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REVIEW OF THE USE OF PF AND RELATED RESINS FOR MODIFICATION OF SOLID WOOD

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SUMMARY

Wood is a porous, hygroscopic and anisotropic material. This means it takes up water by an adsorption process, hydrogen bonds with it, and shrinks/swells differently across individual planes. Uptake of water also makes it vulnerable to decay. Thermosetting resins have long been used to modify wood to improve a number of properties such as moisture uptake, stability, mechanical properties and decay resistance. The chemical composition of resins, their method of application and wood species used have all been found to influence quality of modification. This review introduces the types of resins used and products manufactured. The proposed mechanisms for stabilisation, methods used to examine resin modification of wood and the resulting changes in wood properties are discussed.

KEYWORDS: Resin, modification, wood property changes

INTRODUCTION

Wood is an anisotropic, porous material whose structural and conducting elements vary depending on location in the stem, within species and between species. This variation influences sorption and movement of water in wood. Major longitudinal elements (cells) in softwoods are the tracheids, with vessel elements and fibres in hardwoods. Flow paths within and between these cells influence movement of fluids within wood. Wood cell walls are comprised of three major polymers: cellulose, hemicellulose and lignin, combined to form microfibrils, the cell wall building blocks. The presence of accessible hydroxyl groups on hemicellulose and amorphous cellulose, allows for sorption/desorption of water (liquid or vapour) when exposed to fluctuating environmental conditions. This influences wood moisture content, external dimensions, mechanical and physical properties and influences decay susceptibility.

Much work has been undertaken to reduce the interaction of wood with water using wood modification, with laboratory studies dating back to the 1920's (Furuno *et al.*, 2004; Pizzi and Belgacem, 2016). The type of modification selected depends on the end use of the wood. Concerning solid wood, modifications are largely designed to improve dimensional stability, strength, hardness and biological durability (Cofta *et al.*, 2004; Franke, 2017; Furuno *et al.*, 2004; Gascon-Garrido *et al.*, 2015; Hansmann *et al.*, 2006; Hill, 2007; Xie *et al.*, 2013). Thermosetting resins may be used to develop polymer composites (wood and resin) for commercial applications. This review draws together publications on the modification of solid wood with thermosetting resins, with a focus of phenol-formaldehyde resins (PF), resin chemistry, resin/wood interactions, methods of analysis and changes on wood properties.

RESIN IMPREGNATION TREATMENTS 'HISTORIC' MATERIALS (IMPREG AND COMPREG)

Wood impregnation with PF resins has been studied since the early 20th Century (Stamm and Seborg 1962, Gascon-Garrido *et al.*, 2015). Impreg and Compreg were materials developed in the 1960's in the United States (Gabrielli and Kamke, 2010; Pizzi and Belgacem, 2016).

Both involve the impregnation of wood veneers with PF resin:

- For Impreg, following PF resin treatment, veneers are dried at temperatures of 87°C (presumably to reduce resin pre-cure) to moisture contents of 10%. Resin is then cured at high temperatures retaining the wood cell wall in a swollen state.
- Compreg treatment involves curing resin under compression increasing wood density and strength and further improves dimensional stability.
- Both processes have uses in tool handles, musical instruments and electrical instruments (Pizzi and Belgacem, 2016).
- Stamm and Seborg, 1962 reported on Impreg and noted:
 - Form of resin was important, with unreacted PF components performing better than those part-cured because the latter are larger and less able to penetrate the cell wall.
 - Importance of achieving resin penetration of the cell wall to optimise dimensional stability and the usefulness of a diffusion period in achieving this.
 - That treating veneers overcame problems associated with resin penetration into larger pieces and
 - That naturally occurring extractives in resinous softwoods interfered with PF resin cure.
- Stamm and Seborg also reported the concentration of PF resin in treating solution influenced its location in the wood structure following cure, with high resin concentrations >40%, resulting in some resin curing in the cell lumens since cell wall voids were already saturated with resin.

Impreg and Compreg were the first commercially available PF-impregnated wood composites. These materials showed great improvement in dimensional stability with anti-swelling efficiency (ASE) values of 75 and 95% at weight percent gains (WPGs) of 35 and 30% for Impreg and Compreg, respectively.

Vinyl monomers have been used for the modification of solid wood in laboratory studies. Commercially available vinyl monomers trialled with wood include acrylonitrile, glycidyl methacrylate, methyl methacrylate (MMA), hydroxyethylene methacrylate and styrene (Ibach and Ellis, 2005; Pizzi and Belgacem, 2016; Xie *et al.*, 2013). Modification using vinyl monomers has been shown to improve tensile, bending and compression properties of wood (Yildiz *et al.*, 2005). However, since most vinyl monomers do not penetrate the wood cell wall, and since dimensional stability relies on reducing moisture sorption by the cell wall, this is better achieved using thermosetting resins.

