Enhancement on Physicomechanical Properties of Short-Rotation Teak Woods by Non-Biocide Chemical and Thermal Treatments

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Lactic acid (LA), citric acid (CA), and glycerol (G) are renewable and environmentally friendly chemicals that could improve the qualities of short-rotation teak (SRT) woods. This study investigated the effect of thermal and chemical modification using 20% aqueous solutions (w/w) of LA, CA, and G and their mixtures in the same composition on physical and mechanical properties of SRT teak wood. The impregnation process was initiated by vacuum process for 1 h and pressure (12.2 bar) for 2 h, followed by thermal (150 °C) treatment for 6 h on the SRT wood samples after being removed from the vacuum-pressure tube. Retention (R), weight percent gain (WPG), density (D), anti-swelling efficiency (ASE), leachability (WL), modulus of elasticity (MOE), and modulus of rupture (MOR) were measured. FTIR spectrometry and SEM analyses were performed. The wood impregnated with a mixture of 10% LA + 10% CA provided the highest ASE values of 50.1%, and the lowest leaching resistance of 1.54%. Based on wood strengths (MOE and MOR) and physical properties, as well as supported by FTIR and SEM analysis, the use of 10% LA + 10% CA is the most prospective as an impregnant formula for SRT wood modification of this research.

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INTRODUCTION

The harvesting cycle of teak woods with good strength, durability, and dimensional stability could normally take place when the teak stands reach a minimum of 50 years old (Soerianegara and Lemmens 1995; Jha 2016). The older the stand ages, the better the qualities of the teak woods would be. The demand for teak wood as raw materials for furniture and handicrafts is around 2 to 2.5 million m³/year, while production, especially from the Indonesia State owned Forest Enterprise (Perhutani), is only around 0.7 million m³/year (BPS-Statistics Indonesia 2019). Due to the declining supply of high-quality long rotation teak wood (above 50 years old stand), the wood processing industry has been currently undergoing a major structural change from the production of timber products using long rotation teak to short rotation teak. There are numerous short-rotation teak (SRT) woods developed and then traded in the local markets, which are harvested at less than 16 years old. Unfortunately, SRT woods exhibit inferior strength, dimensional stability, and durability against wood-destroying organisms (Rizanti *et al.* 2018; Martha *et al.* 2021a; Basri *et al.* 2022). However, it is possible to improve the properties of SRT wood by non-biocidal thermal and chemical modifications so that SRT wood can be used for

longer life services of both interior and exterior wood products.

Chemical modification refers to conducting reactions between chemical reagents and free hydroxyl (OH) groups as well as other free polar groups of wood chemical components (*e.g.*, cellulose, hemicellulose, lignin) at the wood cell walls (Hill 2006). The covalent bonds that form between the reagents and the wood's functional OH groups with or without a catalyst can have important effects, but they are prone to hydrolysis (Hill 2006; Rowell 2013; Sandberg *et al.* 2017). The wood's free OH groups are regarded as the most reactive sites; they are responsible for the wood's hygroscopicity, which could lower wood dimensional stability (Dirna *et al*. 2020). Those reactive OH sites should be converted to be less polar/hygroscopic sites through a substitution reaction using specific chemicals, as one attempt in the wood chemical modifications (Ross 2021). Consequently, in accordance with several researchers (Rowell 2013; Papadopoulos *et al.* 2019; Mantanis *et al.* 2020), the main target of chemical modification is to enhance dimensional stability and improve wood resistance against lignocellulose destroying organisms.

Chemical modification followed by heat treatment will increase crosslinking to accelerate polymerization so that chemically modified wood results in lower equilibrium moisture content (Berube *et al*. 2017; Larnøy *et al*. 2018; Mubarok *et al*. 2020). Heat treatment changes the wood's chemical structures, *e.g.*, cellulose, hemicellulose, and lignin, into permanently degraded components (Zhang *et al.* 2022). The wood chemical components that are degraded due to heat treatment (up to 80 to 100 °C) are initially the amorphous, short-chained branched amorphous hemicelluloses, followed by cellulose, and then lignin as the temperatures get higher and higher (Blanchet *et al.* 2016). As a result of heat treatment, the woods become more dimensionally stable and more resistant to the destroying organisms, without polluting the environment, especially the surrounding-air (Pratiwi *et al.* 2019; Priadi *et al.* 2019; Mubarok *et al.* 2021).

Citric acid (CA= $C_6H_8O_7$), lactic acid (LA= $C_3H_6O_3$), and glycerol (G= $C_3H_8O_3$) are inherently non-biocidal chemicals, and they could be prospectively useful for wood chemical modification. CA with molecular weight (MW) of 192.124 g/mole and LA with MW of 90.08 g/mole structurally belong to the weak organic acids (carboxylic acids). The former has three COOH and one OH groups (Lambros *et al.* 2022), while the latter has one COOH group and one OH groups (IUPAC 2014). Therefore, both LA and CA exhibit hydrophilic character. G (MW = 92.09 g/mole) is categorized as an alcohol with three free OH groups, and it also exhibits hydrophilic properties (Pavlov and Terentyev 1970). The created ester polymers ([G-LA/CA]$_n$) as well as ([LA-CA]$_n$) could provide an effective cross-linking (bridging) between the adjacent wood fibres and cellulose/hemicellulose chains (Berube *et al*. 2017; Teacă and Tanasă 2020). All those phenomena could contribute to the impregnated woods having better qualities, *e.g.*, high physical and mechanical properties.

