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Wood modification with resin impregnation technology for value-added services

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Abstract:

Plantation forests have taken the responsibility for sustainable supply of wood resources for household and industries as mankind increasingly faces the challenge of wood shortage. Resin impregnation technology has been taken to modify the low-quality plantation wood for more than half a century which is comprehensively mentioned herein. Various chemical polymers were tried onto dozens of wood species resulting to a common fact, i.e., resin impregnated wood can be enhanced dimensionally, mechanically, microbially, or else. Some modern advanced methods were proven feasible in analyzing the uptake and distribution of impregnated resins in wood. There should be a theoretic critical resin gain value to exactly saturate cell wall of approximately 35wt%. Excessive resin will merely act as the physical filler of the macropores while less may mean deficiency. The resin-impregnation technology shows its superiorities and prospectivity for fast-grown wood modification with comparable or even better properties to those from natural forests.

Keywords: Plantation wood, wood modification, resin impregnation, weight percent gain, anti-swelling efficiency

1. Introduction

Wood, a biomass with natural affinity to human beings, has been accepted as a necessity by mankind since the prehistoric ancient times, and is increasingly showing its state-of-the-art superiorities in competition with plastics, concrete, or steel. Decades of experience in Europe, North America, and recently in China, has proven that a balance can be reached between a secure ecosystem and a sustainable log-fetching industry, provided that forests are well-managed and wood is quality utilized. In practice, wood, especially those from fast-growing forests, features susceptibility to attacks by microorganisms, termites, submarine insects, or a conflagration; to be dimensionally unstable once exposed long in moist surroundings; and to be breakable once subjected to slightly heavy duties. In that context, some modification or enhancement measures should be taken, such as the resin impregnation technology.

The research on wood modification with resinous substances can be dated back to the 1930s (Stamm and Seborg 1939). Their work on "Resin-treated plywood" successfully developed two veneer-based products, i.e., Impreg and Compreg (Stamm and Seborg 1941). This can be viewed as the very beginning of resin impregnation of wood, which has since created a timespan of sixty years. In the coming forty years (1940s to 1980s), however, only limited publications were available on resin-impregnated wood (Tarkow et al 1966; Smith and Côté 1971, 1972; Shiraishi et al 1972; Ellis and Rowell 1984). Later, along with the vast demand for wood resources worldwide and the globally deeper knowledge of plantation wood, the 1990s saw the swarming up of related studies. Such fast grown species as the Norway spruce (Picea abies L, Karst), Scots pine (Pinus sylvestris L.), Japanese cedar (Cryptomeria japonica), poplar (Populus euramevicana cv.), Chinese fir (Cunninghamia lanceolata Lamb. Hook), and Douglas fir (Pseudotsuga douglasii) were mostly chosen to treat (Table 1). It's noted that most tabulated are coniferous low-density wood species which used to be restricted in light-duty applications. Such species like Albizia (Paraserianthes falkata, Shams et al 2006) with an extremely low density of 0.23g/cm3 can't be applied for heavy-loading structural use without highly enhancement.

