and 160° (with PTES). Thus, the treated wood surfaces demonstrated superhydrophobic behaviour, with water droplets sliding off the surface. In a study by Kong et al. [119] high-density zinc nanorods were demonstrated to give not only water-repellency but also photostability and flame retardancy to wood.

Silica nanoparticles were used by Jia et al. [120] to prepare superhydrophobic wood that also had high wear resistance. The nanoparticles were added to the wood in a hydrothermal process with vinyl triethoxy silane (VTES) and ethanol in sealed containers that were placed in the oven at 100 °C for 90 min. This process was repeated three times to obtain treated samples. Similar samples were also prepared on wood that had received a mild sodium hydroxide pretreatment, and this gave rise to very high contact angles, whereas the nanoparticle and VTES treatment alone did not. A further treatment includes sodium hydroxide in the single step hydrothermal treatment with the SiO<sub>2</sub> and VTES, giving contact angle values that were almost as high as the pretreated SiO<sub>2</sub> and VTES samples. The wear resistance of the pretreated SiO<sub>2</sub> and VTES treated wood was tested using abrasion tests (with sandpaper and knife-scratches), and a boiling procedure, in all cases the high contact angle was retained [120].

Other surface modifications have been attempted using bio-derived extracts. Filgueira et al. [121] used water insoluble condensed tannins and hydroxypropylated condensed tannins extracted from *Pinus radiata* bark to increase hydrophobicity on the surface of beech wood. The process was enabled using laccase at pH 10 to produce a heterogenous modification. The hydrophobicity of the surface of beech wood (*Fagus sylvatica* L.) was improved by this treatment.

## 5.2. Self-Healing

The development of new nanotechnology-based coatings brings the need for robust and wear resistant surfaces. Some researchers have begun to address this, either considering the abrasion resistance [120], or through developing self-healing surfaces [122]. A silane modification was used by Tu et al. [122] as a pretreatment for the wood, followed by spray coating with TiO<sub>2</sub> nanoparticles dispersed in a waterborne perfluoroalkyl methacrylic copolymer. The coating performed well in abrasion tests, retaining a high contact angle and only small increase in sliding angle (where the water droplet rolls off the surface). The

silane pretreatment was shown to assist in long-term UV exposure tests, whereas samples prepared with only the nanoparticles in copolymer suspension showed decreasing contact angle with duration of UV.

### 5.3. Indoor Environment Improvement

Comfort of the interior environment is an issue that is becoming more of a design feature. There is a perception that natural materials create more comfortable environments, and wood can contribute significantly to this [123]. Some of this perception is psychological but there is also a physical effect based on temperature and humidity. Hygroscopic materials such as wood have been shown to affect humidity in the indoor environment via moisture buffering—i.e., absorbing moisture in high humidity environments and conversely releasing moisture in low humidity environments [124,125]. This can help keep room humidity in the comfortable zone for most people. This moisture buffering also affects temperature via differences in latent heat of sorption [126,127]. Different wood types have different moisture buffering effects and therefore different effects on room comfort [128]. There is a challenge to maintain moisture buffering (which relies on hygroscopicity) whilst also protecting wood against liquid water. Lozhechnikova et al. [129] have used Carnauba wax in a non-continuous film to treat Spruce wood and showed that good moisture buffering and good water repellence was obtained. In comparison to full wax films and lacquers reduced moisture buffering significantly whilst linseed oil did not provide enough hydrophobicity. Adding zinc oxide to the Carnauba wax [130] and using a layer-by-layer deposition increased both the hydrophobicity and the UV resistance of the wood whilst maintaining the moisture buffering capability.

Other functionalised woods have been developed with indoor environmental comfort in mind. Montanari et al. [75] developed a transparent wood which incorporated a phase change material within the PMMA main polymer. Phase change materials have been an area of development within building design in recent years. Transparent wood has already demonstrated good thermal insulation properties, with potential to outperform traditional glazing [65,66]. The intention of the study was to allow thermal regulation of the indoor environment, while also permitting light to be transmitted into the building. It was found that the transparent wood with thermal energy storage was superior to normal glass, with its combination of thermal energy storage and thermal insulation properties. A thermal conductivity of  $0.30 \text{ Wm}^{-1}\cdot\text{K}^{-1}$  was reported for the transparent wood, compared with  $1.36 \text{ Wm}^{-1}\cdot\text{K}^{-1}$  for glass [75]. The low thermal conductivity of transparent wood for glazing applications was also demonstrated by Mi et al. [62], with an even lower value of thermal conductivity,  $0.19 \text{ Wm}^{-1}\cdot\text{K}^{-1}$ , however, did not incorporate phase change materials.