This paper deals with test results on thermal and chemically modified SRT woods using LA, CA, and G, which are considered to be renewable and non-biocidal chemicals. These compounds were tested in some treatments combinations, with attention paid to their effects on the physical and mechanical properties of the wood. The microstructures of the treated (modified) and untreated SRT wood samples were observed visually using a scanning electron microscope (SEM) instrument, and chemical analysis of them were performed with Fourier-transform infrared (FTIR) device.

EXPERIMENTAL

Materials

Three trees of 13-year-old teak (*Tectona grandis* L.f.), were obtained from the forest area of the Wanabakti Nusantara's Housing Cooperation (WHC), Bogor Regency, West Java Province. It is located at 6º 33' 15" South latitude and 106º 40' 07" East longitude. The diameter of the selected teak trees was 27 cm (at breast height), the height of branch-free stems was 10 m, and the stem was relatively straight upwards. Other environmental conditions were rainfall in 2000 to 3000 mm/year, and temperature from 15 to 31 °C.

The teak logs of 200 cm length were taken from the base of stems, and they were then sawed with a bandsaw tangentially into 3 cm thick boards. All the boards were air dry conditioned, reaching approximately 15% moisture content. The sawn boards (at 15% MC) were cut into several samples with varying dimensions based on the intended tests on physicomechanical properties. The test samples of 20 mm (longitudinal/L) by 20 mm (radial/R) by 10 mm (tangential/T) were prepared for testing the moisture content (MC), density (D), weight percent gain (WPG), and dimensional stability (Pfriem *et al.* 2012). Test samples of 30 mm (L) by 15 mm (R) by 5 mm (T) were prepared for leaching tests, based on the NF X41 (NF 2014). The bending strength test (MOE and MOR) referred to the ASTM D143-22 (2022) using 300 mm (L) by 20 mm (R) by 20 mm (T) test specimens. All the wood samples were taken from the heartwood portion. Before chemical modification, all the specimens were dried in the oven at 103±2 °C for 48 h. Their weight values and size dimensions were measured.

Methods

Chemical and thermal treatment

The three kinds of chemicals used as the impregnants were lactic acid (LA), citric acid (CA), and glycerol (G). They were further manipulated into eight varying formulations of impregnants. Each of those 8 mixture compositions were dissolved in pure distilled water at the ratio 1:4 (w/w); or in other words, 20% of each composition was mixed with 80% of water (Table 1). The mixing results were then called impregnant solutions.

The impregnation of each formulated solution into the wood structure was initiated by applying a vacuum for 60 min, followed by a pressure of 12 kPa for 120 min. Afterwards, all samples were removed and allowed to become air dry. The air-dry specimens were weighed and measured their dimension (for retention test), then wrapped in aluminum foil, further heated in the oven at 150 °C for 6 h. This was intended to render the chemical impregnants (*e.g.* LA, CA, and G) more perfectly and firmly reacted with and bonded to the wood fibers, as well as wood chemical components.

Table 1. Kinds of Chemicals, Formula, and Manipulated Mixture Composition of Chemicals

Kinds of Chemicals	Chemical Formula	Mixture Compositions of Chemicals (%) [1]							
		K0	K1	K2	K3	K4	K5	K6	K7
Impregnants:									
Lactic acid (LA)	$C_3H_6O_3$	- [3]	20	-	-	10	10	-	5
Citric acid (CA)	$C_6H_8O_7$	-	-	20	-	10	-	10	5
Glycerol (G)	$C_3H_8O_3$	-	-	-	20	-	10	10	10
Solvent:									
Water	H_2O	-	80	80	80	80	80	80	80

Remarks: K0 = untreated/control; [1] each replicated 5 times

Measurement of retention, weight present gain, density

The retention (R) of each chemical impregnant solution into the wood samples was calculated after the samples were conditioned for 2 days, using Eq. 1, while the calculation of weight present gain (WPG) and density (D) used Eqs. 2 and 3, respectively,

$$R \text{ (kg/m}^3) = \frac{B_1 - B_0}{V} \text{ x 100 x } K \qquad (1)$$

where B_1 is weight of the sample after the impregnation (kg), B_o is weight of the sample before the impregnation (kg), K is concentration of the chemical impregnant (%), and V is oven-dry volume of the sample before impregnation (m^3).

$$WPG \text{ (\%)} = [(W_1 - W_0) / W_0] \text{ x 100} \qquad (2)$$

In Eq. 2, WPG is the percentage of weight gain due to the chemical thermal modified (CTM) treatment, W_0 is the initial weight of wood sample before treatment, W_1 is the weight of wood sample after CTM.

$$\text{Density (g/cm}^3) = B_0/V_0 \text{, or } B_1/V_1 \qquad (3)$$

In Eq. 3, B_0 is the initial weight of wood sample before CTM, B_1 is the weight of wood after CTM treatment, V_0 is the initial volume of wood before CTM, V_1 is the volume of wood after CTM treatment.

