The Effect of High Temperature Superheated Steam Drying on the Mechanical and Physical Properties of Rubberwood

Anatta Patcharawijit

A Thesis Submitted in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in Chemical Engineering
Prince of Songkla University
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Major Program	Chemical Engineering

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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์	อิทธิพลการอบแห้งด้วยไอน้ำร้อนยิ่งยวดอุณหภูมิสูงต่อคุณสมบัติเชิงกลและกายภาพของไม้ยางพารา
ชื่อผู้เขียน	นางสาวอนัตตา พัชรวิจิตร
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ปีการศึกษา	2561

บทคัดย่อ

การศึกษานี้วัตถุประสงค์เพื่อศึกษาผลของการทรีตเมนต์ด้วยไอน้ำร้อนยิ่งยวดต่อคุณสมบัติเชิงกายภาพและเชิงกลของไม้ยางพารา โดยท่อนไม้ยางพาราที่นำมาใช้ในการศึกษาครั้งนี้ ได้ผ่านการอบแห้งด้วยลมร้อนจากโรงงานแปรรูปไม้ยางพาราจนมีความชื้นเฉลี่ย 10±2% (ฐานแห้ง) การทดลองได้ดำเนินการที่สภาวะไอน้ำร้อนยิ่งยวดอุณหภูมิ 140 150 และ 160 องศาเซลเซียส เป็นระยะเวลา 1, 2 และ 3 ชั่วโมง ภายใต้ความดันบรรยากาศ จากนั้นนำไม้ยางพาราที่ผ่านการทรีตเมนต์มาวิเคราะห์คุณสมบัติต่าง ๆ พบว่าคุณสมบัติเชิงกลของไม้ยางพาราส่วนใหญ่ปรับค่าดีขึ้น โดยเมื่อพิจารณาร้อยละการเปลี่ยนแปลงเทียบกับตัวอย่างไม้ยางพาราควบคุมในแต่ละสภาวะ ค่าที่เพิ่มขึ้นสูงสุดอย่างมีนัยสำคัญของความแข็งและความต้านทานการอดอัดขนานกับเสี้ยน มาจากตัวอย่างไม้ยางพาราที่ผ่านการทรีตเมนต์ด้วยสภาวะ 160 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง และ 140 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง ตามลำดับ นอกจากนี้ยังพบว่าค่าความต้านทานแรงกระแทกและความต้านทานแรงดึงในทิศทางตั้งฉากกับเสี้ยนของตัวอย่างไม้ยางพาราหลังจากผ่านการทรีตเมนต์ในแต่ละสภาวะ มีค่าสูงขึ้นแต่ไม่มีนัยสำคัญเมื่อเทียบกับตัวอย่างไม้ควบคุม

จากการวิเคราะห์คุณสมบัติการดูดซับความชื้น พบว่าในทุกช่วงความชื้นที่ทำการทดลองตัวอย่างไม้ยางพาราที่ผ่านการทรีตเมนต์จากทุกสภาวะ มีปริมาณความชื้นสมดุลลดลง จากนั้นวิเคราะห์ไอโซเทอมการดูดซับด้วย Hailwood-Horrobin model และหาปริมาณความชื้นการดูดซับชั้นเดียว (monolyer) และปริมาณความชื้นการดูดซับหลายชั้น (polylayer) ของตัวอย่างไม้ยางพารา พบว่าปริมาณความชื้นการดูดซับชั้นเดียวของตัวอย่างไม้ยางพารามีค่าลดลงอย่างเห็นได้ชัดเมื่อผ่านการทรีตเม้นต์ด้วยอุณหภูมิสูงขึ้นและระยะเวลานานขึ้น ในขณะที่ปริมาณความชื้นการดูดซับหลายชั้นมีค่าลดลงเล็กน้อย นอกจากนี้พบว่า ตัวอย่างไม้ยางพาราที่ผ่านสภาวะ 160 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง มีความหนาแน่นของพื้นที่การดูดซับความชื้นต่ำสุด ซึ่งชี้ให้เห็นว่าเป็นสาเหตุของ

การดูดซับสมดุลที่ลดลง จากการวิเคราะห์การเปลี่ยนแปลงสีที่ผิวของไม้ยางพารา พบว่าเมื่อสภาวะที่อุณหภูมิสูงขึ้นและเวลานานขึ้น ส่งผลให้ผิวไม้มีสีเข้มขึ้น ซึ่งพิจารณาได้จากค่าความสว่าง (L*) ที่ลดลง และตัวอย่างไม้ยางพาราที่มีค่าความแตกต่างของสีโดยรวม (ΔE*) มากที่สุด คือไม้จากสภาวะ 160 องศาเซลเซียส เวลา 3 ชั่วโมง