THERMOSETTING RESINS FOR WOOD MODIFICATION

Formaldehyde-based resins

Formaldehyde (also known as methanal or methyl aldehyde) is produced on a global scale for a number of industrial uses but almost 70% of production is used for synthesising formaldehyde based resins (Conner, 1996; Salthammer *et al.*, 2010).

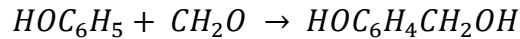
Formaldehyde has long been known to be a cross linking agent for cellulose (Goldstein, 1977) hence it has long been used as a resin base in the wood industry. Formaldehyde based resins are primarily amino resins, which encompass any thermosetting synthetic resin, formed by polymerisation of amine with aldehydes. The most common amino resins are: Urea-formaldehyde (UF), Melamine-urea-formaldehyde (MUF), Phenol-formaldehyde (PF), Phenol-urea-formaldehyde (PUF) and Melamine-formaldehyde (MF). One should be mindful that the chemistry and exact formulations of these resins vary with manufacturer, but the general chemistry remains constant. Table 1 summarises the advantages and disadvantages of major formaldehyde-based resins and study references for wood modification.

Table 1: Advantages and disadvantages of commercial formaldehyde resins and wood modification studies

| Resin type | Description | Advantages | Disadvantages | Wood modification study |
|---|--|---|---|---|
| Urea-formaldehyde (UF) | UF resin is manufactured by combining urea ($\text{CH}_4\text{N}_2\text{O}$) and formaldehyde to produce branched and linear polymers with a three-dimensional structure in cured resin. | Low cost Suitable for a variety of curing conditions Fast curing Colourless Microbial and abrasion resistance | Poor hydrolysis resistance High quantities of free HCHO | (Deka and Saikia, 2000; Shi et al., 2007) |
| Melamine-urea-formaldehyde (MUF) | copolymerisation of urea and melamine during resin formation give superior resin qualities | Compromise between UF and MF in terms of strength and cost Good hydrolysis resistance Lower cost than MF | Melamine is High Cost Slow curing (Dunky, 1998) | (Gindl et al.,(Cai et al., 2007) 2007) |
| Phenol-formaldehyde (PF) | There are two major forms of PF: resols and novolacs | Low phenol to formaldehyde ratio helps reduce cost Fast curing Good hydrolysis resistance Colour customisation | Dark-coloured High cost Reduced mechanical properties | (Franke, 2017; Furuno et al., 2004; Gabrielli and Kamke, 2010; Gascon-Garrido et al., 2015; Goldstein, 1977; Kielmann et al., 2018; Xie et al., 2013) |
| Melamine-formaldehyde (MF) | Manufactured in a similar fashion to UF resin, but urea is replaced with melamine ($(\text{C}_3\text{N}_3)(\text{NH}_2)_3$). | Good hydrolysis resistance (Dunky, 1998) | High cost Slow curing | (Homan and Jorissen, 2004; Altun and Tokdemir, 2017). |
| Methyolated melamine formaldehyde (MMF) | | No colour change Increased hardness and thermal properties Microbial resistance Low cure temperatures | High cost | (Barroso Lopes et al., 2014; Behr et al., 2014; Epmeier and Kligler, 2005; Mahnert et al., 2015; Su et al., 2011a; Westin et al., 2006) |

Phenol-formaldehyde (PF) and phenol-urea-formaldehyde (PUF)

PF resins are formed through a stepwise polymerisation reactions that can be acid or alkaline based. Several variations of PF resins can be produced depending on their desired end-use. Phenol reacts with formaldehyde at the 2nd, 4th and 6th sites (*ortho* and *para*), allowing up to three units of formaldehyde to attach to the ring (mono, di, tri methylol phenols). The initial reaction in all these cases involves the formation of hydroxymethyl phenol.



PF resins are formed by the catalysed combination of phenols from petroleum and formaldehyde. In resol formation, methylation takes place on all the positions of the phenol ring to produce mono-, bi-, or tri-methylated structures. These structures bind together by methylene or ether links to form the resin structure on cure with exclusion of water (condensation reaction). Resol PF resins have high formaldehyde to phenol ratios, 1.8:1 to 2.0:1. Novolacs are formed by the acid catalysis of the reaction. They are lacking in methylated groups, hence a hardener must be used as well as elevated temperatures to form a resin. The addition of the hardener releases formaldehyde, which aids the formation of methylene links between molecules. Other, custom phenolic formulations may include other monomers which can enhance reactivity and potentially lowering energy requirements (Lee, 2007). Some of these may include resorcinol, hydroquinone, and cresol which are more reactive than phenol.