Measurement on dimensional stability and leaching resistance

Dimensional stability was determined by measuring the volumetric swelling (S_v), water up-take (WU), and anti-swelling efficiency (ASE). The values were calculated using Eqs. 4, 5, and 6, as follows,

$$S_v \text{ (\%)} = (V_w - V_d)/V_d \qquad (4)$$

where S_v is the percentage of volumetric swelling of the wood sample, V_w is the wet volume, after wood sample immersion in water (cm^3), and V_d is the dry volumetric of the oven-dried sample, before immersion in water (cm^3).

$$WU \text{ (\%)} = [W_w - W_d)/W_d] \text{ x 100\%} \qquad (5)$$

In Eq. 5, W_w is wet weight, after immersion in water (g), W_d is dry weight of the oven-dried sample,

$$ASE \text{ (\%)} = [(S_{v_u} - S_{v_t})/S_{v_u}] \text{ x 100\%} \qquad (6)$$

where S_{v_u} is volumetric shrinkage of the control sample without chemical thermal modified (CTM) treatment, S_{v_t} is volumetric shrinkage after CTM treatment.

$$WL \text{ (\%)} = ([W_{io} - W_{fo}]/W_{io}) \text{ x 100} \qquad (7)$$

In Eq. 7, WL is the percentage of weight loss of untreated or treated wood due to leaching, W_{io} is the weight of wood after the CTM treatment, and W_{fo} is the weight at 103 ºC of untreated and CTM treatment wood after the leaching process. If the WL values were high, then the woods would be easily leached by water (less water-resistant), and adversely if the WL values were comparatively low.

MOE and MOR in bending test

MOE and MOR of the untreated as well as the chemical thermal modified (CTM) SRT wood samples were tested using a Universal Testing Machine (UTM) Instron 4667 and then measured in accordance with the ASTM D143-22 (2022). As many as 5 wood samples were used for each treatment (Table 1).

Fourier-transform infrared spectrometer (FTIR) analysis

The FTIR analysis was used to indicate the presence of free particular (*e.g.*, OH, COOH, *etc.*) and non-free (hydrogen bonds, ether bonds, ester bonds, *etc.*) functional groups in untreated and chemical thermal modified SRT wood samples. The samples were dried at 25 °C, and then scanned with the FTIR instrument in the wavenumber range of 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}. The FTIR device was of the Perkin-Elmer Spectrum UATR Two brand type, from United Kingdom.

Scanning electron microscopy (SEM) analysis

The untreated and chemical thermal modified SRT wood samples were prepared into dimensions of 0.5 cm [L] by 1 cm [R] by 1 cm [T]. The samples were observed by field emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDS) under high vacuum with 5000x magnification. The device was of the Quattro S brand type.

Data Analysis

The physical-mechanical data of short rotation teak wood (SRT) modified using lactic acid (LA), citric acid (CA), glycerol (G), and combinations were examined using a single-factor completely randomized (RAL) design. The factor or treatment consisted of 8 levels chemical compositions (T). Each level was measured in 5 replications.

Variance analysis of the observed data was analyzed using the SPSS ver. 26. The mean difference test among the level was carried out using the Duncan Multiple Range test at a significance level of 5%.

RESULTS AND DISCUSSION

Physical Properties

Table 2 shows that the moisture content (MC) and water uptake (WU) values of the modified short rotation teak (SRT) followed by heat treatment at 150 °C were significantly lower than the values of the untreated woods (except for glycerol-treated wood). The modified woods' density (*D*) and ASE values were significantly higher than the untreated wood. Regarding the density, the values for G-treated woods were not significantly different from those of untreated woods. Retention describes the quantity of impregnants (*e.g.*, preservatives, stabilizing agents, *etc.*) that enter the wood sample per volume unit, expressed in *w/v*. The SRT woods' impregnant retention (as gross retention values) measured shortly after the impregnation ranged from 85 to 95 kg/m^3. This result indicated that a chemical solution impregnated with a pressure of 12.2 kPa for 2 h was easily penetrated SRT wood structures, though the SRT wood is difficult to be penetrated due to its small pore size, rare pore frequency, and its narrow rays (Martawijaya *et al.* 2014). After being impregnated (with high absolute pressure) and then put at the room temperature on release of impregnation pressure, the free water in the woods would evaporate back into the environment, causing a decrease in retention value (*i.e.*, net retention value) (Hunts and Garrat 1982). The SRT wood-modified samples's net retention values (NRV) before the thermal treatment ranged from about 35.6 to 60.1 kg/m^3 (Table 2).

The SRT wood modified by thermal-chemical treatment at 150 °C generated a low MC value up to 5% (Table 2), except for the MC of G (glycerol)-treated woods. This might be attributed to the three hygroscopic free OH groups G. Further, short-chained, branched, hygroscopic, and amorphous hemicellulose of the woods underwent severe fragmentation due to 150 °C heat treatment, thereby reducing the numbers of polar free -OH groups at the wood cell walls and hence decreasing the wood hygroscopicity (Lodge and Hiemenz 2020). Reducing the hygroscopic -OH groups could also occur through the OH replacement into the less-hygroscopic groups. Such replacement occurs due to the esterification reaction between those free -OH groups and the carboxylic (COO-) groups of the impregnants; this can result in forming fewer hygroscopic ester (-OOC-R) groups at the wood cell walls (Shmulsky and Jones 2019). The MC of SRT woods impregnated with 20% G was the highest among the levels of more than 10% (Table 2). Glycerol has three free hygroscopic OH groups (without COOH groups), which led to the creation weak hydrogen bonds with OH groups of the cell walls not imparting strong ester bonds (Seyhan 2004; Eslami *et al*. 2023). This phenomenon indicates that the polymerization did not occur between glycerol and wood fibres or cellulose chains so that impregnated wood with G would absorb moisture back from the surrounding air (Pavlov and Terentyev 1970). This caused the MC of SRT wood treated with G to be higher than that of LA/CA-treated wood (Table 2).