วิธีมาตรฐาน ASTM D-1413 และ ASTM D3345-74 ถูกนำมาใช้ในการประเมินความต้านทานเชื้อราและปลวกใต้ดินของตัวอย่างไม้ยางพาราตามลำดับ ผลการทดลองพบว่าสภาวะการทรีตเมนต์ด้วยไอน้ำร้อนยิ่งยวดส่งผลให้ความต้านทานการผุกร่อนของไม้ยางพาราเพิ่มขึ้นอย่างมีนัยสำคัญ โดยอุณหภูมิ160 องศาเซลเซียส เวลา 3 ชั่วโมง เป็นสภาวะที่ทำให้ไม้ยางพารามีความต้านทานเชื้อราและปลวกมากที่สุด เนื่องจากน้ำหนักที่สูญเสียของตัวอย่างไม้ระหว่างการทดลองมีค่าต่ำที่สุด

การวิเคราะห์การเปลี่ยนแปลงผนังเซลล์ของตัวอย่างไม้ยางพารา ดำเนินการด้วยเทคนิค FTIR spectroscopy พบว่า เมื่อไม้ยางพาราผ่านการทรีตเมนต์ด้วยอุณหภูมิสูงขึ้น จะส่งผลให้ปริมาณของหมู่ไฮดรอกซิลลดลง รวมทั้งส่งผลให้ปริมาณเซลลูโลสของผนังเซลล์ไม้มีความเป็นผลึกมากขึ้น นอกจากนี้การวิเคราะห์ผิวไม้ด้วย SEM micrographs ทำให้ทราบว่าปริมาณอนุภาคแป้งของตัวอย่างไม้มีค่าลดลงต่อเนื่องจากอุณหภูมิการทรีตเมนต์ที่เพิ่มขึ้น

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ABSTRACT

The effects of superheated steam treatment on the physical and mechanical properties of rubberwood (*Hevea brasiliensis*) were investigated. The wood boards were conventional pre-dried from a manufacturer to an average 10±2% moisture content, prior to the superheated steam treatments in this study. The treatments were carried out at three different superheated steam temperatures (140, 150 and 160°C) and three different times (1, 2 and 3 h) under atmospheric pressure and in the presence of air. The results indicated that the mechanical properties were improved as the percentage increase relative to the control samples of each condition. The greatest values for both hardness and compression parallel-to-grain were found in the samples treated at 160°C for 3 h and 140°C for 1 h respectively. In addition, impact strength and tensile strength perpendicular-to-grain of each treatment condition were increased but there are no significant difference ($p<0.05$) between treated and untreated samples.

The results of adsorption properties show decreased equilibrium moisture content for all heat-treated cases throughout the hygroscopic range. The Hailwood-Horrobin model was used to analyze the sorption isotherms and determine monolayer and polylayer moisture contents for untreated and heat-treated rubberwood. The monolayer moisture content clearly decreased with treatment temperature and duration, whereas the reduction in polylayer moisture was relatively smaller. Moreover, the least density of water adsorption sites was found in wood after treatment at 160°C for 3 h, indicating this as the cause for reduced equilibrium adsorption. At higher temperatures and for a long time, the treated samples became darker as indicated by a decrease of brightness (L*), and the greatest total color changes (ΔE*) were observed in samples after treatment at 160°C for 3 h.

The standard methods of ASTM D-1413 and ASTM D3345-74 were used to evaluate the decay resistance from white-rot decay fungus and subterranean termite of rubberwood samples, respectively. Results revealed that superheated steam treatment significant increases the resistance of rubberwood samples. Treated sample at 160°C for 3 h yielded the best performance with the lowest weight loss on both fungal and termite test. Furthermore, FTIR spectroscopy was used to investigate the change in cell-wall components. It was found that high superheated steam temperature caused the number of accessible hydroxyl groups to decrease and the relative cellulose crystallinity to increase. Also the SEM micrographs of wood surface showed that the starch particles decreased consistently with increasing in treatment temperature.

