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Physical Properties of Hydrothermally Treated Rubberwood [*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.] in Different Buffered Media

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Abstract: The dimensional instability of rubberwood [*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.] is one of the major drawbacks that limits its utilization. Therefore, treatment is needed to improve these properties. Hydrothermal treatment in different buffered media is one of the techniques that improve its dimensional stability. The physical properties of hydrothermally treated rubberwood in different buffered media (pH 4, 6, 8, 10) and tap water (pH 7.43) with different temperatures (160 °C, 180 °C and 200 °C) were studied. In this study, physical properties such as equilibrium moisture content (EMC), density (ϱ), mass loss (ML), water absorption (WA), volumetric swelling coefficient (VSC), thickness swelling (TS) and anti-swelling efficiency (ASE) were investigated for both treated and untreated specimens. Both the buffered media and temperature significantly affected the physical properties. The results indicated that the EMC (%), ϱ (kg/m^3), ML (%), VSC (%), TS (%) of treated rubberwood samples reduced as the treatment temperature increased. With the exception of WA (%), as WA increased when the treatment temperature increased from 160 °C to 180 °C but started to decrease when the temperature was further increased to 200 °C. The research study also exhibited that hydrothermal treatment using buffered media at different temperatures enhanced the dimensional stability of the treated samples. Alkaline media gave the best results on the physical properties compared to other treatment medias.

Keywords: hydrothermal treatment; buffered media; thermal treatment; rubberwood; physical properties; dimensional stability

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1. Introduction

Rubber trees [*Hevea brasiliensis* (Willd. ex A. Juss.) Müll. Arg.] were introduced into Peninsular Malaysia more than a hundred years ago. Rubber trees are the main source of natural latex, a distinctive biopolymer of significant economic importance and an important commodity in Southeast Asian countries [1]. The rubber tree is commonly cut down after 30 years when its latex production capability starts to slow down and it stops being economical. Owing to its light color, rubberwood is a favorable wood for the production of furniture. However, rubberwood is a lignocellulosic material that is considered as non-homogeneous in nature and its density is not uniform [2]. One of the major drawbacks of rubberwood is its dimensional instability when in use [3]. To improve this disadvantage, thermal treatment can be employed and has been recognized as an

effective technique to enhance the stability of this wood [4]. Unfortunately, a reduction in strength properties following thermal treatment is one of the major limitations.

Thermal treatment of wood can be carried out under different treating media such as air, nitrogen, water and oil [5,6]. Wood treated in different media results in varying property alterations. Dissimilarly to thermally treated wood under air conditions, the latter (nitrogen and oil) aims to block off the oxygen that would lead to an oxidative process, which reduces the strength of the treated wood. Thermal treatment using water as a treating medium is also of interest and is one of the most prominent thermal treatment techniques for wood [7,8]. Hydrothermal treatment is the most commercially advanced technique for treating wood [9]. It is an alternative way of treating wood without using chemicals and the wood's properties can be enhanced considerably by converting hydrophilic (-OH) groups into more hydrophobic groups; it also reduces the wood's equilibrium moisture content. In addition, it is different from other methods because of the existence of a hydrolysis step. Nowadays, hydrothermal treatment of wood has been implemented by several researchers [7,8,10,11]. The efficacy of hydrothermal treatment is mainly dependent on treatment temperature, duration and also the heating media [12]. When wood is treated using a hydrothermal treatment, some alterations are found such as the removal of extractives, the reduction of hydroxyl groups, the degradation of hemicellulose and a change in cellulose and lignin materials [13,14]. The presence of free water affects the chemical structure of thermally modified wood and heat is easily transferred into the wood. The wood's properties can be improved considerably by converting hydrophilic (-OH) groups into more hydrophobic groups.

Hydrothermal treatment using buffered media is also known as an effective technique to control and neutralize the destructive effects of the acids that form through the destruction of carbohydrates during the treatment. A buffered solution is a non-chemical solution that does not pollute the environment [15,16]. Formic and acetic acid are generated during the thermal treatment of wood under moist conditions. Therefore, buffered solution is used in order to nullify the effect of the acid generated during thermal treatment [17]. The acidity or pH level of a hydrothermal medium may become more acidic due to hydrothermal treatment. The buffered medium can be used to ensure a lower change in pH level due to the hydrothermal process in order to control the destructive effects caused by the released acid [18,19]. Acidic conditions and high temperatures can degrade wood by hydrolysis. Under acidic conditions, the degradation rate of carbohydrates is high, which is promoted by the high availability and low crystallinity of hemicelluloses [19]. On the other side, an alkaline medium can control the degradation of hydroxyl (OH-) groups. Furthermore, buffered media, especially those of pH 7 and 8, neutralize the released acids and fix the pH to a neutral level. They also buffer the medium in hydrothermal treatment to a neutral level, which prevents strength loss and extends the usage of heat-treated beech (*Fagus orientalis* Lipsky) wood in load-bearing applications [20]. However, until now, information regarding the influence of more acidic and alkaline buffer solutions on the properties of wood is scarce. Several techniques have already been implemented to enhance the physical properties of rubberwood, such as thermal treatment, oil-heat treatment and chemical modification. However, there has been no scientific information available so far on the hydrothermal treatment of rubberwood using different buffered media, especially on physical properties. Therefore, the aim of this research work was to determine the effects of hydrothermal treatment using buffered media of varying pH levels and temperatures on the selected physical properties of rubberwood.

