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EFFECT OF ANATOMICAL STRUCTURE ON DIMENSIONAL STABILITY OF LOW MOLECULAR WEIGHT PHENOL-FORMALDEHYDE IMPREGNATED WOOD

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ABSTRACT

This research deals with low molecular weight-phenol formaldehyde (LMW–PF) impregnation on sepetir (*Sindora* spp), nyatoh (*Palaquium* spp.), and pisang putih (*Mezzettia* spp.) woods to determine the effect of different anatomical structure on weight percent gain and dimensional stability improvement. The wood samples were impregnated using LMW–PF solutions with 7, 8, 9, 10, and 11% of concentrations (w/w), vacuum-pressured (–98 kPa, 15 min, 350 kPa, 4 h), and re-immersed in 80°C for 3 h. According to the findings, LMW–PF impregnation reduced coefficient of swelling by 9.64–29.95%, and increased anti-swelling efficiency by 12.24–29.91%. Additionally, the water absorption and thickness swelling reduced by 2.43–38.75% and 15.94–34.21%, respectively, indicating the improvement of dimensional stability. Microscopy and NIR analysis revealed the presence and reaction of LMW–PF within porous wood matrix. The effect of diverse anatomical structures caused complexity on LMW–PF impregnation. Sepetir-treated wood with fewer anatomical barriers resulted in better dimensional stability improvement than others.

KEYWORDS: Dimensional stability, impregnation, low molecular weight phenol-formaldehyde, wood anatomical structure.

INTRODUCTION

Since wood is a heterogeneous lignocellulosic material that is susceptible to dimensional changes, therefore, it is insufficient for long-term applications (Huang et al. 2014, Essoua et al. 2016, Cai et al. 2019). Therefore, numerous researchers have developed a variety of countermeasures. Impregnation process involves treating wood with a monomer/impregnating agent that diffuses into the cell walls, followed by polymerization to alter the wood's desired properties (Hill 2006). Many impregnating agents have been utilized, among them, thermosetting resin is still the preferred choice, particularly conventional PF resins (CPF). This type of impregnant has several advantages, including good moisture resistance, superior mechanical and electrical properties, heat and flame resistance, and lower smoke production during combustion compared to other resins (Nor Hafizah et al. 2014, Hamad et al. 2019). However, CPF-treated wood has poor penetration on a nanometer scale due to high molecular weight (Laborie 2002, Nor Hafizah et al. 2014). Furuno et al. (2004) stated that only a small amount of high molecular weight PF permeated the cell walls (in the tracheids walls of earlywood and latewood), indicating a negligible effect on the dimensional stability. Therefore, low molecular weight PF (LMW–PF) is one of the solutions to overcome the limitation of CPF.

The characteristics of LMW–PF differ from CPF, particularly in terms of molecular weight, solubility, penetration, etc. The LMW–PF has several advantages, such as water-soluble, lower cost, easy to be applied, and non-toxic (Huang et al. 2014). The LMW–PF has a molecular weight ranging from 290–600 g/mol (Wan and Kim 2006, Izreen et al. 2011, Nor Hafizah et al. 2014, Purba et al. 2014). Huang et al. (2014) and Laborie (2002) added that LMW–PF is composed of small oligomers that can easily fit into small cavities (nanometer scale), such as void cells or tiny spaces between fibers, thus polymerizes *in situ*. Furuno et al. (2004) reported that LMW–PF penetrating the wood more easily, depositing almost entirely on the cell wall and forming a wall polymer after curing, with little or no deposit in the cell cavity. It also helps to increase its retention and penetration, thereby significantly increasing dimensional stability (Kajita and Imamura 1991). Izreen et al. (2011) reported that treated wood using LMW–PF could give anti swelling efficiency (ASE) around 27.7–35.4%; 14.0–15.8%; and 14.4–26.0% with 20%, 30% and 40% resin concentrations. Furuno et al. (2004) reported that resin loading at a concentration of 1% to 15% is around 5.9–62.5% for LMW–PF resin-treated wood. In addition, bulking coefficient and reduction in water absorption (WA) were 12.6% and 37.1%, respectively, with ASE values around 65% at 10% concentration.

Variation in morphological anatomical structure within and between species increases the difficulty of a particular LMW–PF impregnation process. Numerous researchers have investigated the distribution and penetration of LMW–PF into wood cells using their native wood species both in softwood and hardwood (Furuno et al. 2004, Izreen 2011, Huang et al. 2014, Wang and Zhao 2022). According to previous studies, at 1% to 5% LMW–PF deposition is primarily observed on the lumina of tracheids and ray parenchyma cells of Japanese cedar. At 10% and 15% concentration, a few dispersed phenolic in their lumina as well as cell wall were seen after treatment (Furuno et al. 2004). Wang and Zhao (2022) revealed that resin is primarily dispersed in vessels and tracheids of poplar samples, with only a few spread throughout the fiber. In contrast, resin deposition in Chinese fir samples is more abundant and penetrates to a greater depth. Despite all past study, it is widely known that depth and capacity of penetration are prone to be influenced by how internal cavities at the microscopic level communicate with each other. However, few attempts have been made to evaluate the effect of anatomical structure in various wood species on LMW-PF impregnation, particularly employing Indonesian native wood.

Therefore, this study was evaluated the effect of anatomical structure on dimensional stability of LMW–PF impregnation, particularly using lower concentration levels (7, 8, 9, 10, and 11%). Thereby, it will reduce the costs, as well as fewer causes of an increase in weight gain of wood, while still providing a significant improvement in their wood properties. In addition, it was also necessary to analyze the difference of anatomical structure among low, middle and high specific gravity wood species in relation to their treatability.