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Anatta Patcharawijit

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CHAPTER 1

Introduction

1.1 Background and Rationale

Rubberwood (*Hevea brasiliensis*) is one of the most important wood resources in Thailand and Southeast Asia. The rubberwood sawn-timber is the main and primary raw material in furniture manufacturing because consumers can accept rubberwood by its density, medium fine grained and cream-colored. Besides, the rubberwood is often compared to teak, another close grained tropical wood species, and it is sometimes preferred over teak because rubberwood is a sustainable product. Consequently, the rubberwood industry is becoming an increasingly important as it replaces more expensive wood from natural forest. However, some properties of rubberwood, in particular hygroscopicity and durability (Umar et al. 2016), are inferior compared to most commercial species. The wood volume and shape change when the wood absorbs or releases moisture, and it is degraded by biological agents such as fungi, mold and insects. These characteristics of rubberwood can be improved by impregnation with chemicals. Nevertheless, environmental awareness has led to an increased requirement for environmentally friendly method as thermal treatment.

Thermal treatment is one of the environmentally friendly processes and has been suggested as making the wood more durable, dimensional stability and reduced hygroscopicity. When treating wood with heat at specific temperature, it may possible to reduce appetizing to insects in the wood-fiber. The wood properties, particularly water in wood, are improved by heat treatment: weather resistance, lower equilibrium moisture content, as well as less moisture deformation (Calonego et al. 2010; Schneid et al. 2014). This wood modification can play an important role in improving the aforementioned properties of wood without using any chemical treatment such as boric acid and borax which would open the Thailand rubberwood industry to environmentally control markets under the EU. Rubberwood application in the furniture industry has been long recognized, but with the advent of high temperature treatment of wood in order to produce Thermowood during the past decade, there is a potential for additional application of rubberwood as outdoor/indoor furniture or playground equipment.

There are several different types of thermal treatment of wood, depending on the medium and temperature applied. The most well-known types of thermal treatment are ThermoWood in Finland, retification process and bois perdure in France, plato-wood in The Netherlands and oil-heat treatment in Germany (Esteves et al. 2013). Superheated steam technique (steam with temperature higher than its vaporization or boiling point at the absolute pressure) has been used to apply wide range of products including food, sludge, agricultural materials, wood, etc. The use of superheated steam has been known for quite a long time. The advantages of superheated steam include environment-friendly method, prevention of fire and explosion hazards, low energy consumption, high-drying rate, and high quality of dried products under certain conditions.

In previous studies, that investigated the properties of heat-treated wood, the wood was initially in its green condition, specifically without pre-drying to some desired moisture content. Therefore, in this research, pre-dried rubberwoods were used rather than fresh rubberwood in order to make the application of this superheated steam treatment more favorable for the rubberwood factories as they would not have to invest and modify their process as much as they would for a complete drying process.

The aim of this research was to access the influence of superheated steam on the mechanical and physical properties of pre-dried rubberwood at various temperatures and durations. To achieve this objective, the samples were treated at 140, 150 and 160°C for 1, 2 and 3 h.

1.2 Theoretical Background

1.2.1 Rubberwood

Hevea brasiliensis is the botanical name of the rubber tree (Fig. 1-1). It is also known as plantation hardwood, parawood, or "Hevea", with the major product is rubber latex. It is grown predominately in Southeast Asia region. Thailand, Indonesia, and Malaysia are the greatest plantation capacities of rubber in the world with total plantation representing more than 80% of the global output. In Thailand, rubber has been exploited since the 1990s as a source of timber and fuel wood (Win 2017).

Fig. 1-1 Rubber tree.

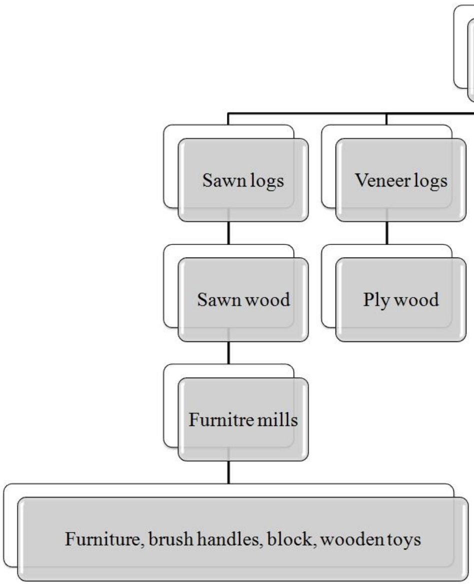

Fig. 1-2 Rubberwood materials and products.

In 2017, rubber plantation area in Thailand area totaled 22.79 million rai (about 3.65 million hectares) (Rubber Authority of Thailand 2018.). The rotation period of rubber tree is about 25 to 30 years when the amount of rubber latex reduces extremely, then cut down for replanting and obtained rubberwood. For several decades in the past, the rubberwood was used primarily as fuel in many countries until it has became to one of the most wood products on world markets. It is a product of plantations rather than deforestation, this why the rubberwood is referred as an environmentally friendly and also an important consideration among buyers today.

