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Chemical, Crystallinity and Morphological Changes of Rubberwood (*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.) Hydrothermally Treated in Different Buffered Media

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Abstract: Hydrothermal treatment is an efficient and environmentally friendly method of enhancing the dimensional stability and durability of wood. The destructive effects of formic and acetic acids generated during thermal treatment, on the other hand, are known to have a negative impact on wood strength. As a result, hydrothermal treatment in different buffered media (acidic, neutral, and alkaline buffer) was performed in this study to mitigate the effects of the acids. As heating media, acidic buffer (pH 4 and 6), alkaline buffer (pH 8 and 10), and tap water (pH 7.43) were used to treat rubberwood at three different temperatures (160 °C, 180 °C, and 200 °C). The effects of different buffered media and treatment temperatures on the chemical components, crystallinity, and morphological changes in treated and untreated rubberwood were studied. The results of the experiments revealed that the chemical constituents of rubberwood changed along with the pH of the buffered media and treatment temperature. Rubberwood treated in alkaline media showed the least degradation, whereas water medium caused the most severe degradation. The crystallinity of wood increased initially (from 160 to 180 °C) and then decreased further at 200 °C. In addition, minimal damage to the wood cell was observed in an alkaline medium.

Keywords: hydrothermal treatment; buffered media; chemical constituents; rubberwood; crystallinity

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1. Introduction

Rubber trees [*Hevea brasiliensis* (Wild. ex. A. Juss.) Müll. Arg.] are found in the majority of the world's tropical and subtropical regions. It is a member of the Euphorbiaceae family and one of the most economically important species because its milky latex is the primary source of natural rubber. Rubberwood is a good wood for furniture production because of its light color, according to Ali et al. [1]. However, one of the major disadvantages is dimensional instability and low natural durability due to the lack of differences between sapwood and heartwood [2]. Heartwood is substantially more durable than sapwood because it contains significantly less starch and has hollow cells loaded with extractives that are occasionally poisonous to fungi and insects.

Due to the aforementioned issues, rubberwood and its wood-based composite have been modified using a variety of methods to improve its dimensional stability and biological durability, with thermal treatment being the most studied modification method [3–10]. Thermal treatment is preferred because it is environmentally friendly and does not use any chemicals during the treatment process [11]. Tarasin et al. [12], for example, thermally treated rubberwood at high temperatures (185, 200, or 215 °C) and found that the rubberwood treated at the highest temperature provided the best resistance to subterranean termites *Coptotermes gestroi* (Wasmann). Meanwhile, Umar et al. [13] treated rubberwood in hot palm oil at temperatures ranging from 172 to 228 °C. The decay resistance of rubberwood to the white rot fungus, *Pycnoporus sanguineus*, was improved, especially when treated at a higher temperature, according to the authors. White rot fungi break down all three cell wall polymers, whereas brown rot fungus tends to selectively eliminate carbohydrates and primarily attack softwoods [14]. Thermal treatment was also found to improve the dimensional stability of rubberwood [15,16] due to the removal of hydrophilic hemicellulose by high temperature.

The heating medium for the thermal treatment methods mentioned above was air or oil. When a heat media is utilized, studies on the changes in chemical composition and crystallinity have indicated that lignin and benzene-alcohol extractive rise while cellulose and holocellulose decrease [17]. Hydrothermal treatment, using water as the heating medium, is another method that has been employed by many researchers [18–22]. The efficacy of hydrothermal treatment is primarily determined by the treatment temperature, duration, and heating medium [23]. Unfortunately, despite its effectiveness in improving both the dimensional stability and biological durability of the treated wood, thermal treatment is known to cause a reduction in strength properties due to the formation of formic and acetic acid during thermal treatment by accelerating the degradation of hemicellulose [24,25]. As a result, various buffered media (acid, neutral, and alkaline) were used as a heating medium for hydrothermal treatment to neutralize the destructive effects of the formed and acetic acids [18]. The primary advantage of the buffered solution is that it is non-chemical that does not pose threat to the environment [26]. Talaei and Karimi [27] discovered that beech wood treated in buffered media with pH 5, 7, and 8 showed varying degrees of strength reduction, with those treated in pH 7 (neutral) and pH 8 (alkaline) showing less strength reduction, furthermore, when exposed to the white rot fungus, beech wood treated in neutral and alkaline media lost the least weight compared to beech wood treated in acidic medium [28]. A similar observation was also shown by several studies reported on oil palm wood [23–30] and bamboo [31].

Rubberwood hydrothermally treated in various buffered media had not previously been reported, except for our previous study [1]. The study reported on the effects of buffered media pH on the physical properties of rubberwood. Rubberwood treated in alkaline media showed little reduction in density and mass (pH 8 and pH 10) compared to neutral and acidic media. Furthermore, rubberwood treated in alkaline media showed the least thickness swelling and the highest anti-swelling efficiency, indicating better dimensional stability. However, the morphological and chemical changes in buffered media as a function of pH have yet to be reported. The goals of this study are to investigate the effects of hydrothermal treatment in different buffered media on chemical constituents, crystallinity, and morphology of the rubberwood.

2. Materials and Methods

2.1. Experimental Design

The schematic diagram shows the experimental design of the present study (Figure 1).