2. Materials and Methods

2.1. Buffer Preparation

An acidic buffer (pH 4, 6), an alkaline buffer (pH 8, 10) and tap water (pH 7.43) were selected as the hydrothermal treatment media. The buffer solutions were prepared by using disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$) and monosodium dihydrogen phosphate

($NaH_2PO_4 \cdot 2H_2O$). Hydrochloric acid and sodium hydroxide were used to adjust the pH of the buffered media. All the chemicals were purchased from R&M Chemicals, Malaysia.

2.2. Sample Preparation

Matured rubberwood logs, aged more than 25 years, were purchased from a rubberwood processing company in Pahang, Malaysia. Each girth of each log was 100–125 cm and divided into butt, middle and top positions. All the logs were fair and free from natural defects. The rubber logs were then processed and cut into sample sticks with dimensions of 300 mm × 20 mm × 20 mm (length × width × thickness) in longitudinal, tangential and radial measurements (Figure 1).

Figure 1. Photograph of prepared rubberwood samples with dimensions of 300 mm × 20 mm × 20 mm (length × width × thickness) for hydrothermal treatment.

The sample sticks were predried to 10–11% moisture content (kiln dry basis) before hydrothermal treatments. In addition, the samples (having a density of around 650 kg/m^3) were then randomly divided into 16 groups (15 hydrothermal treatment groups and 1 untreated group as a control). Each of the treatment groups had an equal number of replicates [21].

2.3. Heat Treatment

Hydrothermal treatment was carried out in 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.

2.4. Color Changes

The color measurement was performed on the treated and untreated rubberwood samples. The surface colors of the specimens were measured using the Color Reader (CR-10, Minolta Co., Ltd.; made in Japan; 9229-1865-11) with an illuminated area of 8 mm before and after treatment. All color measurements were performed using conditions of the standard illuminant D65 with specular component included (SCI). Three measurements were taken at the middle position on each treated and untreated sample. Herein, measurements were performed on 3 samples. The color was defined using the CIE L*, a*, b* system, which

was established by the International Commission on Illumination in 1976. This system comprises three perpendicular axes, where the color coordinate L* is the lightness from 0 (dark) to 100 (white) or the black–white relation, a* is the red–green factor and b* is the yellow–blue factor. The total color change ΔE* caused by the various treatments were calculated as follows:

$$\Delta E* = \sqrt{\left(\Delta L*^2 + \Delta a*^2 + \Delta b*^2\right)} \quad (1)$$

where ΔL* is the change in value of the black–white coordinate, Δa* is the change in the value of the red–green coordinate and Δb* is the change in the yellow–blue coordinate.

2.5. Wet Chemical Analysis

For the evaluation of wet chemicals, 6 cm long conditioned splints were taken from each of the treated and untreated samples. Herein, the splints were ground into powder form. Afterwards, the particles were screened using a 40- to 60-mesh (0.4 to 0.6 mm) sieve in order to obtain homogeneous particle sizes. The powdered samples were then analysed for holocellulose, cellulose, hemicelluloses, lignin and extractive content.

2.6. Physical Properties

Physical properties were evaluated to assess the efficiency of the hydrothermal treatment in different buffered media. For the evaluation of physical properties, 10 samples were cut into dimensions of 20 mm × 20 mm × 20 mm after the treatments were performed. When all the samples reached a constant weight, equilibrium moisture content (EMC%), wood density ϱ (kg/m^3) and mass loss (ML%) were calculated by using the procedure given in the British-adopted European standard test method [22]. These properties were calculated as follows:

$$\text{EMC } (\%) = \frac{(M_u - M_O)}{(M_O)} \times 100 \quad (2)$$

where EMC (%) is the equilibrium moisture content, M_O M_O is the mass (g) of the oven-dried sample and M_u is the mass (g) for the equilibrium moisture content state;

$$\text{ML } (\%) = \frac{(W_{1OD} - W_{2OD})}{(W_{2OD})} \times 100 \quad (3)$$

where ML (%) is the mass loss (%), W_{1OD} is the oven-dried weight (g) of the samples before treatment and W_{2OD} is the weight (g) of the oven-dried samples after treatment.