MATERIAL AND METHODS

The logs with a length of 120 cm and a diameter of 50 cm of sepetir (*Sindora* spp.), nyatoh (*Palaquium* spp.), and pisang putih (*Mezzettia* spp.), which are classed as lesser-used wood species, were acquired from a forest concession area in North Kalimantan Province, Indonesia. The logs were cut from the bottom of the tree trunk. The logs were sawed into 2 cm thick boards, air-dried to a moisture content of 12–15%, and then converted into wood samples in 6 categories (Tab. 1) for studying various wood characteristics of untreated and treated wood, including weight percent gain (WPG), coefficient of swelling (CS), anti-swelling efficiency (ASE), water absorption (WA), and thickness swelling (TS). Only samples of wood devoid of knots, mold, fungi, and other visible faults were analyzed. There were 270 samples used for this research (6 treatments x 15 replications x 3 species).

Tab. 1: Type and code of treatments, and size of samples for impregnation process.

No.	Treatments		Size (cm)
	Type	Code	
1	Untreated	C	2 x 2 x 2
2	Impregnated, then hot soaked within 7% LMW–PF	LMW–PF–7	
3	Impregnated, then hot soaked within 8% LMW–PF	LMW–PF–8	
4	Impregnated, then hot soaked within 9% LMW–PF	LMW–PF–9	
5	Impregnated, then hot soaked within 10% LMW–PF	LMW–PF–10	
6	Impregnated, then hot soaked within 11% LMW–PF	LMW–PF–11	

Tab. 2: Characterization of LMW-PF resin.

Evaluation item	Conditions (°C)	Unit	Result
Color	-	-	Dark reddish brown transparent
Specific gravity	25	-	1.146
Viscosity	25	mPa·s	19
Gelation time	150	s	147
Nonvolatile content*^{1}	135	%	50
pH	25	-	8.8
Water soluble	25	times	7

Note: *1 - the value should be used as the resin content of the PF.

Impregnation process

The volume of each sample was determined and weighed before impregnation by vacuum-pressure. The samples were placing in LMW–PF solutions (PR-51138C Sumitomo Bakelite Co., LTD, Tab. 2) with 7, 8, 9, 10, and 11% of concentrations (w/w), vacuuming at –98 kPa for 15 min, and applying 350 kPa of pressure for 4 h, followed by immersion in 80°C of each impregnating solution for 3 h. The treated wood was then covered in aluminum foil and cured for 24 h at 103 ± 2°C. Before testing, every sample was conditioned for a full night. The weight percent gain (WPG) was calculated according to Eq. 1:

$$\text{WPG (\%)} = \frac{\text{W1} - \text{W0}}{\text{W0}} \times 100 \qquad (1)$$

where: w_0 = weight of oven-dried samples before treatment (g), w_1 = weight of oven-dried samples after treatment (g).

Dimensional stability

Before proceeding to the next steps, untreated and treated samples were measured to obtain their oven-dried volume and then weighed. One cycle of the drying-soaking process was conducted. The samples were immersed in distilled water for 24 h, ensuring that no sample floated on the water surface. Then, all samples were dried at 103 ± 2°C, re-measured and re-weighed after the process. The sample dimensions were determined by length, width, and thickness at marked positions on the sample. The CS, ASE, WA, and TS values were determined using Eqs. 2-5:

$$\text{CS (\%)} = \frac{\text{V2} - \text{V1}}{\text{V1}} \times 100 \qquad (2)$$

$$\text{ASE (\%)} = \frac{\text{S1} - \text{S2}}{\text{S1}} \times 100 \qquad (3)$$

$$\text{WA (\%)} = \frac{\text{Bss} - \text{Bsb}}{\text{Bsb}} \times 100 \qquad (4)$$

$$\text{TS (\%)} = \frac{\text{Tss} - \text{Tsb}}{\text{Tsb}} \times 100 \qquad (5)$$

where: V1= volume of oven-dried samples (cm^3), V2 = volume of immersed samples (cm^3), S1 = volumetric swelling coefficients of untreated samples (%), S2 = volumentric swelling coefficients of treated samples (%), Bsb = weight of oven-dried samples (g), Bss = weight of immersed samples (g), Tsb = thickness of oven-dried samples (mm), Tss = thickness of immersed samples (mm).

NIR and SEM analysis

Near infreared (NIR) spectroscopy was carried out on cross-sections in both untreated and treated wood using the UV-Vis-NIR Spectroscopy, Shimadzu UV-3600 Plus. NIR spectrum was obtained by transforming the spectrometer in reflectance diffuse mode. The wavelength of the NIR spectrum used ranges from 1000-2500 nm. Spectrum was carried out in 3 replications for each sample. Using scanning electron microscopy (SEM) images, the anatomical structure and microscopic changes that occur in both untreated and treated wood were examined.

The samples were vacuum-dried at 40°C for 24 h, and their cross-sections were sputter-coated with gold (Au) for 120 s and 30 mA using a JEOL JEC-3000FC Auto fine coater before being examined under a SEM (JEOL JSM-6510LV, Japan) operating at 15 kV. Multiple pictures at various magnifications were acquired for each sample group.

Statistical analysis

Randomization was applied to two experimental parameters, namely wood species (three levels) and concentrations (six levels). The data were displayed as a mean and standard deviation. The influence of species and concentrations on WPG, dimensional stability, including CS, ASE, WA, and TS in untreated and treated wood was evaluated using analysis of variance (ANOVA). If there are substantial variations between each factor and the interaction, Duncan's multiple distance test was performed.

RESULTS AND DISCUSSION

The average values of WPG, CS, ASE, WA, and TS for sepetir-, nyatoh-, and pisang putih- in untreated and treated samples, respectively, can be found in Tab. 3. Tabulated result of ANOVA for every parameter and factor is presented in Tab. 4. In addition, a cross-section of each type of wood, both in untreated and after being subjected to any treatment, is presented in Fig. 1.

Tab. 3: Average values of WPG, CS, ASE, WA, and TS in each treatment.