Species	Specimen description ^[1]	Literatures	
Norway spruce (<i>Picea abies L, Karst</i> , 0.42g/cm ³)	10(L)x12(T)x30(R) mm ³	Gierlinger et al 2005	
	60(L)x75(R) x10(T) mm ³	Deka et al 2007	
	20(L)x 20(R)x 10(T) mm ³	Croitoru et al 2015	
	20x20x40 mm ³	Gindl et al 2003	
	60(L)x1.5(R) x40(T) mm ³	Shams et al 2006	
	70(L)x12(R) x12(T) mm ³	Žlahtič et al 2017	
Scots pine (Pinus sylvestris L.)	10(L)x20(R) x20(T) mm ³ ;	Lukowsky et al 1998	
	10(L)x20(R) x20(T) mm ³ ;	Lukowsky et al 2002	
	150(L)x3(R) x90(T) mm ³	Wallstrm et al 1999	
	20(L)x20(R) x50(T) mm ³	Klüppel et al 2013	
	50x5x0.8 mm ³	Ebrahimzadeh 1998	
	20x20x40 mm ³	Gindl et al 2003	
	70(L)x12(R) x12(T) mm ³	Žlahtič et al 2017	
Japanese cedar (<i>Cryptomeria japonica</i> , 0.34g/ cm ³)	500 (L)x 38(R)x 100(T) mm ³ , drilled	Fukuta et al 2008	
	3.5mm thick, 40mm diameter	Nishida et al 2017	
	10(L)x20(R) x20(T) mm ³	Baysal et al 2004	
	5(L)x30(R) x30(T) mm ³	Furuno et al 2004	
	60(L)x6(R) x40(T) mm ³	Shams et al 2004a,b	
	60(L)x1.5(R) x40(T) mm ³	Shams et al 2005	
	60(L)x1.5(R) x40(T) mm ³	Shams et al 2006	
Chinese fir (Cunninghamia lanceolata Lamb.	20 x 20 x 20 mm ³	Ma et al 2016	
<i>Hook</i> , 0.355g/cm ³)	1000(L)x38(R) x89(T) mm ³	Yue et al 2017	
Douglas fir (<i>Pseudotsuga douglasii</i> , 0.50g/cm ³)	60(L)x1.5(R) x40(T) mm ³	Shams et al 2006	
Hybrid poplar (<i>Populus deltoidesx</i> , 0.54-0.57g/ cm ³)	50(L)x25(R)x 15(T)mm ³	Lykidis et al 2019	
Loblolly pine (<i>Pinus taeda L</i> .)	10(L)x5(R) x5(T) mm ³	Wang et al 2016	
Corsican pine (Pinus nigra)	10(L)x20(R) x20(T) mm ³	Cardias et al 1999, 2003	
Anthocephalus cadamba Miq.	80(L)x10(R) x5(T) mm ³	Deka et al 2000,2002	
Beech (Fagus sylvatica)	50(L)x15(R) x20(T) mm ³	Engonga et al 1999	
European larch (Larix decidua Mill.)	20x20x40mm ³	Gindl et al 2003	
Red oak (Quercus rubra L.)	50(L)x20(R) x20(T) mm ³	Xu et al 2016	
Albizia (Paraserianthes falkata, 0.23g/cm ³),	60(L)x1.5(R) x40(T) mm ³	Shams et al 2006	
Red lauan (Shorea sp.,0.36g/cm ³),			
Elm (<i>Ulmus sp.</i> ,0.51g/cm ³),			
Japanese beech (<i>Fagus crenata</i> , 0.64g/cm ³),			
Japanese birch (<i>Betula maximowicziana</i> , 0.71g/ cm ³)			
Chestnut (<i>Castanea sativa</i>),	70(L)x12(R) x12(T) mm ³	Žlahtič et al 2017	

Table 1. Typical tree species for resin impregnation applied in selective publications

[1] Specimen dimensions marks: L-longitudinal, R-radial, and T-tangential. Otherwise fails clear introduction in cited literatures.

Resins used to impregnate wood vary in different times in the cited publications (Fig.1). Many studies focused on waterborne polymers like phenolic-, melamine-, urea-formaldehyde or isocyanate resins, among which phenolic resin were most frequently chosen partially due to its dark brown color similar to some natural tree species. Till in the 1990s melamine resins were more applied in some treating processes. Other chemical agents like Dimethyloldihydroxyethyleneurea (DMDHEU, e.g., Ashaari et al 1990a, b), furfuryl alcohol (FA, e.g., Westin et al 2003), methyl methacrylate (MMA, e.g., Hamdan et al 2011), poly (ethylene oxide) [PEO, or poly (ethylene glycol), PEG, e.g., Ebrahimzadeh 1998], or unsaturated polyester resin (UPR, e.g., Ma et al 2016) can be found occasionally in individual experiments. Unlike the petroleum-based resins, it's noticeable that some scientists paid unique attentions to lignocellulose-borne impregnating chemicals from fruits, seeds, or wood itself like tung oil (Žlahtič et al 2017), rosin (Dong et al 2016), or teak extractives (Balfas 2019).