### 5.4. UV Resistance

As mentioned above,  $\text{TiO}_2$  can be used to promote UV resistance, for example during weathering [21,101]. The preparation of  $\text{TiO}_2$  particles of various sizes on wood surface has been demonstrated. Sun et al. [101] reported a one-pot method for hydrothermal treatment of wood creating sub-micron sized particles of  $\text{TiO}_2$ . Yang et al. [131] showed that anatase  $\text{TiO}_2$  has greatest use for photocatalysis, whereas rutile form shows greater UV blocking capability. Sun et al. [101] created anatase and rutile  $\text{TiO}_2$  on wood surfaces using different reaction conditions, and showed that the rutile form had greater UV hindering capacity. Colour change analysis after QUV weathering exposure revealed the lowest change for the rutile  $\text{TiO}_2$  treated wood, with anatase  $\text{TiO}_2$  showing intermediate colour change, and untreated wood the greatest change.

Copper micro-particle deposition on wood was studied by Gascon-Garrido et al. [132] and demonstrated a reduction in UV induced strength loss. A pulsed-arc discharge plasma was used to deposit the copper microparticles on the wood surface. Micro-veneers with and without the copper surface treatment were exposed to accelerated weathering (EN 927-6), then analysed by various techniques including FTIR, SEM-EDAX, zero span tensile test and blue stain fungal test (EN 152). The FTIR results indicated that lignin degradation

was not inhibited by the presence of copper, whereas the strength results indicated that UV-initiated degradation of the polysaccharides was inhibited. The stain fungi were unable to colonise the copper coated surface of the wood. The results are therefore promising for exterior weathering conditions, where mould and stain fungi frequently contribute to discoloration of wood surfaces.

Ultra-violet protection was also reported by Gan et al. [82] in a study that generated magnetic wood by deposition of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles in the wood, followed by an octadecyltrichlorosilane (OTS) modification to provide hydrophobicity and UV resistance. The OTS treatment used a room temperature immersion followed by 50 °C oven drying step. Colour change on UV exposure was substantially reduced for the combined treatment. The combination of  $\text{CoFe}_2\text{O}_4$  particles with the OTS increased the contact angle from 100° for OTS only, to 150°, although the use of nanoparticles on their own gave a very low contact angle of 7°, which was lower than the wood itself.

### 5.5. Photochromic Behaviour

The potential to give wood photochromic properties has been demonstrated by Hui et al. [133] who used spironaphoxazine, an organic photochromic compound with good fatigue resistance. This compound alternates between a colourless (closed ring structure) and coloured (open ringed structure) on the presence of UV light. In the study the photochromic material was incorporated in a surface coating of polyvinyl alcohol (PVA) and dextrin [133]. A second formulation incorporated octadecyltrichlorosilane (OTS) to increase hydrophobicity of the coating. The presence of OTS also slowed the colour change seen during weathering test, but did not hinder the photochromic effect.

### 5.6. Acoustic Properties

One interesting additional use of wood modification is to change the acoustic properties of the wood either for sound adsorption or sound production. Noise pollution is a factor of modern life and yet it can have serious impacts on wellbeing. Modification to increase the sound adsorption of wood could therefore be a highly useful procedure to increase wellbeing of occupants of buildings. Kang et al. [134] used steam explosion to increase the permeability of yellow poplar, resulting in 15 to 50% increase in sound adsorption in the fibre direction, (dependent on the treatment). Wang et al. [135] used microwave treatment to significantly increase sound absorption of Scots pine, especially in mid-range frequencies, via increased permeability due to micro-cracks and voids formed in the wood.

Thermal treatments have been used with higher temperatures appearing to be the most effective in increasing acoustic properties of the wood. Thermal treatment of *Paulownia tomentosa* between 100 °C and 200 °C had an insignificant effect on permeability and therefore sound absorption [136] although heat treatment of Mulberry at 145 °C to 165 °C was shown to increase absorption coefficients in the 250 Hz range [137]. In contrast, high temperature treatment (190 °C) of Malas wood increased permeability in the longitudinal direction with a resulting increase in sound adsorption [138]. Even higher temperature treatments (200–240 °C) have been used to increase the sound absorption coefficient of *Larix kaempferi*, with a particular increase in the absorption of high frequencies [139]. At lower temperatures, using a hygrothermal treatment on *Paulownia coreana* at 110 °C did produce good results, with an 81.8% improvement of the sound absorption coefficient [140].