2.2. Buffered Media Preparation

The hydrothermal treatment mediums in this study were primarily two types of buffer media: acidic buffer (pH 4, 6) and alkaline buffer (pH 8, 10). Tap water (pH 7.43) was used as a neutral medium. Disodium phosphate ($Na_2HPO_4 \cdot 2H_2O$) and monosodium phosphate ($NaH_2PO_4 \cdot 2H_2O$) were used to make acidic buffer (buffer 4, 6) and alkaline buffer (buffer 8, 10), respectively. The pH of the phosphate buffer solution was adjusted by adding acid (HCl) or alkali (NaOH). All the chemicals were supplied by R&M Chemicals in Petaling Jaya, Malaysia.

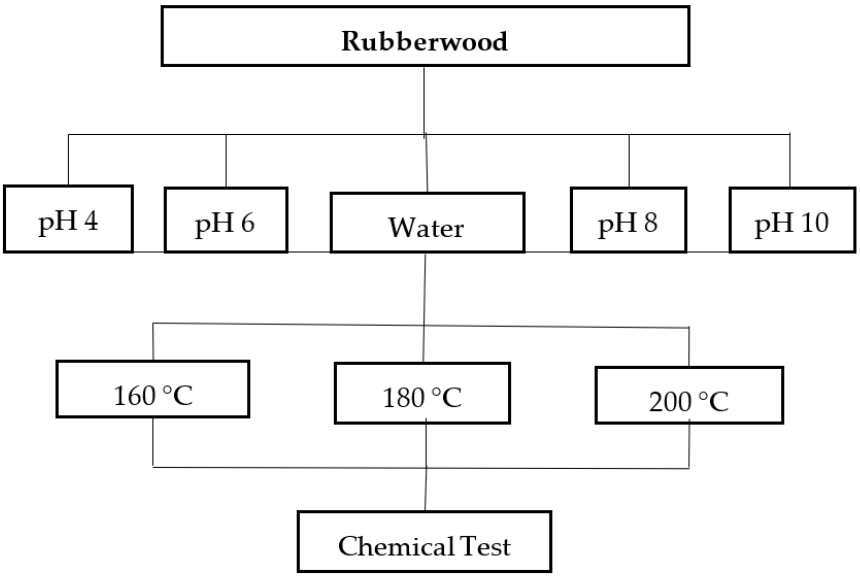

Figure 1. Schematic diagram of experimental design.

2.3. Rubberwood Sample Preparation

Rubberwood was used as the raw material for this study. A rubberwood processing company in Pahang, Malaysia, supplied matured rubberwood logs with the age of more than 25 years. Each log's girth was 100–125 cm and was divided into bottom, middle, and top positions. All of the logs were in good condition and free of natural defects. The rubber logs were then processed and cut into sample sticks with longitudinal, tangential, and radial dimensions of 300 mm × 20 mm × 20 mm (length × width × thickness). Before hydrothermal treatments, the sample sticks were pre-dried to 10%–11% moisture content (kiln dry basis). Furthermore, the samples (with a density of around 650 kg/m^3) were randomly divided into 16 groups (15 hydrothermal treatment groups and 1 untreated group as a control).

2.4. Hydrothermal Treatment in Different Buffered Media

Hydrothermal treatment was carried out using the laboratory digester (model no: GDT-15L; origin country: Korea). The cylinders were filled with wood specimens and the aqueous media (tap water and buffer solutions) separately. The temperatures used were 160 °C, 180 °C, and 200 °C and the treatment duration was 2 h. For each treatment, 10 samples were used. Other conditions were kept unchanged for all treatments. Untreated samples (controls) were used for comparison purposes. After heat treatment, the cylinders were gradually cooled to avoid any defects in the wood. The treated specimens were then placed in a conditioning room to attain equilibrium moisture content. The room temperature was about 28 °C and had a relative humidity (RH) of 75%. A total of 15–20 days were required for the samples to attain constant weights. The equilibrium moisture content was investigated and the test result revealed that the highest and lowest EMC values of the treated rubberwood samples were 9.05% at pH 8 at 160 °C and 7.03% at pH 4.0 at 200 °C, respectively, while the untreated sample (control) had a value of 10% [1].

2.5. Evaluation of Chemical Properties

Conditioned splints of 6 cm long were taken from 5 treated and untreated samples for chemical property evaluation. The splints were ground into fine particles using a Wiley mill. To obtain homogeneous particle sizes, the particles were screened using a 40 to 60-mesh (0.4 to 0.6 mm) sieve according to the TAPPI standard method of T257 cm-02 [32]. Wet chemical, XRD, and FTIR analyses were then performed using these grounded particles.

2.5.1. Wet Chemical Properties

The chemical components of the treated and untreated samples were determined using the TAPPI standard protocols. All treated and untreated samples were analyzed in triplicate for extractives, holocellulose, alpha-cellulose, and lignin content. First, the extractive content of the samples was removed using T 204 cm −97 [33]. A thimble was filled with approximately 2 g of wood particles (OD sample). The round bottom flask was then filled with 160 mL of ethanol-toluene solution. After that, the sample was extracted for 6 to 8 h. The liquid was then boiled by heating it on an electric mantle. A rotary solvent evaporator was used to remove the solvent from the extraction flask. The flask was then dried in an oven at 103 ± 2 °C until it reached a constant weight. Using the equation, the extractive content (%) was calculated.

$$\text{Extractive Content } (\%) = \frac{W_E}{W_{OD}} \times 100$$

where, W_E is the oven-dried (OD) weight of ethanol-toluene solution (weight of the extraction flask containing the OD residue subtracted the weight of the extraction flask (g), and W_{OD} is the OD weight of the samples (g).