PF resins are widely used in the wood industries as adhesives. This relatively low molecular weight resin interacts with hydroxyls in wood forming hydrogen bonds and if in the cell wall, it plasticises improving dimensional stability, decay resistance and mechanical properties (Gabielli and Kamke, 2010; Gascon-Garrido *et al.*, 2015).

Phenol-urea-formaldehyde (PUF)

One drawback to using resol PF resin, is that high quantities of formaldehyde are emitted (Adawiah *et al.*, 2012). Such resins contain high amounts of methylol groups which are often released when the final product is exposed to high temperature and humidity. Formaldehyde is polar and will readily react with water, hence when exposed to high moisture the product emits its unbound formaldehyde. Therefore, a scavenger of free-formaldehyde is often utilised. Urea added to phenolic resin (PUF) is designed to chemically bind to the excess formaldehyde left over on curing. Other additives can be used such as ammonia but urea is of relatively low cost. Few investigations have been conducted on impregnation of solid wood using PUF. Adawiah *et al.*, (2012) evaluated the use of low molecular weight PUF resin for modification of sesenduk (*Endospermum diadenum*) and jelutong (*Dyera costulata*) used in *Compreg*. The results found that formaldehyde emissions were significantly less than wood treated with PF resin, but the strength properties were reduced. ASE results were good, up to 60%, indicating that the resin had entered the cell and caused bulking. Fitiri *et al.*, (2017) also reported significant reduction in formaldehyde emissions from sesenduk treated with PUF compared with PF prior to and following ageing tests.

Other resins (non-formaldehyde)

Formaldehyde is harmful to health and legislation is in place that places limits on emissions from products to reduce impacts on indoor air quality. Wood modified using formaldehyde-based resins, do emit formaldehyde into the atmosphere. As such there have been alternative, non-formaldehyde resins developed, such as isocyanate-based adhesives.

Methylene Diphenyl di-isocyanate (MDI)

MDI is manufactured from aniline, formaldehyde and phosgene. It is unique in that it reacts with both the moisture in the material and the hydroxyl groups of the material (Papadopoulos *et al.*, 2002). The adhesive properties result from the covalent bonded urethane bridges, which are formed with the terminal hydroxyl groups of the cellulose molecules in the wood. This chemical bond is very strong and moisture resistant. Despite the fact that such resins are more costly than UF, the quantities of resin required to produce excellent bonding qualities are less (by dry weight) and therefore MDI is commonly used for MDF and particleboard production. A slightly different alternative is to use polymeric MDI (PMDI) resins, which are produced to have a quicker cure time.

1,3-Methylol-4,5-dihydroxyethyleneurea (DMDHEU)

DMDHEU is an N-methylol compound used as an anti-wrinkle finish in the textile industry (Pizzi and Belgacem, 2016; Xie *et al.*, 2013) as well wood modification with the product Belmadur. DMDHEU treated wood has improved weathering properties as the treatment reacts with hydroxyl groups of lignin, creating a crosslink between the cell wall structure and improved dimensional stability (Homan and Jorissen, 2004). DMDHEU has a molecular weight of 178, penetrates the wood cell wall (Xie *et al.*, 2013) and reduces pore size by occupying void space within the cell wall (Pizzi and Belgacem, 2016) thereby reducing hygroscopicity. Due to its ability to improve wood weathering Dieste *et al.*, (2008) evaluated use of DMDHEU to treat wood to produce exterior grade plywood. The study revealed that dimensional stability was significantly increased but MOE and bending strength was unaffected and hardness decreased. Homan and Jorissen, (2004) also reported DMDHEU had little influence on strength. A study conducted by Xie *et al.*, (2007) found wood modified with DMDHEU using magnesium chloride (MgCl₂) catalyst, reduced the strength of wood as a result of hemicellulose degradation and that DMDHEU incorporated into the cell wall of fibres increased brittleness making it less suitable for veneer modification. A number of studies found DMDHEU reduces susceptibility to decay by wood rotting fungi (Pizzi and Belga 2016). A study conducted by Verma *et al.*, (2009) found that with increasing weight percent gain (WPG) in pine and beech, decay susceptibility reduced. It was concluded that “full protection” was reached with a WPG of 15% for beech and 10% for pine. Another study conducted by the same authors found that fungal activity continued on wood with high WPG of DMDHEU treated wood, showing that the DMDHEU did not act a fungicide (Verma *et al.*, 2008). Therefore, it was not considered a long-term preventative measure against fungal decay as the fungi were still active after 12 weeks.