The highest WPG value (22.30%) of the modified SRT woods was achieved using the CA impregnant (Table 2). The lowest WPG (14.95%) was obtained using 20% G, as described previously. The CA contained free COOH groups (Fig. 1), and thereby it was able to form stronger covalent ester bonds with OH groups of wood fibers/carbohydrates (Seyhan 2004; Shmulsky and Jones, 2019). The mechanism by which citric acid forms ester bonds with the hydroxyl groups of polysaccharides might involve the formation of anhydride rings as an intermediate. It was noted that formation of an acid chloride may happen prior to the esterification (Cumpstey 2013). Meanwhile, G contained only free OH groups, and it forms hydrogen bonds with free OH groups and other polar functional groups at wood cellulose/hemicellulose (Blomquist *et al.* 1993; Shmulsky and Jones 2019). Hydrogen bonds are less effective in lowering the wood hygroscopicity than covalent bonds (Jakes *et al.* 2019). The mixture or combination between the impregnants with free COOH groups (LA and CA) could cause an esterification reaction, creating strong ester bonds, further sustaining the polymerization, which can release the condensed water (H_2O). The impregnants with free COOH groups (LA, CA, and LA+CA) could create ester bonds, further sustaining the polymerization (forming polymers of *e.g.* $[CA]_n$, $[CA+LA]_n$), which further released the condensed water (H_2O) (Seyhan 1994; Lodge and Hiemenz 2020). Two critical parameters are high temperature and particular time, which could accelerate the H_2O evaporation and concurrently create covalent bonding between the polymerized-esterified impregnants and the cell walls, thereby increasing the WPG values (Halpern *et al.* 2013).

These phenomena were confirmed by other related research (Mubarok *et al.* 2020; Basri and Saefudin 2021; Kurkowiak *et al.* 2021), which described the ester bonds between G and CA as more optimally occurring at temperatures above 150 °C. The reduction of the amorphous part (disoriented cellulose chain polymer aggregates mixed with short-chain hemicellulose polymers) due to heat treatment at 180 °C would bring the microfibrils or fibrils parallel and close to each other, forming crystallites, thus strengthening the wood structure (Sjostrom 1993; Basri and Saefudin 2021). The increase in WPG values of thermally modified SRT woods was in line with the increase in their density (Table 2). The lowest density value of was 0.55 g/cm^3, which was obtained with 20% G. The density of SRT woods impregnated with other chemicals could reach values greater than 0.60 g/cm^3. This could happen because G contained only free OH groups (not free COOH groups), while others (CA, LA, LA+CA, LA+G, CA+G, and LA+CA+G), besides containing free

OH groups, also had free COOH groups. The OH groups could only create weaker hydrogen bonds with the OH groups of wood fibers/carbohydrates, while the COOH groups could afford stronger covalent ester bonds.

ASE values of the chemically modified (impregnated and heat-treated) SRT woods were higher than those of untreated SRT woods. As such, the increase in the ASE values was in line with the decrease in the volumetric swelling (S_v) and WU values (Table 2). Impregnants and their concentration could determine the ASE values. The mixture of 10% LA+10% CA produced the highest ASE value of about 50% and the lowest in WU. ASE values below 40% were obtained by the impregnants 20% G, 10% LA+10 % G, and 10% CA+10% G. These results were in accordance with the published result by Essoua *et al.* (2016). In that wood, dimensional stability (ASE, S_v, and WU) was determined by the covalently chemical reaction between the impregnated compounds, especially containing free COOH and free OH groups at the wood cell walls. Intensive esterification indicatively/allegedly occurred in 20% CA and the mixture of 10% LA+10% CA. Such reactions were demonstrated through an increase in peak C=O intensity (Fig. 2; Table 2). The two esters underwent condensation polymerization, forming long-chained, large-sized LA+CA polymers and LA+CA+G polymers, which could create a covalent bond with the polar OH groups of the wood components and also created an effective cross-linking bond between the cellulose fibers from wood structure. Accordingly, all these phenomena could bring positive effect on wood's physical properties (Table 2).

