Valorisation of Acacia mangium Bark for Sustainable Bio-Based Wood Preservatives: Tannin Extraction and Boron Complexation with Additives

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Abstract

The increasing demand for sustainable and environmentally benign wood protection systems has prompted the exploration of natural polyphenolic compounds such as tannins. This study investigates the valorisation of *Acacia mangium* bark, a plantation byproduct, as a source of condensed tannins for bio-based wood preservatives. Tannin extraction was conducted using three solvent systems: hot water, 70% acetone, and a sulfite-based solution (2% Na_2SO_3 + 0.5% Na_2CO_3). Among these, the sulfite-based method demonstrated superior performance, yielding the highest tannin content (56.24%) and purity (Stiasny number = 70), along with elevated phenolic content as measured by UV-Vis spectrometry. The extracted tannins were complexed with boron-tannin and further modified with various additives—formalin, ϵ-caprolactam, hexamine, and low molecular weight phenol-formaldehyde resin—to enhance leach resistance, gelation time, and viscosity. Among the formulations, BTCHF (boron-tannin-caprolactam-hexamine-formalin) showed the most balanced performance with improved water resistance (40% insoluble matter), moderate viscosity (11.45 cP), and near-neutral pH (6.12). FTIR analysis confirmed the formation of stable crosslinked structures and reduced free –OH groups, indicating successful boron-tannin complexation. This study provides a novel approach to producing high-performance, renewable wood preservatives from *A. mangium* bark. The findings highlight the potential of tannin-boron systems as durable and eco-friendly alternatives to synthetic preservatives, supporting sustainable forestry and green construction initiatives in tropical regions.

Keywords: boron, acacia mangium, tannin, tannin extraction

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1. Introduction

Although boron serves as a versatile wood preservative, its primary drawback remains its tendency to leach from treated wood. The complexes that form when boron interacts with tannins in wood provide resistance to decay and insect infestation, as demonstrated in earlier studies [1]. Borate esters, which are highly soluble in water yet partly retained in wood, arise when boric acid reacts with hydroxyl groups in wood components such as cellulose, hemicellulose, and tannins [2]. Through these reactions, boron compounds become complexed with cell wall constituents—particularly tannins—and penetrate the wood structure, forming boron-tannin networks that protect against insects and fungi, contributing to more sustainable and climate-resilient wood products, which aligns with Asia's wider sustainable development and energy transition goals [3–5]. This crosslinking of tannin molecules with boron ions yields a more stable compound that is less water-soluble than boron alone. Although polymerisation with certain additives does not always fully prevent boron leaching, the tannin network can significantly reduce this loss under exposure [6].

In Sabah, Sarawak, and Peninsular Malaysia, *Acacia mangium* (Fabaceae) is widely planted as a non-native forest plantation species. In Sabah alone, 106,581 hectares out of 130,655 hectares of plantation forests are stocked with *A. mangium*, making it the most common plantation tree species in Southeast Asia [7]. This species originates from the Maluku and Irian Jaya regions of eastern Indonesia, as well as Papua New Guinea and northern Australia [8]. Typically, *A. mangium* reaches harvestable size after 7 to 15 years [6]. Its rapid growth and adaptability have made it widely established and, in some areas, invasive beyond its native range [9]. Well known for its industrial applications, *A. mangium* supports pulp and solid wood production, bioenergy, and agroforestry systems, providing multiple economic and ecological benefits [9].

Tannin compounds, abundant mainly in tree bark, occur across various plant species, including both gymnosperms and angiosperms. These natural polyphenols play a protective role against UV radiation, desiccation [10], and biological deterioration by animals, insects, fungi, and bacteria [11]. Tannins exist mainly in two types: hydrolysable and condensed. Hydrolysable tannins consist of simple phenolic acids such as ellagic or gallic acid, while condensed tannins comprise flavonoid units without a sugar core [12]. Mangrove, hemlock, wattle, and quebracho species are known to contain high levels of condensed tannins, whereas species such as chestnut and myrobalan contain predominantly hydrolysable tannins [13].

Extraction of tannins is typically performed using water or mixed solvents such as methanol, ethanol, acetone, or alkaline solutions like sodium hydroxide. According to Antwi-Boasiako and Animapauh [14], hot water extraction produces favorable yields; however, other studies have shown that methanol-water mixtures can further improve extraction efficiency [15,16]. For instance, Paridah and Musgrave [17] demonstrated that tannins extracted from mangrove species such as *Rhizophora mucronata* and *R. apiculata* achieve significant yields when sulphite is used as the extraction medium. Hydrolysable tannins can be hydrolyzed by weak acids or bases, releasing glucose and phenolic acids.

