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Physicomechanical properties of Japanese cedar wood modified by high-temperature vapour-phase acetylation (HTVPA), a simultaneous acetylation and heat treatment modification process

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ABSTRACT

Wood modification can be broadly categorized into chemical and physical processes, with acetylation and heat treatment being two of the most common methods in each category, respectively. This study, for the first time, combines these two modification methods and investigates the effects of high-temperature vapour-phase acetylation (HTVPA) on the physicomechanical properties of Japanese cedar (*Cryptomeria japonica*) wood in the temperature range of 145 to 220 °C for 2 to 16 h. Additionally, the acetylation variations within the wood were evaluated. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and near infrared spectroscopy (NIR) spectral analysis showed that the hydroxyl group of Japanese cedar wood reacted with acetic anhydride to form an acetyl group by HTVPA process. When the HTVPA temperature was 220 °C, dehydration and deacetylation of wood occurred. Furthermore, based on the weight percent gain (WPG) and physicomechanical properties of the treated wood, the 200 °C/8h was considered the optimal HTVPA treatment condition. The profiling analysis results showed that the acetylation depth in the longitudinal direction was 40 mm, while the depth in the tangential and radial directions was 3–4 mm. However, the theoretical WPG of the surface of HTVPA treated Japanese cedar wood was 30.0–31.6 %.

Introduction

Wood possesses excellent mechanical properties, pleasing aesthetics, ease of processing, and the ability to regulate environmental temperature and humidity. Additionally, it can effectively capture carbon dioxide from the atmosphere, thereby mitigating climate change and leading to a gradual increase in global forest resource development and utilization. In recent years, the importance of environmental protection and conservation of natural resources has been increasingly recognized worldwide, prompting extensive discussions on the efficient and rational utilization of wood resources. However, wood is susceptible to the effects of moisture absorption, leading to material shrinkage and expansion. This results in poor dimensional stability. Furthermore, wood is susceptible to biological hazards, such as bacteria, fungi, insects, termites, and marine borers. These factors collectively impact the quality of wood products [1]. According to earlier research findings, when appropriately treated with chemicals, wood material can be chemically modified to effectively address the aforementioned drawbacks of wood and impart different properties, thereby expanding the range of applications in wood processing [2,3]. Among various chemical modification methods, one commonly used technique involves the esterification reaction between wood hydroxyl groups and agents, such as fatty acid chlorides and anhydrides [4–7]. Among these methods, acetylation using acetic anhydride (AA) has gained significant attention [8], and commercial products based on this technique are already available in Europe and Japan [9].

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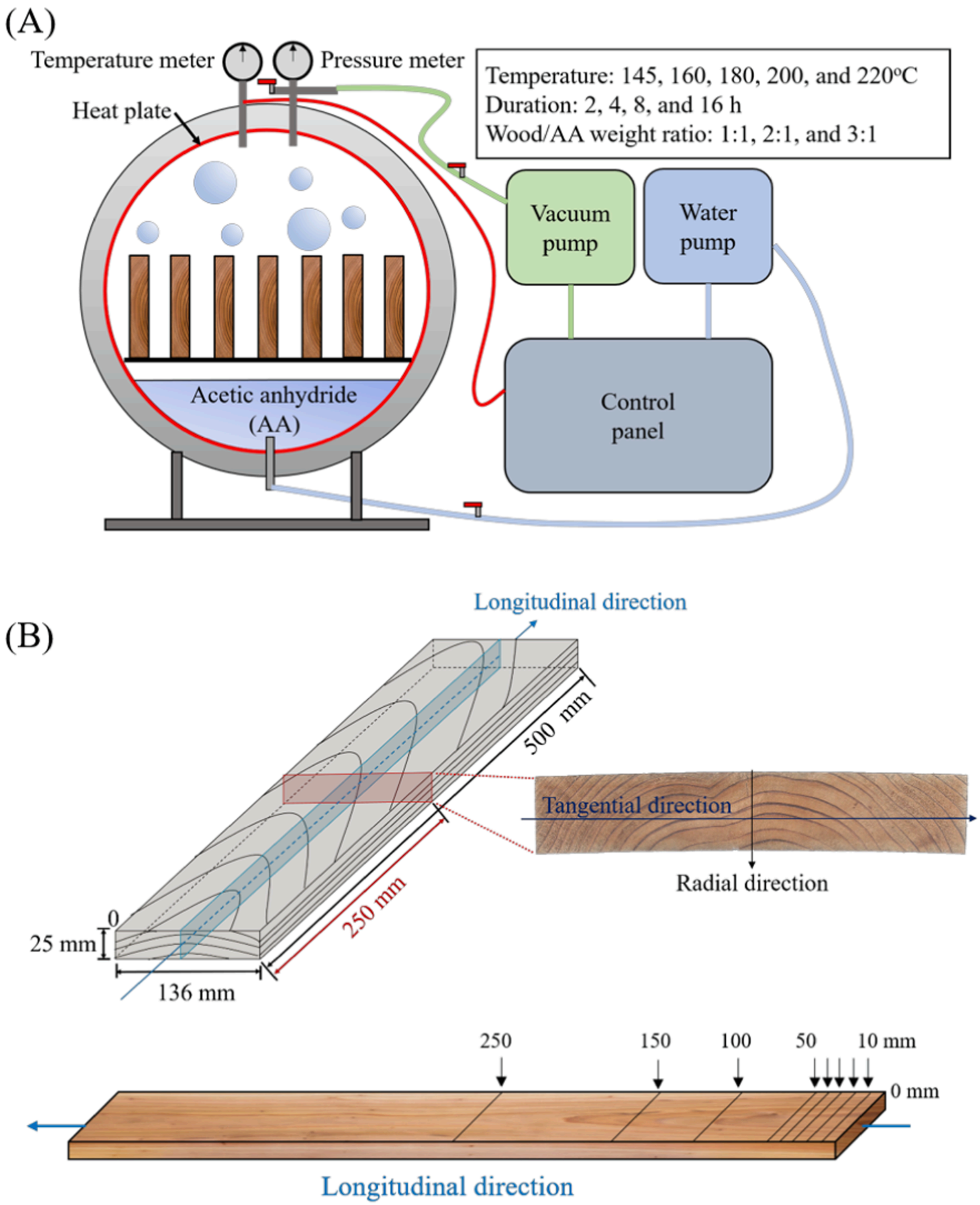

Fig. 1. (A) Schematic diagram of the HTVPA process, and (B) schematic diagrams for longitudinal, tangential, and radial WPG profile analysis of HTVPA treated specimens.