Water absorption (WA %), volumetric swelling coefficient (VSC%), thickness swelling (TS%) and anti-swelling efficiency (ASE%) were calculated by using the equations below [23]:

$$\text{WA } (\%) = \frac{(Wt - Wo)}{(Wo)} \times 100 \quad (4)$$

where, WA (%) is the water absorption (%), *Wt* is the weight (g) of the wet samples after reconditioning and Wo is the weight (g) of the oven-dried samples;

$$\text{VSC } (\%) = \frac{(Vw - Vo)}{(Vo)} \times 100 \quad (5)$$

where, VSC (%) is the volumetric swelling coefficient, Vw is the green-state volume of the sample and Vo is the oven-dried volume of the sample. V is the volume calculated from the longitudinal (L), tangential (T) and radial (R) directions;

$$\text{TS } (\%) = \frac{(T_2 - T_1)}{(T_1)} \times 100 \quad (6)$$

where, TS (%) is the thickness swelling, T_2 is the thickness of the saturated samples and T_1 is the oven-dried thickness of the samples (T is the thickness calculated from the tangential direction);

$$\text{ASE } (\%) = \frac{(S_u - S_t)}{(S_u)} \times 100 \quad (7)$$

where, ASE (%) is the anti- swelling coefficient, S_u is the thickness swelling coefficient of the untreated samples and S_t is the thickness swelling coefficient of the treated samples.

2.7. Statistical Analysis

The test results were analyzed by two-way analysis of variance (ANOVA) (CRD factorial) using SAS (Version 9.4) to evaluate the effect of the buffered media and temperature of the hydrothermal treatment on the physical properties of the rubberwood. The significant differences between the mean values of the testing groups were investigated using Tukey's test (95% significant level).

3. Results and Discussion

3.1. Acidity Variation in Rubberwood

A pH meter was used to measure the acidity variation in the rubberwood samples before and after each hydrothermal treatment in different buffered media. Figure 2 depicts the pH change after hydrothermolysis in various buffered media and tap water at temperatures of 160 °C, 180 °C and 200 °C. The acidity of the wood samples varied according to pH and temperature. After treatment, the wood became more acidic. Regardless of buffered media, samples treated at 160 °C showed a pH range of 3.97 to 7.18 while samples treated at 200 °C had a pH range of 3.15 to 4.66. The trends indicated that the acidity of the wood increased along with an increasing treatment temperature. These findings supported a previous study in which the authors discovered a change in acidity from pH 6.7 (water) to 3.49 and pH 8.0 to 6.85 as samples were treated at 140 °C for 2 h [24].

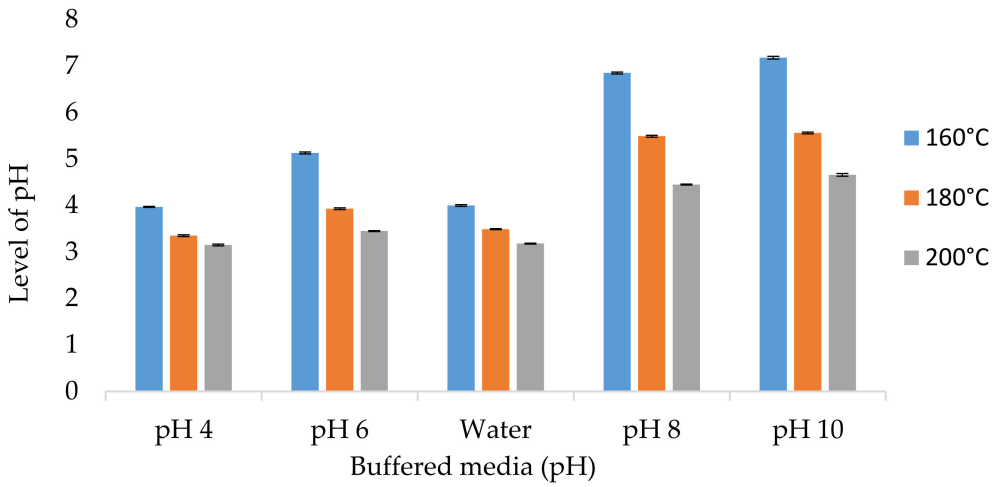

Figure 2. The acidity variation of samples in buffered media and tap water after the hydrothermal treatment.

The removal of carbonic acids and acetic acid caused by the breaking of acetyl groups in hemicellulose increases the acidity of the wood during hydrothermal treatment [7,25]. According to Tjeerdsma et al. [26], the formation of formic and acetic acid during moist thermal treatment increases the acidity of the wood. The findings also demonstrated that hydrothermal treatment in buffered media could control the destructive effects and resist the formation of removed acid, which was consistent with previous research [18,27,28]. Furthermore, buffered media can neutralize and regulate the acidity of the media [29,30].

3.2. Color Changes of Rubberwood

Figure 3 displays the visual observation of the color changes of the rubberwood after being treated in different buffered media and temperatures.