Careful control of the solid-to-solvent ratio and extraction temperature is critical to maximizing yield and quality [15,18–24]. For example, Sujarnoko et al. [25] reported increased concentrations of phenols, tannins, and condensed tannins in Acacia bark when extraction was performed at 120°C compared to 70°C. Using 50% methanol or acetone has been shown to raise tannin yield by up to 17.5% [26], and Makkar [27] recommended 70% acetone for its balance of polar and non-polar properties when extracting tannins from various plant sources.

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This research focuses on examining the properties of *A. mangium* bark tannins extracted using three different solvents, assessing key parameters including pH, solids content, gross and net yields, and the Stiasny number. The study also investigates the interaction between extracted tannins and boron, together with several additives, to enhance wood preservative properties. This dual investigation provides a detailed analysis of tannin extract characteristics alongside the behavior of the resulting boron-tannin complexes.

By offering a comprehensive approach to sustainable wood preservation, this work expands current understanding of *A. mangium* tannin extraction efficiency and boron-tannin complexation with additives such as hexamethylenetetramine (hexamine), ϵ-caprolactam, formalin, and low-molecular-weight phenol-formaldehyde resin. Systematic examination of these interactions helps clarify the mechanisms behind their physicochemical properties and highlights practical potential for greener wood protection systems. This contribution aims to bridge knowledge gaps while supporting future industrial applications in environmentally responsible wood treatment technologies.

2. Materials AND Methods

2.1. Preparation of A. mangium bark powder

About 100 kg of air-dried bark from 7–8-year-old *A. mangium* was obtained from the debarking section in the processing area of Aramijaya Sdn. Bhd. Mill located at Pasir Gudang, Johor (Figure 1). The bark was then cut into roughly 10 cm x 5 cm using a table saw (Jingda MJ113.5B) before the chipping process. The bark was first dried to a moisture content (MC) of 16% and then chipped into 2-3 cm-sized particles, followed by further flaking to less than 1 mm. After that, the flakes were ground using a Wiley mill into fine particles of about 0.5 mm. The bark was then dried to 16% moisture content (MC), and then chipped to 2-3 cm particles, and further flaked to less than 1 mm. The flakes were finely ground to approximately 0.5 mm using a Wiley mill. This process ensured a uniform particle size for subsequent experimental procedures.

2.2. Preparation of crude tannin extract

Tannin extraction was conducted using three different extraction methods and solvents: boiling in water, 70% acetone using the Soxhlet method [28] and boiling in 2% sodium sulphite and 0.5% sodium carbonate [29] (Table 1). The fine bark was then extracted with hot water at 65°C for 4 hours. The second extraction process was using 70% acetone and water, boiled in a boiling flask under reflux for two hours, with the liquor/bark ratio of 15:1. The liquor was then filtered under a vacuum by using a Büchner funnel. Each treatment was replicated five times. The third extraction process was by using a mixture of water, 2% sodium sulfite, and 0.5% sodium carbonate for 4 hours of cooking.

Table 1: *Acacia mangium bark extraction methods with different extraction mediums*

Types of Solvents	Method	Temperature (°C)	Reaction Time (hours)	References
Water	Boiling	65	4	
Acetone 70%+water	Soxhlet method	60	0.5	[28]
Water+2% sodium sulfite+0.5% sodium Carbonate	Boiling	65	4	[29]

Figure 1: *Peeled Acacia mangium bark*

2.3. Characterisation of A. mangium tannin

The characterisation of the tannin extracts was done to determine percentage yield, total dissolved solids content, the pH, amount of tannin or total phenol, reactive tannin and colour of the tannin yield from different media of extractions. The composition of tannins in the sample was assessed through UV-visible and Fourier-Transform Infrared Spectroscopy (FTIR) studies [30].

2.3.1 Determination of percentage yield of extract

The percentage of chemical products was calculated based on the dry weight of the barks. After the extraction process, the tannin extracts were cooled to about 50°C and filtered through a fine screen filter (140 mesh). The extracts were then dried in an oven at 50°C until the weight was constant. About 5 g of aqueous extracts were placed in petri dishes and evaporated in an oven at 105°C for 4 hours until a constant weight. The percentage of solid content (Equation 1), gross yield (Equation 2) and net yield (Equation 3) were calculated using the formulas as follows:

$$\text{Solid Content (\%)} = \left(\frac{\text{Oven-dried weight of solid residue}}{\text{Weight of aqueous solution}} \right) \times 100 \tag{1}$$

$$\text{Gross Yield (\%)} = \left(\frac{\text{Total weight of solid in the extract}}{\text{Oven-dried weight of bark}} \right) \times 100 \tag{2}$$

$$\text{Net Yield (\%)} = \left(\frac{\text{Total weight of solid in extract} - \text{Total weight of sodium salts used}}{\text{Oven-dried weight of bark}} \right) \times 100 \tag{3}$$

2.3.2 pH determination of each extraction medium

The fine *A. mangium bark* (2 g) was soaked in 20 mL distilled water at 25°C for 30 min. Then, the pH of the solutions was measured using a digital pH meter, and the value was registered after four minutes of electrode contact with the solution. This measurement was repeated three times for each sample.