Traditionally, the chemical modification of wood involves immersing the wood in chemical agents and conducting reactions through heat conduction. This method requires a substantial amount of chemical agents and longer reaction times to achieve desired modification effects. Consequently, it increases the manufacturing costs, leads to energy waste, and imposes environmental impacts. Therefore, the current and future focus in the development of green processes for wood chemical modification is centred around reducing chemical agent usage, shortening process times, decreasing energy consumption, enhancing reaction efficiency, minimizing environmental impacts, and reducing harm to human health. Since the reactivity of general chemical agents is better in the gas phase, vapour-phase chemical modification should be capable of reducing reaction times and diminishing agent usage, thus addressing the limitations of the liquid-phase chemical modification. Therefore, applying vapour-phase reactions for the acetylation of wood could help reduce modification costs and enhance product competitiveness. Furthermore, wood heat treatment has significantly increased over the past few decades and is still growing as an industrial process to improve some wood properties [10]. However, there is currently very limited research on the simultaneous application of acetylation and heat treatment to the processing of large-sized solid wood timber. To fill this research gap, the aim of this study is to investigate the effects of various treatment factors of high-temperature vapour-phase acetylation (HTVPA), a simultaneous acetylation and heat treatment modification process, on the properties of acetylated wood. Additionally, our study assesses the extent of the reaction penetration within solid wood timber, providing valuable insights for future modification treatments of solid wood timber.

Materials and methods

Materials

Japanese cedar (*Cryptomeria japonica* D. Don) (40–45 years old) timber, which is the most common domestically produced wood in Taiwan, was supplied by Jang Chang Lumber Industry Co., Ltd. (Hsinchu, Taiwan). Flat-sawn timbers with dimensions of 3,600 mm × 136 mm × 25 mm and an average density of 396 kg/m^3 were prepared from conventionally kiln-dried wood with an average moisture content of 14 %. To mitigate the impact of the biological variations among specimens, this study followed the guidelines of CNS 14630 [11], a standard for coniferous structural timber, and conducted mechanical grading on the specimens. During testing, a span-to-depth ratio of 18 and a loading rate of 5 mm/min were used as the testing conditions for the four-point bending test. After recording the load and deformation at 3000 N, the modulus of elasticity (MOE) was calculated, enabling the selection of specimens that conformed to the range of E70 ($5.9 \leq \text{MOE} < 7.8$ GPa). These selected specimens were intended for subsequent HTVPA treatment at different treatment temperatures and times. Each treatment group consisted of 14 replicates. Analytical grade acetic anhydride (AA, boiling point approximately 140 °C) was purchased from Easchem Co., Ltd. (Taipei, Taiwan).

High-temperature vapour-phase acetylation (HTVPA) treatment of the timber

This study used a semi-industrial-level treatment chamber with controlled temperature and pressure (San Neng Ltd., Chiayi, Taiwan) for HTVPA treatment, as shown in Fig. 1A. To obtain accurate weight percent gain (WPG) values, the specimens were initially placed in the treatment chamber and dried at 105 °C for 48 h, with the oven-dry mass recorded before the experiment. Subsequently, as the treatment chamber temperature was decreased to 80 °C, Japanese cedar specimens and AA were introduced in ratios of 1:1, 2:1, and 3:1 (w/w). The specimens were elevated using a rack to prevent direct contact with the AA. Next, the pressure inside the chamber was reduced to 25 kPa using a vacuum pump, and the temperature was raised to different target temperatures (145, 160, 180, 200, and 220 °C) at a heating rate of 2 °C/min, followed by HTVPA treatment for durations of 2, 4, 8, and 16 h at the given temperatures. At the end of the reaction, the acetylated samples were dried at 105 °C for 24 h, and the oven-drying method was used to calculate the WPG of the acetylated samples. In addition, all specimens were conditioned to constant weight in an environment at 20 °C and 65 % relative humidity (RH) for subsequent testing.

Theoretical consumption of AA

Specimens with dimensions of 500 mm (longitudinal) × 136 mm (tangential) × 25 mm (radial) were dried at 105 °C for 48 h in the treatment chamber, and their masses were determined before and after HTVPA treatment. The theoretical consumption of AA (TC_{AA}) for different treatment conditions was then calculated using the following equation: $TC_{AA}\ (\%) = [(m_1 - m_0) \times 102]/(m_{AA} \times 42) \times 100$, where m_0 and m_1 are the oven-dry mass of the specimen before and after HTVPA treatment, respectively, and m_{AA} is the mass of AA used. A molecular weight of 42 corresponded to the difference between the acetyl group and hydroxyl group, and a molecular weight of 102 represented that of AA.

Characterizations of wood properties

To determine the physicomechanical properties of the untreated and acetylated Japanese cedar timbers, several determinations, including air-dry density, equilibrium moisture content (EMC), moisture excluding efficiency (MEE), and flexural properties, were conducted. In brief, the air-dry density and EMC of the specimens with dimensions of 500 mm × 136 mm × 25 mm were measured according to CNS 451 [12] and CNS 452 [13], respectively. The MEEs were measured according to ASTM D1037 [14]. The flexural properties were determined according to CNS 454 [15] via a universal testing machine (Shimadzu AG-10kNX, Tokyo, Japan). In brief, the modulus of rupture (MOR) and modulus of elasticity (MOE) of the specimens with dimensions of 500 mm × 136 mm × 25 mm were determined by a three-point static bending test with a loading speed of 5 mm/min and a span of 350 mm. All tests were carried out in an air-conditioned room at 20 °C. Nine replicate specimens were used for each determination.

Acetylation variations within the reacted wood

In this experiment, a Spectrum 100 FTIR spectrometer (PerkinElmer, Buckinghamshire, UK) equipped with a deuterated triglycine sulfate (DTGS) detector and a MIRacle ATR accessory (Pike Technologies, Madison, WI, USA) was used for the analysis. The profiling scans were conducted on the cross-sections of acetylated specimens with dimensions of 500 mm × 136 mm × 25 mm in the tangential, radial, and longitudinal directions. The scanning resolution used was 4 cm^{-1}, with 32 scans and a wavenumber range of 4000 to 650 cm^{-1}. As shown in the schematic diagram in Fig. 1B, the depths of acetylation were analysed at the cross-section located at half the length of the specimen (250 mm). The variations in tangential acetyl groups were scanned with an interval of 4 mm along the centreline of the specimen thickness. On the other hand, the variations in radial acetyl groups were scanned at intervals of 3 mm along the centreline of the specimen width. Regarding the longitudinal variations in acetyl groups, scans were performed at the centre point of the specimen's cross-section at longitudinal positions of 0, 10, 20, 30, 40, 50, 100, 150, and 250 mm. In addition, referring to our previous paper [16], the method for evaluating the WPG of acetylated wood involved regression analysis of the ratio of absorption peak intensities at wavenumbers 1740 cm^{-1} and 1030 cm^{-1} (I_{1740}/I_{1030}) against the WPG. Subsequently, based on the obtained regression equation, the modification gradient variation of vapour-phase acetylated specimens was estimated. The degree of acetylation profiles was visualized using SigmaPlot 12.5 software (San Jose, California, United States).

NIR spectral measurements

A PerkinElmer Spectrum Two N (Buckinghamshire, UK) NIR spectrometer was used to determine functional group changes on the surfaces of the untreated and acetylated specimens. The spectra were collected by co-adding 32 scans at a resolution of 8 cm^{-1} in the 4000 to 10,000 cm^{-1} range.

Analysis of variance

All the results are expressed as the mean ± standard deviation (SD). The significance of differences was calculated by Scheffe's test or Student's *t* test, and p values < 0.05 were considered to be significant.