RESIN MODIFICATION AND DIMENSIONAL STABILISATION

Dimensional stabilisation of wood is highly-desirable, and most wood modification processes aim to improve this property. It is achieved by preventing water accessing and binding with free hydroxyl groups in the cell wall. In resin modification, this is achieved by one or more of the following:

- Occluding flow paths to restrict movement of water throughout the wood structure.
- Coating the cell wall/lumen interface to restrict water access to water-binding sites in the cell wall.
- Occupying pores in the cell wall where these binding sites are located. Once here, resin obstructs entry of water, occupies space that might otherwise be occupied by water (leading to wood bulking) and reacts with binding sites (Gascon-Garrido *et al.*, 2015).

The last provides the best method of achieving dimensional stability provided a good level of bulking is achieved and resin remains ‘fixed’ in the pores. Although cured resin in lumens can reduce rate of uptake it does not prevent this (Xie *et al.*, 2007).

Impregnation of dry wood with PF resin diluted in water results in swelling indicating resin accesses hydroxyl sites in the cell wall. Once cured by heating, it forms an insoluble cross-linked three-dimensional polymer reinforcing the wood structure (Kamke and Lee, 2007; Wan and Kim, 2007; Xie *et al.*, 2013; Gabrielli and Kamke, 2010; Hosseinpourpia *et al.*, 2016). That wood is bulked following curing indicates PF resin rather than just water has accessed the cell wall and remained in-situ following cure.

The effectiveness of PF resins at improving dimensional stability and the permanence of modification has been assessed using a range of techniques set out below. Factors found to influence modification and their influence on commercial use are set out.

Lignocellulosic materials naturally have a difference in rates of sorption and desorption of moisture, generating a hysteresis effect. This is a result of a lag in response the cell wall matrix to water molecules coming and going in different environments (Hosseinpourpia *et al.*, 2016). But when wood is modified with a thermosetting resin, the cured resin matrix increases the stability and stiffness of the wood so that it can no longer swell to accommodate moisture (Hosseinpourpia *et al.*, 2016). This does result in other properties of wood changing, sometime, adversely. However, a benefit of this modification of wood is that a number of other properties are improved and the chemical structure of the wood cell wall remains the same (Hosseinpourpia *et al.*, 2016).

Wood structure and resin distribution

Resin penetration of wood is seldom without difficulty, so impregnation of individual lumens and cell walls may not be uniform throughout the piece (Furuno *et al.*, 2004). Flow is influenced by wood anatomy and varies with species, region of the stem from which wood is obtained (Kamke and Lee, 2007; Reinprecht, 2016)), wood extractives (Gindl *et al.*, 2003; Xie *et al.*, 2013), resin viscosity, wood moisture and method used to apply the resin. The dimension of the piece being impregnated is also likely to influence resin distribution and is an important consideration when stepping up from lab-scale to commercial production.

Getting PF resin into the wood cell wall is complex and governed by many factors. The main features of the wood cell wall are the middle lamella, a thin primary wall and a compound secondary wall. The middle lamella is not strictly part of the cell wall, but it holds adjacent cells together. The primary wall is approximately 0.1-0.2 μ m thick in softwood tracheids (Keey *et al.*, 2012) and resin penetrating into the cell wall must first pass through this layer into the secondary wall. In studies with MMF resin it was found to be concentrated in the primary wall flow path (Mahnert *et al.*, in press). The secondary wall is comprised the S₁ (0.1-0.3 μ m thick), S₂ (1-5 μ m thick depending on early or latewood), and S₃ (0.1 μ m thick) layer (Keey *et al.*, 2012). Cell walls are able to transmit gases and polar liquids due to their microporous structure which has vacant pores (1-80nm diameter) lined with hydroxyl and other polar composites. In the presence of polar liquids, macromolecules repel each other, further increasing the porosity of the cell wall, hence potential for diffusion and capillary transport continuously increase (Reinprecht, 2016). The sizes (diameters) of these pores relative to the resin molecules, influences penetration.

Wood moisture content and resin distribution/penetration

Wood moisture content influences resin impregnation at macroscopic and ultrastructural levels. It has been reported that moisture content prior to impregnation should be less than 30% (Cofta *et al.*, 2004) as recommended for pressure treatment using preservatives. Free water in lumens

above fibre saturation point (nominally 30%) has the potential to dilute resin and it occupies space, preventing resin gaining access to some regions. However, for some wood species/stem regions, drying wood to low moisture contents <30%, promotes pit aspiration which can retard flow of liquids in wood. For large section sizes it is unlikely that moisture content of 30% will be achieved throughout the section, but a gradient will exist.