2.3.3 Determination of tannin content

The Stiasny number was determined by reacting the tannin extract with formaldehyde under acidic conditions, precipitating the reactive condensed tannin fraction, which was then dried and weighed to calculate the proportion of reactive tannins relative to the total dissolved solids [31]. Approximately 50 ml of a 0.4% (w/w) tannin solution was carefully transferred into a 150 ml flask. To this solution, we added 10 ml of aqueous formaldehyde (37%) and 5 ml of concentrated hydrochloric acid (10N). The resulting mixture underwent reflux heating for 30 minutes and was subsequently filtered through a sintered glass crucible (porosity 2), which had been pre-dried to a constant weight. The resulting precipitate was washed with warm distilled water and then subjected to drying in an oven at 105°C until a constant weight was achieved. The Stiasny number, representing the ratio of the oven-dried weight of the precipitate to the total dissolved solids content of the tannin extract, was expressed as a percentage. The calculation of the Stiasny number was carried out using Equation 4.

$$\text{Stiasny number (\%)} = \left(\frac{\text{Oven-dried weight of the precipitate}}{\left(\frac{\text{Dissolved solid content}}{100} \times 50 \right)} \right) \times 100 \tag{4}$$

2.3.4 Total phenol by using UV spectrophotometry

The Folin-Ciocalteu reagent of 2.5 ml (diluted 10 times) and 2 ml of an aqueous solution of sodium carbonate (75 g/l) were added to 0.5 ml of diluted extract, and the mixture was kept at 50∘C for 5 minutes. Then, after the mixture was cooled by using the UV-Vis Spectrophotometer, the absorbance of phenol content at 760 nm was recorded. An aqueous solution of catechin and gallic acid (8-40 µg/ml) was used as a standard. The calibration curve was constructed for both catechin and gallic acid using the solutions of 8, 16, 24, 32, and 40 μg/mg and applying the procedure described above for the extract samples. Three replicates for each point were used.

2.4. Preparation of boron-tannin based preservatives

The preservative formulation consisted of Boron (2%) mixed with 10% and 20% of tannin with water. The mixture was then stirred until it reached a uniform consistency.

2.5. Characterisation of boron-tannin formulation

Characterisation of the boron-tannin mixture was to determine the pH value, viscosity, gelation time, and water-insoluble matter. The composition of the boron-tannin mixture was assessed through FTIR spectroscopic studies.

2.5.1 Determination of pH of boron-tannin formulation

A beaker filled with 50 ml of a boron-tannin-based formulation mixture was kept at 25°C for 30 min before pH measurement using a digital pH metre. This measurement was repeated three times for each sample.

2.5.2 Viscosity of the boron-tannin formulation

At room temperature, 75 ml of a boron-tannin mixture was added to a 100 ml beaker. The mixture's viscosity was measured using a Brookfield Viscometer DV2T with a suitable spindle spinning at 1 rpm. Then, the spindle was lowered until the notch was submerged in the mixture. The viscometer spindle was positioned in the center of the beaker, and the reading was taken a few minutes after the viscometer monitor displayed the data.

2.5.3 Determination of boron-tannin formulation gelation time

ASTM [32] was used in the determination of the gelation time of each formulation of boron-tannin-based preservatives. The mixture was heated in a water bath at 90±2 ∘C and stirred with a glass rod until it had formed a gel (until the product had solidified sufficiently, easily removed from the side of the beaker). Then, a soft spiral wire was inserted into the tannin solution (test tube) to examine the gel state. The gel time required for this to take place is gelation or gel time. The test was duplicated 3 times for each treatment.

2.5.4 Determination of boron-tannin formulation water-insoluble matter

The determination of water-insoluble matter of the solution was adopted from the MS 995 [33]. The dried solutions were accurately weighed, approximately 10 g of the test sample, into a 250 ml beaker. Then, 100 ml of distilled water was added to dissolve the sample for about 30 minutes. Then, the solution was filtered through a tared Gooch crucible containing a medium asbestos pad. The crucible and the residues were dried to a constant weight in an oven at 105∘C for 24 hours and then cooled in a desiccator and weighed to measure the percentage of water-insoluble matter. The calculation was as in Equation 5. These tests were repeated three times.

$$\text{Water-insoluble matter (\% w/w)} = \left(\frac{A \times 100}{B}\right) \tag{5}$$

where A is the weight of residue, g, and B is the weight of the boron-tannin solid taken, g.