Table 1
The weight percent gain (WPG), end pressure, theoretical consumption of acetic anhydride (TC_{AA}), air-dry density, equilibrium moisture content (EMC), and moisture excluding efficiency (MEE) of the acetylated Japanese cedar wood with different HTVPA temperatures and durations (W/A ratio = 2/1).

Item	Temperature (°C)	Duration (h) 2	4	8	16
Pressure (MPa)	145	0.03	0.05	0.05	0.06
	160	0.03	0.05	0.05	0.05
	180	0.05	0.10	0.10	0.12
	200	0.10	0.15	0.27	0.25
	220	0.20	0.33	0.39	0.59
TC_{AA} (%)	145	11.8	19.4	19.6	22.9
	160	10.5	13.6	19.5	35.2
	180	17.0	19.3	26.5	38.1
	200	19.2	29.8	39.6	39.8
	220	15.2	15.5	24.7	08.3
WPG (%)	145	2.5 ± 0.8^{Bbc}	3.9 ± 0.4^{Ab}	4.1 ± 0.6^{Ab}	4.8 ± 0.8^{Ab}
	160	2.2 ± 0.4^{Cc}	2.8 ± 0.6^{Cb}	4.0 ± 0.4^{Bb}	7.2 ± 1.0^{Aa}
	180	3.5 ± 0.7^{Cab}	4.0 ± 1.0^{Cb}	5.3 ± 0.4^{Bb}	7.9 ± 1.2^{Aa}
	200	3.9 ± 0.4^{Ca}	6.3 ± 1.5^{Ba}	8.2 ± 1.7^{Aa}	8.2 ± 1.7^{ABa}
	220	3.2 ± 0.9^{Bab}	3.2 ± 0.9^{Bb}	5.1 ± 1.3^{Ab}	1.7 ± 0.8^{Cc}
Density (kg/m^3)†	145	$429 \pm 33^{Aa}_{ns}$	$474 \pm 44^{Aa}_{ns}$	$479 \pm 79^{Aa}_{ns}$	$457 \pm 61^{Aa}_{ns}$
	160	$448 \pm 32^{Ba}_{ns}$	$543 \pm 46^{Aa***}$	$439 \pm 63^{Bab}_{ns}$	$460 \pm 37^{Ba}_{ns}$
	180	$437 \pm 29^{Ba}_{ns}$	$505 \pm 62^{Aa*}$	$471 \pm 33^{ABab}_{ns}$	$449 \pm 51^{Aba}_{ns}$
	200	$462 \pm 26^{Aa}_{ns}$	$469 \pm 63^{Aa}_{ns}$	$447 \pm 32^{Aab}_{ns}$	$424 \pm 44^{Aa}_{ns}$
	220	$438 \pm 49^{Aab}_{ns}$	$461 \pm 65^{Aa}_{ns}$	$398 \pm 30^{Bb*}$	$421 \pm 27^{Aab}_{ns}$
EMC (%)†	145	$6.1 \pm 0.3^{Aa***}$	$5.9 \pm 0.7^{ABa***}$	$5.9 \pm 0.9^{ABa***}$	$5.1 \pm 0.5^{Ba***}$
	160	$6.3 \pm 0.5^{Aa***}$	$5.9 \pm 0.5^{ABa***}$	$5.5 \pm 0.4^{Ba***}$	$4.7 \pm 0.5^{Ca***}$
	180	$6.2 \pm 0.3^{Aa***}$	$5.6 \pm 0.7^{Aa***}$	$4.7 \pm 0.4^{Bb***}$	$3.0 \pm 0.4^{Cb***}$
	200	$5.0 \pm 0.4^{Ab***}$	$3.9 \pm 0.9^{Bb***}$	$2.2 \pm 0.1^{Cc***}$	$2.1 \pm 0.2^{Cc***}$
	220	$4.3 \pm 0.3^{Ac***}$	$2.4 \pm 0.6^{Bc***}$	$2.2 \pm 0.1^{Bc***}$	$1.2 \pm 0.4^{Cd***}$
MEE (%)	145	51 ± 2^{Bc}	52 ± 5^{ABc}	52 ± 7^{ABc}	59 ± 4^{Ad}
	160	49 ± 4^{Cc}	53 ± 4^{BCc}	56 ± 3^{Bc}	62 ± 4^{Ad}
	180	50 ± 3^{Cc}	55 ± 6^{Cc}	62 ± 3^{Bb}	76 ± 3^{Ac}
	200	59 ± 3^{Cb}	71 ± 7^{Bb}	82 ± 1^{Aa}	83 ± 2^{Ab}
	220	65 ± 3^{Ca}	81 ± 4^{Ba}	83 ± 1^{Ba}	90 ± 3^{Aa}

Values are the mean ± SD ($n = 9$). Different capital letters within a row indicate significant differences among the various durations by one-way ANOVA and the Scheffé test ($p < 0.05$). Different lowercase letters within a column indicate significant differences among the various temperatures by one-way ANOVA and the Scheffé test ($p < 0.05$). ns: nonsignificant; *: $p < 0.05$; ***: $p < 0.005$, compared with untreated specimens by Student's t test. †The air-dry density and EMC of untreated specimens are 447 ± 52 kg/m^3 and 12.4 ± 0.4 %, respectively.

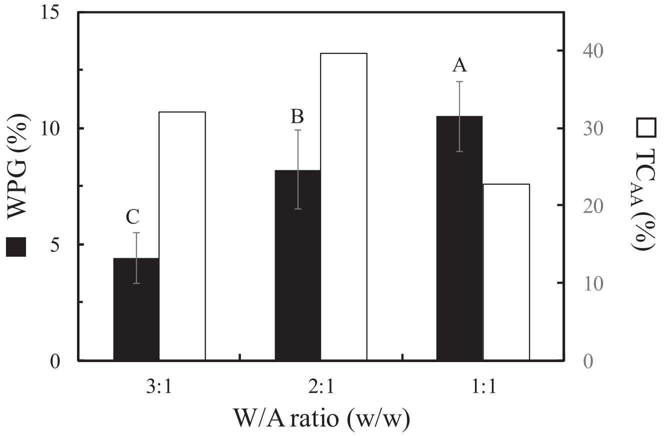

Fig. 2. WPG and the theoretical consumption of acetic anhydride (TC_{AA}) of HTVPA treated Japanese cedar wood with different W/A ratios (200 °C/8h). Values are the mean ± SD ($n = 9$). Bars with different capital letters indicate significant differences among various W/A ratios by one-way ANOVA and the Scheffé test ($p < 0.05$).