The holocellulose content was analyzed according to Wise's sodium chlorite method [34] and carried out in a fume hood. From the extractive free samples, approximately 2 g of OD sample was mixed with 100 mL of distilled water, 1.5 g of sodium chlorite ($NaClO_2$), and 5 mL of 10% acetic acid (CH_3COOH). The mixture was added into a 250 mL beaker before being placed in a water bath maintained at 70 °C. The beaker was kept closed with a small petri dish. A total of 5 mL of 10% acetic acid was added after 30 min. After another 30 min, 1.5 g of $NaClO_2$ was added. The addition of CH_3COOH and $NaClO_2$ was repeated again alternately every 30 min until the total $NaClO_2$ is 6 g. The mixture was heated for 30 min after the last addition of $NaClO_2$ before it was cooled down in an ice bath. Then, the mixture was filtered in a coarse-porosity glass crucible and rinsed with distilled water at 20 °C, followed by the addition of acetone for the final rinse. The residue was air-dried until it was free from acetone and a constant weight was attained. The holocellulose content was determined in percentage by using the equation as follows:

$$\text{Holocellulose Content } (\%) = \frac{W_H}{W_{EF}} \times 100$$

where, W_H is the air-dried (AD) weight of holocellulose (weight of the crucible containing the residue subtracted the weight of the crucible (g), and W_{EF} is the OD weight of the extractive free samples (g).

The alpha-cellulose content was analyzed based on TAPPI Standard T203 cm-09 [35]. First weigh the sample from holocellulose and put into the 250 mL beaker. Then, of 75 mL of 17.5% NaOH was put into the burette. Firstly, 15 mL of 17.5% NaOH was added gently into the beaker and stirred for 1 min. After that, 10 mL of 17.5% NaOH was added gently into the beaker and stirred for 45 s. Again, 10 mL of 17.5% NaOH added gently into the beaker and stirred for 15 s. The mixture was stirred and allowed to stand for another 3 min. After that, the following sequence of steps was followed with 10 mL of 17.5% NaOH added and mixed with a stirring rod for 2.5 min. This step was repeated four times continuously. The mixture was stirred and allowed to stand for another 30 min. A total of 100 mL of distilled water was added and stirred for another 30 min. Next, the diluted mixture was filtered into a medium- or coarse-porosity glass crucible. The residue was rinsed with 25 mL of 8.3% NaOH solution and all the fibers were quantitively transferred to the crucible. Then, rinsed with 650 mL of distilled water. After the pump was stopped, the crucible was filled with 2N acetic acid (CH_3COOH) and was allowed to stand for 5 min. The suction was re-applied and rinsed with 150 mL of distilled water. The crucible was dried in an oven at 105 °C until a constant weight was reached. The following equation was to evaluate the alpha-cellulose content.

$$\text{Alpha-Cellulose Content } (\%) = \frac{W_C}{W_{OD}} \times 100$$

where, W_C is the oven-dried (OD) weight of alpha-cellulose (the weight of the crucible containing the OD residue subtracted the weight of the crucible (g), and W_{OD} is the OD weight of the samples (g).

The hemicellulose content was determined in percentage using the following equation.

Hemicellulose Content (%) = Holocellulose—Alpha-Cellulose

Lignin content was determined as acid-insoluble Klason lignin by following the TAPPI standard method T 222 om-02 [36]. The process was started by weighting the extractive-free samples to approximately 1 g in a 50 mL beaker. Then, 15 mL of 72% sulphuric acid (H_2SO_4) was added carefully using a glass pipette. The beaker was covered by watch glass. The mixture was slowly stirred and allowed to stand for 2 h. Next, the mixture was transferred into a conical flask and added approximately 500 mL of distilled water that is resulted in the conical flask equal to 575 mL. Then, the mixture was boiled with condenser reflux for 4 h. When the refluxing was completed, the insoluble lignin was recovered by filtration through the crucible after allowing the lignin to settle to facilitate filtration. The lignin was rinsed with hot distilled water. Then, the crucible containing the lignin was dried in an oven at 105 °C, cooled by the desiccators, and weighed. The percentage of lignin content was calculated based on the OD weight of the samples using the equation.

$$\text{Lignin Content } (\%) = \frac{W_L}{W_{OD}} \times 100$$

where, W_L is the oven-dried (OD) weight of lignin (the weight of the crucible containing the OD residue subtracted the weight of the crucible (g), and W_{OD} is the OD weight of the samples (g).

2.5.2. Fourier Transform Infrared (FTIR) Analysis

FTIR measurements were conducted using an ATR- FTIR instrument (4 cm^{-1} resolution, 32 scans) in the Laboratory of Biocomposite Technology at the Institute of Tropical Forestry and Forest Product (INTROP), UPM. The FTIR analysis was carried out to qualitatively determine the functional group that existed and to relate the result of alteration in chemical composition from the wet chemical analysis between the treated samples after hydrothermal treatment and the untreated samples. The measurements were conducted using an FTIR spectrophotometer (Thermo Scientific Nicolet iS10, Madison WI, USA) equipped with a smart iTR attenuated total reflectance (ATR) sampling accessory with diamond crystal (Thermo Fisher Scientific, Madison WI, USA). The particles were measured in the absorption mode at wavenumber ranging from 400 to 4000 cm^{-1} and all spectra were plotted using the same scale on the transmittance axis.

2.5.3. Crystallinity Index

The crystallinity of wood is defined as the weight fraction of crystalline material. X-ray Diffractometer (XRD) is a well-established method for determining the crystallinity of partially crystalline materials. The crystalline structures of hydrothermally treated and untreated rubberwood samples were conducted analyzed using an X-ray diffraction (XRD) spectrometer (Shimadzu, Model: XRD 6000 analyzers, Kyoto, Japan) with Cu Kα radiation operated at 30 kV and 30 mA at the range of 2–800 with a scanning speed of 4° min^{-1}.