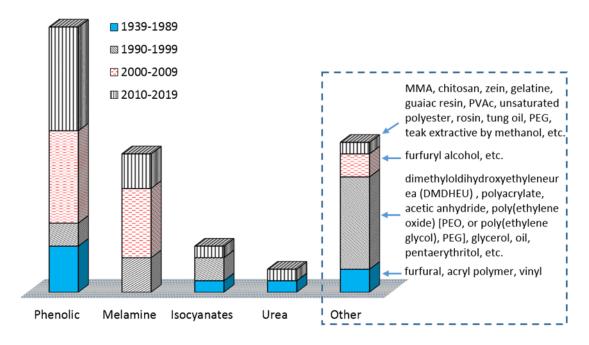


Fig.1 Resins applied for wood impregnation in different development periods

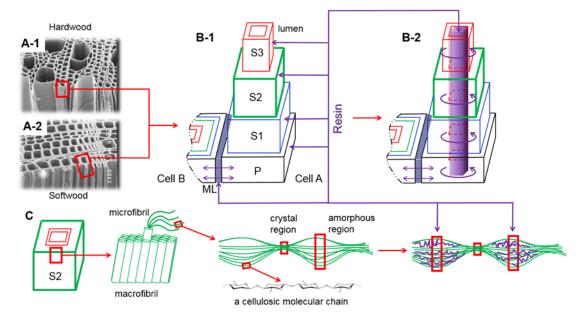
Nowadays, resin modified wood products have found their industrial applications and markets more in Europe, North America, and a few other regions such as Japan. To compare, in other parts of the world like China, the industrial promotion of resin-impregnated wood (lumbers or veneers) is still limited. Plantation wood is primarily utilized in these regions as the raw materials for composites, e.g., plywood, particleboard, or fiberboard, while few for further value-added, heavy-duty wood products for the residential buildings, sports stadiums, bridges, containers, or even aircrafts. Therefore, it's necessary to systematically sum up the relevant aspects of resin-impregnation of wood to the public to promote the industries.

1. Basic theoretic aspects

The accessibility of resinous substances into wood depends on a variety of factors. Stamm and Seborg (1939) proposed three essential criteria for effective resin treatments of wood, i.e., sufficiently small resin molecules against the voids in wood, full solubility of the resins in polar solvents via which to fully diffuse into cell wall, and a strong affinity between resinous polymers and the polar macromolecular components of wood.

1.1 Porous structure of wood

Regardless of coniferous and needlelike species, wood owns a similar anatomic microstructure comprised of cells with normally a hollow lumen enclosed by the wall (Fig. 2A). A wood block actually comprises of two parts, i.e., the solid lignocellulosic substances and voids. The latter may be manifested as macropores (including inter-cellular canals, cell lumens, pit chambers, Fig. 2B) or nano-dimensional micropores in the amorphous regions among micro- fibrils in the cell wall (Fig. 2C). The voids of green wood are initially occupied by air and liquid or gaseous water. The impregnation of a wood block is essentially the process of displacement of water or air by an invading resinous entity. In this process, the three criteria proposed by Stamm and Seborg (1939) apply. The induced resinous substances may reside in the voids physically, chemically, or both. If covalent bonds can be effectively set up between the resinous entities and wood components, the impregnating treatment can achieve a strong "grafting", otherwise merely a transient "filling" which may lose effectiveness during service especially in an outdoor environment.





A-1. SEM of typical hardwood microstructure (Populus deltoidesx); A-2. SEM of typical softwood microstructure (Cunninghamia lanceolata Lamb. Hook); B
 -1. Resin penetrates from outside through cell wall invading amorphous region; B-2. Resin flows into lumens and invades cell wall from inside through amorphous region; C. Nanostructure of a cell wall exemplified by the S2 layer of a secondary wall, resin penetrating into the amorphous regions.

1.2 Molecular size control of resinous polymers

Size matching for a resin molecule against the voids in wood seem to be a crucial precondition for resin impregnation. Anatomically, the macropores in wood can reach a size of microns or even millimeter level, which is readily accessible for most polymeric molecules; while the micropores in cell walls are heterogeneous in size of 2-4 nm on average (Tarkow et al., 1966; Hill 2006) which are merely accessible for small molecules.

It's noted that moisture content may alter the porosity of wood remarkably. The macropores in wood (such as the cell lumen, pit chambers, intercelluar voids, etc.) may exist permanently regardless of uptake or loss of the moisture, although the sizes may vary accordingly. However, the micropores in cell wall may be transient. With enough water they are open, otherwise may close once dehydrated (Stamm 1964). Other polar solvents may also have the effect to "open" the micropores (Gindl et al 2003).

Following the size requirement by the inborn pores of wood, resins should be restricted in a pre- polymerized stage (Astaged). Furuno et al (2004) investigated the influence of molecular weight of PF resins on the impregnation performance of Japanese cedar. The resins with 270 g/mol or 490 g/mol number average molecular weight (Mn) penetrated into wood cell wall readily, while the larger molecules (Mn=820 g/mol) filled merely the cell lumen as pillar-shaped or cylindrical forms. Large molecules have high viscosity which hinders resin penetration as well. Small molecules have the tendency to choose cell wall to stay in priority rather than cavities, and only excessive resins may fill in the lumens. In this way, the efficiency of resin impregnation can be improved.

Another option to improve the permeability of impregnants is taking a two-step method. Monomers of small molecular sizes other than prepolymerized resins can easily enter wood cells, followed by in-situ polymerization with heating, radiation, et al (Hamdan et al 2011). Monomers have a bulking effect on wood cell wall, which can help "open" the microvoids. Shiraishi et al. (1972) studied the polymerization of methylmethacrylate (MMA) in the cell wall of Japanese cedar wood. SEM images disclosed that the MMA-treated wood had a high degree of cell wall swelling. A bias effect of monomer impregnation is that some polymerizing reactions may occur in lumens or intercellular cavities, which means only part the chemicals can reside in cell wall (Hill 2006).