Results and discussion

Impact of the different HTVPA conditions on the physical properties of Japanese cedar wood

Weight percent gain (WPG)

To understand the impact of different HTVPA treatment conditions on the WPG of acetylated Japanese cedar, experiments were conducted using various treatment temperatures, treatment times, and wood-to-AA (W/A) ratios. From Table 1, when the HTVPA temperature was below 200 °C, the WPG of acetylated wood ranged from 2.2 to 8.2 % and tended to increase with longer treatment times. Specifically, at an HTVPA temperature of 145 °C, the WPG after 2 h of treatment was 2.5 %. For treatment times of 4, 8, and 16 h, the WPGs were 3.9, 4.1, and 4.8 %, respectively. No significant difference was observed among these values, indicating that the reactivity of HTVPA at 145 °C gradually diminished after 4 h. This phenomenon was likely due to HTVPA being a heterogeneous treatment method. The reaction proceeded from the outer layers of the wood in a concentric manner towards the inner layers. After the reaction, the smaller hydroxyl groups on the cell wall were replaced by larger acetyl groups, leading to cell wall swelling. Consequently, the subsequent penetration of vapour-phase AA into the interior of the wood for reaction became less effective [17,18]. In contrast, when the temperature was increased to 200 °C, the WPGs of acetylated wood after 2, 4, 8, and 16 h of treatment were 3.9, 6.3, 8.2, and 8.2 %, respectively. This result indicated that the highest WPG was achieved after 8 h of treatment at 200 °C, and no significant difference was observed between these values. This result was likely due to the higher saturated vapour pressure of AA at 200 °C compared to 145 °C (Table 1), providing more available vapour-phase AA for the reaction. However, as the treatment temperature was increased to 220 °C, the WPG showed a decreasing trend due to the thermal degradation of the wood material. Hence, 200 °C/8h was considered the optimal treatment temperature and time. Furthermore, to explore the influence of the W/A ratio on the degree of modification, experiments were performed under three W/A conditions: 3:1, 2:1, and 1:1. As shown in Fig. 2, at 200 °C for 8 h, when the W/A ratios were 3:1, 2:1, and 1:1, the WPGs were 4.4, 8.2, and 10.5 %, respectively. Among them, the 1:1 ratio had the highest WPG, which was approximately 28 % higher than that of the 2:1 ratio; however, the 2:1 W/A ratio appeared more suitable due to the lower reagent consumption.

Since the generation of vapour-phase AA was related to treatment temperature and pressure, the pressure was recorded at the endpoint of the HTVPA reaction as a reference for evaluating the degree of modification. From Table 1, the pressure of HTVPA increased with higher treatment temperatures and longer treatment times. At a treatment temperature of 160 °C, the pressures after 2 and 4 h of treatment were the same as those at 145 °C, but the WPGs were lower and determine to be 2.2 % and 2.8 %, respectively. Conversely, when the treatment temperature exceeded 180 °C, the endpoint pressures were higher than those at 145 °C. This result indicated that conducting HTVPA at higher temperatures could lead to a greater vaporization of AA, which subsequently reacted with the wood. However, when the treatment temperature reached 220 °C, the highest pressure range (0.20–0.59 MPa) was attained, while the WPG showed a trend of initially increasing and then decreasing with prolonged reaction time. This phenomenon occurred because the HTVPA temperature of 220 °C reached the thermal degradation temperature of the wood, leading to an influence of thermal degradation during acetylation and causing a decrease in the WPG. Additionally, referring to our previous research [19], when the heat treatment condition was set at 160 °C for 4 h, the mass loss of Japanese cedar wood was 2.7 %. Under this treatment condition, the WPG of acetylated wood was 2.8 %, which was lower than the 3.9 % achieved for acetylated wood prepared at 145 °C (Table 1). Furthermore, when both the heat treatment and acetylation were carried out at a temperature of 220 °C, the mass loss ranged from 6.4 to 13.0 %, while the WPG ranged from 1.7 to 5.1 %. Therefore, despite this temperature having the highest pressure range (0.20–0.59 MPa), its mass loss from thermal degradation was much higher than the WPG achieved through acetylation. As a result, the weight gain was reduced. However, when the heat treatment and acetylation were both conducted at 200 °C, the mass loss and WPG of Japanese cedar ranged from 4.2 to 8.7 % and 3.9 to 8.2 %, respectively, both of which increased with longer treatment times. The primary reason for this phenomenon was potentially caused by the thermal degradation of the hemicellulose-lignin matrix on the cell wall, altering the structure of the cell wall and enabling the vapour-phase AA to more effectively penetrate into the interior of the wood [20].

Theoretical consumption of acetic anhydride (TC_{AA})

To further understand the required reagent amounts for practical reactions under various HTVPA conditions, the TC_{AA} was investigated. As shown in Table 1, when the reaction temperature was 145 °C, the TC_{AA} for the reaction times of 2–16 h ranged from 11.8 to 22.9 %. However, when the reaction temperature was increased to 200 °C, the TC_{AA} increased to 19.2–39.8 %, an increase of approximately 50–100 %. This phenomenon was likely due to the higher HTVPA temperature leading to an increase in the saturated vapour pressure in the environment, which facilitated the vaporization of more AA. However, when the reaction temperature reached 220 °C, the TC_{AA} decreased to 8.3–24.7 %. This potentially occurred because the thermal degradation of wood at 220 °C was faster than the acetylation rate, resulting in a decrease in the WPG. Furthermore, during the thermal degradation of hemicellulose in wood, mainly consisting of xylose, mannose, arabinose, and galactose degrade, produced gases, such as carbon monoxide, carbon dioxide, methane, and water. This increased the saturated vapour pressure in the environment and consequently decreased the concentration of vapour-phase AA, leading to a reduction in the rate of acetylation [21–23]. From Fig. 2, under the treatment condition of 200 °C/8h, the W/A ratio of 2:1 exhibited the highest TC_{AA} (39.6 %). Conversely, when the amount of AA was increased with a W/A ratio of 1:1, the TC_{AA} dropped to only 22.7 %, indicating that approximately 80 % of the reagent remained unreacted. As a result, increasing the W/A ratio did not increase the total amount of AA that could be vaporized; it merely led to unnecessary waste of the reagent.

Air-dry density, equilibrium moisture content (EMC), and moisture excluding efficiency (MEE)

As shown in Table 1, except for the specimens modified at 160 °C/4h, 180 °C/4h, and 220 °C/8h, no statistically significant differences in density between untreated and acetylated wood were observed. The air-dry densities of the various specimens ranged from 398 to 543 kg/m^3. On the other hand, acetylation treatment could generally reduce wood's moisture absorption and enhance its dimensional stability, thereby extending its lifespan and expanding its range of applications [24,25]. Therefore, the EMC and MEE of untreated and acetylated Japanese cedar at 20 °C and 65 % relative humidity (RH) were measured with the aim to explore the influence of different HTVPA conditions on these properties. As shown in Table 1, the EMC of the untreated Japanese cedar wood was 12.4 %, while the EMC of the various acetylated wood samples ranged from 1.2 % to 6.3 %; all values showed significant differences from those of the untreated wood. Specifically, at a reaction temperature of 145 °C, the EMC decreased as the reaction time increased, and similar trends were observed across the different reaction temperatures. These results indicated that the hydrophilic hydroxyl groups on the wood were replaced by hydrophobic acetyl groups through HTVPA treatment, resulting in a lower EMC. Additionally, when comparing results with the same reaction time, no significant difference in the EMC values between the reaction temperatures of 145 °C and 160 °C were observed. However, when the reaction temperature exceeded 180 °C, the EMC of the acetylated Japanese cedar wood decreased as the reaction temperature increased. This phenomenon was likely due to the thermal degradation of hydrophilic hemicellulose during the HTVPA treatment. Notably, to understand the correlation between the EMC and WPG of the acetylated wood mentioned above, the EMC was plotted against the WPG for both the untreated and acetylated wood. As shown in Fig. 3, when the reaction temperature was below 220 °C, the EMC of different acetylated wood decreased as the WPG increased. However, when the reaction temperature reached 220 °C, the acetylated wood with a low WPG (1.7 %) also exhibited a low EMC (1.2 %). This result potentially occurred because at this temperature during HTVPA treatment, the rate of the thermal degradation of wood exceeded the rate of acetylation, resulting in a lower WPG. Moreover, the degradation of hydrophilic hemicellulose in wood contributed to the reduction in EMC. This discrepancy in trend at 220 °C was potentially due to this unique interaction of factors not observed under the other treatment conditions.