Parameters	Treatments	Wood species		
		Sepetir	Nyatoh	Pisang Putih
WPG (%)	C	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
	LMW–PF–7	4.26 ± 0.56^{c}	3.02 ± 0.36^{b}	2.68 ± 0.14^{b}
	LMW–PF–8	5.84 ± 0.28^{fg}	4.98 ± 0.31^{cde}	4.73 ± 0.03^{cd}
	LMW–PF–9	5.41 ± 0.49^{def}	4.60 ± 0.43^{cd}	4.47 ± 0.49^{c}
	LMW–PF–10	5.60 ± 0.59^{efg}	4.20 ± 0.29^{c}	4.89 ± 1.05^{cde}
	LMW–PF–11	6.31 ± 0.70^{g}	4.33 ± 0.28^{c}	4.56 ± 0.36^{c}
CS (%)	C	11.92 ± 1.65^{de}	11.70 ± 1.36^{cde}	12.55 ± 0.97^{e}
	LMW–PF–7	9.05 ± 1.15^{a}	9.69 ± 0.29^{abc}	11.34 ± 1.36^{bcde}
	LMW–PF–8	8.62 ± 0.68^{a}	9.09 ± 0.11^{ab}	9.34 ± 1.72^{ab}
	LMW–PF–9	9.42 ± 0.72^{ab}	9.77 ± 1.48^{abcd}	10.46 ± 1.36^{abcde}
	LMW–PF–10	8.96 ± 0.69^{a}	8.79 ± 0.34^{a}	10.60 ± 2.08^{abcde}
	LMW–PF–11	8.35 ± 0.26^{a}	8.50 ± 0.26^{a}	9.38 ± 1.78^{ab}
ASE (%)	C	-	-	-
	LMW–PF–7	24.06 ± 9.61^{bc}	20.29 ± 3.21^{bc}	12.24 ± 9.00^{ab}
	LMW–PF–8	27.68 ± 5.75^{c}	22.28 ± 0.95^{bc}	25.56 ± 13.71^{bc}
	LMW–PF–9	20.94 ± 6.07^{bc}	23.35 ± 10.65^{bc}	16.67 ± 10.83^{bc}
	LMW–PF–10	24.81 ± 5.77^{bc}	24.83 ± 2.90^{bc}	21.04 ± 9.91^{bc}
	LMW–PF–11	29.91 ± 2.15^{c}	27.38 ± 2.21^{c}	25.25 ± 14.20^{bc}
WA (%)	C	94.40 ± 3.05^{e}	99.51 ± 9.56^{cde}	132.68 ± 20.02^{f}
	LMW–PF–7	84.17 ± 5.23^{bcd}	83.35 ± 4.40^{bcd}	92.27 ± 8.73^{cde}
	LMW–PF–8	92.10 ± 1.26^{cde}	88.95 ± 2.36^{bcde}	98.65 ± 2.66^{de}
	LMW–PF–9	74.36 ± 9.49^{abc}	87.35 ± 10.34^{bcde}	88.27 ± 6.02^{bcde}
	LMW–PF–10	75.18 ± 16.63^{abc}	86.06 ± 11.08^{bcde}	84.49 ± 13.30^{bcd}
	LMW–PF–11	57.82 ± 8.30^{a}	72.29 ± 8.45^{ab}	95.98 ± 8.32^{de}

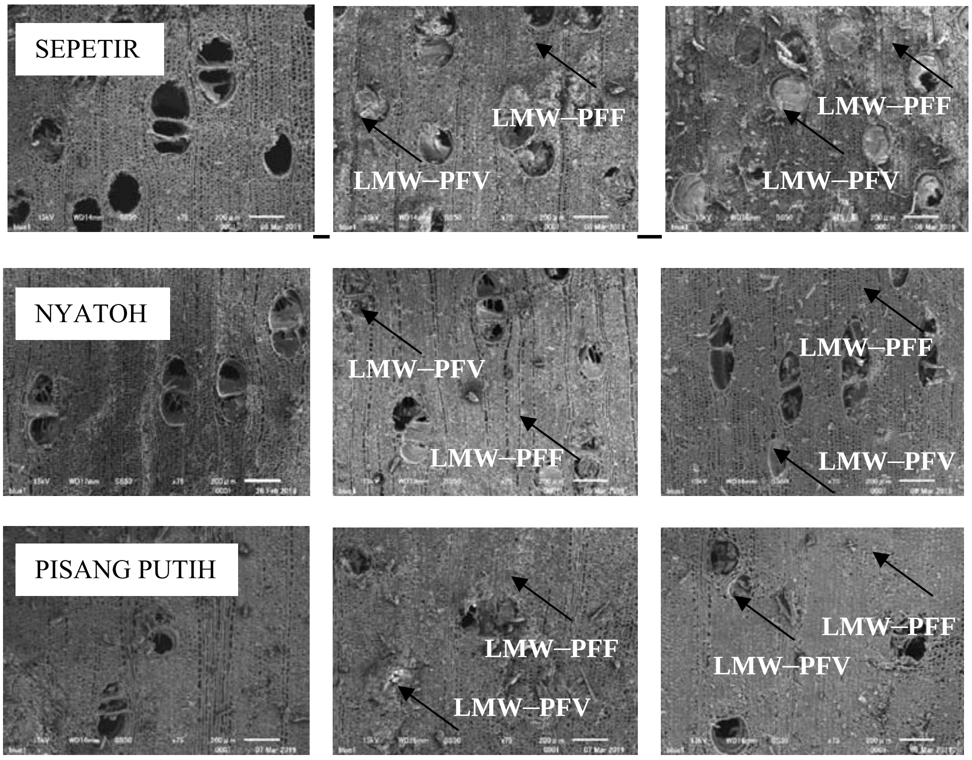
TS (%)	C	6.43 ± 0.66^{a}	6.46 ± 0.40^{a}	8.36 ± 0.29^{a}
	LMW–PF–7	5.03 ± 0.78^{c}	5.43 ± 0.48^{b}	6.01 ± 0.69^{b}
	LMW–PF–8	4.85 ± 0.45^{fg}	5.18 ± 0.37^{cde}	5.86 ± 0.43^{cd}
	LMW–PF–9	5.34 ± 0.66^{def}	5.16 ± 1.08^{cd}	5.95 ± 0.35^{c}
	LMW–PF–10	4.91 ± 0.53^{efg}	4.91 ± 0.35^{c}	6.42 ± 0.57^{cde}
	LMW–PF–11	4.23 ± 0.47^{g}	4.56 ± 0.22^{c}	5.99 ± 0.98^{c}

Note: Those values are averages of 15 replicates with standard deviation. Values within a column followed by the same letters are not significantly different at 5% significance level using Duncan's multiple range test.