The modified SRT woods with the lowest leaching (WL) values (1.54%) resulted from the treatment of 10% LA+10% CA (Table 2). This is because the mixture of 10% LA + 10% CA impregnants contained free OH groups as well as free COOH groups, where the latter could strongly fix or bond with the OH groups of wood fibres/celluloses, forming stronger covalent ester bonds (*i.e.*, more resistant to water). These results indicate that there occurred strong effective fixation between the impregnants and the wood fibres, thereby resulting in greater resistance to the water leaching. Conversely, the glycerol and their mixture with other impregnants produced higher leaching values between 6.30 and 12.65% (Table 2). These results suggest that the G fixation with the wood fibre components was not as strong as those using LA+CA impregnants, as the G only afforded weak hydrogen bonds (with the wood fibres). Thereby the connections were easily hydrolyzed and then partially dissolved by the water, as presented by the high WL value of teak wood in G-based impregnants. This is in accordance with the opinion of Hoadley (2000) that if impregnated chemicals have no covalent bond with wood, then the ester bonds will be leached into water. The LA and CA were easily soluble in water, but they became difficult to dissolve in water after esterification and the polymerization of esters. This result indicates that effective fixation occurred between the impregnated chemicals and components of wood cell walls. Conversely, the roles of G, which has only free OH groups, seemed smaller in those chemical fixation phenomena. This strengthened the previous allegation that the G could only impart the hydrogen bonds with the OH groups of wood components. The hydrogen bonds are weaker than covalent bonds, *i.e.* 10 to 40 kJ/mol *vs.* 200 to 800 kJ/mol, respectively, as previously described (Seyhan 1994). Thus, hydrogen bonds are prone to water leaching, thereby dissolving the glycerol into the water, as shown by the significantly high WL (Table 2).

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Table 2. Physical Properties of Untreated and Chemical Thermal Modified Short Rotation Teak (SRT) Woods

| Treatment (Kinds and manipulated mixture proportions of impregnants) [2]	Physical Properties [1]							
	Retention (kg/m^3)	Moisture Content (%)	Weight Percent Gain (%)	Density (g/cm^3)	Volumetric Swelling (%)	Water Uptake (%)	Anti-Swelling Efficiency (ASE), %	Water Leaching (WL), %
Citric acid (CA) 20%, K1	35.65	5.47[b]	20.30[c]	0.61[b]	5.43[b]	53.81[b]	46.23[c]	4.71[b]
Lactic acid (LA) 20%, K2	41.03	5.71[b]	18.46[b]	0,59[b]	5.85[c]	60.94[c]	42.06[b]	4.87[b]
Glycerol (G) 20%, K3	47.19	10.39[e]	14.95[a]	0.55[a]	6.42[d]	66.33[d]	35.33[a]	12.65[f]
LA 10% + G 10%, K4	60.07	7.79[d]	18.29[b]	0.61[b]	6.54[d]	70.52[e]	35.16[a]	10.41[e]
LA 10% + CA 10%, K5	50.90	5.02[a]	19.84[c]	0.60[b]	5.01[a]	46.95[a]	50,10[d]	1.54[a]
CA 10% + G 10%, K6	58.01	5.77[bc]	18.29[b]	0.60[b]	6.39[d]	65.73[d]	36.89[a]	6,30[c]
CA 5% + LA 5% + G 10%, K7	51.33	5.92[c]	19.40[bc]	0.60[b]	5.07[a]	50.96[b]	48.75[d]	7.56[d]
Control (untreated/unmodified), K0	-	12.17[f]	-	0.53[a]	10.07[e]	89.76[f]	-	1.43[a]

Note: [1] Average of 5 repetitions; the same letters above are not significantly different, based on the Tukey / HSD tests (α = 0.05)
[2] Please refer to Table

Mechanical Properties

The MOR and MOE values for the untreated and chemical thermal modified SRT wood samples, are presented in Table 3. The mean values of MOE and MOR for untreated wood were 98,300 kg/cm^2 and 880 kg/cm^2, respectively. The MOE and MOR values of treated SRT wood increased slightly after chemical and thermal modification, except for the MOE of SRT wood treated with G or combining CA, LA, with G, which tended to be lower than untreated. Meanwhile, the increased physical properties of the modified SRT wood (Table 2) might lead to an increase in MOE and MOR values (Table 3). However, MOE and MOR values decreased slightly by 3% in G, 10% and 11% in LA+G, and 2% and 4% in CA+G-treated followed by heating at 150 °C. This result is in line with the findings of Martha *et al.* (2021b), who reported a decrease in MOE and MOR of SRT wood, by 3% and 14% respectively, when treated with glycerol maleic anhydride and by furfurylation, both followed by heating at 150 °C. This confirmed that G impregnants afforded only weak hydrogen bonds with the wood fibers/carbohydrates, and thereby they were unable to cope with the degradation of wood fibers/carbohydrates. The decrease in MOE/MOR which treatment with G can be explained as being due to the heat-induced depolymerization of wood polymers caused by exposure to 150 °C after the impregnation (Sejati *et al.* 2016; Martha *et al.* 2021b), as already described previously. Meanwhile, the CA and LA compounds could each polymerize to form CA and LA polymers. The polymerization between CA and LA monomers can occur since each pair of CA/LA monomers contains at least two distinct free functional groups, *i.e.* -OH ≠ -COOH, which can react with each other, forming strong covalent ester or -COOR bonds (Lodge and Hiemenz 2020). This behavior is due to the fact that the strength of covalent bonds (200 to 800 kJ/mol) is far greater than that of hydrogen bonds (10 to 40 kJ/mol) (Walker 1993; Seyhan 1994), as already described. The CA monomer (Fig. 1) and the polymers resulting from its reactions could have large-sized molecules (Odian 2024), which seemed effective in creating hydrogen bonds and ester bonds with wood fibers and providing cross-linking between the fibers, ultimately all bringing out the impregnated woods using CA, as well as incorporating LA with high MOE/MOR values.
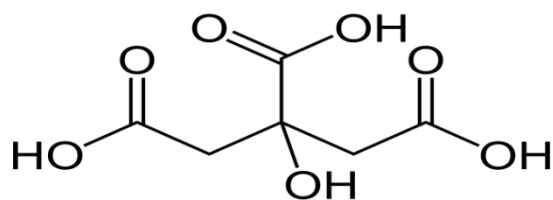
Fig. 1. Chemical building formula of citric acid (CA), as monomer (IUPAC 2014)