In Thailand, especially the South of Thailand, rubberwood is one of exported product of Thailand which shipping to abroad over 65%. The rubberwood production in Thailand was predicted by Economic Intelligence Center (EIC) that it will increase by 3% from 2016 to 2020 (Panels & Furniture Group n.d.). Group of dressed and flat sawn timber is the main exported wood product of Thailand in 2017 as Fig. 1-3.

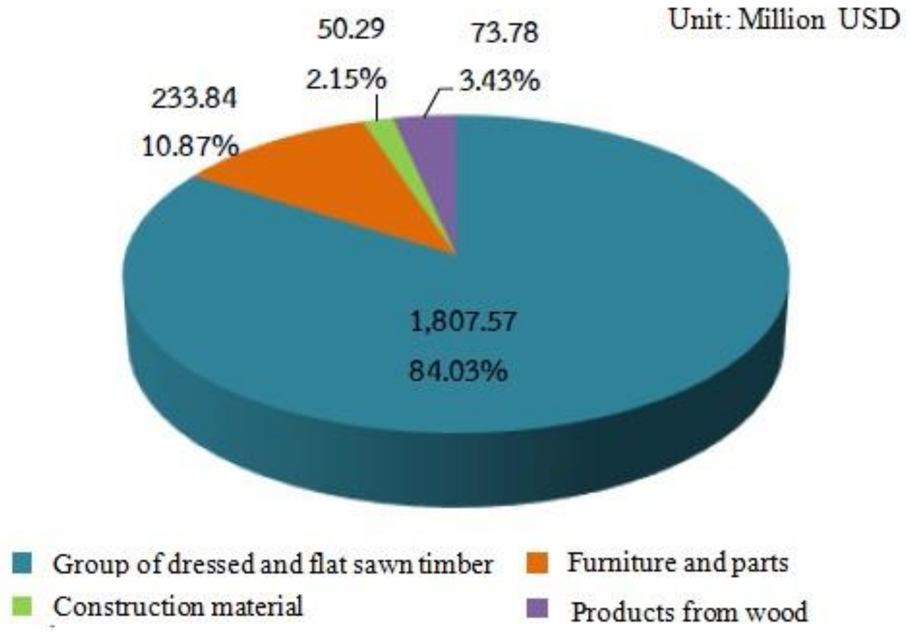

Fig. 1-3 Ratio and total values of rubberwood exports of Thailand (January – September 2017) (Office of Industrial Economics 2017).

The creamy color is the one attractive property of rubberwood as well as easy machining and processing properties. The rubberwood is classified as a light hardwood, has an air-dry density ranging from 560-640 kg/m^3 and has medium strength properties comparable with several wood materials. This wood species usually used in construction, flooring, furniture, children toys, playground equipment and other applications (Killmann and Thong 2000).

Table 1-1 and Table 1-2 show the characteristics of rubberwood, physical and mechanical properties of rubberwood as compared to teak, respectively.

Table 1-1 Characteristics of rubberwood (Department of Agriculture and Fisheries, 2018).

Characteristic	Description
Color	Whitish yellow when freshly cut, turned into brown on exposure.
Grain/Texture	Straight to shallowly interlock and medium texture.
Features	
□ Sapwood	□ Not distinct from heartwood.
□ Heartwood	□ Whitish yellow when freshly cut, turned into brown on exposure.
□ Texture	□ Medium texture/ open grain texture.
Properties	
□ Density	□ 640 kg/m3 at 12% moisture content.
□ Durability	□ Little natural resistance.
□ Hardness	□ •Work with machine and hand tools easily.
□ Workability	□ Good workability (sawing, drilling, turning, nailing, gluing)

Table 1-2 Strength properties of (air-dried) rubberwood and other species (Meier 2008).