Tab. 4: ANOVA results of each parameters and factors.

Parameters	Factors		
	JK	CC	JK × CC
WPG	**	**	*
CS	**	**	ns
ASE	ns	**	ns
WA	**	**	*
TS	**	**	ns

Note: ns = not significant; * = significantly different at 5% significance level; ** = significantly different at 1% significance level; JK = wood species, CC = concentration.



(a) (b) (c)

Fig. 1: Cross-section of each wood species: (a) untreated wood, (b) treated wood with LMW–PF 7%, and (c) treated wood with LMW–PF 11% (75×). LMW–PFF = LMW–PF deposited in fiber cells, LMW–PFV: LMW–PF deposited in vessel cells.

Weight percent gain

At a 5% significance level, the interaction between wood species and concentration has a substantial impact on WPG values (Tab. 3). The WPG values obtained using vacuum-pressure method discussed previously were significantly lower than that maximum theoretical levels. Furuno et al. (2004) revealed that the resin loading at 1% to 15%

concentration for LMW–PF resin-treated wood is between 5.9 and 62.5%. This may be a result of the LMW–PF solution's characterization and the lower concentration employed in this study. The LMW–PF solution had a viscosity of approximately 19 mPa·s, which enabled the solution to penetrate lumina cells and microvoid cells (Tab. 2). Observation with SEM revealed that LMW–PF has covered half and/or full area in the vessel and fiber cells, as well as some area in the vessel's pits (Fig. 1). This phenomenon was agreed by Furuno et al. (2004), the lumina of tracheids and ray parenchyma cells has a little or no phenolic resin at 1% to 5% concentration, even the increase of concentration up until 15% still gives small number and also scattered phenolic resin-filled cell wall.

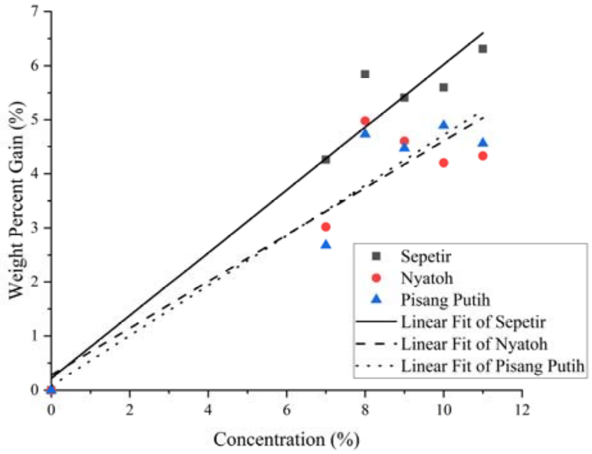


Fig. 2: Relation between average values of WPG with concentration of LMW–PF in each wood species.

The average WPG value of each species is varies depending on its wood treatability. Wood treatability is directly linked to permeability and penetrability as wood has a capillary structure that allows liquid to penetrate the cell wall and/or lumen cells (Flynn 1995, Taghiyari 2012, Wen et al. 2014, Augustina 2019). Sepetir has the highest WPG values than that of nyatoh and pisang putih (Tab. 3). Correlation between WPG and concentrations of LMW–PF for sepetir ($y = 0.58x + 0.22$; $R^2 = 0.95$), nyatoh ($y = 0.43x + 0.09$; $R^2 = 0.85$), and pisang putih ($y = 0.46x + 0.07$; $R^2 = 0.90$) served as evidence for these findings (Fig. 2). Sepetir has more LMW–PF-filled area, particularly in the vessel and fiber cells, as well as vessel's pit area (Fig. 1). While in nyatoh, LMW–PF filled half portion of vessel cell, and some of fiber cells, whereas pisang putih has scattered LMW–PF-filled area in both vessel and fiber cells.

This phenomenon was related to the different treatability among wood species which is categorized as low, middle, and high specific gravity (SG). According to previous works related to these species, the average SG values were 0.35, 0.44, and 0.52 for sepetir, nyatoh and pisang putih, respectively (Augustina et al. 2022). Higher WPG values for sepetir in accordance with its lower initial SG and anatomical structure, i.e. the greater void volume, than other wood species. Void volume percentage for these species were 76.45, 70.29, and 72.57% for sepetir, nyatoh and pisang putih, respectively (Augustina et al. 2020). Lower SG with higher portion of void volume indicates that the wood is more porous, which results in better treatability due to an adequate open capillary system (porosity). The inverse phenomenon occurred in higher SGs.

Dimensional stability

The dimensional stability of treated wood can be approached by CS, ASE, WA, and TS values (Tab. 3). It can be seen that interaction among wood species and concentration has a significant effect on dimensional stability at a 5% significant level, except for ASE values between each wood species, while interaction within wood species and concentration was not significantly affected, except for WA values (Tab. 4). The results show that sepetir resulted in better dimensional stability improvement than other wood species. Meanwhile, the dimensional stability of treated woods had improved significantly compared with their untreated. Treated wood had a lower CS value (reduced by 9.64–29.95%) compared with untreated and ASE values ranging from 12.24–29.91%. In addition, WA and TS values for treated wood decreased by 2.43–38.75% and 15.94–34.21%, respectively from their untreated. The dimensional stability of treated wood tended to increase with an increase in LMW–PF concentrations.