Other workers have found moisture content influences penetration of the cell wall by low molecular weight PF resins. It was found to be faster where walls had high moisture contents (Haygreen and Gertjens, 1971; Wan and Kim, 2007). Xie *et al.*, (2007) also stated penetration of water-based resins into wood walls is easier where moisture contents are high. Gindl *et al.*, (2003) reported that for MF resins, high cell wall moisture contents and high-water contents in resins promoted MF resin penetration of the wall. It is hypothesised that moisture in the cell wall opens pores and facilitates diffusion of resin from lumens into the walls.

Wood and resin interaction

Water-based resins such as PF and amino resins can separate, as water is absorbed into the cell wall, leaving behind the high molecular weight polymer in the lumens or at pit membranes (Kamke and Lee, 2007). Additionally chemical interactions between resin components and the cell wall can restrict flow (Kamke and Lee, 2007).

A resin/reagent must be able to gain access to and penetrate the micropore network. Cell wall pores can be subdivided into, macropores (>50nm), meso pores (2-50nm) and micropores (<2nm) (Kojiro *et al.*, 2010; Yin *et al.*, 2015). These pores play a crucial role in wood behaviour including mechanical properties as well as porosity and dimensional stability. The volume of meso and micropores are different in sapwood and heartwood, early wood and late wood. Initially liquids (water or reagents) enter into the macropores (lumens) and then diffuse into the cell wall through the meso and micropores. In heartwood there is a decrease in the volume of mesopores compared to heartwoods, which can be attributed to the accumulations of extractives during heartwood formation (Yin *et al.*, 2015). The earlywood of sapwood develops rapidly during springtime and it is thought that this rapid development generates more mesopores. Whereas in latewood, where the growth is slower in autumn, there is a greater volume of micropores (Yin *et al.*, 2015). So, when considering wood impregnation and cell wall penetration, it is important to consider if the wood is all sapwood and what the proportion to early and late wood is.

The state, swollen or shrunk, of the cell wall also has an influence on the cell wall structure and consequently penetration. In a fully swollen state, the accepted maximum diameter of a cell wall micro-pore is 2-4 nm (Hill, 2007). However, to gain access the wood must first be in a swollen state, as in a dry condition the micro-pores collapse and are inaccessible to resin. Also, the resin molecules themselves must be small enough to penetrate these micro-pores otherwise penetration and dimensional stability remain poor.

Resin properties

Resin properties are tailored to their specific end-uses. Major properties such as molecular weight, viscosity, solids contents and surface tension of the resin can influence penetration into wood (Kamke and Lee, 2007). For example, MDI are of lower molecular weight and surface tension than PF resins and can penetrate deeper into the wood structure (Kamke and Lee, 2007). The chemical composition can also play a role in wood modification. A study conducted by Leemon *et al.*, (2015) modifying phenolic resin with a nanoclay resulted in higher reduction in water absorption (RWA) compared to unmodified PF and untreated wood. Additionally, adding 1.2% nanoclay to the PF resin improved the strength properties of the wood. Shi *et al.*, (2007) reported on the use of nano-SiO₂ in UF resin to treat poplar (*Populus tomentosa*) under different

resin production criteria. The results showed that all resins improved hardness, ASE and resistance to water uptake. NaOH is added to high molecular weight resins to improve swelling of cell walls to increase resin uptake (Kamke and Lee, 2007). However, this can lead to detrimental effects such as weakening of the cell wall structure (Wan and Kim, 2007). The addition of acid-based catalysts to DMDHEU can also negatively affect wood structure. Acid catalysts hydrolyse hemicelluloses and cellulose gradually reducing mechanical properties of treated wood (Xie *et al.*, 2007).

The molecular size of the impregnating chemicals affects their penetration into the wood cell wall and has the biggest impact on impregnation success (Furuno *et al.*, 2004; Gabrielli and Kamke, 2010; Gascon-Garrido *et al.*, 2015; Kamke and Lee, 2007; Wan and Kim, 2007; Xie *et al.*, 2007). Resins of a monomer structure (oligomers) are preferred as these stand a better chance of getting into the cell wall (Kluppel and Mai, 2013). PF resol resins of lower molecular weight (290-480) (Adawiah *et al.*, 2012; Xie *et al.*, 2007) can better penetrate the wood cell wall (Franke, 2017; Hosseinpourpia *et al.*, 2016). Furuno *et al.*, (2004) observed that resins of low molecular weight were deposited extensively in the wood cell walls reducing cell wall swelling on water immersion. However, excess resin that cannot penetrate the wood cell wall is deposited in the lumens sometimes as a coating or sometimes blocking them (Furuno *et al.*, 2004). This is not uniform and under a light microscope areas of resin build-up/blockages were observed sporadically throughout the structure.