Wood specie*	**Density (kg/m^3)**	**MOR* (MPa)**	**MOE* (MPa)**	**CP//* (MPa)**	**Hardness (N)**	**Durability**	**Common Uses**
Rubberwood	640	71.9	90,700	42.1	4,280	Low	Furniture, cabinetry, interior millwork, kitchen woodenware
Rosewood	1,035	171	16,380	117	10,790	High	Fine furniture, turned objects, musical instruments
Burma Padauk	865	138.8	14,140	62.3	9,550	High	Furniture, flooring, musical instruments, tool handles
Afzelia, Doussie	805	122.3	14,440	74.1	8,050	High	Furniture, cabinetry, flooring, docks, boatbuilding
Teak	655	91.7	12,280	54.8	4,740	High	Ship and boatbuilding, furniture, exterior construction
Balau	850	122.3	16,950	70.9	7,120	slightly	Plywood,veneer, general construction, flooring
European Ash	680	103.6	12,310	51	6,580	slightly	Flooring, millwork, boxes/crates, tool handles
European Beech	710	110.1	14,310	57	6,460	Non	Flooring, boatbuilding, furniture, musical instruments
Red Oak	700	99.2	12,140	46.8	5,430	Non	Cabinetry, furniture, interior trim, flooring
Yellow Meranti	565	80.8	10,680	44.5	3,120	Non	Plywood, interior furniture, and general construction
Radiata Pine	515	79.2	10,060	41.6	3150	Non	Veneer, plywood, paper (pulpwood), boxes/crates

*MOR: Modulus of rupture; MOE: Modulus of Elasticity; CP//: Compression parallel to grain

** Rubberwood (*Hevea brasiliensis*), Rosewood (*Dalbergia cochinchinensis*), Burma Padauk (*Pterocarpus macrocarpus*), Afzelia or Doussie (*Afzelia spp.*), Balau (*Shorea spp.*), European Ash (*Fraxinus excelsior*), European Beech (*Fagus sylvatica*), Red Oak (*Quercus rubra*), Teak (*Tectona grandis*), Yellow Meranti (*Shorea spp.*), Radiata Pine (*Pinus radiata*).

1.2.2 Physical structure of wood

The trunk is composed of different substances from the outside to the inside of the tree, namely, outer bark, inner bark, vascular cambium, sapwood, heartwood, and the pith. The inner bark is protected from mechanical from the outer bark and the outer bark also helps to reduce the rate of water loss. Food or sugars of the tree are formed by photosynthesis and transported by the inner bark tissue from the leaves to the roots or growing parts of the tree. The vascular cambium is located in the the bark and each year the wood will produces both these tissues. The sapwood is the existence section of the wood which is located between the cambium and heartwood. Water is transported from the root through this sapwood to the leaves and color of the sapwood is normally lighter than the heartwood. While the heartwood acts as the mechanical support to the tree. The pith is located at the trunk center which is the remnant of early growth before wood.

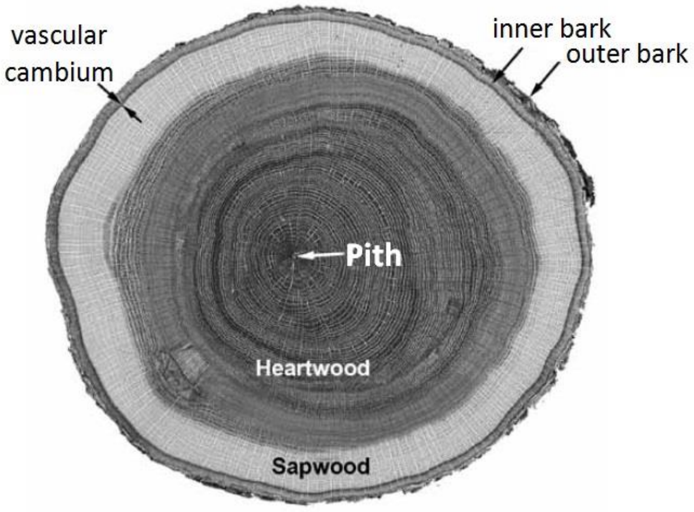

Fig. 1-4 Macroscopic view of a transverse section of a Quercus alba trunk (Rowell 2013).

1.2.2.1 Softwood

Softwoods are simple and regular in their structure. There are two different kinds of cell in softwoods tracheids (approximately 90% - 95%) and parenchyma. The main functions of these tracheids are contribution the strength and transportation capabilities to the softwood tree. The strength is provided by the tracheids that found in latewood, while the transport capability is associated with the tracheids in the earlywood. The amount of parenchyma cells in softwoods is approximately 5-10%, mostly found in rays and around resin canals. These parenchyma cells have living protoplasm and act as the storage of nutrient in sapwood. While the nutritious protoplasm is lost, during heartwood formation.

1.2.2.2 Hardwoods

Hardwood is more complicated and heterogeneous in structure than softwood. Libriform fibres perform the mechanical strength, while vessels are involved in the movement of liquid. Vessels are not interconnected by bordered pits and they have an open structure.