Coefficient of swelling (CS) and anti-swelling efficiency (ASE)

The CS values prior to the impregnation process (untreated) were 11.92, 11.70, and 12.55% for sepetir, nyatoh, and pisang putih, respectively. The initial CS values for sepetir and nyatoh were quite similar, while for pisang putih tended to be higher (Fig. 3). This phenomenon indicated that pisang putih has an unstable condition regarding to its swelling behaviour, eventhough it has higher SG values. This could be due to higher portion of raycells, i.e. multiseriate (Fig. 1a), which could accelerate the swelling behaviour. According to Elaieb et al. (2019), ray proportion is positively correlated with basic density as well as SG values. Furthermore, Hernandez (2007) convinced that volumetric swelling in tropical hardwood has a positive correlation with dry basic density.

After applying impregnation process, the CS values tended to decrease among wood species as concentation increased. The CS values among wood species were 9.05 and 8.35% for sepetir, 9.69 and 8.5% for nyatoh, as well as 11.34 and 9.38% for pisang putih at 7 and 11% concentration, respectively. Correlation between CS and concentrations of LMW–PF for sepetir ($y = -0.31x + 0.06$; $R^2 = 0.88$), nyatoh ($y = -0.28x + 0.04$; $R^2 = 0.92$), and pisang putih ($y = -0.26x + 0.08$; $R^2 = 0.70$) served as evidence for these findings (Fig. 3).

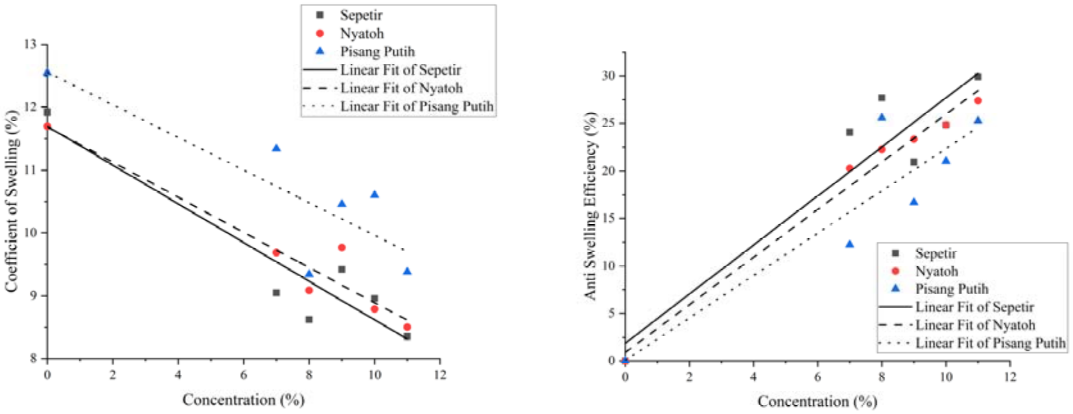


Fig. 3: Relation between average values of CS and ASE with concentration of LMW–PF in each wood species.

As shown in Tab. 3, the CS values decreased along until 8% of concentration was applied, and slightly increased to 9% of concentration, then continued to decrease until 11% of concentration. Meanwhile, the inverse phenomenon occurred in ASE values. According to Wang et al. (2019), these two values have a negative correlation, a smaller CS value results in a larger improvement in ASE values, and vice versa.

The ASE tended to increase as concentration increased (Tab. 3). Those values among wood species were 24.06 and 29.91% for sepetir, 20.29 and 27.38% for nyatoh, as well as 12.24 and 25.25% for pisang putih at 7 and 11% concentration, respectively. Correlation between ASE and concentrations of LMW–PF for sepetir ($y = 2.58x + 0.48$; $R^2 = 0.88$), nyatoh ($y = 2.50x + 0.16$; $R^2 = 0.98$), and pisang putih ($y = 2.23x + 0.52$; $R^2 = 0.82$) served as evidence for these findings (Fig. 3). Those high R-square values indicates that the correlation between CS and ASE with concentrations of LMW–PF were quite significant.

Sepetir had a lower CS values with higher ASE values than that of nyatoh and pisang putih. Better improvement in both values for sepetir-treated wood could be due to higher WPG (5.48%) than nyatoh- (4.23%) and pisang putih- (4.27%) treated wood as shown in Tab. 3. It indicates that more impregnating agent reached and/or deposited in wood cells, which could prevent the swelling mechanism of the wood cells. It was agreed by Wan and Kim (2006) stated that high polymer loading will significantly increase the dimensional stability of wood by controlling the volumetric swelling while improving the ASE value. An increase in WPG values in treated wood was predicted due to the penetration of LMW–PF into wood cell walls. This could be due to the low molecular weight of impregnating material used in this research which can be easily penetrated the wood cells. According to Furuno et al. (2004), LMW–PF is depositing heavily in the cell wall, forming a wall polymer that can effectively reduce the CS value while producing a higher ASE value. Eventhough, LMW–PF could give an improvement for each wood species, but those values were rather small compared with another research. Furuno et al. (2004) reported that LMW–PF resin-treated wood resulted in ASE values around 65% at 10% concentration.

Water absorption (WA) and thickness swelling (TS)

The WA values prior to the impregnation process (untreated) were 94.40%, 99.51%, and 132.68%, while that of TS were 6.43%, 6.46%, and 8.36% for sepetir, nyatoh, and pisang putih, respectively. These values convinced that pisang putih is unstable, eventhough it has higher SG.