Noise, at least in the form of music, also has a mostly beneficial impact on wellbeing and wood is used in a myriad of musical instruments. Of course, the influence of humidity and dimensional movement can have serious effects on these instruments both in terms of tone and tuning, and in strain or catastrophic failures when joints and timber are placed under high tension. Wood modification has therefore been used to alleviate some of these issues. Of the chemical methods acetylation, has been tested [141] to solve the issues of dimensional changes on wood in instruments. It was found that whilst stabilising the wood, both the sound velocity and sound adsorption were reduced, although no conclusions on

sound quality were made. Succinylation, however, did not improve acoustic properties although in the same study crosslinking with glyoxal and carboxymethyl cellulose did [142]. Vapour formaldehyde treatment of a violin [143] was shown to improve the tone of a violin whilst also protecting it against humidity effects. Further treatments [143,144] using low molecular phenolic resin or vapour formaldehyde combined with saligenin impregnation were found to affect tone and timbre of wooden instruments. Ahmed et al. [145] compared acetylation, phenol formaldehyde, and furfurylation treatments to thermal treatments of a number of woods. They identified a range of differing modulus of elasticity to damping coefficient ( $\tan\delta$ ) ratios that would be beneficial for differing instruments. Most modifications produced better acoustic properties compared to the original wood types though thermally modified wood and acetylated wood showed the most potential. Conversely phenol formaldehyde and furfurylation treatments showed the least potential.

Seeing that thermal modification seems to give good results Mania et al. [146] report that the most resonant wood has a high modulus of elasticity and low density. Thermal modification decreases both density and hygroscopicity. Modification at 160 °C increased the modulus of elasticity and acoustic parameters such as sound propagation and acoustic impedance, (determined by the modulus). Pfriem [147] found that thermal modification at 160 °C to 180 °C in low oxygen gave good improvements of acoustic properties. Hydrothermal treatment at temperatures between 100 °C and 140 °C has also been used [148] to decrease density and increase Young's modulus of mulberry wood to improve acoustic properties. However, if intermediate relative humidities, e.g., 29–64%, are used for the hydrothermal treatment then gains are actually reversible and so provide no long term solution [149]. Mania and Gasiorek [150] found hot oil treatment to have different effects based on the size of the element being treated. Small pieces absorbed comparatively high levels of oil which increased density and decreased acoustic performance. In contrast larger pieces showed more of an increase in MOE which overcame the increase in density to result in a small increase in acoustic parameters.

### 5.7. Electrical Conductivity

Several different approaches have been taken to introduce electrical conductivity to wood in various forms. Polymer impregnation or polymer grafting have been demonstrated by Lv et al. [151] with polypyrrole, and Trey et al. [55] with polyaniline. Proposed applications were for use in supercapacitors and in anti-static applications, respectively. Others have looked at different approaches, such as creation of a fine mesh of conductive nanowires on the wood surface. Guo et al. [152] used copper nanowires, and developed a fusion welding process, based on photonic curing, to ensure good mesh formation and avoid degradation of the thermally sensitive wood substrate during this process. In other transparent materials both copper and silver nanowires have been used, however, the greater abundance of copper leads to greater potential for widespread use in flexible electronics. The use of silver nanoparticles for conductive wood was investigated by Gao et al. [108]. In their study, a post-treatment with a fluoroalkyl silane led to a superhydrophobic surface, using the texture of the nanoparticles combined with the hydrophobicity of the silane. Another method is the impregnation of the wood scaffold with metals [153], however this requires high temperatures, to melt the metal, and could lead to wood thermal degradation, so it is most frequently performed on charred wood, rather than untreated wood, and falls outside the scope of this review. Unlike metals, many of the semiconducting metal oxides (such as  $\text{TiO}_2$ ) show potential for adaptation to introducing electrical conductivity to material substrates, including wood, and could be further tailored to offer sensing properties [95]

There is interest in using wood as a scaffold for electrically conductive or semiconducting materials for various reasons. One is the potential of the wood grain to contribute to different levels of conductivity in different orientations along or across the wood, relating to the distribution of conductive polymer or metal within cell lumina, or as

a coating on the cell wall of each lumen space. The flexibility of wood veneers was also listed as an advantage by Lv et al. [151], the flexible wood-polyppyrrrole material had high capacitance, and showed potential for use in energy storage.