2.5.5 FTIR Analyses

FTIR was performed with a Perkin Elmer 1600 infrared spectrometer in the wavenumber range of 500 – 4000 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans. The position of significant transmission peaks at one wavenumber was tracked with the Nicolet software.

2.5.6 Statistical analysis

The statistical analyses of the experimental results were conducted using the One-way analysis of variance (ANOVA) function in SPSS software. The Duncan test was also used to compare the mean values between the two groups at a significance level of 0.05 ($p \leq 0.05$). Results were summarised using each sample's average and standard deviation (SD).

3. Results and Discussion

3.1. Characterisation of A. mangium tannin extracts from three different extraction solvents

Table 2 displays the characteristics of tannin extracts obtained from various extraction solvents. The pH levels of tannin extracts differed depending on the extraction solvents used (Table 2). When *A. mangium* tannin extracts were heated in boiling water, they exhibited an acidic pH value of 4.95, and in 70% acetone, the pH was 5.22. Extracts treated with sulfitation (2% sodium sulfite and 0.5% sodium carbonate) had a pH of 7.35.

The solid content percentage of each tannin extract increased by 1.24%, 2.4%, and 7.35% after being extracted with water, 70% acetone, and sulfitation, respectively. When water was utilized for tannin extraction at 65 °C, the net yield of tannin was 24.8%, the lowest among the tested conditions (Table 2). Acetone (70%) was the second most effective solvent for extracting tannins, yielding 48%. The sulfitation process produced the highest tannin production, with a gross yield of 57.67% and a net yield of 56.24%.

Table 2: *Tannin extracts properties*

Extraction Solvent	Method	Temp (°C)	Time (Hr)	pH	Solid Content	Gross Yield (%)	Net Yield (%)	Stiasny No. (%)
Hot water	Boiling	60	4	4.95c (0.02)	1.24b (0.21)	24.8c (0.40)	24.8c (0.40)	33c (0.08)
Acetone (70%)	Soxhlet method	65	2	5.22b (0.08)	2.40a (0.60)	48.0b (0.16)	48.0b (0.16)	62b (0.04)
Sulphite (Na_2SO_3 2%, Na_2CO_3 0.5%)	Boiling	60	4	7.35a (0.02)	2.78a (0.24)	56.24a (0.40)	56.24a (0.40)	70a (0.32)

Note: Means that share the same letter within the same column are not considered significantly different at a significance level of $p \leq 0.05$, as determined by Duncan's test.

This study's results support the findings of Wina et al. [25] on tannin production from different extraction procedures. Water extraction resulted in the lowest yield of 8.37% at 100°C for 40 minutes, whereas acetone (50%) and Na_2SO_3 (2%) extraction yielded 27.17%. Na_2SO_3 (4%) extraction yielded 26.83% tannin, while Na_2SO_3 (6%) extraction yielded 31.2% tannin. Our study expands on the findings of Wina et al. [33] by highlighting the use of the sulfitation method to extract tannins from *A. mangium* bark. This method utilises a 2% solution of Na_2SO_3 and demonstrates its effectiveness by achieving a significant yield of 31.2%. This method adds new information to the comprehension of tannin extraction procedures. This approach utilises a solution containing 2% sodium sulfite and 0.5% sodium carbonate. This extraction procedure was shown to be efficient by obtaining a high yield of 57.67% and an elevated Stiasny number of 70.

The Stiasny number is used to measure the purity of tannin extracts. Sulfite-based extraction produced extracts with the greatest tannin concentration of 70%, outperforming hot water (33%) and acetone-based (62%) extraction procedures in the trial. The high Stiasny number found is likely caused by sulfonation resulting from the sulfite treatment. Sulfitation demonstrates surface-active characteristics, which change the distribution of molecule sizes [34]. Introducing a sulfonic group through sulfitation increases polarity, enhancing tannin reactivity and solubility by expanding the heterocyclic ring during extraction. Sulfite consumption in the process enhances the extraction of high-molecular-weight oligomers by boosting their solubility.