After applying impregnation process, the WA and TS values tended to decrease among wood species as concentration increased (Tab. 3). The WA values among wood species were 84.17 and 57.82% for sepetir, 83.35 and 72.29% for nyatoh, as well as 92.27 and 95.98% for pisang putih at 7 and 11% concentration, respectively. Correlation between WA and concentrations of LMW–PF for sepetir ($y = -2.61x + 1.12$; $R^2 = 0.57$), nyatoh ($y = -1.86x + 0.62$; $R^2 = 0.69$), and pisang putih ($y = -4.03x + 0.91$; $R^2 = 0.83$) served as evidence for these findings (Fig. 4). Meanwhile, the TS values among wood species were 5.03 and 4.23% for sepetir, 5.43 and 4.56% for nyatoh, as well as 6.01 and 5.99% for pisang putih at 7 and 11% concentration, respectively. The correlation between TS and concentration of LMW–PF for sepetir ($y = -0.17x + 0.04$; $R^2 = 0.84$), nyatoh ($y = -0.16x + 0.01$; $R^2 = 0.98$), and pisang putih (y = -0.22x + 0.06; R² = 0.79) served as evidence for these findings (Fig. 4). Those high R-square values indicates that the correlation between WA and TS with concentrations of LMW–PF were quite significant. Lower WA and TS values were produced by treated wood with 11% of concentration. Both values are lower than that of untreated. This is evidenced by SEM observations (Fig. 1). It can be seen that LMW–PF compound was able to partially cover up the vessel and fiber cells at 7% of concentration and its role as a blocking agent was increasingly seen as the concentration increased. This could be due to the increasing number of areas that were completely covered by impregnating agents. The more areas covered by impregnating agent would make it difficult for water to enter or fill up the cell cavities of wood, thus eventually decreasing both the WA and TS values. The same phenomenon was reported by Kajita and Imamura (1991).

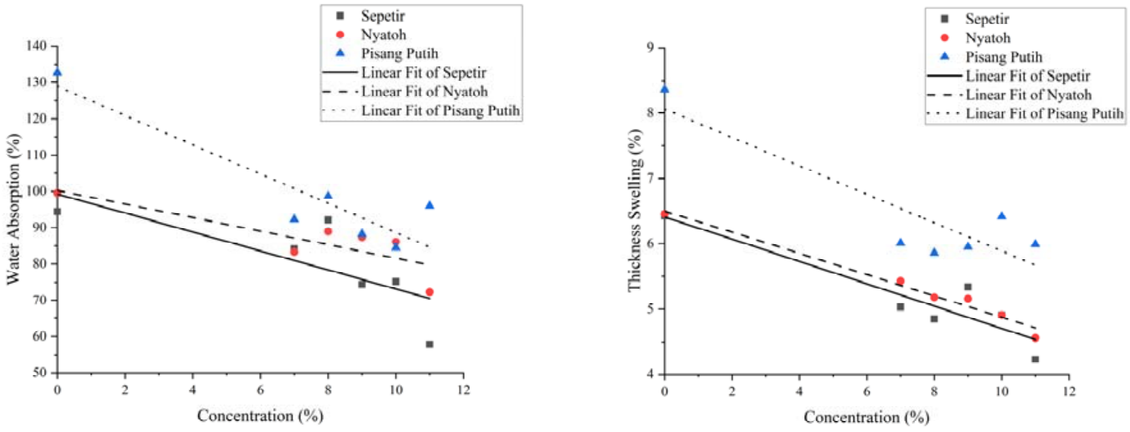


Fig. 4: Relation between average values of WA and TS with concentration of LMW–PF in each wood species.

As previously stated that LMW–PF can enter wood cells easily and effectively via a liquid-pathway, either longitudinally through vessels or transversely through pit and ray cell tracheids, thus filling up empty spaces in wood cells (Wan and Kim 2006, Kamke and Lee 2007, Wang et al. 2019). The LMW–PF will be deposited in it and form a wall polymer, thus making it difficult for water to enter the wood (more hydrophobic) (Furuno et al. 2004). Frihart (2004) added that there are four possible scenarios for resin or adhesive penetration into cell walls. First, resin simply fills the empty spaces between cell walls, allowing it to withstand the swelling and shrinkage of wood cells, thus reducing wood hygroscopicity. Second, the resin penetrates the cell walls and forms molecular interdigitation, known as mechanical interlocking. Third, the resin forms a separate network within the cell wall that acts as a cross-link on either the surface nor completely or can be interpreted as a polymer network. Fourth, the resin components chemically react with the cell wall components and forms cross-links with each other. The four possible scenarios can be the basis for understanding the reaction of PF resin, especially LMW–PF, with wood to improve its dimensional stability, especially its WA and TS values.

Near infrared spectroscopy (NIR) analysis

The impregnation process using LMW–PF will alter the bonds and/or active groups. In general, PF resins are synthesized from phenols and aldehydes using specific catalysts. The reaction of phenol and aldehyde in alkaline conditions produces hydroxymethyl phenol. If the hydroxymethyl phenol polymerizes before reaching the gelling point, it will transform into a water-soluble PF resol-type which is capable of self-polymerization (Liu et al. 2012). Those reactive hydroxymethyl phenol groups will form chemical bonds with the hydroxyl groups in the wood structure (Li et al. 2020). LMW–PF treatment of wood results in a decrease of hydroxyl group and an increase of the number of hydroxymethyl phenol groups. The increase number of those groups can be followed in the near infrared spectra.

Raw spectras absorbance of untreated and treated wood are presented in Fig. 5. Untreated has a pronounce lower raw absorbance compared with that of treated wood. A continuous increase in the band heights can be observed due to an increase in the WPG and the increase of hydroxymethyl phenol groups, respectively, due to LMW–PF treatment of wood mainly at 1450 nm. According to Lin et al. (2014), absorption spectra for the control PF adhesive occurred at 1458 nm which is assigned to the C-H vibrations of the CH_2 and CH_3 groups and included the typical vibrations for the methoxyl groups. These wavelength is nearly identical to that obtained by Poljanšek and Krajnc (2005) who examined the PF characteristics of prepolymer resins. According to Poljanšek and Krajnc (2005), peaks at 1498 and 1594 nm are associated with C=C vibrations in the aromatic ring, while peak at 1478 nm corresponds to the methylene bridge C-H bend. In addition, a slightly increase in the band heights also occurred at 1682 which is associated with CH_3 groups in hemicellulose (Schwanninger et al. 2011).