Free COOH groups (especially in the case of the LA/CA impregnants) afforded more significant roles to interact with free OH groups at wood fibre chains, forming strong cross-linking ester bonds laterally between cellulose chains/fibres and thereby strengthening the wood cell walls (laterally as well as axially) and fibre-to-fibre bonds (laterally). Further, in the material bending test, the compression and tension stresses are highest at the upper and lower surface of the material, gradually diminishing to zero at the neutral plane (Shmulsky and Jones 2019). Conversely, shear stresses are maximum at the neutral plane, gradually reaching a minimum at the surface. The phenomena concerning stronger wood cell walls (laterally/axially) and fibre-to-fibre bonds (laterally) in the impregnated SRT woods could relate positively to such tension/compression occurrence,

thereby increasing the wood MOE/MOR strengths.

Judging from the assessment results on the desired physical/mechanical properties of the impregnated SRT woods, *e.g.*, low hygroscopicity, low leaching, high dimensional stability, high density as well as strengths (Table 2 and 3), the results imply that the impregnants of 10% LA+10% CA followed by thermal at 150 °C were the most promising.

Table 3. Mechanical Properties (MOE, MOR) of Untreated and Chemical Thermal Modified Short Rotation Teak (SRT) Woods

Treatment [2]	Mechanical Properties [1]	
	MOE	MOR
	(kg/cm^2)	(kg/cm^2)
Control (untreated/unmodified), K0	98,262.41[b]	880.46[bc]
Lactic acid (LA) 20%, K1	104,990.55[c]	909.84[c]
Citric acid (CA) 20%, K2	117,511.81[e]	915.22[c]
Glycerol (G) 20%, K3	95,019.46[b]	848.01[b]
LA 10% + G 10%, K4	87,684.66[a]	785.74[a]
LA 10%+CA 10%, K5	107,535.91[d]	913.56[c]
CA 10% + G 10%, K6	96,014.55[b]	843.86[b]
LA 5% + CA 5% + G 10%, K7	104,837.40[c]	853.81[b]

Note: [1] Average of 5 repetitions; the same letters above are not significantly different, based on the Tukey / HSD tests (α = 0.05); [2] Please refer to Table 1
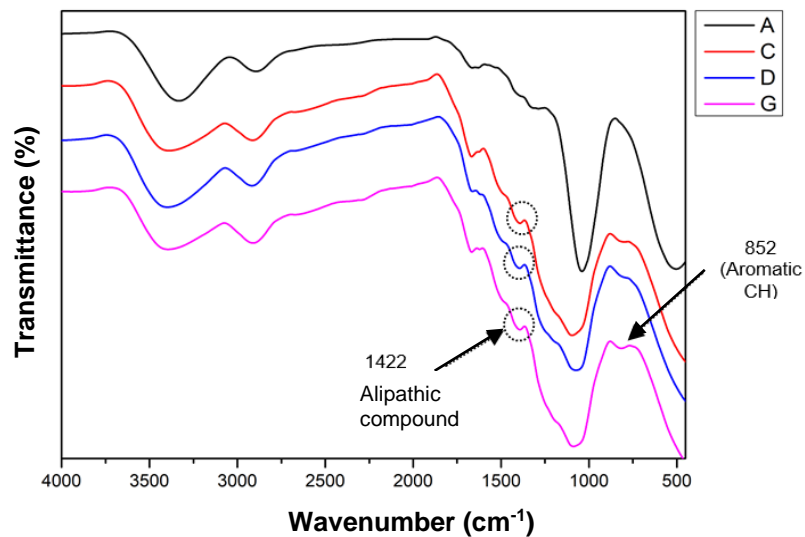
FTIR Analysis

Figure 2 shows the FTIR spectra of the treated (modified) SRT wood samples using 10% LA + 10% CA, 20% CA, and 20% LA followed by thermal at 150 °C over the 4000 to 500 wavenumber range. Figure 3 shows the FTIR spectra of all the Klason lignin fractions for those treated and untreated SRT woods.