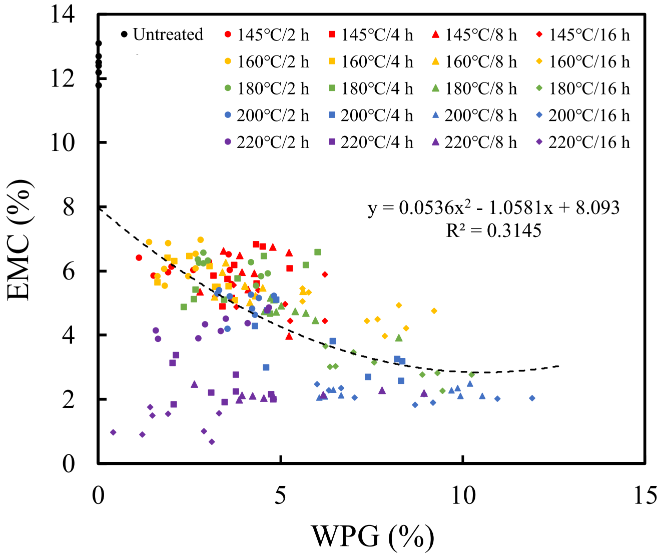

Fig. 3. Correlation between the WPG and EMC of untreated and HTVPA treated Japanese cedar wood at 20 °C and 65 % RH.

Additionally, the MEEs of the various acetylated wood samples were calculated at 20 °C and 65 % RH. From the results in Table 1, when the reaction temperature was 145 °C, the MEEs ranged from 51 % to 59 % and increased with longer reaction times. Similarly, at the same reaction time, the MEEs of the acetylated samples also increased with higher reaction temperatures. The MEEs increased from 51 to 59 % at 145 °C to 65–90 % at 220 °C; this result indicated that HTVPA treatment at temperatures ranging from 145 to 220 °C effectively enhanced the wood's MEE. These results were consistent with those of Chang and Chang [26], who observed a decrease in EMC to 6.51 % and an increase in the MEE to 47.79 % in an acetylated maple wood treated at 120 °C. Moreover, our results were in agreement with the research conducted by Xu et al. [19] on different heat-treated Japanese cedar wood, which also showed an improved MEE with increasing treatment time and temperature. Compared to the aforementioned studies, the acetylated Japanese cedar wood prepared in this research exhibited an even lower EMC and higher MEE. Thus, the HTVPA treatment at high temperatures could combine the effects of both the heat treatment and chemical modification.

Table 2
Modulus of elasticity (MOE) and modulus of rupture (MOR) of untreated and HTVPA treated Japanese cedar wood.

Temperature (°C)	MOE (GPa)			MOR (MPa)		
	2 h	8 h	16 h	2 h	8 h	16 h
Untreated	7.2 ± 0.5			60 ± 8		
145	$7.2 \pm 0.5^{Aa}_{ns}$	$7.5 \pm 0.7^{Aa}_{ns}$	$7.1 \pm 0.5^{Aa}_{ns}$	$58 \pm 4^{Aa}_{ns}$	$61 \pm 6^{Aa}_{ns}$	$60 \pm 5^{Aa}_{ns}$
160	$5.6 \pm 0.5^{Ab***}$	$5.3 \pm 0.5^{Abc***}$	$5.4 \pm 0.5^{Ab***}$	$55 \pm 8^{Aa}_{ns}$	$53 \pm 6^{Aa}_{ns}$	$54 \pm 11^{Aa}_{ns}$
180	$5.3 \pm 0.3^{Ab***}$	$5.7 \pm 0.7^{Abc***}$	$5.4 \pm 0.5^{Ab***}$	$55 \pm 8^{Aa}_{ns}$	$54 \pm 10^{Aa}_{ns}$	$50 \pm 6^{Abc*}$
200	$5.7 \pm 0.4^{ABb***}$	$6.1 \pm 0.9^{Ab***}$	$5.2 \pm 0.4^{Bb***}$	$59 \pm 8^{Aa}_{ns}$	$51 \pm 8^{Aa}_{ns}$	$39 \pm 5^{Bcd***}$
220	$5.1 \pm 0.5^{Ab***}$	$4.8 \pm 0.3^{Ac***}$	$4.8 \pm 0.6^{Ab***}$	$40 \pm 12^{Ab***}$	$39 \pm 5^{Ab***}$	$35 \pm 8^{Ad***}$

Values are the mean ± SD ($n = 9$). Different capital letters within a row indicate significant differences among the various durations by one-way ANOVA and the Scheffé test ($p < 0.05$). Different lowercase letters within a column indicate significant differences among the various temperatures by one-way ANOVA and the Scheffé test ($p < 0.05$). ns: nonsignificant; *: $p < 0.05$; ***: $p < 0.005$, compared with untreated specimens by Student's t test.

Influence of different HTVPA conditions on the flexural properties of Japanese cedar wood

Generally, the acetylation treatment does not significantly affect the mechanical properties of wood [16]. However, in this study, the HTVPA temperature used ranged from 145 °C to 220 °C, which overlapped with the temperature range of the wood heat treatment, known to have mostly negative effects on mechanical properties [27]. Therefore, to understand the impact of various HTVPA conditions on the mechanical properties of wood, the flexural properties of the untreated and acetylated Japanese cedar wood were examined, as listed in Table 2. The results showed that when the reaction temperature was 145 °C, the MOE values for the acetylated wood with reaction times of 2, 8, and 16 h were 7.2, 7.5, and 7.1 GPa, respectively. These values did not exhibit statistically significant differences when compared to untreated wood (7.2 GPa). This outcome was consistent with the findings of Li et al. [28] regarding liquid-phase acetylation of Japanese cedar wood. This phenomenon occurred because the hydrophilic hydroxyl groups on the cell walls of wood were replaced by hydrophobic acetyl groups, leading to a decrease in the EMC of the wood and subsequently an increase in the strength. Conversely, acetylated wood also experienced cell swelling, resulting in a reduced quantity of fibres per unit volume and causing a decrease in strength. Due to the combined effects of these two factors, no significant difference was observed in the MOE values between the untreated and acetylated wood [27,29]. However, when the reaction temperature was increased to 160–220 °C, the MOE values decreased with increasing reaction temperature, and the values significantly differed from those of the untreated samples. Among these temperatures, the MOE reduction was the most pronounced at 220 °C, ranging from 29 % to 33 %, indicating that thermal degradation had a negative impact on the MOE of Japanese cedar wood.