Piezoelectric energy generation using wood-based materials has also been considered. Sun et al. [154] used delignified balsa wood as a 'wood sponge' with greater deformability than untreated wood, and a higher piezoelectric yield on deformation. A large-scale demonstrator used 30 wood sponges connected in to power a commercial LCD screen through compression in a flooring element. This holds considerable potential for wearable electronics and other motion-based energy supply.

### 5.8. Fire-Retardant Properties

A desirable area for development in modified wood is fire retardancy, either as an indirect result of deposition of the types of inorganic materials used in some of the emerging nanotechnology-based modifications listed above, or as a deliberate effort to move commercially modified timbers into higher performance applications within buildings. As a result, the tests used to claim that new modified woods demonstrate fire retardancy can vary widely, from small lab experiments such as thermogravimetric analysis up to the more thorough fire test standards used on construction sized timber elements or assemblies. Both have their role to play in understanding the many mechanisms through which fire retardancy may be achieved, and an excellent overview can be found in Lowden and Hull [155]. This understanding is especially important as new generation fire-retardant treatments are developed. In this review we made effort to clarify how the reported levels of fire retardancy were tested, to help differentiate between these different scales.

Martinka et al. [156] has shown that thermal treatment can change the fire properties of timber. Thermally treated spruce had a lower total heat release and heat rate comparing to untreated timber in a cone calorimeter study. During thermal treatment, hemicellulose and some of the extractives which have the lowest combustion temperature are decomposed. The absence of these components can explain the thermally modified wood better reaction to fire. Others have shown the opposite, indicating a higher burn rate for thermally modified wood from higher temperature processes, for example Čekovská et al. [157], who used spruce wood in their study, which used a novel 45° ignition method. The treatment conditions chosen (180 °C and 210 °C) were representative for the Thermowood S and Thermowood D product categories, respectively. However, according to Luptakova et al. [158], in order to have any beneficial effect on fire performance of thermally modified timber, the treated temperature should be over 200 °C. Working with larch timber in a cone calorimeter tests, Xing and Li ([159] observed that the heat release rate and mass loss rate curves for thermally treated larch (180 °C, 190 °C and 210 °C) were suppressed, which concords with other cone calorimetry studies, such as Martinke et al. [156]. It should be pointed out that no thermally modified timber, regardless of the temperature conditions used, has sufficient gain in fire retardancy in the full-scale tests required to meet the building regulations in Europe. Therefore, it is highly likely that additional treatments will continue to be required to protect thermally modified timber. Gasparik et al. [160] showed that the application of a two-substance fire-retardant coating can improve the fire performance of thermally treated oak. This was a commercially available product, using three layers of a foaming formulation containing oxalic acid, ammonium phosphates and fire-retardant additives, which was followed by an acrylic cover lacquer.

Acetylated wood also shows a small change in flammability, as a result of the chemical modification, however this is insufficient to provide fire resistance. Mohebbi et al. [161] tested acetylated beech plywood in an ignitability test on small samples. They reported a delay in ignition for the acetylated beech, and a reduction in observed glowing, which they attributed to the weight percent gain from the acetylation treatment.

In 2007, an Australian collaborative project was funded by the Commonwealth Scientific and Industrial Research Organization (CSIRO) to develop a single step treatment that could provide fire protection and preservation to wood. According to Marney and



Russell [162], to produce a multifunctional system to act both as fire retardant and wood preservative there are four different approaches. The first approach would be to modify an existing preservative with the addition of fire-retardant chemical. Another approach would be to treat or chemically modify the wood with fire retardants that have proven to have good biocidal performance. A similar approach would be the usage of preservatives that have shown good fire resistance when fixed into the wood structure. The fourth approach would be the wood modification with inorganic substances forming a wood-inorganic composites.