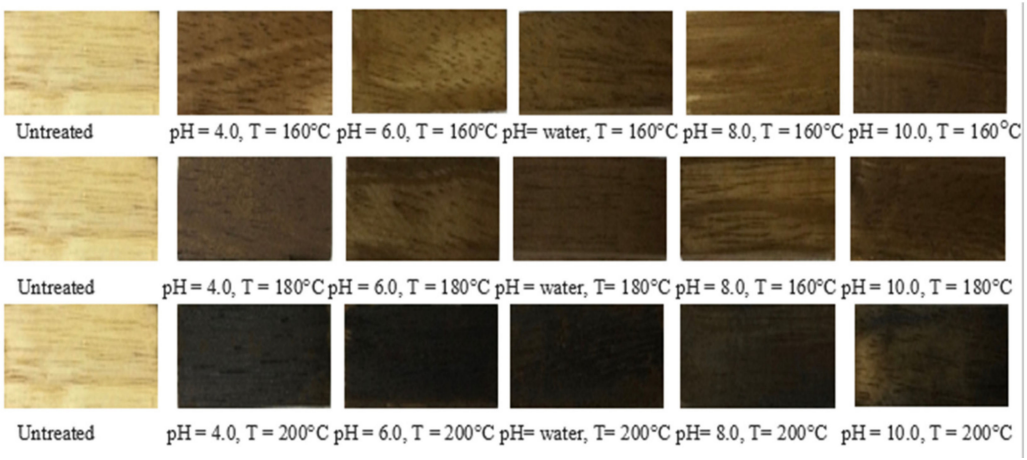

Figure 3. Visual observation of the color changes of untreated and hydrothermally treated rubberwood samples.

The most visible effect of treatment was a darkening of the color of the wood. Figure 3 depicts photographs of wood samples treated with hydrothermal treatment at various temperatures in different buffered media (acidic, water and alkaline). As can be seen in Figure 3, increased treatment temperatures increased the intensity of discoloration. Different media exhibited color differences at low temperatures, but there were no discernible changes in color at high temperatures. Lower temperatures (160 and 180 °C) caused less color changes in pH 6, 8 and 10 compared to acidic and water media, while high temperatures (200 °C) caused the most color changes. The hydrothermal treatment changed the color of the sample significantly as the treatment temperature increased [31–33]. This finding was consistent with the research findings in [34]. Color changes (wood darkening) are frequently attributed to the formation of oxidation and degradation elements from wood components [35,36]. The decrease in lightness caused by thermal treatment primarily indicates the formation of several components that absorb visible light [37]. According to Chen et al. [36], the condensation reactions of lignin and some extractives, as well as the formation of biproducts, contribute to an increase in the intensity of red tone in wood samples. Table 1 shows the chromatic value changes of treated and control rubberwood samples.

The chromatic values L*, a* and b* were measured for evaluating the overall color changes (ΔE*). Table 1 shows that the lightness (L*) values of all treated wood samples decreased when compared to untreated wood, indicating that the wood darkened after treatment. The L* value of the untreated wood was 76.91. The L* value on the wood treated by hydrothermal treatment with different media decreased as the temperature increased. In general, treatment temperature had a greater impact on the darkening of wood than the buffered media. Rubberwood treated with pH 6 at 160 °C had the smallest reduction in L* value (52.43). Meanwhile, the most severe reduction in lightness was observed in rubberwood treated in tap water at 200 °C. The decrease in lightness with increasing temperature during the hydrothermal treatment in different buffered media in this work could be attributed to extractive migration on the wood surface [38].

Table 1. Changes in chromatic value of treated and untreated samples of rubberwood.

Group	Temp. in °C	Lightness (L*)	Red–Green Factor (a*)	Yellow–Blue Factor (b*)	ΔE*
Control	-	76.91 ^{a} (0.95)	4.97 ^{e} (0.84)	21.69 ^{a} (1.57)	-
pH 4	160	46.85 ^{c} (1.76)	9.52 ^{a} (0.10)	13.60 ^{cd} (0.72)	31.46
	180	41.94 ^{e} (0.58)	6.79 ^{d} (0.50)	8.28 ^{fg} (0.99)	37.50
	200	33.82 ^{f} (0.18)	0.58 ^{f} (0.31)	0.04 ^{hi} (0.20)	48.42
pH 6	160	52.43 ^{b} (1.01)	9.46 ^{a} (0.40)	16.94 ^{b} (0.52)	25.34
	180	41.66 ^{e} (0.66)	7.37 ^{cd} (0.26)	9.72 ^{fg} (0.90)	37.31
	200	34.84 ^{f} (0.31)	1.20 ^{f} (0.13)	0.89 ^{hi} (0.07)	47.08
* Tap water	160	43.78 ^{de} (0.79)	8.21 ^{abcd} (0.30)	11.08 ^{def} (0.16)	34.93
	180	41.30 ^{e} (1.07)	6.90 ^{d} (0.45)	7.69 ^{g} (0.97)	38.32
	200	33.62 ^{f} (0.45)	2.20 ^{f} (0.44)	−1.23 ^{i} (0.20)	49.06
pH 8	160	50.84 ^{b} (0.80)	9.27 ^{ab} (0.09)	15.42 ^{bc} (0.22)	27.15
	180	45.13 ^{cd} (0.79)	8.38 ^{abcd} (0.62)	12.86 ^{cde} (0.81)	33.17
	200	34.51 ^{f} (0.85)	2.14 ^{f} (0.24)	1.97 ^{h} (0.15)	46.85
pH 10	160	45.88 ^{cd} (0.89)	8.77 ^{abc} (0.24)	13.61 ^{cd} (0.79)	32.30
	180	41.09 ^{e} (1.12)	7.78 ^{bcd} (0.69)	10.21 ^{efg} (1.68)	37.74
	200	34.82 ^{f} (0.17)	2.21 ^{f} (0.46)	1.91 ^{h} (0.29)	46.59