1.2.3 The wood cell wall

Cell wall structure of wood consists mainly of three main organic compounds: cellulose, hemicellulose, and lignin (Fig. 1-5). Table 1-3 shows the main chemical constituent of some wood species.

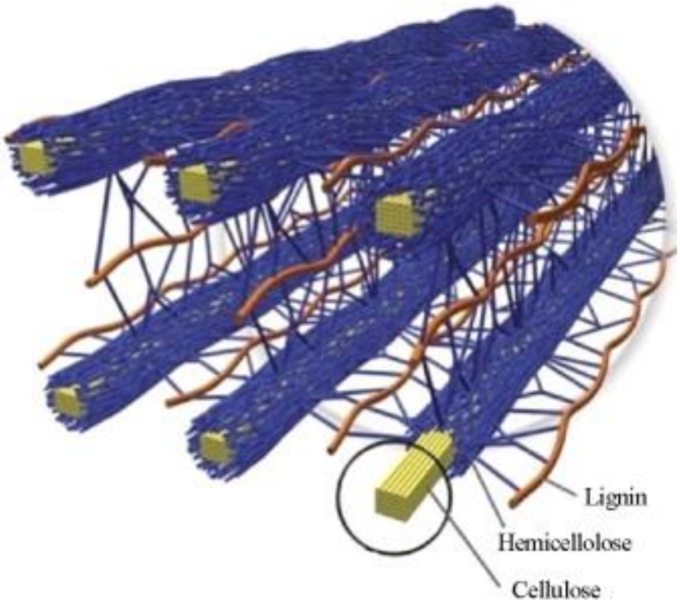

Fig. 1-5 Cell wall containing cellulose, hemicellulose, and lignin (Doherty et al. 2011).

Table 1-3 Chemical composition of some wood species.

Wood Specie	**Constituent (%)**			
	Cellulose	**Hemicellulose**	**Lignin**	**Extractives**
Scot pine (Pinus sylvestris)[a]	40.0	28.5	27.7	3.5
Spruce (Picea glauca)[a]	39.5	30.6	27.5	2.1
Eucalyptus (Eucalyptus camaldulensis)[a]	45.0	19.2	31.3	2.8
Silver birch (Betula verrucosa)[a]	41.0	32.4	22.0	3.0
Rubberwood (Hevea brasiliensis)[b]	39.0	29.0	28.0	4.0

a:(Sjostrom 1993), b: (Petchpradab et al. 2009)

1.2.3.1 Holocellulose (cellulose and hemicellulose)

Holocellulose is constituted principally of cellulose and hemicelluloses polymers with small amounts of other sugar for example pectin and starch (Stamm 1964). Cellulose content ranges from 40% to 50% of the dry wood weight, and hemicelluloses range from 25 to35%. These polymers are made up of simple sugars, mainly, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid, and lesser amounts of other sugars such as L-rhamnose and D-fucose. There are high densities of hydroxyl groups in these polymers which responsible for moisture sorption through hydrogen bonding.

1.2.3.2 Cellulose

Cellulose is the structural constitutive of the primary cell-wall of green plant as well as is the most occurring organic polymer on earth. These are called microfibrils in wood and it accounts for 40 to 50% in wood (Fengel and Wegener 1989). . The chemical formula of cellulose is $(C_6H_{10}O_5)_n$. It is consisted of monomer unit of Beta-D-glucose (Fig. 1-6a) that are upside down to bulid cellobiose (the repeating unit of the cellulose) dimeric units, (length about 1.03 nanometer) (Fig. 1-6b). This yields in the cellulose to be linear structure (Fig. 1-6c, d). The cellulose polymer is made from the cellobiose units that link together through glycosidic linkages. The degree of polymerization (DP) is the number of glucose units in one of cellulose molecular chain. The DP and chain length contribute to the various properties of cellulose. An approximate cellulose molecular weight value is about 10,000 to 150,000 (Rowell 2013). This factor significantly influences solubility, the efficiency of enzymatic hydrolysis of lignocellulosic biomass, as well as the mechanical properties of lignocellulosic biomass and derived products.