Sweet et al. [163] tested a variety of fire retardants in combination with wood preservatives. This follows point two of Marney and Russel's suggested four potential approaches [162], in this case the examples are based on treatments rather than wood modifications, in the strict sense, however the list is included here to show the range of substances currently under investigation. Sweet et al. [163] tested the compatibility of the different products in leaching, indicating their ability to fulfil the requirements for external usage. According to their findings urea dicyandiamide phosphoric acid and formaldehyde (UDPF), melamine dicyandiamide phosphoric acid and formaldehyde (MDPF), dicyandiamide phosphoric formaldehyde (DPF) and dicyandiamide phosphoric acid (DP) were the fire retardant candidates to show resistance to leaching and be compatible with the chromated copper arsenate (CCA), didcyl dimethyl ammonium chloride (DDAC), DDCA with 3-iodo-2-propynyl butyl carbamate (NP-1), ammoniacal copper quaternary (ACQ), zinc naphthenate, waterborne emulsion (ZnNaph-wb) and ammoniacal copper arsenate (ACA) preservatives. Their study concluded that the combinations UDPF with DDAC and MDPF with NP-1 were the most effective system to provide both fire resistance and durability before and after weathering. Similarly, many researchers have used different combinations of fire retardants with wood preservatives such as zirconium and borate salts and urea phosphoric acid and ethanol with a mixture of boric acid and borax pentahydrate [162]. An example of wood modification combined with fire retardant is seen in the work of Baysal [164], who showed that the melamine formaldehyde with boric acid and borax improved the fire performance of wood. However, the efficiency of the system as preservative was not investigated in this study as it was assumed that boric acid would provide sufficient performance.

Lewin [165] tried the approach of chemically modify wood with proven fire-retardant substances. Yellow pine and spruce were subjected to bromination of lignin with bromate-bromide resulting to improved fire and decay resistance while being resistant to leaching. Moreover, the brominated timber did not show any significant reduction in mechanical properties while improving hydrophobicity and swelling. Moreover, in situ production of phosphoramides within Loblolly Pine and Sweetgum timber using phosphorus pentoxide and amines has been reported to provide good decay and fire resistance [162,166].

In an attempt to fix a substance into wood in order to provide fire and decay resistance properties, Tsunoda [167] proposed a boron vapor treatment and showed that there was no difference between fire performances of the suggested application with the application of boron in a liquid state. However, this study did not include any data about leaching after weathering. To fix the leaching problem of boron substances in a fire-decay resistance modified wood, Kartal et al. [168] introduced a chemical modification using allyl glycidyl ether (AGE) in combination with methyl methacrylate (MMA), grafted in situ into timber that had been treated with disodium octoborate tetrahydrate (DOT). Their findings were that the modified Japanese cedar timber showed improvement in dimensional stability, leaching, decay and termite resistance, however they did not include fire performance testing. Another approach to fix the boron into the treated wood was proposed by Baysal et al. [169] with the application of various water repellent agents, including styrene, isocyanate, paraffin wax and methyl methacrylate, as a post borate impregnation treatments. A vacuum impregnation system and thermally induced cure step (90 °C, 4 h) was used to cure the monomers in situ. They found that styrene application provided the most effective results in reducing borate leaching, yet they did not present fire performance data.



Jiang et al. [170] used a N-methylol resin to fix a guanidylurea phosphate (GUP) and boric acid (BA) fire-retardant system into wood. The resin was DMDHEU (which is a known wood modification agent) was connected to an increase in flammability, when used alone, but with the GUP/BA treatment suppressed combustion. The treated wood was tested in full-scale tests and demonstrated class  $B_{fl-s1}$  performance, suitable for certain building applications.

Yue et al. [171] used boric acid that was incorporated into phenol formaldehyde resin during synthesis to enhance the fire retardancy of PF modified wood. The treated wood was assessed in cone calorimetry tests, and showed a suppression of HRR, which became more prominent as the percentage of boric acid PF resin within the wood increased. Smoke formation was also reduced. Interestingly, the mechanical properties of the boric acid PF treated wood were greater than those of the PF treated wood. In a development of this work, Yue et al. [172] showed that compression of the boric acid PF resin impregnated timber led to further gains in combustion resistance, and increased mechanical properties.

Different silane compounds and different treatment methods have been investigated as systems to provide inorganic fire resistance and durability to timber and timber-based products with some promising results. However, some of the treatments could not minimize the leaching issue seen with boron compounds. Other approaches with combination of zinc and boron compounds have been also investigated with interesting results, however many of those studies do not include fire test data and they are focusing on the leachability of their substances [162]. Mineralisation of timber has also been investigated as a fire resistance and hydrophobicity improvement method.  $CaCO_3$  can be found in many exoskeleton species such as corals, egg-shells and crustacean exoskeletons and it provides durability, increase of hardness and water uptake reduction. The incorporation of  $CaCO_3$  into the timber structure as a bio-inspired mineralisation showed a high improvement in fire resistance. This could be an alternative approach to improve fire resistance of timber, however there was no leaching and water absorbing data in this study [79].