Care should be taken in the interpretation of microscopic findings as this might be construed as resin being unable to penetrate the wall rather than it being saturated. Higher molecular weight PF resins above 800-820 (Franke, 2017; Gabrielli and Kamke, 2010; Xie *et al.*, 2007) are deposited in the lumens and had little influence on water absorption and subsequent swelling (Gabrielli and Kamke, 2010; Wan and Kim, 2007). Higher molecular weight PF resins do have potential to penetrate the wood cell wall but are inhibited at a microscopic level, likely due to viscosity (Franke, 2017). There is evidence that high molecular weight resins do still penetrate cell walls resulting in bulking but to a lesser extent than low molecular weight resins (Franke, 2017).

A study by Furuno *et al.*, (2004) suggested that bulking observed using medium to high molecular weight resins is due to smaller fractions of the high molecular weight resin penetrating into the cell wall, leaving behind the majority of the larger resin fractions in the cell lumens. This behaviour was also observed by (Franke, 2017), the final product properties were different, depending on where the resin is located in the wood structure. It has been observed by Furuno *et al.*, (2004) and Franke, (2007) that the use of high molecular weight resins can damage the wood structure rather than improving performance. It was found that, as the resin could not penetrate the wood cell wall, the resin remained in the lumens and when cured caused considerable shrinkage, deformation of tracheids and rays and failure of cell walls.

The solids content (resin loading) can impact cell wall penetration too. It has been reported that a solids content of 30% is required to penetrate wood cell wall and subsequently reduce water absorption and swelling to generate an ASE of 70% (Wan and Kim, 2007). Hansmann *et al.*, (2006) also reported on MF resins of different solids contents and levels of methylolation. The results showed that there were impacts on levels of weathering and surface cracking but concluded that a cell wall penetration is the most critical factor when dealing with thermosetting resins and wood modification. A study conducted by Wan and Kim, (2007) found when impregnating Southern yellow pine, the molecular weight played a greater role in influencing ASE results than solids content. Biziks *et al.*, (2016) also reported that different formulations of PF resin brought about different levels of cell wall penetration and this influenced durability against basidiomycete decay.

Method of processing post-impregnation and quality of resin modification

Quality of resin modification seems not only to depend on getting resin throughout the wood structure using vacuum pressure impregnation but on allowing time for the resin to penetrate the cell wall.

Allowing a ‘diffusion period’ post impregnation is an important step in ensuring a more uniform spread of resin throughout the wood. Differences in resin concentration between the modification solution and wood moisture are equalised through diffusion (Klüppel and Mai, 2013). Hence the greater the initial moisture content of the wood, the more diffusion contributes to distributing the resin throughout the wood. This is especially important for cell wall penetration as it a diffusion-driven process as most cell wall pores are only accessible when the cells are in a swollen state (above fibre saturation point, FSP) (Hill *et al.*, 2004; Klüppel and Mai, 2013). Diffusion rate is affected by cell wall thickness, varying inversely with the square of the cell wall thickness (Goldstein, 1977). If the diffusion stage is included in the impregnation process it is important that the wood be stored under ‘non-drying’ conditions, where the wood is wrapped in impermeable material or kept submerged in impregnation solution (Furuno *et al.*, 2004; Klüppel and Mai, 2013).

In most studies and for material manufacture (Impreg) wood is dried post impregnation and prior to curing. Post impregnation, the chemical concentration in bound water and free water are uniform (Klüppel and Mai, 2013). As the wood starts to dry, the free water from the lumens exits the wood first, increasing the chemical concentration in the wood lumen. Therefore, there is a gradient between cell lumen and cell wall and diffusion of dissolved molecules into the cell wall micropores occurs (Klüppel and Mai, 2013). Without a drying stage and immediate curing after impregnation, the soluble chemicals begin to polymerise, molecular size increases and the chemicals cannot migrate into the cell wall during the curing stage, despite the high temperatures.

However, the method of drying can result in redistribution of resin in the wood structure if not carried out under controlled conditions. When drying wood impregnated with water-based resins such as PF and UF, there is an outward movement of water and migration of solute (urea, phenols etc.) to the surface of the wood. This can result in an uneven distribution of resin and problems with the quality of the piece. It can result in additional stress in the piece as the surface of the wood is dry but the centre is still wet, causing checks, honeycombing and ‘dog-bone’ shaped wood, the latter due to resin being concentrated and bulking ends and outsides (Ashaari *et al.*, 1990; Klüppel and Mai, 2013).