The absorption spectra bands at 3336 cm^{-1}, which was assigned as the stret*c*hing vibration of the hydroxyl group (OH) in wood carbohydrates, predominantly came from the celluloses (Gupta *et al.* 2015; Nandiyanto *et al.* 2023). The decrease in absorbance at that wavenumber (3336 cm^{-1}) occurred at the FTIR spectra of the modified SRT woods (G, D, and C; Fig. 2) following the 150 °C thermal treatment, compared to the spectra of untreated (A=control). Further, at 1032 to 1025 cm^{-1}, which also indicates the presence of free OH groups (Nandiyanto *et al.* 2023), there occurred a decrease in the absorbance bands of G, D, and C, compared to the A (Fig. 2). Such absorbance decrease indicates a lowering of the number of free OH groups and instead the increasing number of bonded-OH groups (as *e.g.* ester; mostly more hydrophobic). All those phenomena indicate the intense evaporation of free water (from woods) as well as the forming of not-free bonded-OH groups, thereby rendering the modified woods more hydrophobic with a low MC value of up to 5% (Table 2). The spectra bands of the G, D, and C presented the increase in the absorbance band at 1723 cm^{-1} (Fig. 2), corresponding to the carbonyl (C=O) stret*c*hing band (Nandiyanto *et al.* 2023), which allegedly came from the ester group at 20% CA, 20% LA, and 10% CA+10% LA modified woods. Meanwhile, the absorbance bands in the spectra between untreated and 20% LA treated were not significantly different in this area (Fig. 2). These indicate the occurrence of esterification and transesterification on the carbonyl (C=O) groups at the carbohydrates, where the FTIR spectral band for SRT impregnated wood using 10% CA and 10% LA + 10% CA. Thus, it can be regarded as the most prospective impregnant.
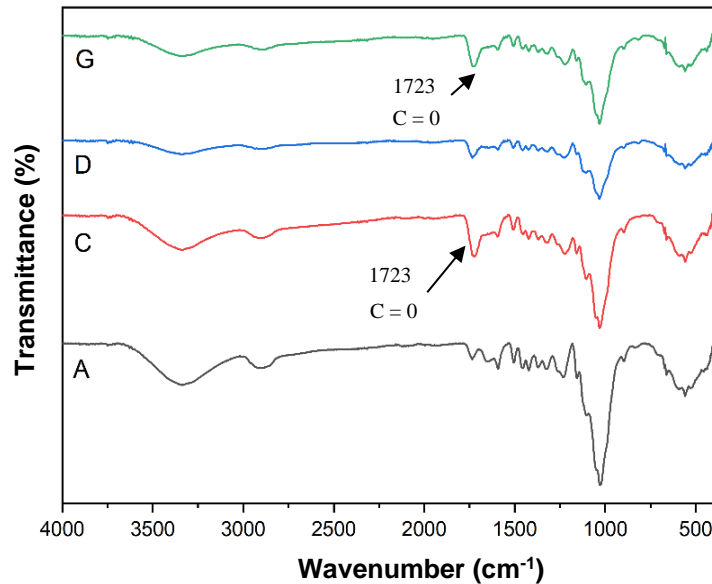
Fig. 2. FTIR analysis of untreated and chemical thermal modified short rotation teak (SRT) wood samples. Note: A = untreated (control); C = 20% citric acid (CA); D = 20% lactic acid (LA); G= 10% CA+10% LA

Fig. 3. Result of FTIR analysis of native Klason lignin on modified SRT wood under thermal chemical treatment. Note: A = untreated (control); C = 20% citric acid (CA); D = 20% lactic acid (LA); G= 10% CA+10% LA

Minor modification of the Klason lignin also occurred at the area 852 cm^{-1} and 1422 cm^{-1} (Fig. 3), especially in the G (10% CA+10% LA) sample. These two small bands are assigned to aromatic ring C-H, out-of-plane band and aliphatic compound, respectively (Nandiyanto *et al.* 2023). These indicate that the polymerization of the G wood sample was completed and the chemical interaction also occurred between the LA+CA and lignin.

The above description indicated esters and bonded-OH groups (more hydrophobic) as well as decreased number of free OH groups in modified wood, especially with LA+CA impregnant (through the FTIR analysis). These changes resulted in modified wood with more hydrophobic characteristics (*e.g.* lowest MC, water leaching, water up, volumetric

swelling, and the largest ASE), as well as higher in MOE and MOR. Further, those indicated ester and bonded-OH groups could be formed from the LA+CA esterification, LA+CA polymerization (resulting in large-sized polymers), and cross-linking between the wood fibres-impregnant-fibres. All those phenomena resulted in the 10% LA+ 10% CA-modified SRT wood having the greatest physical and mechanical properties (Tables 2 and 3).

SEM Analysis

Scanning electron microscopy (SEM) observation focused on the selected samples (10% LA + 10% CA, 20% CA, 20% LA and untreated), as presented in Fig. 4 (A-D).