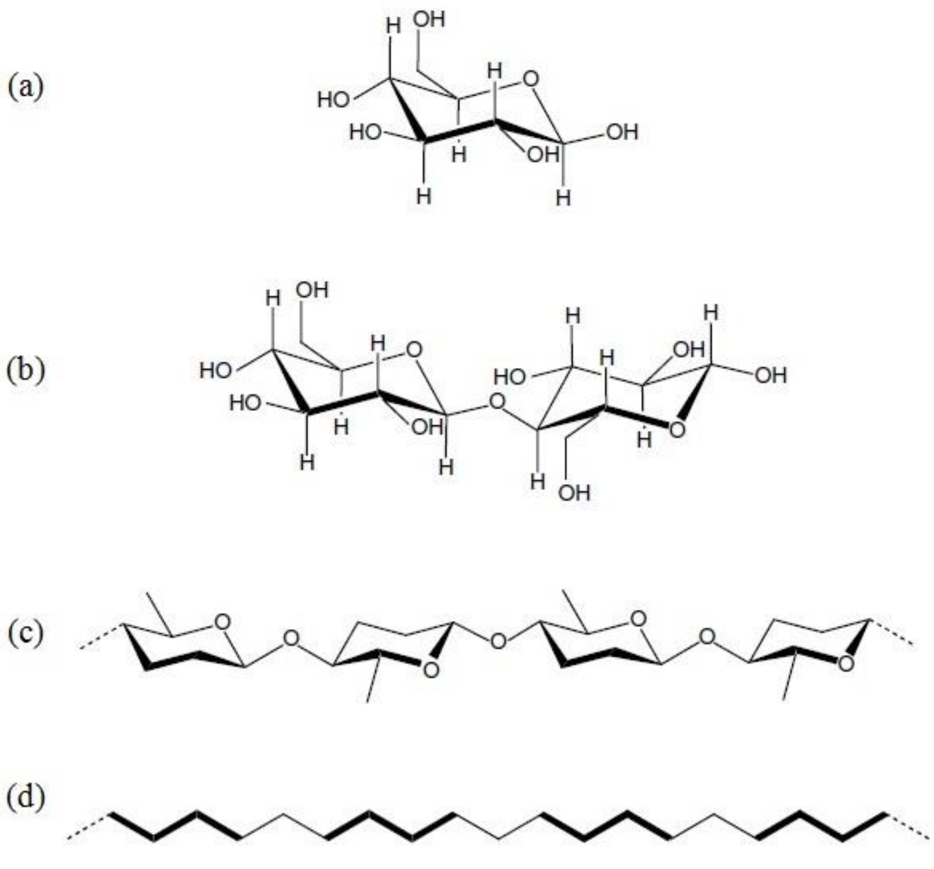

Fig. 1-6 The molecular structure of β–D-glucopyranose (a), cellobiose (b), cellulose glucopyranose backbone (c), and (d) a schematic of the glucopyranose units linear arrangement.

Crystalline cellulose will occur when the cellulose chains are regularized evenly, with respect to each other in some parts of the microfibril. While the cellulose chains are not regularized evenly, it is called amorphous cellulose. The crystalline nature of cellulose is due to stacking of layers of long cellulose chains one above the other held together by hydrogen bonds (Fig. 1-7). It is an excellent fiber forming polymer and thus offers strong structural support. The amorphous region of cellulose is hygroscopicity while the crystalline is not. These dissimilar regions of the cellulose provide dissimilar moisture characteristic.

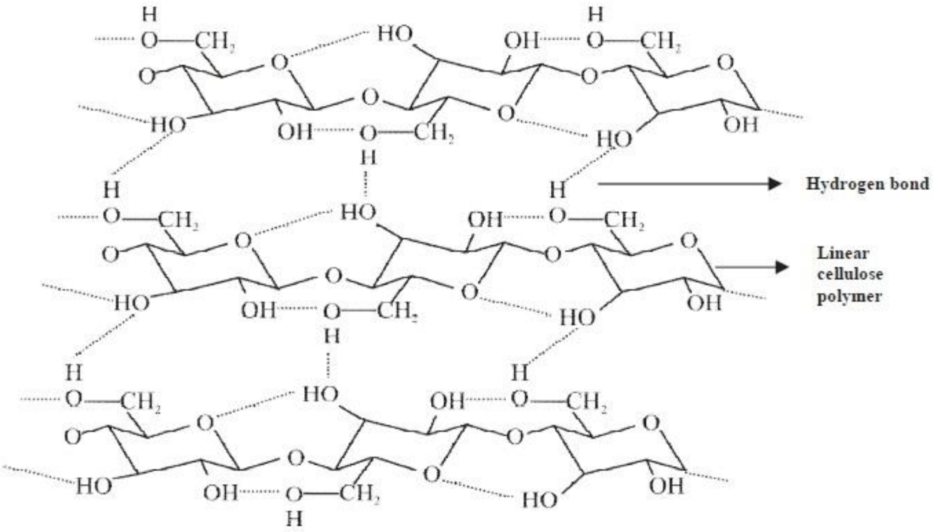

Fig. 1-7 Structure of cellulose showing hydrogen bonds within and between the cellulose molecules.