The crystallinity index (Crl) was determined as:

$$\text{Crystallinity index (Crl)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

where, I_{002} represents the intensity of the crystalline peak while and I_{am} denotes the intensity of the amorphous peak in the diffractograms.

2.5.4. Morphological Changes

The morphology of the wood samples was determined using scanning electron microscopy (SEM). It studied the anatomical microstructure, pits, and pit membranes on both heat-treated and untreated material. The morphological features of hydrothermally treated and untreated samples were investigated using a JSM-IT100 IntouchScopeTM (Tokyo, Japan) scanning electron microscope.

2.5.5. Statistical Analysis

The test results were analyzed using two-way analysis of variance (ANOVA) (CRD factorial) in SAS (Version 9.4, developed by SAS Institute, USA and used for Malaysia) to determine the effect of buffered media and hydrothermal treatment temperature on the chemical properties of rubberwood. Tukey's test was used to examine the significant differences in the mean values of the testing groups (95% significant level).

3. Results and Discussion

3.1. Chemical Properties of Rubberwood

The effects of hydrothermal treatment in different buffered media (acidic, water, alkaline) on the content of extractives, holocellulose, cellulose, hemicellulose, and lignin of rubberwood are shown in Table 1.

Table 1. Table of chemical analysis of rubberwood.

Group	Temp. in °C	Extractives (%)	Holocellulose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Control	-	2.59 ^{i} (0.27)	77.38 ^{a} (0.54)	37.41 ^{h} (0.46)	39.97 ^{a} (0.52)	28.13 ^{bcde} (0.90)
pH 4	160 °C	4.78 ^{gh} (0.25)	74.49 ^{de} (0.63)	45.89 ^{de} (0.58)	28.59 ^{ef} (0.60)	30.96 ^{ab} (0.55)
	180 °C	7.30 ^{de} (0.24)	72.14 ^{fghi} (0.54)	51.42 ^{ab} (0.48)	20.72 ^{hi} (0.27)	30.18 ^{abc} (1.60)
	200 °C	9.80 ^{b} (0.64)	70.51 ^{i} (0.30)	47.06 ^{cd} (1.00)	23.45 ^{g} (0.63)	32.16 ^{a} (1.20)
pH 6	160 °C	4.52 ^{h} (0.49)	75.23 ^{bcd} (0.58)	37.63 ^{h} (1.10)	37.60 ^{b} (0.55)	29.13 ^{abcd} (1.18)
	180 °C	6.91 ^{def} (0.60)	73.03 ^{efg} (0.69)	46.23 ^{de} (0.53)	26.80 ^{f} (0.48)	28.56 ^{bcd} (0.53)
	200 °C	8.13 ^{cd} (0.38)	71.41 ^{ghi} (0.52)	42.03 ^{g} (0.85)	29.38 ^{de} (0.36)	29.00 ^{abcd} (1.00)
Tap water (pH 7.23)	160 °C	7.07 ^{de} (0.25)	74.82 ^{cd} (0.21)	45.33 ^{def} (0.85)	29.49 ^{de} (0.99)	29.20 ^{abcd} (1.58)
	180 °C	9.93 ^{b} (0.67)	72.61 ^{fgh} (0.60)	53.83 ^{a} (0.79)	18.78 ^{i} (0.82)	27.12 ^{cde} (1.17)
	200 °C	12.01 ^{a} (0.63)	70.96 ^{hi} (0.61)	49.06 ^{bc} (0.86)	21.90 ^{gh} (0.31)	31.09 ^{ab} (1.08)
pH 8	160 °C	4.93 ^{gh} (0.43)	76.83 ^{ab} (0.77)	37.33 ^{h} (0.85)	39.50 ^{ab} (0.26)	29.00 ^{abcd} (0.99)
	180 °C	6.18 ^{efg} (0.51)	74.41 ^{de} (0.38)	43.23 ^{fg} (0.99)	31.18 ^{cd} (0.60)	29.00 ^{abcd} (1.02)
	200 °C	8.9 ^{bc} (0.52)	71.76 ^{ghi} (0.49)	39.08 ^{h} (1.04)	32.68 ^{c} (0.98)	27.12 ^{cde} (1.10)
pH 10	160 °C	5.56 ^{fgh} (0.53)	76.23 ^{abc} (0.69)	37.8 ^{h} (0.58)	38.43 ^{ab} (0.78)	27.00 ^{cde} (0.98)
	180 °C	7.86 ^{cd} (0.57)	73.63 ^{def} (0.60)	44.56 ^{ef} (1.16)	29.07 ^{de} (0.92)	25.00 ^{e} (0.52)
	200 °C	9.18 ^{bc} (0.54)	71.16 ^{hi} (0.55)	38.78 ^{h} (0.65)	32.38 ^{c} (0.70)	27.00 ^{de} (0.57)

Note: Means with different letters are significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD).