The modification of timber in order to provide durability has an effect on the fire performance. Rabe et al. [173] investigated the fire performance of acetylated (Accoya), thermally treated and N-methylol crosslinked (Belmadur) timber, and compared them to untreated timbers of the equivalent species. In addition, Scots pine and a tropical hardwood (Meranti) were included to investigate species effects. They used four test systems: Thermogravimetric analysis, bomb calorimetry, heat release capacity and dual cone calorimetry to conduct tests, in a comprehensive study. All of the treatments except for the acetylated timber showed a partial flame retardancy. The introduced acetyl groups into acetylated wood are producing volatile compounds with low ignition temperatures during pyrolysis in the event of fire which they negatively affect their fire resistance [173,174]. However, it seems that for the timbers investigated by Rabe et al. [173], the timber species had a greater effect on fire performance than the wood modification treatment itself. When species with higher lignin content (which is associated with higher char yield) were used, the improvement in fire performance became more prominent.

## 6. Discussion

This review has considered the functionalisation of modified timber and the modification of timber to provide (multi)-functionality as two overlapping fields (Figure 1). Additionally, we have identified rapid expansion in the field of nanotechnology applied to wood, whether this is in combination with wood modification; or as a wood modification process in its own right; or as a process with potential for application to modified wood through future research. Our intention has been to highlight the many parallel research fields, and some of their inter-connectivity, which leads to multifunctionality in new generation wood. Throughout the review we have encountered similar active substances, combined in different sequences, or different combinations.

It is clear from the review that for some properties, the commercially available modified timbers may be easily subjected to a secondary treatment, to deliver additional

functionality. A good example is the addition of hydrophobicity to thermally modified wood, often at the same time as introducing UV stability and weathering resistance. Another example is where thermally modified timber is routinely available with a secondary commercially applied fire-retardant formulation of the same type as is used on unmodified timber, to deliver fire retardancy. In this particular example, we have not presented formulation data, or scientific journal citations, as this is typically proprietary information available from the timber merchant or fire-retardant treatment company. Similarly, Accoya have stated that the fire class of their timber for European cladding applications is class D-s2, but note that fire-retardant treatment using commercially available systems can be used to achieve higher requirements, up to class B, with appropriate systems [175].

As a contrast, at a laboratory research level, various groups have looked to alter the wood modification processes to incorporate fire-retardant agents, or to trap active chemicals that were previously applied (e.g., using resin impregnation systems), or to modify the wood so that it is more receptive to secondary fire-retardant treatments, and better able to retain these active components during leaching or other weathering and exposure tests. This is an essential process, and can provide good results, suitable for future incorporation in commercial systems or development into new stand-alone products.

A similar mix of strategies can be seen in other fields of adding functionality to modified wood, or adding functionality through the modification process. Examples of adding functionality to modified wood that we have seen include: resistance to mould growth (by adding biocides, or by adding secondary modifications); termite resistance (by adding active agents before or during the thermal modification); promotion of UV resistance on resin modified woods (by incorporating dye in resin, or including HALS in the resin, or the use of surface coatings, or use of pre-modification with succinic anhydride); improvement of biodegradability (through the use of biopolymers rather than the traditionally chosen polymers and resins); and adding novel functionality through new polymer impregnants (leading to pH response, electrical conductivity, or energy storage by inclusion of phase change materials within the resin).

There have been examples of combining two modification systems to successful effect. Notably this is the basis for forming transparent wood by using delignified wood with polymer impregnation; but is also well demonstrated in the various chemical pretreatments (silanes, anhydrides) to enhance resin adhesion in resin modified timber. Some pretreatments have also been developed that could essentially be considered to be modifications, for example the use of NaOH to increase cell wall texture prior to grafting or deposition of other components, or the delignification of wood to alter nanostructure and chemical functionality.