The extraction temperature applied is a crucial aspect in this technique [35]. Temperature influences the concentration of tannins and the amount of extract produced. Table 2 shows a direct correlation between the rise in temperature and the increase in extraction rate for the

acetone (70%) extraction medium. Sirisangsawang and Phetyim [36] discovered that the number of tannins extracted from *Quercus infectoria* galls increased with rising temperature but decreased as the temperature approached the boiling point when using distilled water. At 78 °C, the tannin concentration is 9.495 ± 0.525 mg/g dry and 6.825 ± 0.425 mg/g dry. The conditions of extraction, particularly the temperature, can greatly affect the ability to remove tannins. Increasing temperatures improve the efficiency of tannin extraction. Increasing temperature boosts the kinetic energy of solvent molecules, accelerating the extraction process. This increased level of energy helps in breaking down plant cell walls and releasing tannins from the plant structure. Higher temperatures lead to a faster and more efficient extraction process, resulting in larger tannin yields in a specific period. Tannin extraction success depends on factors such as solvent type, plant species, temperature, and extraction length. When extracting tannins from *Quercus infectoria* galls using distilled water, the tannin production increased as the temperature rose but reduced as it reached the boiling point. There was a direct relationship between the extraction rate and temperature, leading to a quicker attainment of equilibrium. Extraction conditions, especially temperature, have a substantial impact on the extractability of tannins. Most tannins are soluble in water. During the wort collection process in brewing, it is important to keep the temperature below 170°F (77°C) and the pH below 5.8 to limit tannin extraction.

3.2. Total phenolic content by using a UV spectrophotometer

Figure 2 shows that the aqueous sulphite extract achieves the highest total phenolic content (0.6892 g/mL GAE), followed by the 70% acetone extract (0.6874 g/mL GAE) and the hot water extract (0.682 g/mL GAE). The relatively higher phenolic concentration obtained with the sulphite solution indicates that the addition of a mild alkaline agent improves the efficiency of phenolic compound recovery. These findings are consistent with previous reports suggesting that solvent polarity and the presence of ions can significantly influence the extraction of tannin and other polyphenols from lignocellulosic biomass. Overall, the results support the selection of the sulphite method as an effective approach for recovering phenolic-rich extracts suitable for wood preservative formulations.

Figure 3 displays the UV-Vis spectrum with the highest absorbance at 730 nm, followed by acetone at 729 nm and water at 726 nm. The highest phenolic content was detected in the aqueous sulphite extract at 0.6892 g/ml, followed by acetone at 0.6874 g/ml and water-based extraction at 0.682 g/ml. The highest absorbance was recorded at 730 nm for the aqueous sulphite extract, followed by acetone at 729 nm and water at 726 nm. The sulphite extraction method yielded the highest tannin content, measured at an absorbance of 730 nm. Various extraction solvents can selectively extract distinct phenolic compounds, with aqueous sulfite extraction being particularly effective for tannins. The variations in phenolic content between solvents arise from their polarities, impacting extraction efficiency. Increased phenolic content in extracts improves wood protection against decay and insect damage. The concentration of the extract is more important for antifungal activity than individual compounds [37].

3.3. Properties of boron-tannin mixture for preservatives

When selecting an optimal boron–tannin formulation for wood preservation, four interdependent performance criteria must be balanced: leach resistance (indicated by a high percentage of insoluble matter for long-term durability), penetration capacity (reflected by low viscosity to enable deep wood absorption), curing efficiency (determined by a practical gelation time for manageable application), and pH compatibility (maintaining near-neutral pH to minimise wood

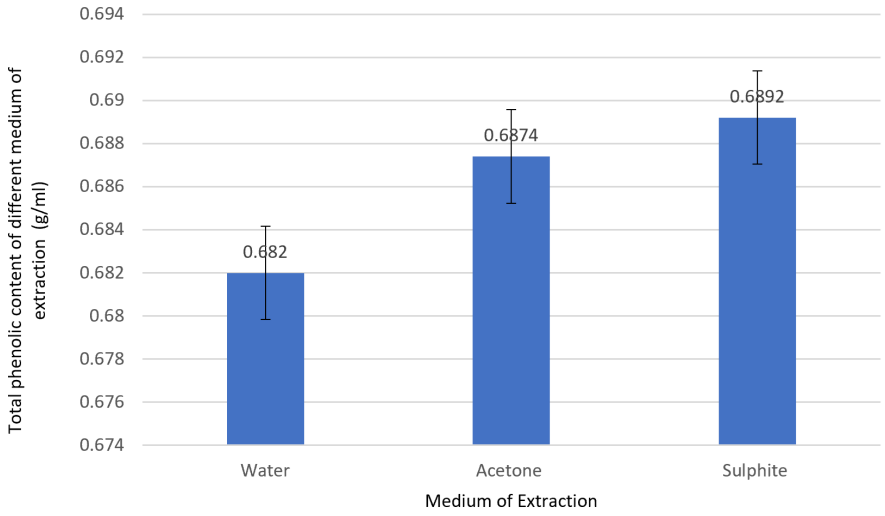

Figure 2: *Total phenolic content of A. mangium bark extracts obtained using water, 70% acetone, and sulphite-based extraction methods*

fibre degradation and ensure chemical stability). These factors collectively define a formulation's suitability for different preservation needs, with trade-offs between deep penetration and robust long-term protection requiring careful consideration according to the intended exposure and service conditions.