From Table 1, the extractives content of untreated rubberwood was 2.59%. The extractive content of the treated samples ranges from 4.52 to 12.01% after treatment, depending on the temperature and buffered media used. One of the most notable findings was that the extractive content increased as treatment temperatures increased. In terms of buffered medium, the rubberwood treated in a water medium (neutral) at 200 °C had the highest extractives content of 12.01%. Aside from the degradation of existing substances and the formation of new degradation products, the variations in extractive content can be attributed to a large number of parallel reactions. This finding was consistent with other studies [37–40]. The general increase in extractives content was primarily caused by the degradation of the hemicellulose fraction of the polysaccharides fraction in the wood. The extent to which the chemical components of wood materials change is determined by the hydrothermal treatment conditions. The primary organic acids (acetic and formic acid) that are formed by cleavage of the acetyl and formyl groups of hemicellulose play the most important role in hydrothermal action. These volatile organic acids degrade hemicellulose and, in part, subsidize the amorphous content of cellulose, as well as result in the dissolution of lignin and, finally, degrade monosaccharides.

Table 1 also showed the holocellulose content of rubberwood as a result of hydrothermal treatment in different media at various temperatures. It is evident that the proportion of holocellulose decreased as the treatment temperature increased. Rubberwood samples treated in alkaline media displayed higher holocellulose content compared to that of rubberwood treated in acidic and neutral media. The holocellulose content of untreated samples is 77.38%. The highest and lowest holocellulose content, 76.83% and 70.51%, were observed in the treated samples at 160 °C at pH 8.0 and 200 °C at pH 4.0, respectively. This decrease in holocellulose was caused by a significant decrease in hemicelluloses [37,41]. Furthermore, the research findings were consistent with previous studies using other wood types [37,42], which concluded that holocellulose damage in hydrothermally treated wood occurs primarily through the degradation of non-cellulosic polysaccharides. When compared to other media, the decrease in holocellulose content in alkaline media was minimal compared to other conditions (acidic, water). Alkaline media can control the destructive effect of acid released, so OH- group decrements are lower than in other media [27].

The changes in alpha-cellulose content after hydrothermal treatment in various media were also shown in Table 1. In this study, the untreated sample contained 37.41% alpha-cellulose. When compared to untreated wood, the majority of the treated wood showed inconsistent variations in cellulose content with treatment temperature. The cellulose content deformation was minimal at low temperatures (160 °C) and increased at 180 °C, then declined further as treatment temperatures increased (Table 1). Among the treatment media, alkali media exhibits the least cellulose deformation when compared to acidic and water media. Among wood constituents, alpha-cellulose is the most important and plays a critical role in wood strength. Alpha-cellulose is more stable than hemicellulose due to its higher molecular weight and crystalline structure, which provides great stability to the cellulose chains and protects them from acid attack during hydrolysis. Furthermore, cellulose crystallinity increases due to amorphous cellulose degradation, which affects the accessibility of OH- groups to water molecules [43–45].

Table 1 showed the hemicellulose content of treated and untreated rubberwood in various buffered media. As a result of thermal treatment, hemicellulose is the most affected wood chemical constituent. The hemicellulose content of untreated rubberwood is 39.97%. The hemicellulose content of hydrothermally treated rubberwood is lower than that of untreated rubberwood, ranging from 18.78% to 39.50%. Rubberwood treated at 180 °C in a water medium had the lowest hemicellulose content of 18.78%. This phenomenon demonstrated that hemicellulose, which was thought to be quite unstable, was highly susceptible to degradation during the hydrothermal treatment. When compared to acidic and water media, alkaline media showed the least amount of decrement. After hydrothermal treatment, the decrement of hemicellulose was greater than that of cellulose, indicating that alpha-cellulose is more thermally stable than hemicellulose due to its crystalline structure. Several studies have revealed similar research findings [37,40,42]. Furthermore, hemicellulose is the most vulnerable component, degrading faster than cellulose during thermal treatment [46]. Furthermore, because hemicellulose is very hydrophilic, it reduces the free hydroxyl groups (OH-). Furthermore, hemicellulose degrades easily due to its amorphous structure and lower molecular weight than alpha-cellulose [47].

After hydrothermal treatment, the percentage ratio of lignin content increased. This is primarily due to the degradation of hemicelluloses and other components of cell walls, such as pentoses and hexoses [48], rather than the formation of lignin during the thermal treatment process [25]. According to Table 1, the lignin content varied after treatment, ranging from 25.0% to 32.16% compared to 28.13% in control samples. The increase in lignin was caused by lignin condensation reactions with hemicellulose cleavage products [45,48]. Rubberwood treated in alkaline media has lower lignin content than rubberwood treated in acidic or neutral media. This observation could be attributed to the lower degree of cellulose and hemicellulose degradation in alkaline media.

3.2. X-ray Diffraction (XRD) Analysis

The effects of hydrothermal treatment in different media on the 2θ diffraction angle of the rubberwood samples were almost similar. Figure 2 showed that two significant peaks appeared on the curved within the scanning interval of 0–80°, where the first one exhibited at about 2θ = 18°, representing the scattering intensity of the diffraction angle in the amorphous region (I_{am}). On the other hand, the second one was located near 2θ = 22°, denoting the highest strength (I_{002}) of the diffraction angle in the crystalline region.