In terms of the MOR, when the reaction temperature was 145 °C, the MOR values obtained from acetylated wood after reaction times of 2, 8, and 16 h were 58, 61, and 60 MPa, respectively. These values did not exhibit statistically significant differences from the untreated wood (60 MPa), indicating that acetylation via the vapour-phase at this temperature did not impact the bending strength of the wood. However, as the reaction temperature increased to 160 °C, the MOR of acetylated wood decreased to 53–55 MPa and continued to decrease with higher reaction temperatures, reaching 35–40 MPa for the 220 °C treatment. This was a reduction of approximately 33–42 % in the MOR, and all values exhibited significant differences from those of the untreated wood. This

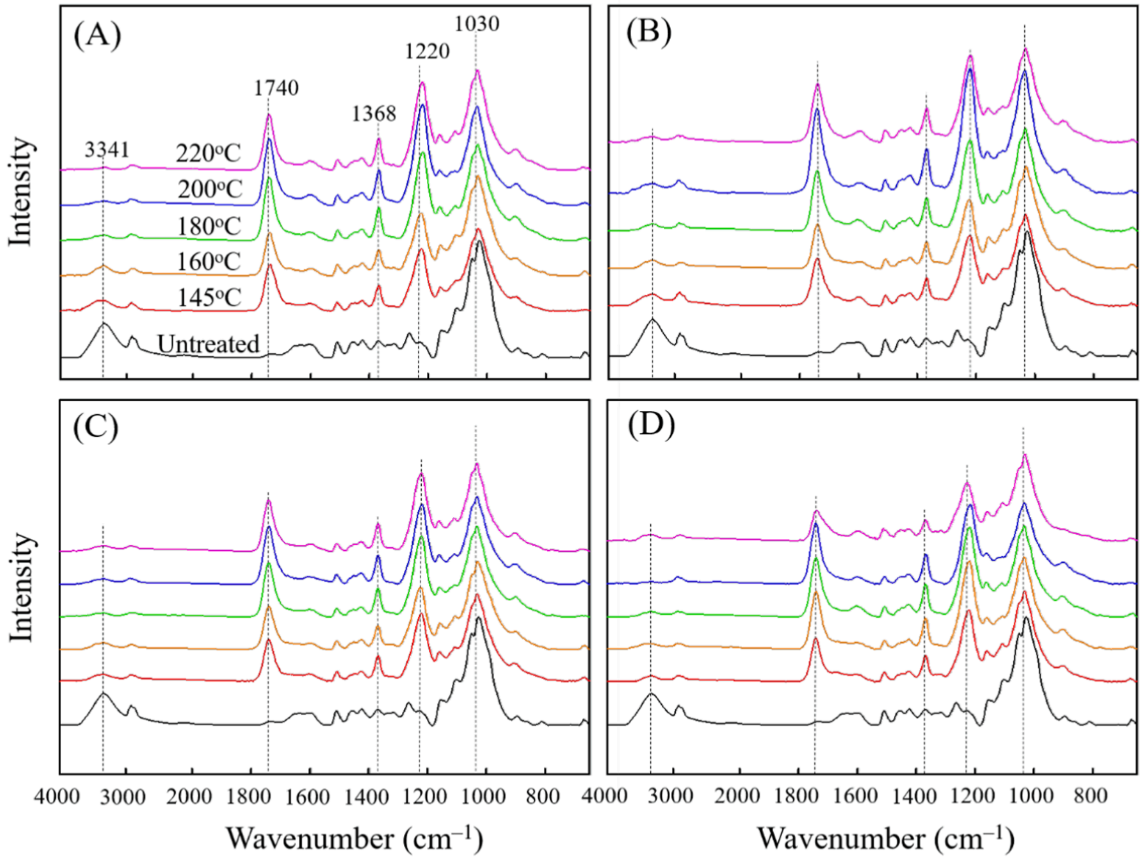

Fig. 4. FTIR spectra of Japanese cedar wood after HTVPA treatment at different temperatures for (A) 2, (B) 4, (C) 8, and (D) 16 h.

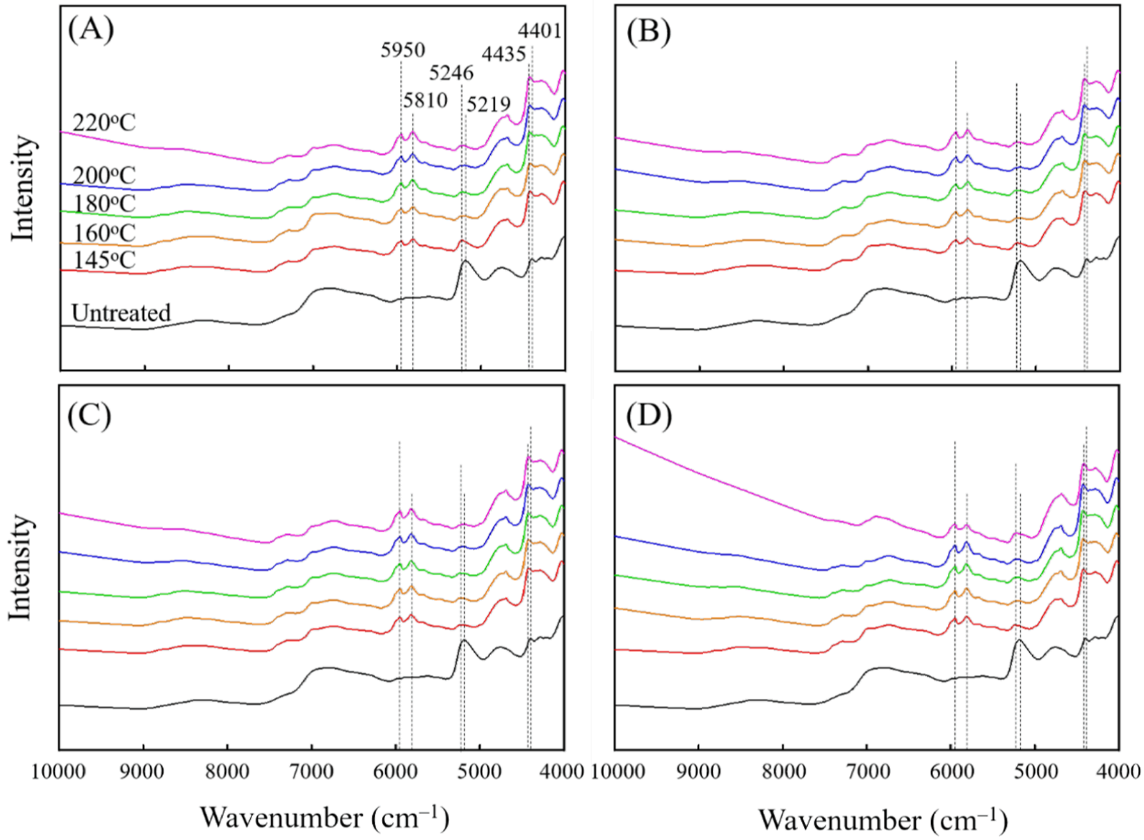

Fig. 5. NIR spectra of Japanese cedar wood after HTVPA treatment at different temperatures for (A) 2, (B) 4, (C) 8, and (D) 16 h.