A. 10% LA + 10% CA

B. 20% CA

C. 20% LA
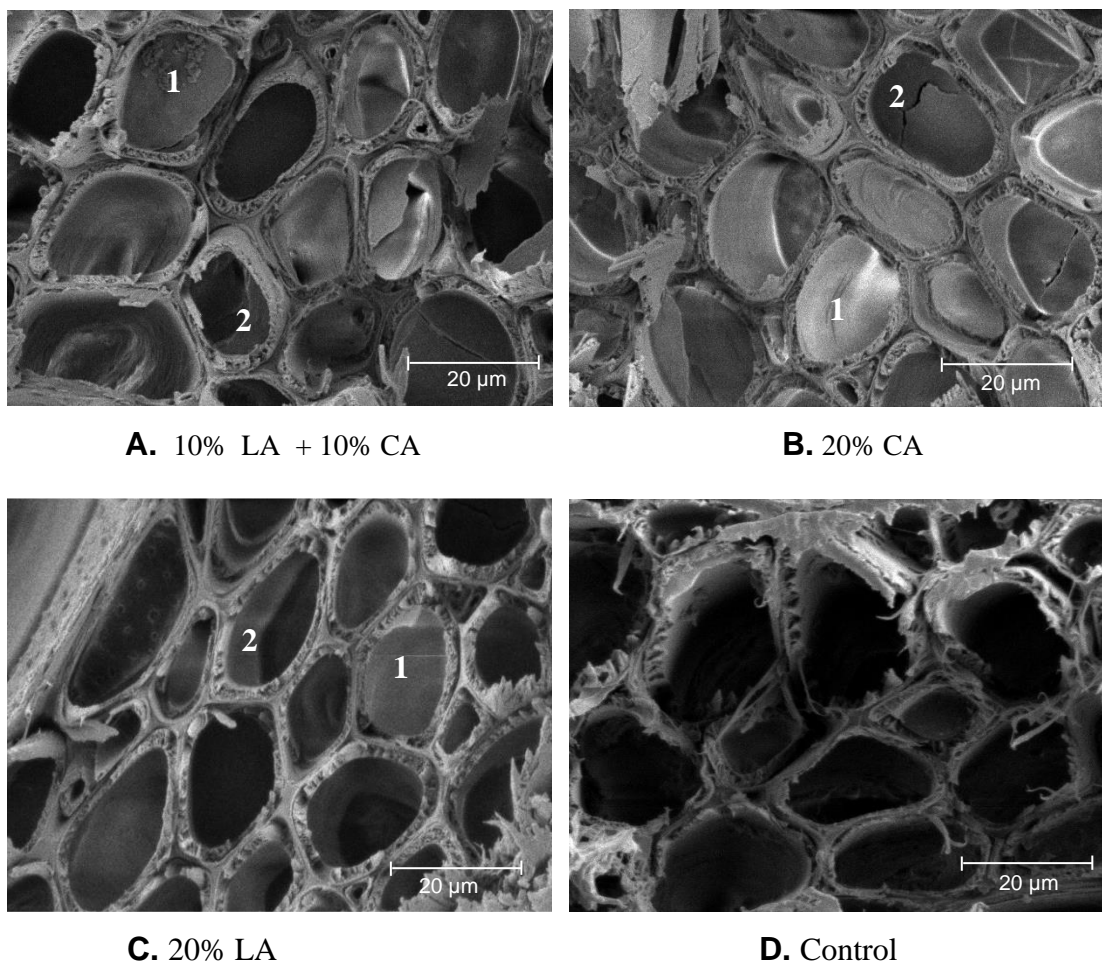
D. Control

Fig. 4. Visual features from SEM analysis of untreated and chemical thermal modified short rotation teak (SRT) wood samples. Notes: LA= Lactic acid; CA=Citric acid; D=Control (untreated); Form of a thick layer in the lumen (1), and which attached to the cell wall (2)

Figure 4 indicates that CA and LA+CA showed many deposits of impregnants after the curing process. The impregnant material adhered to the cell walls and partially covered the wood's pores. Those impregnants showed the presence of a thick layer in the lumens and attached to the inside cell walls. These phenomena strengthened the previous indications that esterification reactions had occurred between LA and CA impregnants, forming LA+CA esters. These subsequently underwent polymerization (polyesterification)

as (LA + CA)n polymers with long chains, large sizes, and high molecular weights (MW). All these phenomena further induced the hydrogen/covalent bonds between the free OH or COOH groups at the polymer and the OH groups at the carbohydrates from wood structure (cellulose, hemicellulose), which allowed the establishment of crosslinking laterally between wood cellulose fibres chains, and accordingly increased the wood physical-mechanical properties (Tables 2 and 3).

SEM analysis results on SRT wood impregnated with 20% LA also showed the presence of a small amount of thick layers in the lumens and attached to the inside of the cell walls. This phenomenon indicates that polymerization of LA also occurred individually, forming LA polymers with molecular weight and size that is not too large. However, it is thought to be still quite effective in crosslinking between carbohydrate chains/wood fibres. Meanwhile, the results of SEM analysis on the untreated SRT woods revealed that visually, there were no deposits in the lumens or the lumens were empty.

CONCLUSIONS

1. The non-biocidal chemical impregnants, consisting of citric acid (CA) and lactic acid (LA), after heating, allowed for the improvement of the physical and mechanical properties of short rotation teak (SRT) wood.

2. The combination of 10% LA+10% CA chemicals, followed by thermal treatment at 150 °C appeared to be the most promising to improve the physical and mechanical properties of the modified SRT woods, *e.g.*, low hygroscopicity, low leaching, high dimensional stability, high density as well as strengths (MOE and MOR).

3. Fourier transform infrared (FTIR) analysis showed evidence of a chemical bond between CA+LA and carbohydrate as well as lignin from modified SRT wood, while observations with scanning electron microscopy (SEM) also showed impregnant material adhering to the cell walls and covering most of the wood pores, thus supporting 10% LA + 10% CA as the most prospective impregnant formula for modifying SRT wood.

Declaration of Competing Interest
The authors declare that they have no potential conflict of interest relevant to this article was reported.

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