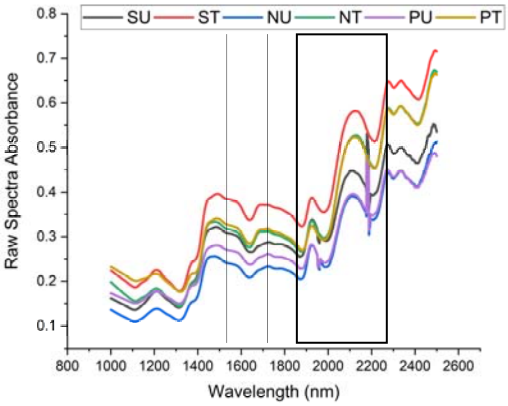


Fig. 5: NIR raw spectra absorbances of untreated and LMW–PF-treated woods. Note: SU = sepetir untreated; ST = sepetir treated; NU = nyatoh untreated; NT = nyatoh treated; PU = pisang putih untreated; PT = pisang putih treated.

Furthermore, a slightly increase in the band heights is also occurred at 1950 and 2180 nm which is associated with H_2O, and cellulose and/or hemicellulose, respectively (Schwanninger et al. 2011). As described before, LMW–PF treatment could produce lower WA values than that of untreated. Increasing the concentration of LMW–PF has been shown to reduce water content after impregnation. Those phenomenon can be seen in the absorption spectra for treated wood which was having higher absorption spectra, especially at 1901–1929 nm than that of untreated (Fig. 5). The increase in concentration also shows stronger absorption spectra. Kobori et al. (2013) agreed with this phenomenon, stating that higher water content causes a decrease in absorbance/absorption spectra. Schwanninger et al. (2011) and Altgen et al. (2023) added absorption spectra at these wavelengths related to the presence of water.

For a detailed investigation of the spectra changes, calculation of the second derivatives should be properly used. The spectra changes between raw spectra absorbance and their second derivatives are quite similar (Tab. 5).

Tab. 5: NIR bands assignment of LMW-PF treated wood.

Observed wavelength (nm)	Functional group
1212	CH and CH_2-groups
1450, 1574	C-H vibrations of the CH_2 and CH_3 groups; typical vibrations for the methoxyl groups; C=C vibrations in the aromatic ring; phenolic O-H group
1696	CH_3 groups
1810	CH groups in aromatic structures, such as phenols
1950	Water
2084	CH groups in aromatic structures, such as phenols
2180	Cellulose and/or hemicelluloses
2280	C-C stretching vibrations in phenols

NIR bands were decreased after LMW–PF treatment, particularly within the range between ca. 1212, 1450, 1574, 1698, 1810, 2084, 2280 nm (Fig. 6). This phenomenon was similar with Altgen et al. (2023), which studied about PF impregnation during wet and dry curing. According to this study, prominent resin bands were observed particularly within the range between pproximately 1600 and 1860 nm and between aprox. 2120 and 2220 nm, which is associated with CH groups in aromatic structures, such as phenols. Prominent decrease of NIR bands can be clearly seen in sepetir-treated wood compared with others wood species (Fig. 6). This could be due to higher WPG produced in sepetir-treated wood during LMW–PF impregnation, which results in prominent spectra changes. This phenomen was agreed by Altgen et al. (2023).

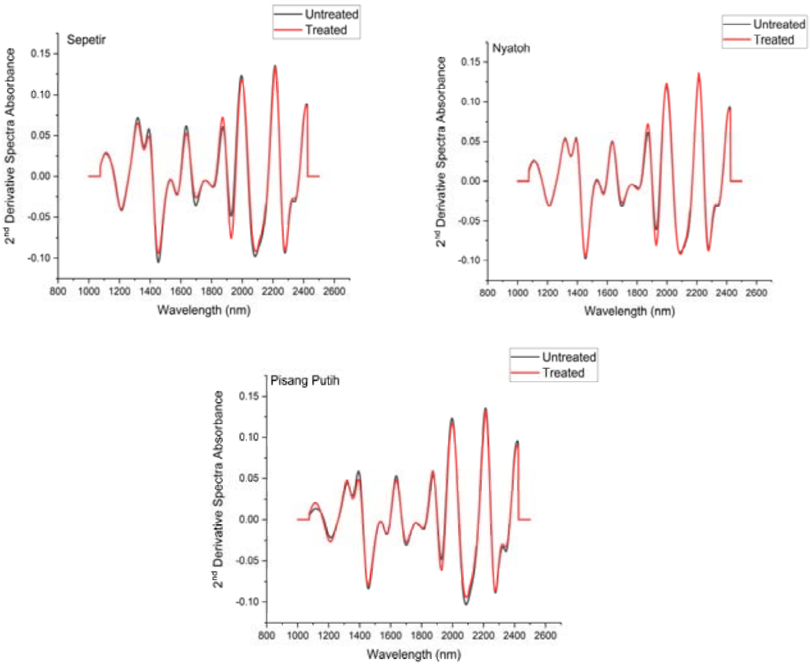


Fig. 6: The 2nd derivative spectra obtained from untreated and LMW–PF-treated in each wood species.

Anatomical structure – impregnation process relationship

The most essential characteristics of wood in terms of impregnation process involve the microscopic interaction between internal cavities. According to Wen et al. (2014), different position and anatomical factors among wood species combine to respond for the variation in chemical impregnation treatability. As shown in Fig. 7, sepetir has a lower anatomical barrier to the impregnation process than other wood species. According to our previous research, sepetir has microscopic characteristics as follows: diffuse-porous with radially arranged vessels, which are usually solitary and in radial multiples of 2-4 cells, simple perforation plates; tyloses absent; cross-field pitting between vessel-ray and vessel-parenchyma with alternate arrangement; rays are typically uni- to biseriate; parenchyma is predominantly paratracheal, vasicentric to aliform (Lemmens et al. 1995, FPL 2010, Augustina et al. 2020). In addition, SEM observation revealed a unique configuration of vessel and intervessel pits in sepetir. As seen in Fig. 7b, vessel pits are alternately arranged, but intervessel pits are scalariform. It also features a modified border pit with a larger aperture (Fig. 7a).