[Note: * denotes pH 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

Green–red coordinate (a*) values of the treated rubberwood increased after treatment at 160 °C and 180 °C in all buffered media (acidic, water and alkaline), indicating that the samples turned redder. However, when the samples were treated at 200 °C, the a* value decreased, indicating that the samples were beginning to turn green. The findings agreed with those of Cai et al. [39] and Lee et al. [40]. The samples treated at 160 °C in pH 6 had the highest a* value, while the samples treated at 200 °C in pH 4.0 had the lowest a* value. The treatment, on the other hand, reduced the yellow–blue coordinate (b*) values. A decrease in b* indicated that the samples became bluer after treatment. Similarly, the highest b* value was recorded in pH 6 media at 160 °C, while the lowest b* value was recorded in tap water media at 200 °C.

Previous studies found that treating the wood surface in different buffered media resulted in color changes due to the removal of extractives, hydrolysis of hemicellulose and oxidation of these components [38,41,42]. To validate the color changes of the wood, the total color differences ΔE* were calculated, which involved changing all color coordinates (ΔL*, Δa*, Δb*). The E* value gradually increased with increasing treatment temperature, as shown in Table 1. Different media displayed different values of ΔE*. The greater color changes caused by hydrothermal treatments in the water media compared to other media (acidic, alkaline) were due to a greater contribution from the chromaticity coordinates, namely ΔL*, Δa* and Δb*. Overall, E* increased as the treatment temperature increased and the effect of the buffered media was less noticeable.

3.3. Physical Properties of Rubberwood

Equilibrium moisture content (EMC %), wood density ϱ (kg/m^3), mass loss (ML%), water absorption (WA%) and volumetric swelling coefficient (VSC%) were evaluated in this study. The equilibrium moisture content of treated and untreated rubberwood samples are presented in Table 2.

Table 2. EMC of treated and untreated samples of rubberwood at 28 °C and 65% RH.

Group	Temp. in °C	Equilibrium Moisture Content (EMC%)
Control	-	10.00 ^{a} (0.30)
pH 4	160	8.52 ^{d} (0.18)
	180	7.20 ^{efg} (0.17)
	200	7.03 ^{g} (0.10)
pH 6	160	8.79 ^{bc} (0.45)
	180	7.39 ^{efg} (0.16)
	200	7.13 ^{fg} (0.10)
* Tap water	160	8.64 ^{cd} (0.24)
	180	7.32 ^{efg} (0.17)
	200	7.10 ^{g} (0.12)
pH 8	160	9.05 ^{b} (0.16)
	180	7.57 ^{e} (0.18)
	200	7.39 ^{efg} (0.14)
pH 10	160	8.96 ^{bc} (0.19)
	180	7.49 ^{ef} (0.20)
	200	7.23 ^{efg} (0.14)

[Note: * denotes pH 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

Table 2 shows that the highest and lowest EMC values of the treated rubberwood samples were 9.05% in pH 8 at 160 °C and 7.03% in pH 4.0 at 200 °C, respectively, while the untreated sample (control) had a value of 10%. There was a significant difference between the samples treated in buffered media with different pH values. As the reduction in EMC of the wood was directly proportional to the intensification of temperature [43], treatment temperatures were found to be a more influential factor in reducing the EMC of the treated samples. On the other hand, alkaline media (pH 8, 10) reduced EMC the least. The main reason for the decrease in EMC was the loss of hydroxyl groups after heat treatment. Due to the lack of these hydroxyl groups, the cell walls were able to absorb less water [44]. Furthermore, the decrease in EMC could be caused by increased cellulose crystallinity, which reduces the availability of hydroxyl (OH-) groups to water molecules [30,31]. The hydrothermal treatment might have an effect on the chemical constituents of the rubberwood samples. When compared to cellulose and lignin, the degradation of OH- groups in hemicellulose occurred even at low temperatures [44]. As a result of the degradation of OH- groups from hemicelluloses, the treated samples had lower EMCs than the untreated samples. As hemicelluloses contain a greater number of OH-groups than cellulose and lignin components, they are more hygroscopic. Table 3 shows the effects of the hydrothermal treatment in various media (acidic, water, alkaline) on the content of holocellulose, cellulose, hemicellulose, lignin and extractives in the rubberwood. A reduction in hemicellulose content after treatment was observed, ranging from 18.78% to 39.50% compared to that of 39.97% in the control samples.