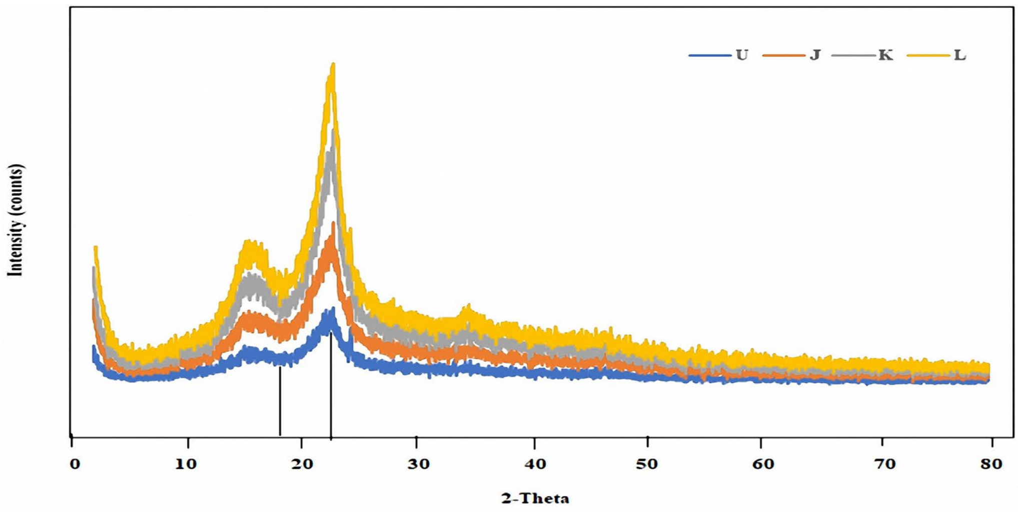

Figure 2. XRD diagram of the untreated and hydrothermally treated rubberwood, (**U**) control, (**J**) 160 °C, pH 8 (**K**) 180 °C, pH 8, and (**L**) 200 °C, pH 8.

The crystallinity changes of hydrothermally treated (acidic, water, alkaline) rubberwood specimens are shown in Table 2. The results revealed that the crystallinity of untreated rubberwood cellulose was 50%. The degree of crystallinity varied depending on the media and temperature used.

It was clear that as the treatment temperature increased, the relative crystallinity index increased. The crystallinity increased from 160 °C to 180 °C and then decreased when the treatment temperature was raised to 200 °C, as shown in Table 2. The highest crystallinity of 70.4% was observed at 180 °C in tap water whereas the lowest of 51.58% was seen at 160 °C in pH 8, respectively. Rubberwood treated in acidic and water media exhibited the highest crystallinity when compared to alkaline media. Crystallinity is a vital factor that affects the wood properties, especially the physical, mechanical, and chemical properties. Cellulose is mainly composed of two-phase structures such as a crystalline region and an amorphous region. The increase in cellulose crystallinity as treatment temperature rises could be due to two factors. First, amorphous cellulose degradation results in decreased accessibility of OH-groups to water molecules [43,45]. Second, according to Akgül et al. [49], crystallization in quasi-crystalline amorphous regions is caused by cellulose molecule reorientation within these regions.

Table 2. The relative degree of crystallinity of untreated and treated rubberwood.

Group	Temp. in °C	Relative Degree of Crystallinity (%)
Control	-	50.0
pH4	160	57.04
	180	69.91
	200	65.90
pH6	160	53.64
	180	68.87
	200	65.7
Tap water (pH 7.43)	160	56.06
	180	70.4
	200	66.8
pH8	160	51.58
	180	65.0
	200	62.03
pH10	160	53.05
	180	66.33
	200	61.87

Furthermore, the hydrolysis of cellulose was not acute between the temperatures of 160 °C and 180 °C, and in this range, the transformation of cellulose's amorphous region into a crystalline region occurred. As a result, the degree of crystallinity was increased in this phase. In the crystalline regions, the part motion of the cellulose chain was augmented as the treatment temperature increased, causing part of the space between the cellulose chain to shrink and a new hydrogen bond to appear, resulting in increased wood crystallinity. It was discovered in this research study that the crystallinity of wood decreased further at a temperature 200 °C probably due to the hydrogen bond being destroyed and the intermolecular force between the cellulose chain being reduced, resulting in decreased wood crystallinity. Birinci et al. [50] thought that the initial increase in crystallinity is primarily due to hemicellulose decomposition, and the subsequent decrease is due to cellulose damage.

3.3. Fourier Transform Infrared (FTIR) Analysis

Figure 3 depicts the FTIR spectra of untreated and treated rubberwood samples at pH 8 and different temperatures. At wavenumbers between 4000 and 400 cm^{-1}, the spectra show the common components or functional groups of hemicellulose, cellulose, and lignin. In most cases, the intensity varies between the treated and untreated samples.

Peaks at 3332 cm^{-1}, 2924 cm^{-1}, 1734 cm^{-1}, 1594 cm^{-1}, 1504 cm^{-1}, 1458 cm^{-1}, 1320~1421 cm^{-1}, and 1236 cm^{-1} were the O-H stretching vibration peak, C-H stretching vibration peak, non-conjugating C=O stretching vibration peak of hemicelluloses (xylose), conjugating C=O stretching vibration peak of lignin, C-C vibration peak lignin benzene ring skeleton, C-H bending vibration peak of cellulose, C-H bending vibration peak of cellulose and hemicellulose, and C-O bending vibration peak of lignin, respectively [51]. The ether bond C-O-C stretching vibration peaks of cellulose and hemicelluloses appeared at 1154 cm^{-1}. C-O stretching vibration peaks of cellulose and hemicelluloses occurred at 1027 cm^{-1}. At 898 cm^{-1} was the C-H bending vibration peak of cellulose and hemicelluloses. The C-H bending vibration peak of the lignin benzene ring skeleton existed at 556 cm^{-1}.