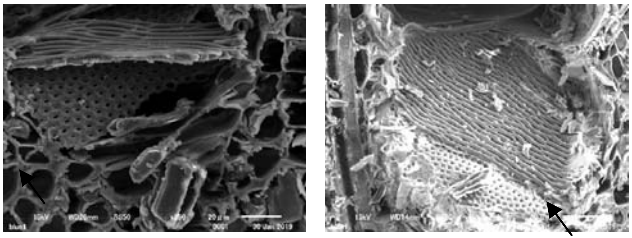

(a) (b)

Fig. 7: Distinct anatomical features in sepetir wood, (a) altered border pit with wider aperture (400×), (b) scalariform intervessel pitting (850×).

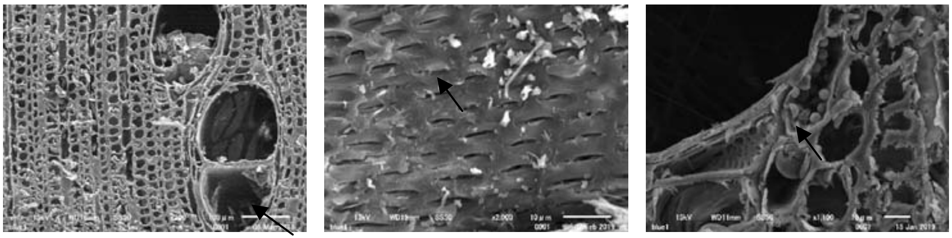

(a) (b) (c)

Fig. 8: Distinct anatomical features in nyatoh wood, (a) scalariform perforation plates (200×), (b) bordered pit with narrow aperture (2000×), (c) deposits in parenchyma cells (1100×).

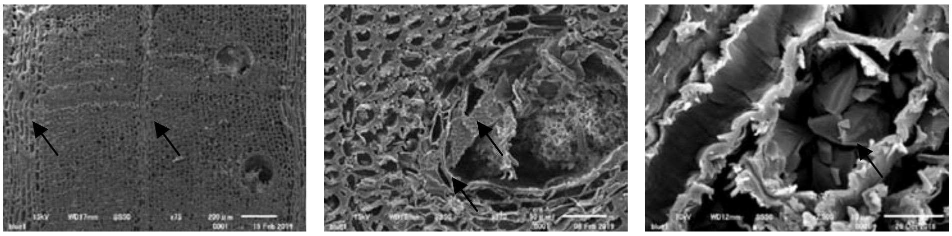

(a) (b) (c)

Fig. 9: Distinct anatomical features in pisang putih, (a) uni- to multiseriate raycells (75×), (b) bordered pit pairs within vessel cells (370×), (c) prismatic crystal grouped in chambered axial parenchyma (2500×).

While for nyatoh and pisang putih have more anatomical barrier which could affects the impregnation process. Microscopic characteristic of nyatoh: growth ring distinct marked by differences in spacing of tangential parenchyma bands; vessel diffuse-porous mainly in radial multiples of 2-4 cells; thin-walled tyloses; rays mainly uniseriate; parenchyma abundant in fine discontinuous or continuous seriate with straight or slightly wavy bands (Soerianegara and Lemmens 1993, FPL 2010, Augustina et al. 2020). In addition, SEM observation revealed that nyatoh has scalariform perforation plates (Fig. 8a), bordered pits with narrow aperture (Fig. 8b), and deposits in the form of silica in parenchyma cells (Fig. 8c). Microscopic characteristic of pisang putih: vessel diffuse-porous, solitary dominant of vessel or radial multiples of 2 cells, simple perforation plates; cross-field and intervessel pitting with the same size and shape; rays with distinct two sizes, uni- to multiseriate (Fig. 9a); axial parenchyma with long tangential band in irregular distance (Koek & Westra 2012, Augustina et al. 2020). In addition, SEM observation revealed that pisang putih has bordered pit pairs within vessel cells (Fig. 9b), prismatic crystal grouped in chambered axial parenchyma (Fig. 9c), and tyloses within vessel cells (Fig. 9b). Those anatomical barriers in nyatoh and pisang putih, such as bordered pits with narrow aperture, scalariform perforation plastes, tyloses, deposits in the form of prismatic crystal and silica in parenchyma cells, as well as arrangement of raycells (multiseriate), could prevent the flow of impregnating agent into cell walls. This statemet in accordance with Olsson et al. (2001), Hansmann (2002), Tarmian et al. (2020). This phenomenon proven by lower WPG values in nyatoh and pisang putih as (Tab. 3) and Fig. 2. This indicated that these two wood species are less permeable, as consequences, the flow may be forced to seek alternative open capillary systems, which expends more energy (pressure) due to considerably smaller openings around obstacle in the flow direction.

CONCLUSIONS

The LMW–PF impregnation process affects by its anatomical structure among wood species. Sepetir has lesser anatomical barriers than nyatoh and pisang putih. Therefore, it results in greater dimensional stability improvement after LMW–PF treatment, especially CS, ASE, WA, and TS values, compared to that of nyatoh and pisang putih. The presence of bordered pits with narrow aperture, scalariform perforation plastes, tyloses, deposits in form of prismatic crystal and silica in parenchyma cells, as well as arrangement of raycells (multiseriate) in nyatoh and pisang putih, could prevent the flow of impregnating agent into cell walls and make them less permeable. After performing impregnation process, treated wood could give WPG around 2.68-6.31%. Treated wood had a lower CS value (reduced by 9.64-29.95%) with higher ASE values ranging from 12.24-29.91% compared with untreated. In addition, WA and TS values for treated wood decreased by 2.43-38.75% and 15.94-34.21%, respectively from those untreated. Distinguish NIR bands spectra for treated wood displayed at 1450 which was related to PF adhesive.

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