Table 3. Chemical analysis of treated and untreated rubberwood.

Group	Temp. in °C	Holocellulose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Control	-	77.38	37.41	39.97	28.13	2.59
pH 4	160 °C	74.49	45.89	28.59	30.96	4.78
	180 °C	72.14	51.42	20.72	30.18	7.30
	200 °C	70.51	47.06	23.45	32.16	9.80
pH 6	160 °C	75.23	37.63	37.60	29.13	4.52
	180 °C	73.03	46.23	26.80	28.56	6.91
	200 °C	71.41	42.03	29.38	29.00	8.13
Tap water (pH 7.43)	160 °C	74.82	45.33	29.49	29.20	7.07
	180 °C	72.61	53.83	18.78	27.12	9.93
	200 °C	70.96	49.06	21.90	31.09	12.01
pH 8	160 °C	76.83	37.33	39.50	29.00	4.93
	180 °C	74.41	43.23	31.18	29.00	6.18
	200 °C	71.76	39.08	32.68	27.12	8.9
pH 10	160 °C	76.23	37.8	38.43	27.00	5.56
	180 °C	73.63	44.56	29.07	25.00	7.86
	200 °C	71.16	38.78	32.38	27.00	9.18

Table 4 shows the density of the rubberwood before and after treatment in different buffered media. Before treatment, the average density of the rubberwood was 644.94 kg/m^3. After treatment, the density of the rubberwood decreased to a different extent. Generally, the reduction in density increased along with increasing temperature. It was observed that the rubberwood treated with the acidic medium (pH 4) had the highest density reduction, particularly those treated at 200 °C, which experienced a 16.3% reduction in density compared to that of untreated samples. Samples treated with an alkaline medium (pH 8 and pH 10) experienced a lower reduction in density. The lowest density reduction of 0.5% was recorded in the samples treated in pH 8 at 160 °C. These findings were in line with previous work where the authors reported density losses that ranged from 1.89%–5.67% in different media (water, acidic, neutral, alkaline) at 160 °C and 2.96%–7.84% at 180 °C, respectively [20].

Table 4. Density of rubberwood before and after hydrothermal treatment at different temperatures and using buffered media.

Group	Temp. in °C	Density, ϱ (kg/m^3)		
Control	**-**	**644.94 (15.11)**		
		Before	**After**	**Reduction (%)**
pH 4	160	644.48 (18.86)	617.36 (14.4)	4.2
	180	645.63(16.56)	560.49 (11.0)	13.2
	200	643.21 (16.11)	538.13 (13.8)	16.3
pH 6	160	645.14 (16.45)	633.85 (14.8)	1.8
	180	643.88 (20.82)	579.33 (15.7)	10.0
	200	644.34 (18.71)	549.69 (15.8)	14.7
* Tap water	160	644.41 (18.56)	622.78 (18.0)	3.4
	180	645.30 (15.6)	575.75 (12.0)	10.8
	200	645.56 (16.76)	544.18 (13.6)	15.7
pH 8	160	645.1 (20.32)	641.72 (18.3)	0.5
	180	644.6 (16.67)	598.89 (12.8)	7.1
	200	645.0 (19. 37)	554.68 (13.1)	14.0
pH 10	160	645.77 (19.98)	638.9 (15.2)	1.1
	180	643.94 (13.90)	594.54 (14.9)	7.7
	200	644.27 (17.49)	551.0 (15.0)	14.5

[Note: * denotes pH 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

Mass loss (ML%) of hydrothermally treated rubberwood samples is presented in Figure 4. Mass loss increased along with the increasing treatment temperature.