1.3 Rheological features of thermosetting resins

The rheological behavior of a resin may play a significant role for its penetration and diffusion in wood. The actual penetration depth of a consolidant depends on the wood permeability to liquids, the impregnation methods, and physicochemical properties of the solution (Thébault et al 2018). Paris and Kamke (2015) reported that resol PF and isocyanates exhibit Newtonian flow over a shear range below 1000s-1, with viscosity of approximately 1300 and 500 centipoises, respectively. Polyvinyl acetate (PVAc), in comparison, showed shear-dependent viscosity behavior, which appeared to thicken at low shear rates but then shear-thinned from 12,000 cP to 2000 cP. Actually, most thermosetting resins, including above-listed resol PF, isocyanates, and other low-molecular resins such as A-staged MF resin, apply the law of Newtonian flow. However, their rheological behaviors may transfer to other mechanisms such as shear-thinning (pseudoplastic) or shear-thickening (dilatant) behaviors along with polymerization process. In those cases, the accessibility of resins into wood gets lower.

Table 2 summarizes the typical mathematical models applied in literatures, which can theoretically help understand the invisible penetrating and diffusing behaviors of resinous fluids in porous wood. Formulas A to C express the diffusion of a liquid in a porous medium under designated adaptable conditions under constant temperature. Formula D, the White-Roller equation, describes the changing law of viscosity of a liquid in its flowing process. Under heated conditions, the viscosity of thermosetting resins may be increased. In all the listed formulas, the parameters involved are from three sources: the impregnant (i.e., viscosity), the medium to be impregnated (i.e., specific permeability, surface tension, contact angle, pore radius, sizes), and the environmental conditions (i.e., pressure gradient, time of flow, temperature). Through these parameters, it's theoretically helpful to clarify the influential factors relevant to resin penetration and diffusion. In practice, wood is much more complicated than an ideal medium with uniform capillary pores. Hence, the practical application of these models may meet with considerable difficulties.

Formula	Parameters	Adaptable conditions	Literature sources
A. the Darcy's law: $Q = K \cdot \frac{A}{L} \cdot \frac{1}{\mu} \cdot \Delta P$	Q-the liquid volume flow; K-the specific permeability of wood; A-the area perpendicular to the liquid flow; L-the sample length in the direction of flow; M-the dynamic viscosity of the liquid; ΔP-the pressure gradient.	For homogeneous porous mate- rials; no interactions between the liquid and the porous materi- al; permeability independent of the porous material length in the flow direction.	Siau 1984
B. the Ebrahimzadeh's equation $D = \frac{\pi}{16} \cdot \frac{h^2}{t}$	D - the diffusion constant; h - the sample thickness; t – the time of flow.	For both sorption and desorp- tion.	Ebrahimzadeh, 1998
C. the Lucas-Washburn equation: $L(t)^{2} = \frac{\gamma_{L} \cdot \cos(\theta) \cdot R}{2\mu}$	t – the time of flow; μ – the dynamic viscosity of the liquid; γ_L – the surface tension; L–the distance into the capillaries; R – the pore radius; θ – the contact angle.	When a porous medium (e.g., paper) is assumed to comprise of a number of vertical, parallel cylindrical pores that are ran- domly distributed.	Thébault et al, 2018
D. the White-Roller equation: $\eta = K e^{E_{\eta} / RT} e^{K(T)t}$	 K- the Arrhenius predisposition factor; Eq- the activation energy of the viscous fluid; R- the universal gas constant; T- temperature; t - time; K(T)- the reaction constant. 	When a thermal-setting polymer is subjected to heating during flow.	White 1974; Roller 1975.

Table 2. Typical mathematical models describing the diffusion of a liquid into porous mediums

2. Processing procedures

Wood impregnation by resins involves generally three steps, i.e., wood pretreatment, resin soaking, and post-treatment of impregnated wood. The specific procedures vary greatly in different published work. Specimens normally in a rectangular shape of small dimensions, i.e., 10-100mm (longitudinal in fiber grain direction) by 10-40mm (tangential) by 1.5-25mm (radical), tend to be applied for lab-scale experiments although occasional studies adopted larger sizes. The random dimensions of specimens bring great challenges to directly compare among various tree species in resin uptake capabilities.