This research has led to some new modification systems: delignification with compression (for flexible functionalised films); and the impregnation or encrustation with inorganic particles. This latter modification is not always considered to be a modification in the truest sense, as it overlaps with the impregnation of micronized copper or other traditional preservative systems. However, in this review we believe it is justified in some cases, where for example the deposition is highly controlled to provide closely spaced nanorods of ZnO as a surface coating, or TiO<sub>2</sub> of the correct crystalline form on the wood cell wall. This is clearly more engineered than simple impregnation with preservatives or FR systems; there is tailoring of crystalline forms and particle sizes. These systems are most closely associated with the treatments giving hydrophobicity and superhydrophobicity.

Many examples of simultaneously adding several functionalities while modifying wood can be found in the transparent wood family of products—where different systems have demonstrated combinations of secondary or tertiary functionalities through added nanoparticles, chemicals, dyes or active substances. Traits that have been achieved include: heat shielding, lasing, luminescence, heat storage and magnetic properties. It is clear from the many publications in this field that there is considerable scope to achieve new combinations through continued research.

Many of these multi-functional materials are not targeting traditional sectors where wood is used as a commodity material. The use of veneers or thin slices of wood for transparent materials in glazing or solar cells is a good example; it is likely to displace glass, rather than replace structural timber. However, good mechanical properties will still be required, to sustain the wear and tear of the domestic environment—weather, cleaning, human activity. Thus, the reported advances in mechanical properties [57,58,61] are a necessary part of the whole product. When transparent wood with energy regulating properties induced by phase change materials is fully developed, will it be used in posts and beams for routine construction? This is unlikely, a more strategic location for these wood materials will be chosen where their light diffusing qualities can be combined with greatest capacity for thermal gain and thermal release. It will be necessary to not embed the functionalised timber into standard wall elements as structural units, but leave them exposed within the wall to ensure a real contribution to the regulation of the interior environment.

A big question is: can multi-functional wood still be defined as wood or modified wood? Looking back at the definition proposed by Hill [3], many of the cases described in this review have retained the necessary traits:

- The action of chemical, physical or biological agents on the cell wall—in the case of this review, primarily chemical processes have been described, but also compression which is a physical process.
- Achievement of property enhancement has been achieved, in a very diverse set of properties.

In his definition, Hill continues to say that “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” [3]. This is probably the more challenging part of the definition, and the answers to different functionalised modified woods described in this review will vary significantly in their toxicity in service, or their likelihood of releasing toxic substances during service life or after disposal or recycling. To consider these questions would take detailed individual study, and during the route to scale-up and commercialisation of novel modified wood products, researchers must continue to ask these questions, to ensure that new products are correctly declaring their sustainable or environmentally benign credentials.

In order to do this, various green chemistry approaches, ecotoxicity studies, life cycle assessment (LCA) studies and other research will be required to answer pertinent questions about end-of-life options for modified wood or functionalised wood. There is clearly much to be done.

Certainly, this review has revealed that the range of modifications covered, and the scope of applications, show that wood modification may no longer be the sole remit of wood scientists but a true inter-disciplinary area. Ongoing work will involve metallurgy, ceramic, electronics, nanotechnology and polymer science on one hand and will involve engineers, designers, and even health professionals on the other.

## 7. Conclusions

Wood modification, by chemical, impregnation or thermal methods, has already been used to address issues such as dimensional instability with changes in moisture content, or by degradation and deterioration due to biotic factors or weathering with varying success. Ongoing research has looked to new chemical modifications and other fields of inspiration such as biomimetics and nanotechnology to further augment the properties of wood. This review has considered two parallel, and closely connected themes: (1) the functionalisation of modified timber and (2) the modification of timber to provide (multi)-functionality. In several examples we have observed new wood modification processes, which are emerging

through the pursuit of functionalised wood for high technology applications such as energy and electronics.

A large body of work is also emerging through nanotechnology approaches that have been tested on wood (but not necessarily applied to modified wood yet). These were noted for their potential to radically change the way that wood is used in future. Wood, and especially delignified wood, is increasingly seen as a scaffold for enhancement through decoration with functional particles. In time, some of these nanotechnology techniques will be applied to modified wood as part of a multi-step process, where the benefits complement or offset the properties of the modified wood.

In the shorter term, a good example that is well advanced is the development of weathering resistant surfaces for thermally modified timber, which boosts the performance of the thermally modified timber in an area where it previously had a weakness. It is clear there are many other treatments and modifications in the pipeline. Certainly, as wood modification moves to render dimensional change negligible for wood, new aspirations for using this stable substrate in precision applications such as electronics or responsive materials have become tangible.

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