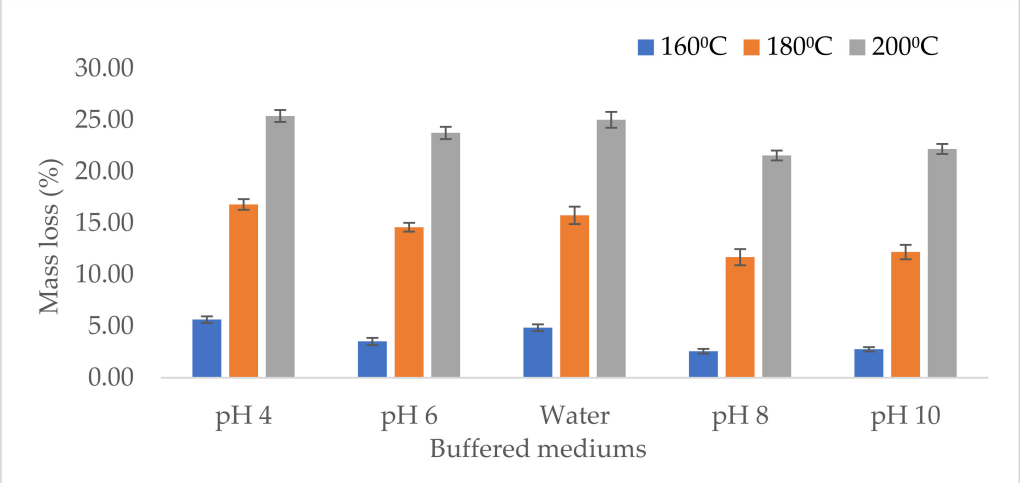

Figure 4. Mass loss (ML%) variations of treated and untreated (control) rubberwood samples in buffered media after the hydrothermal treatment.

Temperatures of 200 °C in pH 4 (25.39%) and 160 °C in pH 8 (2.58%) resulted in the highest and lowest percentage of mass loss, respectively. According to Tjeerdsma et al. [26], acidic hydrolysis at various hydrothermal treatments can significantly increase the degradation rate of wood polymers. According to Theander and Nelson [19], the degradation rate of carbohydrates is high in acidic conditions, which is facilitated by the high availability and low crystallinity of hemicelluloses. In general, the exclusion of hydrogen (H+) and hydroxide (-OH) ions in hydrothermal treatment has no effect on the pH of the hydrothermally treated medium. Furthermore, in hydrothermal treatments using buffered media, the pH can be kept constant at a certain level and the destructive effects of the released acid can be controlled [29].

Untreated samples had a water absorption (WA) of 20.5%. The samples treated in pH 8 at 180 °C had the highest WA value of 25.02%, while the samples treated in pH 4 at 200 °C had the lowest WA value of 22.42% (Table 5). It is worth noting that WA increased as the treatment temperature increased from 160 °C to 180 °C, but began to decrease as the temperature was raised to 200 °C. This phenomenon might be explained by heat-induced damage within the wood structure. This study's findings were consistent with previous studies [5,42,43]. Figure 5 shows the cracks that occurred on the samples after being treated at a higher temperature of 200 °C.

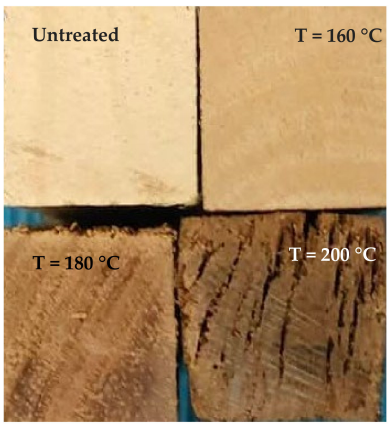

Figure 5. Visual appearance of untreated and treated rubberwood at different temperatures.

Table 5. WA of treated and untreated samples of rubberwood.

Group	Temp. in °C	Water Absorption (WA%)
Control	-	20.56 ^{g} (0.46)
pH 4	160	23.01 ^{cdef} (0.59)
	180	23.56 ^{bcde} (0.17)
	200	22.42 ^{f} (0.10)
pH 6	160	23.99 ^{abc} (0.51)
	180	24.44 ^{ab} (1.06)
	200	22.72 ^{def} (0.73)
* Tap water	160	23.05 ^{cdef} (0.50)
	180	23.64 ^{bcde} (0.63)
	200	22.63 ^{ef} (0.74)
pH 8	160	24.43 ^{ab} (1.03)
	180	25.02 ^{a} (1.01)
	200	23.78 ^{bcd} (0.78)
pH 10	160	24.36 ^{ab} (0.63)
	180	24.68 ^{ab} (0.72)
	200	23.03 ^{cdef} (0.86)

[Note: * denotes 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

Table 6 shows the effects of pH and treatment temperature on the VSC of untreated and treated rubberwood. The VSC of the hydrothermally treated rubberwood was lower than that of the untreated samples (8.09%). When the samples were treated in pH 8 at 200 °C, the lowest VSC value of 6.97% was observed. Similarly, as the treatment temperature increased, the VSC values decreased. Lower VSC values indicated that the samples are more dimensionally stable. In general, alkaline-treated samples had lower VSC values and, thus, better dimensional stability.

Table 6. Volumetric swelling coefficient of treated and untreated samples of rubberwood.