The results demonstrate that the evaluated boron–tannin systems vary substantially in these key attributes. The BTCHF formulation represents the most balanced option for outdoor applications, combining moderate viscosity (11.45 cP), a workable gelation time (45 minutes), improved leach resistance (40% insoluble matter), and a near-neutral pH (6.12), which together enhance retention and durability against moisture and biological degradation. By comparison, the BTLPF system achieves the highest insolubility (72.8%) and fastest curing time (24 minutes) due to its phenol–formaldehyde crosslinking network, but its high viscosity (23.69 cP) limits penetration into deeper wood layers, making it more suitable for surface treatments. In contrast, the base BT formulation offers excellent penetration potential thanks to its very low viscosity (1.5 cP) but shows insufficient leach resistance (16.2%) for long-term outdoor use. The BTC and BTCH variants incorporate additional crosslinking agents but yield only marginal improvements in insolubility (15%) while introducing less favourable acidity in the case of BTC (pH 4.35), likely due to caprolactam content.

Table 3: *Properties of boron-tannin mixture*

Preservative Formulation	pH	Viscosity (cP)	Gelation Time (Min)	Insoluble Matter (%)
BT	5.63a	1.5a	51a	16.2
BTC	4.35b	4.6b	34d	15.2
BTCH	5.79b	5.8b	33c	15.2
BTCHF	6.12c	11.45c	45b	40
BTLPF	5.8d	23.69d	24e	72.8

Note: BT (boron-tannin), BTC (boron-tannin-caprolactam), BTCH (Boron-tannin-caprolactam-hexamine), BTCHF (boron-tannin-caprolactam-hexamine-formalin), BTLPF (boron-tannin-low molecular phenol formaldehyde). Means that share the same letter within the same column are not considered significantly different at a significance level of $p \leq 0.05$, as determined by Duncan's test.

Maintaining a near-neutral pH is critical to minimise chemical degradation of wood fibres over

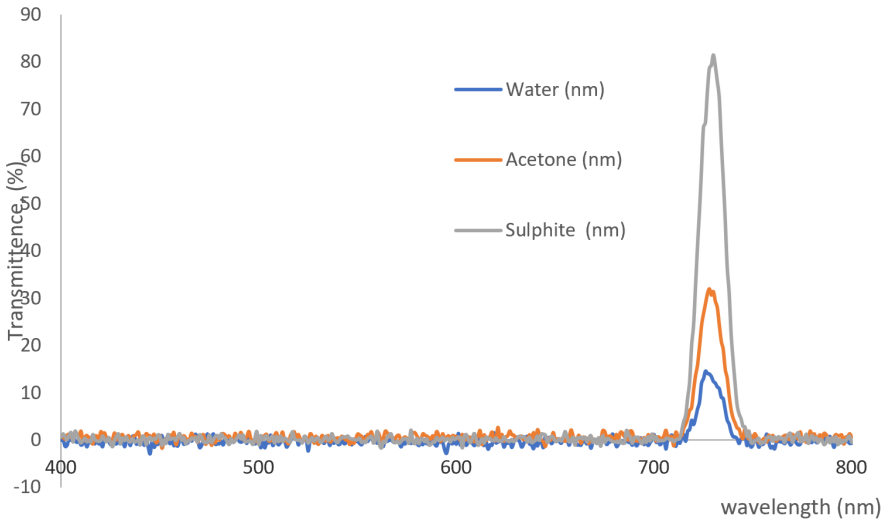

Figure 3: *UV-Vis spectrum of Acacia mangium tannin extracted using different solvent systems*

time. BTCHF (pH 6.12) and BTLPF (pH 5.8) align closely with this requirement, while BTC's lower pH (4.35) raises concerns about potential acid-induced damage, consistent with observations by Tondi et al. [10] that acidic preservatives can compromise wood integrity during extended service life.

Viscosity directly influences penetration and handling properties. A low-viscosity system, such as BT, promotes deep impregnation but lacks sufficient crosslinking for durable leach resistance. Conversely, BTLPF's higher viscosity creates a dense protective layer with strong insolubility but is better suited for surface coatings. BTCHF demonstrates a practical intermediate, providing adequate flow for effective penetration while maintaining a stable, crosslinked network — a balance shown to improve long-term performance [10,38].