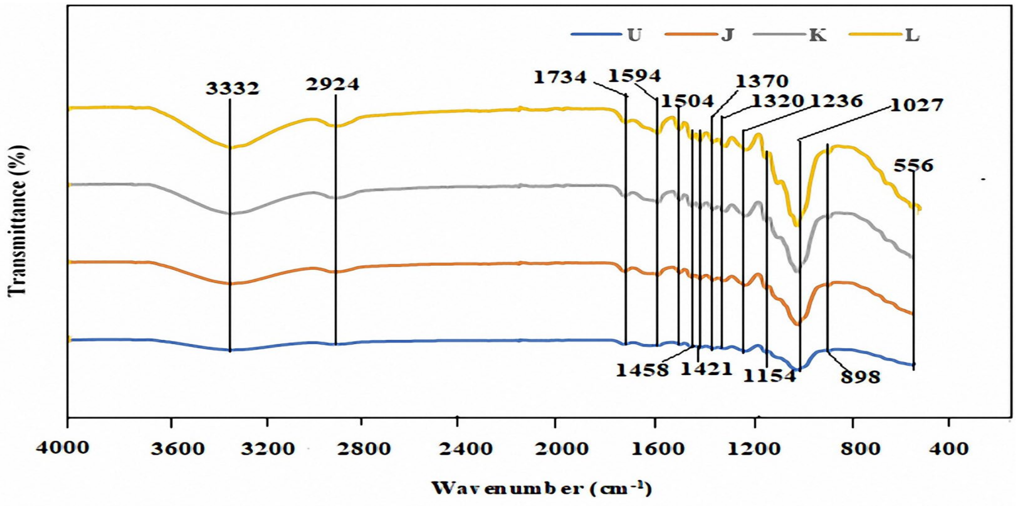

Figure 3. FTIR spectra of untreated and hydrothermally treated rubberwood, (**U**) control, (**J**) 160 °C, pH 8 (**K**) 180 °C, pH 8, and (**L**) 200 °C, pH 8.

The broadening spectra of untreated rubberwood samples were exhibited at 3332 cm^{-1}. This band were shifted to the wavenumber of 3340 cm^{-1}, 3331 cm^{-1}, and 3337 cm^{-1} at temperatures 160 °C, 180 °C, and 200 °C in pH 4. On the other side, at the same temperatures, the band were shifted to the wavenumber of 3333 cm^{-1}, 3339 cm^{-1}, and 3338 cm^{-1} in pH 6; 3338 cm^{-1}, 3333 cm^{-1}, and 3336 cm^{-1} in water; 3332 cm^{-1}, 3334 cm^{-1}, and 3336 cm^{-1} in pH 8; and 3334 cm^{-1}, 3333 cm^{-1}, and 3334 cm^{-1} in pH10, respectively. This wavenumber represents the O-H stretching vibration peak from alcohols, phenols, and acids in cellulose (3600–3300 cm^{-1}). According to Esteves et al. [52] This broadening may have happened due to the increase in carboxylic acids due to primary OH oxidation or hydrolysis of acetyl groups from hemicelluloses. In addition, the change of O-H stretching frequencies can also be due to the modification of cellulose crystallinity influenced by dehydration effects [53].

The presence of absorption at the region between 1700 cm^{-1} and 1800 cm^{-1} which belongs to stretching vibrations of the carbonyl (C=O) functional group of acetoxy groups in xylans was noted at peaks 1735 cm^{-1} [52]. This peak was then shifted to 1734 cm^{-1}, 1719 cm^{-1}, and 1603 cm^{-1} at temperatures 160 °C, 180 °C, and 200 °C in pH 4. At the same temperatures, the bands shifted to 1726 cm^{-1}, 1719 cm^{-1}, and 1601 cm^{-1} in pH 6; 1734 cm^{-1}, 1719 cm^{-1}, and 1604 cm^{-1} in water; 1733 cm^{-1}, 1716 cm^{-1}, and 1598 cm^{-1} in pH 8; and 1734 cm^{-1}, 1719 cm^{-1}, and 1597 cm^{-1} in pH 10, respectively. The enhancement and shifting for smaller wavenumbers with increasing the treatment temperatures may be due to the enhancement of carbonyl or carboxyl groups in lignin or carbohydrates by oxidation [52]. On the other side, Tjeerdsma and Militz [22] conducted a study of heat-treated *Fagus sylvatica* and *Pinus sylvestris* and stated that the band at 1740 cm^{-1} increase was due only to the lignin as there was no intensification in holocellulose. In addition, the carbonyl peak supposedly decreases due to the deacetylation process which caused by the cleavage of acetyl groups during thermal treatment [22,54,55]

The bands at 1027 cm^{-1} were shifted to 1028 cm^{-1}, 1028 cm^{-1}, and 1029 cm^{-1} at temperatures 160 °C, 180 °C, and 200 °C in pH 4; 1026 cm^{-1}, 1029 cm^{-1}, and 1030 cm^{-1} in pH 6; 1029 cm^{-1}, 1028 cm^{-1}, and 1030 cm^{-1} in water; 1024 cm^{-1}, 1028 cm^{-1}, and 1030 cm^{-1} in pH 8; and 1024 cm^{-1}, 1027 cm^{-1}, and 1029 cm^{-1} in pH 10, respectively. These bands were assigned to the bonds of holocellulose. The shift in peaks after hydrothermal treatment indicates the degradation of polysaccharides [56].

Peaks at 556 cm^{-1} was shifted to 557 cm^{-1}, 559 cm^{-1}, and 558 cm^{-1} at temperatures 160 °C, 180 °C, and 200 °C in pH 4; 557 cm^{-1}, 558 cm^{-1}, and 557 cm^{-1} in pH 6; 559 cm^{-1}, 559 cm^{-1}, and 557 cm^{-1} in water; 557 cm^{-1}, 557 cm^{-1}, and 558 cm^{-1} in pH 8; and 556 cm^{-1}, 557 cm^{-1}, and 557 cm^{-1} in pH 10, respectively. The C-H bending vibration peak of the lignin benzene ring skeleton shown a declining trend as the treatment temperatures increased.