Prior to resin impregnation, wood specimens can be pre-treated to help clear up the porous pathways for the entry of resinous impregnants. Wood samples, normally oven- or air-dried, could be subjected to chemical extraction, vacuum exhausting, or physical heating. Deka et al (2000) extracted Anthocephalus cadamba Miq. wood samples with four solvents, e.g., dichloromethane, benzene±ethanol (2:1, v/v), acetone, and methanol, before resin impregnation. Shams et al (2004) soaked Japanese cedar veneers in Sodium Chlorite (NaClO₂) solution at 45°C for 12h followed by rinsing with running water for 6h. The treatment resulted to 2-21% weight loss after 1-4 treating cycle(s) mainly attributed to the removal of lignin. Shams et al (2006) heated Japanese cedar veneers with saturated steam causing slight weight loss (0.7-7.4%) due to the hydrolysis of hemicellulose, but the wood was effectively plasticized with higher compressibility in the resin-swollen condition. As a consequence, a discernible increment in density was achieved at a relatively low pressing pressure (1MPa).

Impregnation of wood under atmospheric environment needs a long duration (Lukowsky and Peek 1998). Hence, a vacuumpressure combined process was widely preferred, regardless of the differential technological parameters (Deka et al 2007; Kluppel and Mai 2013; Žlahtičet al 2017; Lykidis et al 2019; Balfas 2019). The process depends closely on the porosity of wood so that a fluid can interflow freely inwards and outwards. The wood specimens to be treated were enclosed in a closed vessel. The air in the vessel and subsequently the air and gaseous water in wood is expected to be pumped out forcefully, creating a subatmospheric space readily inducing the impregnating solutions into wood. After the vacuum, a positive pressure is exerted onto the solutions speeding up the penetration process. In some researches, a vacuum immersion followed by an atmospheric soaking was also applied (Lukowsky 2002; Furuno et al 2004; Baysal et al 2004; Ma et al 2016). More complicated, however, is the cycled treating procedures with vacuum (Shams et al 2004a, b; 2005; and 2006). Another method called "in-platen pressing" showed its superiority in resin uptake (Fukuta et al 2008). The wood block compressed in a resin solution to a high degree (e.g., 50%) may "inhale" quantitative resin once the compression is suddenly removed.

Timely polymerization of the impregnated chemicals in wood is crucial to fix the resin and the deformation of wood itself. Pre-polymeric resins, e.g., resol PF, are crosslinked to macromolecules under proper conditions like heating. Chemical interactions between resins and wood are highly preferable to fix the impregnants. Normally adopted water-borne resins, e.g., PF, MF, UF, or isocyanates, are reliable to build covalent bonds with wood through the hydroxyls on cellulosic or hemicellulosic molecular chains. Monomers impregnated into wood, e.g., methyl methacrylate, need special conditions such as radiation to be polymerized.

In practice, unlike the small-scale experiments in lab, a proper treating process should be set up according to local conditions. Too complicated procedures may achieve the better results but bring higher costs and longer durations, which may lose marketing attractiveness of treated plantation wood against natural wood. A proper balance should be reached among properties improvement and technical complexity as well as costs.

3. Properties of treated wood

3.1 Weight gain

Resin impregnation is directly manifested as the weight percent gain (WPG) of polymers in treated wood, which has significant influences on the density and other properties. The actual resin uptake levels may be attributed to multiple factors, including: wood species and locations (i.e., density, sapwood or heartwood), specimen sizes in the three anisotropic directions (i.e., lon-gitudinal, radial, or tangential), resin types, chemistry parameters of resins (e.g., molecular weight, viscosity, etc.), treating procedures (mentioned above) and corresponding technical parameters adopted (solid content of polymeric solutions, temperature, duration, degree of vacuum, pressure levels, repetition cycles), and so on. When all the above conditions are designated, a maximum WPG value can be decided since the accumulated volume of all the macro- and micro-pores of wood is constant.

The data from all the cited publications show a heavily disperse distribution of WPG values in accordance with varying treatment conditions. Weight gains of 10% or so can be seen in Lukowsky's work (2002) with modified MF resin of various formaldehyde content (10 wt%), Fukuta and co-workers' investigations (2008) with PF resin (Mn 400, 20wt%), and Balfas's research on teak extractive (2019). Much higher WPGs were found in other literatures. To simplify, WPG is closely correlated with the density of wood regardless of the specific wood species (Table 3). Basically the higher density wood species are more difficult to adopt resin. Although the tendency is not absolutely precise, it's helpful for industries to simply determine the adaptability of a wood species for resin impregnation. It's certainly crucial to expose the transverse cross-section of a specimen fully to the solutions.