EVALUATING QUALITY OF RESIN IMPREGNATION IN WOOD

Ultimately, the critical factor in treating wood is maximising the migration of resin into the wood cell wall. Table 2 shows several methods used to examine where the resin is located within wood and its effects on stability.

EFFECT OF RESIN MODIFICATION ON WOOD PROPERTIES

Wood Colour

Wood impregnated with most thermosetting resins changes colour (Xie *et al.*, 2007). PF resin turns wood red-brown, reportedly due to change in the pH of the wood/resin (Furuno *et al.*, 2004), wood being acidic and PF resin (resole) alkaline. Kielmann *et al.*, (2018) found that PF resin could be further modified to ‘customise’ the colour of the final product with addition of iron salt without adversely affecting the effects of modification. Exposing wood to temperatures high enough to cure PF resin is also likely to lead to darkening of wood (personal observation).

Table 2: Techniques used to evaluate performance of modified woods.

| Method | Description | References |
|--------------------------------------|---|--|
| Weight percent gain (WPG) | A measure of the change in mass of a treated sample of wood as a percentage | (Behr et al., 2014; Biziks et al., 2016; Franke, 2017; Hill et al., 2004; Hosseinpourpia et al., 2016; Leemon et al., 2015) |
| Bulking (B) | A measure of resin in cell wall pores, with little bulking resulting from filling of the lumen | (Franke, 2017; Furuno <i>et al.</i> , 2004; Gascon-Garrido <i>et al.</i> , 2015; Ryu <i>et al.</i> , 1993; Wan and Kim, 2007). |
| Anti-Swelling Efficiency (ASE) | Compares change in volume of resin-treated wood fully-swollen - oven dry against unmodified wood | (Behr et al., 2014; Franke, 2017; Furuno et al., 2004; Leemon et al., 2015) |
| Irreversible swelling (IS) | Used as an indicator of dimensional stability | (Gabrielli and Kamke, 2010; Wan and Kim, 2007) |
| Resistance to water absorption (RWA) | Used to help measure obstructions to flow paths and water binding sites in the cell wall. | (Leemon et al., 2015; Shi et al., 2007). |
| Water repellent effectiveness (WRE) | Used to measure if a treatment has prevented or slowed down the rate of moisture or liquid uptake | (Cai et al., 2007; Trinh et al., 2012) |
| Leaching efficiency (LE) | Examines loss of material from wood following leaching usually in water | (Shi et al., 2007) |
| Microscopy | Used to observe the resin distribution in wood. Including light, scanning electron microscopy (SEM), electron probe X-ray microanalysis (EPMA) and transmission electron microscopy (TEM) | (Biziks et al., 2016; Cai et al., 2007; Furuno et al., 2004; Kielmann et al., 2018; Leemon et al., 2015; Su et al., 2011). |

Modified wood properties are influenced by the type of resin used to impregnate the species of wood. A study conducted by Deka and Saikia, (2000) modifying a softwood species *Anthocephalus cadamba* Miq with PF, UF and MF resins found that for all 3 resins used, a WPG was observed between 33-35%. However, PF resin modified wood resulted in a 70.59% ASE, whereas MF and UF modified wood resulted in ASEs of 68.23% and 48.5% respectively.

Influence on moisture sorption

Hosseinpourpia *et al.*, (2016) examined sorption of moisture over 0% to 95% RH at a constant temperature of 20°C, in Scots pine modified using PF and MF resins. However, PF resin better

penetrated the wood cell wall nanopores than MF resin. It was suggested that the higher moisture sorption was caused by the formation of hydroxyl groups in the resin when cured. With both MF and PF resins, the sorption hysteresis was reduced compared to untreated wood. This is a result of the cured resin matrix hindering swelling and relaxation of the cell wall, reducing lag between sorption and desorption.

Mechanical properties

Thermosetting resin impregnated wood becomes stiffer (increased MOE) as the bulking of the wood cell wall reduces its flexibility (Hosseinpourpia *et al.*, 2016). However, resin deposits in the wood cell wall and its benefits in blocking hydroxyl groups might be offset changes in cell wall structure. However, highly alkaline phenolic resin can cause the decrease of modulus of elasticity (MOE) (Furuno *et al.*, 2004). This could be a result of the swelling of the crystalline cellulose regions and a weakening of the molecular bonding of cellulose.