These research findings are usually consistent with the chemical changes observed in treated rubberwood samples using wet chemical analysis. Hemicelluloses are the first to degrade with the reduction of hydroxyl groups, as demonstrated here by the initial decrease of the 1734 cm^{-1} bands that attributed to xylan acetyl group cleavage.

3.4. Morphological Change

The morphologies for untreated and treated samples of rubberwood are shown in Figure 4 for pH 8. The figures show that the compound middle lamellas of the rubberwood cell were scratched after hydrothermal treatment in different media., particularly acidic and water. The degradation rate increased as the treatment temperature increased. Furthermore, at temperatures (160–180 °C) in pH 4, 6, and water, a few fractures on inter-two fiber cells were visible. Furthermore, at higher temperatures (200 °C), the damage was severe, and the cell wall collapsed. Similar results were obtained for poplar wood, which was subjected to hydrothermal treatment at various temperatures [57], and *Eucalyptus globulus* wood, which was subjected to the same treatment at a temperature of 200 °C for 10 min [58].

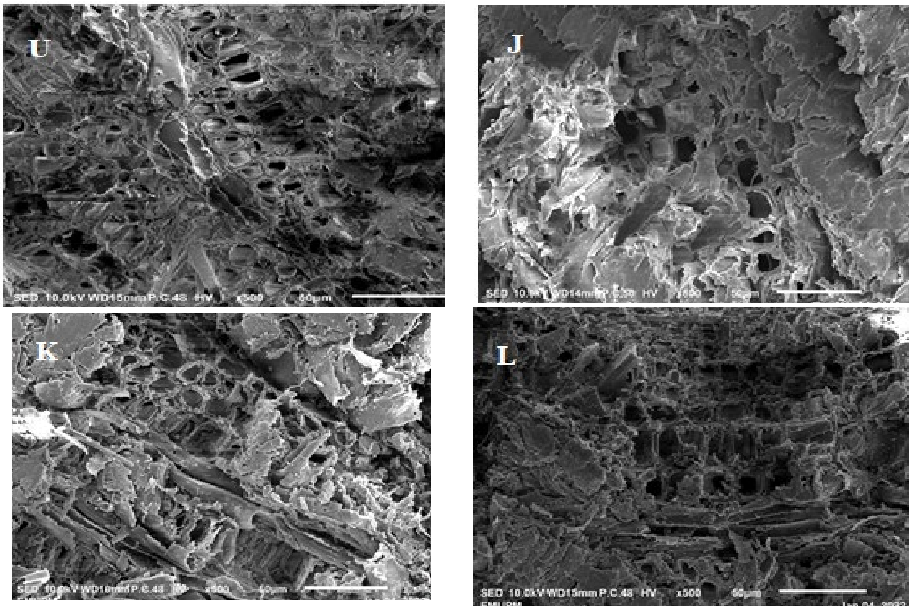

Figure 4. Cross-sections after hydrothermal treatment on control (**U**), pH 8, 160 °C (**J**), pH 8, 180 °C, and (**K**), pH 8, 200 °C (**L**).

Heat increases stresses on wood as the cell structure changes during hydrothermal treatment. When the moisture content is greater than the fiber saturation point (FSP), the variation in free water content in wood material does not normally change the cell wall structure. Furthermore, as the treatment temperature rises, some amorphous polymers, such as hemicellulose and lignin, degrade. According to Rosu et al. [59], such polymers would have a high concentration in the compound middle lamella. As a result, the stress concentration destroyed the cell walls, causing irreversible fractures. Cell wall damage was greater in pH 4 and water media than in pH 6. However, when compared to the untreated samples, the treated samples showed damage to the cell wall components. At higher temperatures of 200 °C in pH 4, 6, and water media, the cell wall structure was severely damaged.

The wood cell walls were minimally broken after hydrothermal treatment in alkaline media with pH (8, 10) and different temperatures compared to acidic and water media, and this destruction gradually increased with increasing the treatment temperature. The cell wall collapsed at 200 °C, which was visible in pH 8 and pH 10. Figure 4 also shows that the fiber cells were separated from each other following the hydrothermal treatment in alkaline media. Similar findings were discovered by Salehian et al. [60] and Shi et al. [57].

4. Conclusions

The changes in chemical constituents, crystallinity index, and morphological changes of rubberwood caused by hydrothermal treatment in different buffered media were investigated in this study. According to the research findings, hydrothermal treatment had a significant impact on the chemical constituents of rubberwood. The holocellulose and hemicellulose content decreased as the treatment temperature increased, while the extractive content increased. Wood crystallinity usually increases at first and then decreases at higher temperatures (200 °C). In terms of buffered media, rubberwood treated with alkaline media exhibited the lowest degradation in hemicellulose and cellulose contents. The wood cell wall also displayed minimal damage when treated in alkaline media. Contrarily, treatment in water media resulted in the most severe degradation. The findings of this study were in agreement with our previous study that the thermal-induced mass loss of rubberwood was the lowest in alkaline media and the highest in water medium. As a result, the dimensional stability of the rubberwood treated in alkaline media was the best compared to the rubberwood treated in acidic and water media (Ali et al. 2022). It can be concluded that the alkaline media could counteract the destructive effects of acetic and formic acids generated during treatment on the rubberwood.

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