Species ^[1]	Density/g.cm ⁻³	WPG/%	Impregnation procedure
Albizia (Paraserianthes falkata)	0.23	48.9	PF (20wt%; Mn300); oven-dried then treated (7 cycles: vacuum impregna- tion 12h+ air conditioning. 12h); air drying 3d; vacuum dried at 50°C for 12h.
Japanese cedar (Cryptomeria japonica)	0.31	72.4	
Red lauan (Shorea sp.)	0.36	43.0	
European spruce (Picea abies)	0.44	47.0	
Douglas fifir (<i>Pseudotsuga douglasii</i>)	0.50	34.7	
Elm (<i>Ulmus sp.</i>)	0.51	42.3	
Japanese beech (Fagus crenata)	0.64	33.7	
Japanese birch (Betula maximowicziana)	0.71	28.1	

Table 3. Weight percent gain of various wood species

[1] Sources: Shams et al, 2006

The concentration and the specific composition of a resinous polymer play important roles on resin uptake by wood specimens. Shams et al (2004) treated Japanese cedar plantation wood with low molecular PF resin (Mw=300g/mol). A sevencycle procedure was applied at various resin solid contents, i.e., 1, 3, 5, 10, and 20wt%, resulting to a proportional increase of weight gain: 5, 12.5, 20, 40, and 60.8wt%, respectively. Lukowsky (2002) synthesized melamine resins to treat Scots pine sapwood. Ten melamine/formaldehyde/methanol ratios at a solid content of 10wt% were applied, i.e., 1: (2.1-5.7): (1.4-4.5). Under a vacuum-atmospheric condition, a series of quite low WPGs of merely 4.8-7.5wt% were reached.

3.2 Resin distribution

As analyzed in Fig.2, resins are thought to be deposited in cell wall, lumen, or inter-cellular cavities. However, more attentions of wood modification focus on the accessibility of polymers into cell wall. With innovated analyzing technologies, it's easier to quantify and visualize the in-depth distribution of resinous substances in cell wall. Furuno et al (2004) induced electron probe X-ray microanalysis (EPMA) technology to detect the presence of resins in impregnated Japanese cedar wood. The micrographs successfully disclosed the presence of the phenol-formaldehyde resin on the transverse section of specimens through Br-Lα1 X-ray maps. The ultra-violet (UV) microscopic spectra can also be used to quantitatively evaluate the MF resin content in wood cell wall (Gindl et al 2003; Deka et al 2007). Through comparing the spectra of pure MF resin, untreated wood, and MF-impregnated wood, the content of MF resin can be calculated. The X-ray computed tomography (XCT) is another useful tool to analyze the resin distribution in wood cell (Kučerová 2012; Paris and Kamke 2015). Paris and Kamke (2015) applied Micro X-ray computed tomography (XCT) to analyze the adhesive penetration behavior of PF, MDI (methylene diphenyl diisocyanate), and hybrid PVAC (with PF) resins of different wood-adhesive bondlines with Iodine as the attenuating element. The 3D images showing the resin penetrated regions of wood were successfully constructed.

3.3 Bulking effect and Critical WPG value

Impregnated resins may replace moisture molecules in wood cell wall and simultaneously bulk the cell wall, similarly as water does. The difference exists in that resin bulking is irreversible (especially if chemical interactions occur between wood and resins), while water bulking is transient and reversible with moisture moves inwards and outwards. Stamm (1964) gave a calculated maximum volumetric swelling in organic liquids of the cell wall of about 38%. In that context, it's theoretically feasible to find out the critical WPG value for a designed type of resin that exactly fills the full volume of the micropores. More resin polymers taken up by wood may be excessively deposited in the macrovoids.

It's understandable that a wood block can be exactly saturated by water molecules in its cell wall at the characteristic moisture content, i.e., the fiber saturation point (FSP), without any excessive water molecules existing in the lumen or intercelluar voids. FSP in that critical state is normally taken as 30% on average for all wood species. Taking the substance density of wood as 1.50g/cm3 and water 0.998g/cm3 (20oC), the volume of water accounts for approximately 31% of wood cell wall following formula (1) and (2). Provided that all the cell wall voids initially occupied by water are fully displaced with cured resinous polymers, the resin weight gain can be acquired by equation (3).

$$V_{H_20} = \frac{0.3.\rho_{wood} V_{wood}}{\rho_{H_20}} \qquad \dots \dots \mathbf{1}$$

$$\frac{V_{H_20}}{V_{wall}} = \frac{V_{H_20}}{V_{H_20} + V_{wood}} = \frac{0.3.\rho_{wood}}{0.3.\rho_{wood} + \rho_{H_20}} \qquad \dots \dots \mathbf{2}$$

$$WPG_T(\%) = \frac{\rho_{resin} V_{H_20}}{\rho_{wood} V_{wood}} \times 100 \qquad \dots 3$$