Epmeier and Klinger, (2005) found that for Scots pine treated with MMF resin MOR improved by 10%, however the MOE remained unchanged and impact strength significantly decreased by 61% compared to untreated Scots pine. Deka and Saikia, (2000) reported that for wood impregnated with PF, MF and UF resins to a WPG between 33-35%, did improve MOR by 12-20% but MOE was less influenced, only 5-12% improvement. Xie *et al.*, (2013) also reported that resin modified wood impacted little on MOE properties. It is evident different resins, resin loadings and processing methods have different effects on mechanical properties.

Xie *et al.*, (2013) reported low molecular weight MF resin penetrating wood cell wall and improving overall hardness. Melamine resins seem to greatly increase the brittleness (reduce in MOR) of wood which can create checking in the cell wall as a result of stresses applied during high temperature curing (Gindl *et al.*, 2007; Xie *et al.*, 2013).

Durability

As part of the carbon cycle, wood decays. Specialised groups of fungi and insects are responsible for this. Other micro-organisms deface wood in service e.g. moulds and stains, which reduce its value. Heartwoods of some timbers are inherently resistant to decay (naturally durable) though their overexploitation has led to sustainable supplies of many becoming limited. With respect to wood preservatives concerns over environmental impact and health has led to their restriction and interest in alternative methods of protection.

A wide range of wood modification techniques have been shown to improve durability including impregnation with some resin types (Gascon-Garrido *et al.*, 2015). Biodeterioration by fungi results from wood having a moisture content above fibre saturation point over a prolonged period. Wood exposed outdoors in Use Classes 3, 4 and 5 will be exposed to periodic or long-term wetting and be susceptible to decay. Therefore, controlling / reducing the amount of water absorbed by wood is one method for reducing decay. The use of resins to reduce uptake of water by the cell wall demonstrates its potential for reducing biodeterioration. Wood impregnated with PF resin has improved decay resistance to fungi and subterranean termites (Wan and Kim, 2007). Table 3 shows studies evaluating decay resistance of PF treated wood.

Table 3: Resin modification and decay resistance

| Study | Resin treatment and wood substrate | Key findings |
|---------------------------------------|---|---|
| (Gascon-Garrido <i>et al.</i> , 2015) | PF treatment of Scots pine sapwood | <ul style="list-style-type: none"> ~ All treated samples expressed greater resistance to termites than unmodified controls ~ Level of feeding markedly reduced ~ After exposure to wood in test 100% termite mortality |
| (Deka and Saikia, 2000) | <i>Anthocephalus cadamba</i> Miq. impregnated with MF, PF and UF resin | <ul style="list-style-type: none"> ~ A resin WPG between 33-35% improved resistance to termite attack |
| (Biziks <i>et al.</i> , 2016) | <i>Fraxinus excelsior</i> impregnated with a range of PF resins | <ul style="list-style-type: none"> ~ PF treated beech has improved decay resistance ~ A WPG of between 8-10% is sufficient to prevent brown rot decay in all PF resin types ~ Higher WPG was needed to prevent white rot |
| (Cofta <i>et al.</i> , 2004) | <i>Pinus sylvestris</i> impregnation with CCA and two types of resin. | <ul style="list-style-type: none"> ~ Different resin impregnation resulted in subsequent mould growth rates ~ Fungicide addition benefitted durability ~ Resistance depended on correct combination of resin and fungicide |
| (Gusse <i>et al.</i> , 2006) | Phenolic resin | <ul style="list-style-type: none"> ~ SEM revealed white rot fungi can decompose pure phenolic formaldehyde polymers ~ Decomposition generates water-soluble by-products ~ Use of white rot decay could offset high energy costing methods currently used to recycle phenolic resin |
| (Klüppel <i>et al.</i> , 2015) | Scots pine sapwood treated with, TEOS PF and MF compared against acetylated and unmodified wood | <ul style="list-style-type: none"> ~ Wood treated with PF resin had the highest WPG ~ Acetylated wood had the highest resistance to ship borer (<i>Teredo navalis</i>), PF resin modified wood had the second |

CONCLUSIONS

Thermosetting resins have long been used to modify wood to improve a number of properties such as moisture uptake, stability, mechanical properties and decay resistance. Impregnation of wood with thermosetting resins is a complicated subject that requires a wide knowledge of wood, wood structure, wood and water interactions and thermosetting resins. Formaldehyde based resin that have proven to be successful in modifying wood and the most successful are phenol based resins. These resins have certain characteristics such as low molecular weight that make it suitable for wood modification. It should be remembered that the type/species of wood and its structure also plays an important role in modification.

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