Curing time further shapes application viability. BTLPF's rapid gelation (24 minutes) facilitates industrial-scale processes requiring fast setting, whereas BT's longer curing time (51 minutes) allows thorough impregnation at the expense of extended processing. BTCHF's moderate gelation time (45 minutes) offers a workable compromise, enabling controlled absorption with acceptable processing speed.

A high degree of leach resistance remains essential for preserving boron's protective efficacy under exposure to moisture. Tannin–boron complexes have been shown to significantly reduce leaching compared to boron-only systems by anchoring boron within a stable tannin matrix, thereby enhancing retention and extending service life [10]. Crosslinked tannin–boron systems can retain up to 70-80% of boron after severe leaching, whereas conventional treatments lose most of their active compound, a performance crucial for meeting standards such as EN 84, which simulate harsh weathering conditions.

Taken together, these structure–property relationships indicate that formulations incorporating formalin (BTCHF) or phenol–formaldehyde resin (BTLPF) offer the most promising balance of penetration, curing, leach resistance, and pH stability for durable wood preservation. Nevertheless, these laboratory findings should be validated through extended field trials under relevant environmental conditions. The proposed crosslinking mechanism between tannin, boron, and additives is illustrated in Figure 4.

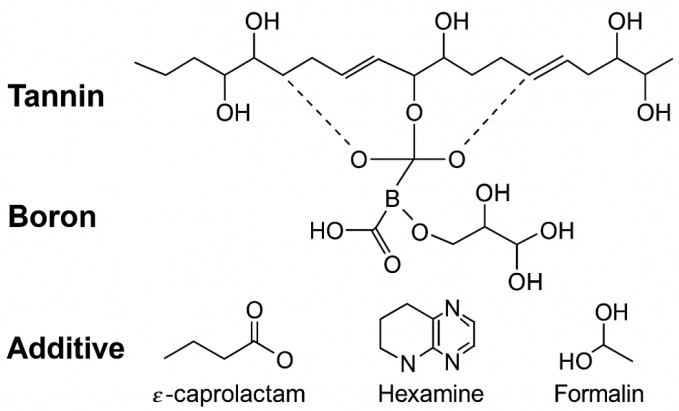

Figure 4: *Proposed schematic of the boron–tannin crosslinking mechanism with additives*

3.4. Fourier Transform Infrared Spectroscopy (FTIR) analysis of boron-tannin based preservatives with additives

The spectra (Figure 5) of the boron-tannin were compared with those of other formulations with additives. Bands in the 3500–3100 cm^{-1} region show the sum of the -OH stretching and hydrogen-bonded hydroxyl [38–40]. This has been confirmed by which is characteristic of polyphenolic extracts, where they also found the same results stating the -OH was in the region of 3500–3100 cm^{-1} [41,42]. It is seen that the intensities of the peaks are reduced for formulation with additives compared to the boron-tannin mixture. This can be due to structural changes that occurred during the crosslinking reaction, where the free –OH groups are used up by boric acid and make changes in the hydrogen-bonded hydroxyls of the mixture [43]. The broad peak observed in the region from 3550 to 3100 cm^{-1} is attributable to –OH bridging groups.

The small peaks near 2920 cm^{-1}, in the spectrum of larch tannin, are due to aromatic C–H stretching vibrations in the benzene rings (44,45). The elongations of the aromatic –C=C– bonds gave absorption bands in the range from 1616 to 1447 cm^{-1}, and the deformation vibrations of the C–C bonds in the phenolic groups gave absorption bands in the range of 1500 to 1400 cm^{-1} [44]. The single peak at 1521 cm^{-1} indicates that procyanidin was predominant in the extracted larch tannin, and the high-intensity band at 1616 cm^{-1} indicates that the extracted larch tannin had a high number of C4–C8 interflavonoid linkages [45]. Aromatic C-O stretching produced bonds at 1280 and 1150 cm^{-1}, and others at 1063 cm^{-1} correspond to aliphatic C–O stretching.

The peak at 2900 cm^{-1} corresponds to the C-H stretching and bending frequencies; this peak was observed in the additive-enhanced formulation. Peak 2360 cm^{-1} was induced by the vibration of the C=O bond, and this was confirmed [46]. The characteristic peaks in the range 1440 – 1395 correspond to the OH bonding (carboxylic acid). Bands in the region of 2824 to 2940 cm^{-1}, produced by the methylene (–CH2–) bridges of LTF resins [47], showed a gradual increase as a function of reaction time. This increase indicates that larch tannin gradually reacted with formaldehyde, forming the –CH2– bridges. The intensity of C–O bonds at 1063 cm^{-1} increased, which may be attributed to the formation of dimethylene ether (–CH2–O–CH2–) linkages. Small peaks at 1125 cm^{-1} in the spectra of LTF resins can be observed. These peaks were caused by the asymmetrical –CH2–O–CH2– stretching (Silverstein and Webster 1998). The peaks at 1038 cm^{-1} were related to –CH2OH bridges, formed in the methylation reaction. Bands in the region of 820