Group	Temp. in °C	Volumetric Swelling Coefficient (VSC%)
Control	-	8.09 ^{a} (0.15)
pH 4	160	7.68 ^{b} (0.19)
	180	7.47 ^{bcd} (0.23)
	200	7.44 ^{bcdef} (0.16)
pH 6	160	7.54 ^{bcdef} (0.30)
	180	7.41 ^{bcdef} (0.19)
	200	7.28 ^{defg} (0.18)
* Tap water	160	7.66 ^{bc} (0.17)
	180	7.45 ^{bcde} (0.24)
	200	7.35 ^{cdef} (0.27)
pH 8	160	7.41 ^{bcdef} (0.23)
	180	7.13 ^{fg} (0.22)
	200	6.97 ^{g} (0.12)
pH 10	160	7.45 ^{bcde} (0.21)
	180	7.15 ^{efg} (0.16)
	200	7.0 ^{g} (0.12)

[Note: * denotes 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

TS and ASE of the treated and untreated rubberwood samples are presented in Table 7.

Table 7. Thickness swelling (TS) and anti-swelling efficiency (ASE) of treated and untreated samples of rubberwood.

Group	Temp. in °C	TS (%)	ASE (%)
Control	-	3.74 ^{a} (0.25)	-
pH 4	160	3.47 ^{b} (0.04)	7.23 ^{j} (0.90)
	180	3.33 ^{bcd} (0.05)	11.07 ^{hi} (1.36)
	200	3.22 ^{cde} (0.08)	13.91 ^{efgh} (1.67)
pH 6	160	3.26 ^{bcde} (0.12)	12.85 ^{gh} (2.28)
	180	3.13 ^{def} (0.10)	16.38 ^{cde} (1.38)
	200	3.06 ^{ef} (0.11)	18.17 ^{bc} (2.01)
* Tap water	160	3.43 ^{bc} (0.06)	8.33 ^{ij} (1.38)
	180	3.25 ^{bcde} (0.10)	13.19 ^{fgh} (2.80)
	200	3.11 ^{def} (0.06)	16.82 ^{cde} (1.54)
pH 8	160	3.14 ^{def} (0.08)	16.05 ^{cdef} (2.31)
	180	3.07 ^{ef} (0.09)	17.80 ^{bcd} (2.33)
	200	2.95 ^{f} (0.09)	21.18 ^{a} (2.42)
pH 10	160	3.17 ^{def} (0.06)	15.13 ^{defg} (1.67)
	180	3.10 ^{def} (0.04)	17.00 ^{cd} (1.16)
	200	2.99 ^{f} (0.08)	20.06 ^{ab} (2.24)

[Note: * denotes 7.43 and means with different letters represent significant differences within groups at the 0.05 probability level by Tukey's test. The values in parentheses represent the calculated standard deviation (SD)].

TS and ASE values varied according to pH and temperature. The hydrothermally treated rubberwood samples had lower TS values than the control samples. The highest TS value for the treated samples was 3.47% at 160 °C in pH 4, while the lowest TS (2.95%) was recorded in the samples treated at 200 °C in pH 8. According to Table 7, the ASE values of the samples ranged from 7.23 to 13.91% (pH 4.0, 160–200 °C), 12.85–18.17% (pH 6.0, 160–200 °C), 8.33 to 16.82% (tap water, 160–200 °C), 16.05 to 21.18% (pH 8.0, 160–200 °C) and 15.13 to 20.06% (pH 10.0, 160–200 °C). Furthermore, both the treatment temperature and the buffered media had a significant effect on ASE values. The samples treated in alkaline media had a lower TS than the samples treated in acidic and water media. These observations were in agreement with the finding that was revealed by Ebadi et al. [18].

4. Conclusions

The changes in selected physical properties of rubberwood caused by hydrothermal treatment in different pH-buffered media at different temperatures were investigated in this study. The study's findings revealed that the acidity of the treated medium increased after hydrothermal treatment in various buffered media. It was found that the buffer solution could reduce and control the destructive effect of acid on the wood components. After hydrothermal modification, there were clear variations in wood acidity. Furthermore, the equilibrium moisture content decreased, which might have had an impact on the decrements in wood quality. According to the findings of the study, hydrothermal treatment could improve the dimensional stability of rubberwood. Wood density was reduced after hydrothermal treatment and was found to be minimal in alkaline media. Mass loss was caused by the degradation of hemicellulose and extractives content, and mass loss was directly proportional to the decline of density and strength properties. It also affected the wood color, and the color changes of rubberwood become darker after treatment. As alkaline media could control the destructive effects of released acid, minimal mass loss was observed when compared to other treatment media. Furthermore, the neutralization effect of buffered media could control the rate of carbohydrate degradation and medium acidity, which could help to improve some of the wood's properties. Among the treatment media, alkaline media at a lower temperature was selected as the best treatment condition to improve the performance of some of the rubberwood's physical properties.

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