Where, V_{H2O} , V_{wood} and V_{wall} are volumes of cell wall micropores, wood substances, and cell wall at a moisture saturated condition, respectively. Densities are 0.998g/cm³, 1.5g/cm³ and 1.15-1.21g/cm³ for water at 20°C (ρ_{H2O}), wood substance (ρ_{wood}), and resins (PF, MF, or UF, ρ_{resin}). This calculated value, i.e., WPG_T=34.5-36.3%, can be accepted as the theoretical critial value for resins like MF, PF or UF. This calculated value conforms to Deka's et al (2000, 2002) report (33.7-34.1%) for *Anthocephalus cadamba Miq.* Sapwood. At the critical WPG levels, bulking coefficients achieved the highest values for PF (14.54%), MF (12.28%) and UF (9.02%) at 33.7%, 34.1% and 33.8% WPG, respectively. The X-ray analysis confirmed that higher WPGs led to excessive filling of cured resin in the lumen cavities.

3.4 Hygroscopicity and Dimensional stability

Resin-impregnated wood differs from untreated wood with less porosity, higher density, and loss of most polar chemical groups such as hydroxyls. These groups used to have active affinity to moisture but are covered by or reacted with impregnated resin molecules. Hence, the chemistry features of wood are altered resulting to inerter hygroscopicity. Croitoru et al (2015) found that water sorption of wood declines with the impregnation of any a biopolymer (i.e., chitosan, zein, gelatine, or guaiac resin dispersed in EMIMCI ionic liquid) of higher hydrophobility (higher contact angles, from the reference 36.850 to 44.63-56.130). The water sorption occurs in two steps, i.e. wetting and swelling of the organic coating followed by an induction time (pseudo-equilibrium state) in which the water diffuses through the organic coating into the wood.

No matter what resins or processes are adopted, impregnated wood is evidently enhanced in its volumetric stability due to the complete or partial loss of the voids and the lignocellulosic hydroxyls that water molecules may build hydrogen bonds with. The anti-swelling efficiency (or termed as "anti-shrinking efficiency" in some literatures, ASE) values from various sources vary significantly. However, a universal fact is: higher ASE values tend to be along with higher resin gains. It's noted that a minus ASE value (-42.3%) occurred in Furuno and co-researchers' study (2004), where high molar weight PF (Mn=820g/mol) was applied. This may be due to the low permeability of resin.

3.5 Mechanical properties

Mechanical enhancement is another key initiative to impregnate plantation wood with resins other than dimensional stabilization. Wood gains cured resin and is densified with less inner voids through physical filling and/or chemical grafting. The hardness and strength (bending or compressing) of wood are hence improved significantly. Deka et al (2007) reported that Norway spruce's hardness in transverse direction increased with higher WPG levels (from 17.6N.mm⁻²-untreated to 27.6, 29.8, and 39.4 N.mm⁻² with WPG of 7.3, 13.2, and 22.9%, respectively). Ma and coworkers' (2016) research on fast-grown Chinese Fir wood with unsaturated polyester resin achieved strengthened bending strength and modulus by 112.85% and 67.13%, respectively, in comparison with the untreated samples.

Resin-impregnation along with thermo-compression may lead to further improvement of the mechanical properties. Shams et al (2004a, b; 2005, 2006a, b) conducted series of work on Japanese cedar. PF resin was applied as the impregnant in an inplaten pressing procedure. Wood was evidently densified from 0.34g/cm3 to 1.1g/cm3. During compression of wood, three regions were distinguished, i.e., elastic region, collapse-dominant region, and post collapse region. The occurrence of cell wall collapse was found to be strain-dependent at a strain level of approximately 0.06-0.08mm/mm. PF resin acted as a cell wall plasticizer and recovery restricter, with which the pressure needed to compress wood to a density of about 0.9g/cm3 was significantly controlled at a low level of 2MPa versus about 15MPa for untreated. In this process, pressure holding had a significant effect on densification and deformation-fixing of wood attributed to its creep mechanism.

The creep deformation of cell walls resulted from merely 30min of pressure holding to initiate collapse happens at a quite low pressing pressure under 2MPa. PF resin-impregnated wood required lower stress to initiate cell wall collapse than untreated wood.

The cured resin systems in wood are advantageous in fixing the deformation and control of high recovery of densified wood, which is a universal difficulty in wood-densification practices with hydrothermal compressing techniques. Since the very beginning of resin treatment of wood, Stamm and Seborg (1939) successfully applied this process to make the Comperg laminates. Lykidis et al (2019) densified poplar wood by impregnation with melamine formaldehyde resin. The resin acts as a means for reducing set-recovery of compressed poplar wood due to the formation of new bonds between cell wall components and MF. In the case of stress application at 10 kg/cm², the stabilization was improved by the use of MF to about 50% compared to water-treated specimens. Higher stress was not suggested in avoidance of outflow of the impregnated resin.