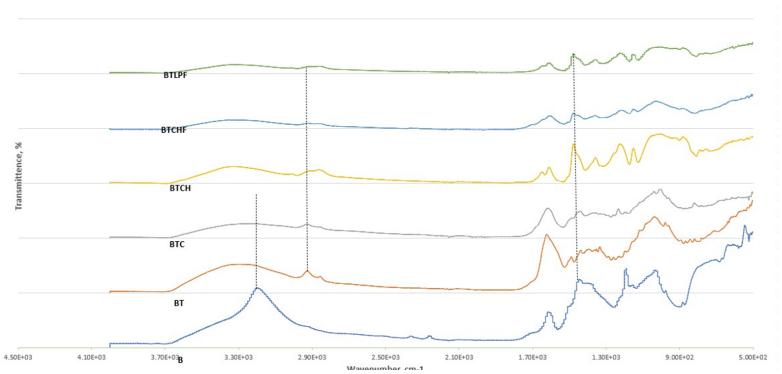

Figure 5: *Fourier Transform Infrared Spectroscopy (FTIR) analysis of Boron-tannin with different additives*

to 775 cm^{-1} resulted from the deformation vibrations of the C–H bonds in the benzene rings [47].

The FTIR spectra of boron-tannin formulations with additives reveal critical structural modifications relevant to the valorisation of *A. mangium* bark tannins. The broad 3500–3100 $^{-1}$ characteristic of polyphenolic –OH stretching [48,49] shows reduced intensity in additive-modified formulations, indicating consumption of free hydroxyl groups during boron complexation [39]. This aligns with *Acacia mangium* tannin's reactivity, where borate crosslinking enhances leach resistance—a key objective in sustainable wood preservative development. Notable peaks at 2920 cm^{-1} (aromatic C–H stretching) and 1616–1447 cm^{-1} (C=C/C–C vibrations) confirm the preservation of condensed tannin structures [46,50]. The 1521 cm^{-1} band (procyanidin dominance) and 1616 cm^{-1} (C4–C8 interflavonoid linkages) mirror findings in Acacia tannins, underscoring their suitability for boron-based preservation [50]. Additive-induced changes are evident in the 2900 cm^{-1} (C–H) and 2360 cm^{-1} (C=O) peaks [51–54]. The progressive intensity increase of methylene (–CH) bridges (2824–2940 cm^{-1}) and dimethylene ether linkages (1063 cm^{-1}) reflects formaldehyde-mediated polymerisation, critical for enhancing Acacia tannin's insolubility. Peaks at 1125 cm^{-1} (–CH–O–CH2–) and 1038 cm^{-1} (–CH2-OH) further validate network formation, while 820–775 cm^{-1} bands confirm aromatic ring stability [50].

4. Conclusion

This study confirms the successful valorisation of *Acacia mangium* bark as a sustainable source of bio-based wood preservatives through an integrated approach combining optimised tannin extraction and boron complexation with functional additives. Among the extraction methods assessed, the sulfite-based technique (2% Na_2CO_3 + 0.5% Na_2CO_3) achieves the highest extraction efficiency, producing tannins with greater purity (Stiasny number of 70%) and elevated phenolic content, as verified by UV-Vis spectrometry. This approach demonstrates a viable, environmentally responsible pathway for recovering high-yield tannins from forestry byproducts.

The combination of boron with *A. mangium* tannins and selected additives—including formalin, hexamine, ϵ-caprolactam, and low molecular weight phenol-formaldehyde resin—substantially enhances the physicochemical performance of the final wood preservative formulations. In particular, the BTCHF system exhibits balanced characteristics, including improved water resistance (40% insoluble matter), near-neutral pH (6.12), moderate viscosity (11.45 cP), and practical gelation time (45 minutes), making it well suited for outdoor wood applications. FTIR analysis confirms the formation of stable boron-tannin networks and additive-induced crosslinking that contribute to increased durability and leach resistance.

Overall, this dual-focused investigation offers a practical and sustainable alternative to conventional wood preservatives by utilising locally available biomass and low-impact chemistry. The findings highlight the feasibility of tannin-boron systems as next-generation wood protection agents, with significant potential for application in tropical forestry and green construction sectors across the ASEAN region. Future research should prioritise long-term field performance trials and compatibility testing with various wood species to support wider industrial adoption.

Declaration of interest: The authors declare no conflicts of interest.

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