trend was similar to the MOE results. Furthermore, when the reaction time was 16 h, the MOR of acetylated wood treated at 180, 200, and 220 °C was 50, 39, and 35 MPa, respectively. This result indicated that the effect of heat treatment on Japanese cedar wood was more pronounced than that of acetylation when the reaction time was 16 h. These findings aligned with the results of Xu et al. [19] in their investigation of the flexural properties of Japanese cedar wood under different heat treatments. They noted that the MOE of Japanese cedar wood decreased with increasing heat treatment time when the temperature exceeded 180 °C. Similarly, when the treatment temperature exceeded 200 °C, the MOR also decreased with increasing heat treatment temperature and time. However, in our study, the MOE and MOR of vapour-phase acetylated Japanese cedar wood began to decrease at 160 and 180 °C, respectively. This was potentially attributed to the byproduct of acetic acid that was generated during HTVPA treatment, accelerating the degradation of hemicellulose and thereby enhancing the temperature's impact on the flexural properties of the Japanese cedar wood.

Impact of the different HTVPA conditions on the chemical properties of Japanese cedar wood

Surface functional groups

As shown in Fig. 4, the FTIR spectra showed that after the HTVPA treatment, specific peaks of acetyl groups at 1740 cm^{-1} (–OCOCH$_3$, C = O), 1368 cm^{-1} (–OCOCH$_3$, C–H), and 1220 cm^{-1} (–OCOCH$_3$, C–O) clearly intensified. Simultaneously, the peak of hydroxyl groups (–OH) at 3341 cm^{-1} significantly decreased; this result indicated the effective conversion of the hydroxyl groups into acetyl groups through the reaction with AA. This finding was similar to the results obtained by Sun et al. [30] in their investigation on the influence of different acetylation durations on the chemical functional groups of pine wood. Furthermore, the FTIR spectrum of the material subjected to a 16 h HTVPA treatment at 220 °C (Fig. 4D) showed that the absorption peak of the acetyl group at 1740 cm^{-1} was weakened and shifted towards lower wavenumbers. Thus, deacetylation reactions occurred during the HTVPA process of the wood, leading to the formation of acidic degradation products. Additionally, the specific C–H absorption peak of cellulose or hemicellulose at 898 cm^{-1} also experienced a decrease in intensity.

NIR spectroscopy is convenient and has rapid detection characteristics; additionally, NIR spectra often contain combination bands of various vibration modes, such as C–O, C–H, O–H, and N–H overtones, or combinations of two or more distinct vibrational modes similar to those found in FTIR spectroscopy [31]. Therefore, NIR was used to observe the changes in the chemical structure of wood after HTVPA treatment. From Fig. 5, after HTVPA treatment of Japanese cedar wood, the C–H combination bands of cellulose, hemicellulose, and lignin at 4401 cm^{-1} not only shifted towards 4435 cm^{-1} but also exhibited increased intensities. Additionally, the C–H first overtone absorption peaks of hemicellulose and lignin at 5810 cm^{-1} and 5950 cm^{-1} showed acetyl group-specific absorption peaks [32], indicating the generation of acetyl groups after HTVPA treatment. Furthermore, the broad peak in the range of 5185–5242 cm^{-1} was mainly attributed to the O–H stretching vibration of water at 5219 cm^{-1} and the second overtone of C = O stretching vibration in hemicellulose at 5246 cm^{-1} [33]. After HTVPA treatment, the intensity of this absorption peak decreased and shifted towards higher wavenumbers. This result indicated the formation of hydrophobic acetyl groups within the wood, leading to a reduction in the moisture content of the wood. Furthermore, a decrease in the intensity of the O–H first overtone absorption peak in the range of 6500–7000 cm^{-1} for cellulose, hemicellulose, and lignin was observed after HTVPA treatment, while an increase in the intensity of the acetyl group C–H second overtone absorption peak was observed at 8583 cm^{-1} [31]. The above results all showed that hydroxyl groups in the wood definitely reacted with acetic anhydride to form acetyl groups. Furthermore, as shown in