Modulus of tension or compression may have controversial results. Most wood-impregnating resins are thermosetting polymers, which tend to show rigidity once cured. Impregnated wood may lose part of its rheological capability due to the bulked cell wall. This may modify the viscoelasticity of wood. In case of compressing, the densification of wood may be contributed through its irreversible collapse of cell wall. In Shams' research (2004b), it's found that with higher WPG values of PF resin (from 5.3% to 10.1%), the pressure to collapse cell wall decreased from 1.6MPa to 1.0MPa. Hence, the final improved strength of impregnated and compressed wood can't ignore the side effect at the micro levels. From this perspective, an innovated resin system with better damping characteristics needs to be developed.

3.6 Weatherability, durability and fire-retardancy

Resin impregnation may also enhance other performances of wood. Cured polymers, except for the biopolymers (e.g., chitosan, zein, gelatine, or guaiac resin, applied in Croitoru's research, 2015), tend to be extremely unpleasant to microbial fungi or termites (Ryu et al 1993; Rapp et al 1996; Ritschkoff et al 1999; Sailer et al 1998). In addition, the resin can be a carrier dragging biocides into wood cell wall, hence ensuring wood with higher bio-resistance grades. Balfas (2019) applied teak extractives for rubberwood and teak wood modification. The treated wood had higher resistance to subterranean termite (Cryptotermis cynocephalus). Fujimura et al (1989, 1990, 1991, 1993, and 1993) used acrylic-copolymer carrying DBT-DL (di-n -butyl tin dilaurate) to treat hemlock (Tsuga heterophylla Raf. Sarg.), 6.075 mg of DBT-DL per gram of wood was required for surpression of the attack by brown rot. The existence of acrylic resin was thought to prevent the chemical elution into nature hence improving the safety of biocides treatment. As for fire-retardancy, a case can be found in Yue's et al (2017) work, where boric-phenol-formaldehyde (BPF) resin was synthesized to treat Chinese fir wood, achieving improved mechanical properties and fire-retardant performance simultaneously. It's, therefore, technologically feasible and economically efficient to enhance the weatherability, durability and fire-retardancy along with the targets of dimensional and mechanical enhancement of wood.

4. Thin veneers impregnation

In case of decorative thin veneers (DTV), the mechanism of resin impregnation is universal, while the practice shows vast difference. Similar to decorative paper for overlaying wood lumbers or composites, DTVs have significantly small thickness, normally ranging among 0.2-0.8mm. Resinous fluids penetrate the wood mostly in tangential direction rather than in the transverse section. In that case, resin impregnation follows type II pattern (Fig.2, B-2). Following the industrial production of decorative papers, thin veneers can be continuously impregnated in a belt pattern (Fig. 3). The impregnated veneers are continuously subjected to air drying for approximately 12-15s at 120-130°C (Tang et al 2016). The resin covering the surface and filling the inner voids of veneers is merely partially polymerized under hot air to eliminate the excessive small volatile molecules for storage. During subsequent overlaying, the resin will be fully cured as the bonding agent. As well, the cured resin acts as a protection film for thin veneers against moisture, contaminations, or daily abrasion. Accordingly, the veneers need to be over-loaded with resin to a WPG level over 60-80% to confirm the overlaying performances (Fig. 4).



Fig.3 Thin veneers being industrially impregnated with MF resin in a continuous floating

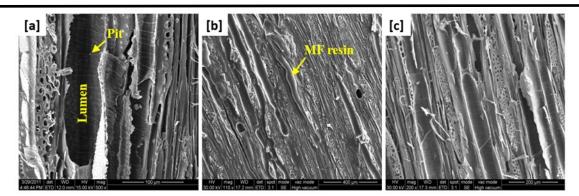


Fig.4 Poplar thin veneers at micro level before and after MF resin impregnation

5. Conclusions

Research and industrial practices of wood modification or enhancement through resin impregnation have a long history span over half a century. However, the work still continues essentially as mankind still faces the global challenge of wood resources shortage and low-quality plantation forests are acting as the main sustainable force in wood industries. With the invention and application of more advanced technologies and analyzing tools, the mechanism of resin impregnation in wood will be more clearly explored, and more precisely controlled processes will be developed. Wood through resin impregnation acquires higher dimensional stability, mechanical strengths or moduli, and/or stronger resistance to weathering, biodegradation, or even fires with combined techniques. To saturate wood cell wall, there should be a theoretic critical value of resin gain of approximately 35wt%, which can be a reference for later research work.

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