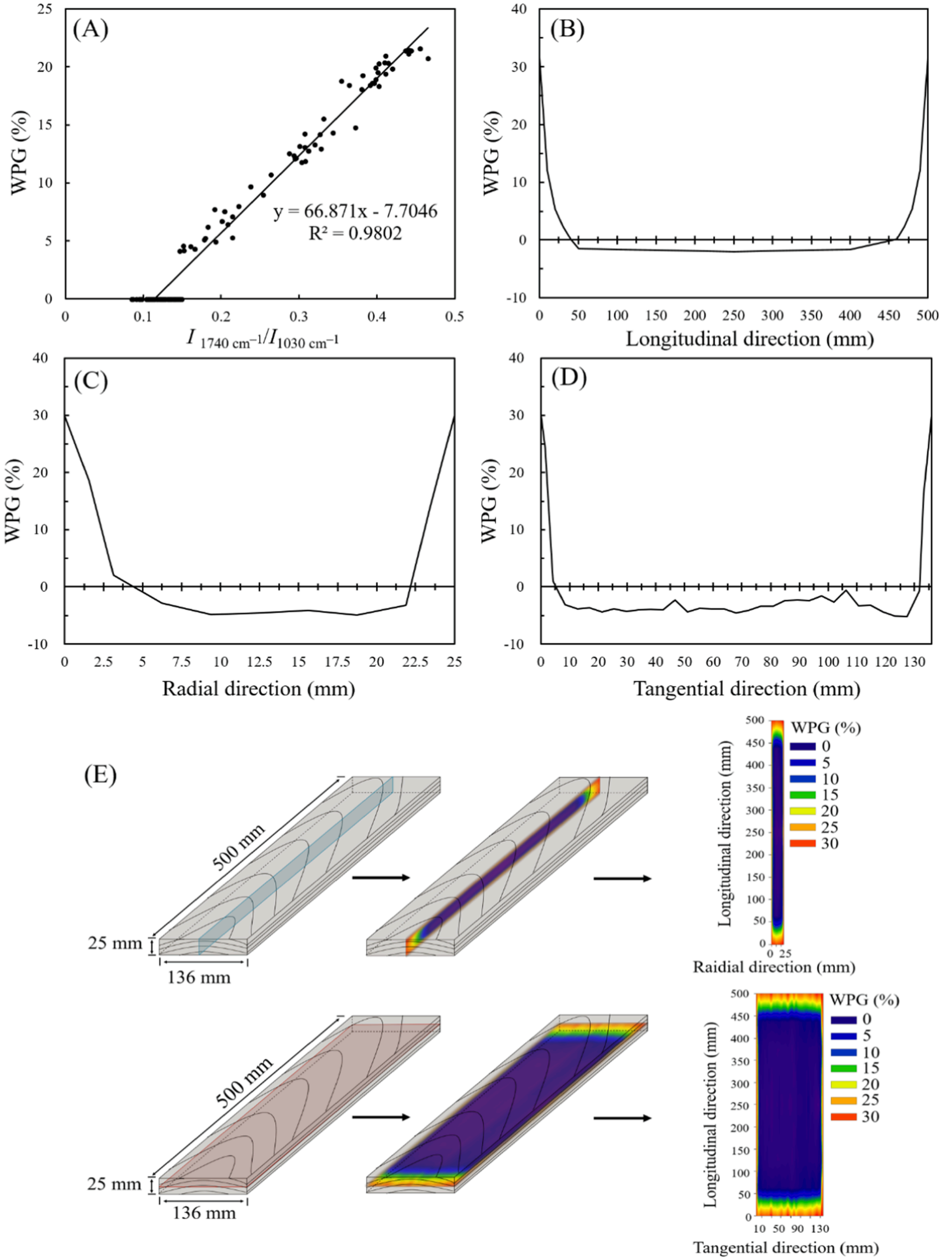

Fig. 6. (A) Regression analysis of the WPG and I_{1740}/I_{1030} ratio of HTVPA treated Japanese cedar wood. (B) Longitudinal, (C) radial, (D) tangential, and (E) two-dimensional (2D) WPG profiles for the central section of the HTVPA treated wood (200 °C/8h) obtained through regression analysis.

Fig. 5D, the absorption intensity in the range of 9000–10000 cm^{-1} increased with increasing reaction temperature for the acetylated wood; thus, the surface colour of the acetylated wood deepened with higher reaction temperatures [34].

WPG profile

To understand the variation in the acetylation gradient in Japanese cedar wood treated with vapour-phase AA, the optimized HTVPA condition (200 °C/8h) was used in this study. For analysis, the FTIR intensity ratio of the absorption peak at 1740 cm^{-1} to 1030 cm^{-1} (I_{1740}/I_{1030}) was used for regression analysis with WPG. The results in Fig. 6A showed that the coefficient of determination (R^2) between I_{1740}/I_{1030} and WPG was 0.9802. According to this regression equation, the theoretical WPG profiles of the longitudinal, radial, and tangential directions of acetylated Japanese cedar samples were calculated using the I_{1740}/I_{1030} ratio value, as shown in Fig. 6B–D. The results for the longitudinal direction of the samples indicated that when the depth was 0 mm (end-side), the theoretical WPG was 31.6 %, whereas at a depth of 40 mm, the theoretical WPG decreased to 0.1 %. Similarly, for the radial and tangential directions, the theoretical WPG was 30.0 % at 0 mm depth. However, at a depth of 3 mm for the radial direction, the theoretical WPG decreased to 2.0 % on one side and –3.2 % on the other side. Similarly, at a depth of 4 mm for the tangential direction, the theoretical WPG decreased to 0.9 % on one side and 1.2 % on the other side. This phenomenon occurred because HTVPA treatment involved the diffusion of vapour-phase AA from the outer surface of the specimen into the interior, initiating a reaction. Wood had optimal longitudinal diffusion characteristics, enabling a penetration depth of up to 40 mm in acetylation. In contrast, radial and tangential diffusions were less efficient, resulting in acetylation depths of only 3–4 mm. Fig. 6E shows the two-dimensional WPG profile. These results were similar to the findings of Hasegawa et al. [35], who investigated the cross-sectional acetylation degree of wood using vapour-phase acetylation at 80 °C. Their results showed that with a processing time of 6 h, the acetylation depth was less than 2 mm. Extending the processing time to 12 h enabled an acetylation depth of 2–4 mm, demonstrating that AA diffused into the wood interior from the outer surface. In comparison, the acetylation depth of the cross-section of Japanese cedar wood prepared in our study at 200 °C/8h was deeper than that of Hasegawa et al. [35] at 80 °C/12 h, indicating that increasing the acetylation temperature could lead to a more complete reaction between AA and wood. Moreover, at 200 °C, the wood cell wall underwent thermal degradation, changing the cell wall structure and enabling more AA to penetrate into the wood interior. Additionally, Zelinka et al. [36] indicated that wood acetylation achieves decay resistance when the WPG reached 18–20 %. Although the WPG of Japanese cedar wood acetylated at 200 °C/8h was only 8.2 %, the theoretical WPG on the surface reached 30.0–31.6 %. Furthermore, as shown in Fig. 6B–D, the internal WPG in the longitudinal, radial, and tangential directions of HTVPA treated Japanese cedar samples all displayed negative values. These negative values were mainly attributed to the reduction of acetyl groups at 1740 cm^{-1} ($–OCOCH_3$, $C = O$), which has been confirmed to be significantly associated with the degradation of hemicellulose during the heat treatment process [19,23,37]. Unlike the gradient changes in surface WPG, the internal WPG remained relatively stable, indicating that the degradation of hemicellulose in HTVPA treated Japanese cedar wood was uniform. Hemicellulose is considered a crucial nutrient and a key factor for the growth of wood-decaying fungi [22]. Therefore, the simultaneous surface acetylation and uniform heat treatment modification process, known as HTVPA, could have potential for enhancing the decay resistance of Japanese cedar wood.

Conclusions

The EMC of the acetylated Japanese cedar wood decreased with increasing vapour-phase reaction temperature and time, leading to an enhancement in its resistance against moisture absorption. In terms of mechanical properties, when HTVPA was performed at 145 °C, no significant impacts on the MOE and MOR of wood were observed. However, as the treatment temperature and time were increased, negative effects on MOE and MOR became apparent. Among these conditions, the most pronounced effects were observed with treatments at 220 °C/8h and 220 °C/16 h. Nevertheless, when treated at 200 °C/8h, the MOE only experienced a modest decrease of 15 %, with no significant impact on the MOR. Furthermore, based on the results from FTIR and NIR analyses, the hydroxyl groups in the Japanese cedar wood reacted with acetic anhydride to form acetyl groups after HTVPA treatment. However, when the treatment temperature reached 220 °C, deacetylation and dehydration reactions occurred during the modification process. Additionally, with increasing treatment temperature and time, organic acids, such as formic acid and acetic acid, were generated within the specimens during HTVPA treatment. When the Japanese cedar wood was subjected to acetylation via the HTVPA method at 200 °C/8h, the optimal longitudinal penetration depth was achieved and reached up to 40 mm, while the penetration depths were only 3–4 mm in the tangential and radial directions. Although the overall WPG of the acetylated wood obtained under this treatment condition was only 8.2 %, the theoretical WPG on the surface was 30.0–31.6 %. Therefore, this HTVPA treatment method could have potential for enhancing the resistance of Japanese cedar wood against biodegradation, warranting further research in subsequent studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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