The application of industrial, cellulose is generally acquired from cotton and pulp of wood. Generally, it is applied to manufacture paper and cardboard and it is altered to a wide variety of derivative products for such as rayon and cellophane in a minor scale. Unlike starch, cellulose is a polymer with straight chain structure where no branching or coiling takes place, and an extended and rather stiff-rod conformation of the molecules are adopted. Cellulose microfibrils are formed when the multiple hydroxyl groups on the glucose unit from one chain forms hydrogen bonds with oxygen atoms on the same or a neighbor chain thus holding them firmly together giving them tensile strength higher. In the cell walls this tensile strength is significant, where the microfibrils are connected into a matrix of carbohydrate, resulting in the plant cells more rigid. The cellulose rigidness is a major limiting factor in the hydrolysis of cellulose.

Cellulose is more crystalline than other glucose polymers like starch. It becomes the amorphous state in water only at 320°C and pressure at 25 MPa. While crystalline-to-amorphous transformation of starch will occur when heated in water to. 60–70°C

1.2.3.3 Hemicelloloses

The second most substantial plant polysaccharides posterior cellulose is hemicellulose that it is not cellulose form. Hemicellulose is not only comprised glucose units, but a number of different pentose and hexose monosaccharides is also contained in it. Moreover, they also have some hydroxyl content that it acetylation occurred naturally and the carboxylate groups are also existed in the structures. Because the hemicelluloses have branches with short side chains composed of different sugars, they are different from cellulose Fig. 1-8. Due to the nature of hemicelluloses amorphous, they contain more hydroxyl content and they are more hydrophilic than cellulose in the cell-wall, more degradation and less thermal stability than cellulose or lignin (Hill 2006). Hemicellulose represent a sort of complex structures of heteropolysaccharides, along with xylose, mannose, glucose, galactose, arabinose, glucuronic acid, fructose, as well as galacturonic acid in many amounts depending on the source. The degree of polymerization of hemicelluloses of the order of 200–300 and usually smaller than cellulose, even though some can form crystalline units (Hill 2006).

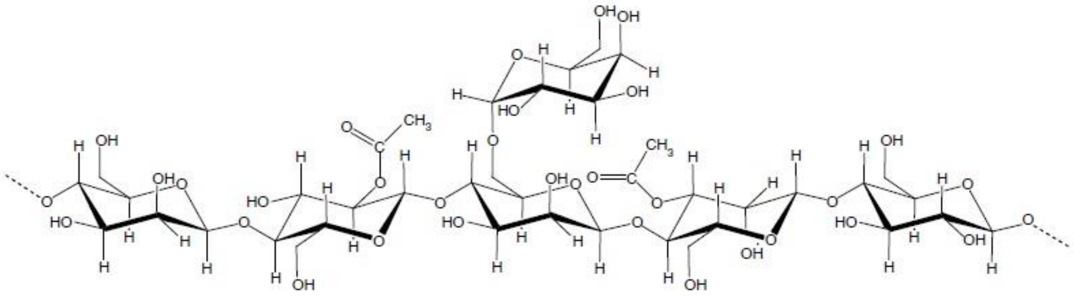

Fig. 1-8 The molecular structure of a hemicellulose (Hill 2006).

1.2.3.4 Lignin

Lignin is one of the most abundant polymeric aromatic organic components of wood cell wall. It is a highly amorphous phenolic polymer and the molecular weight of the lignin network in wood is undetermined. The chemistry of lignin has a varied, unique, and complicated chemical structure due to its three-dimensional molecule structure (Fig. 1-9). Moreover, lignin is the chemical responsible for part of the stiffness to the wood cell wall and also serves to bond individual cells together in the middle lamella region. The content of hydroxyl groups of lignin is lower than polysaccharide components. Hardwood lignins have a syringyl content varying from 20 % to 60 %, whereas softwood lignins have very low syringyl contents (Hill 2006). There is a wide variation of lignin structures within different wood species. The lignin content is commonly in the range of 18-25% and 25-35% of hardwoods and softwoods species, respectively. Lignin is associated with hemicelluloses forming lignin-carbohydrate complexes. There is no evidence that lignin is associated with cellulose (Rowell 2013).

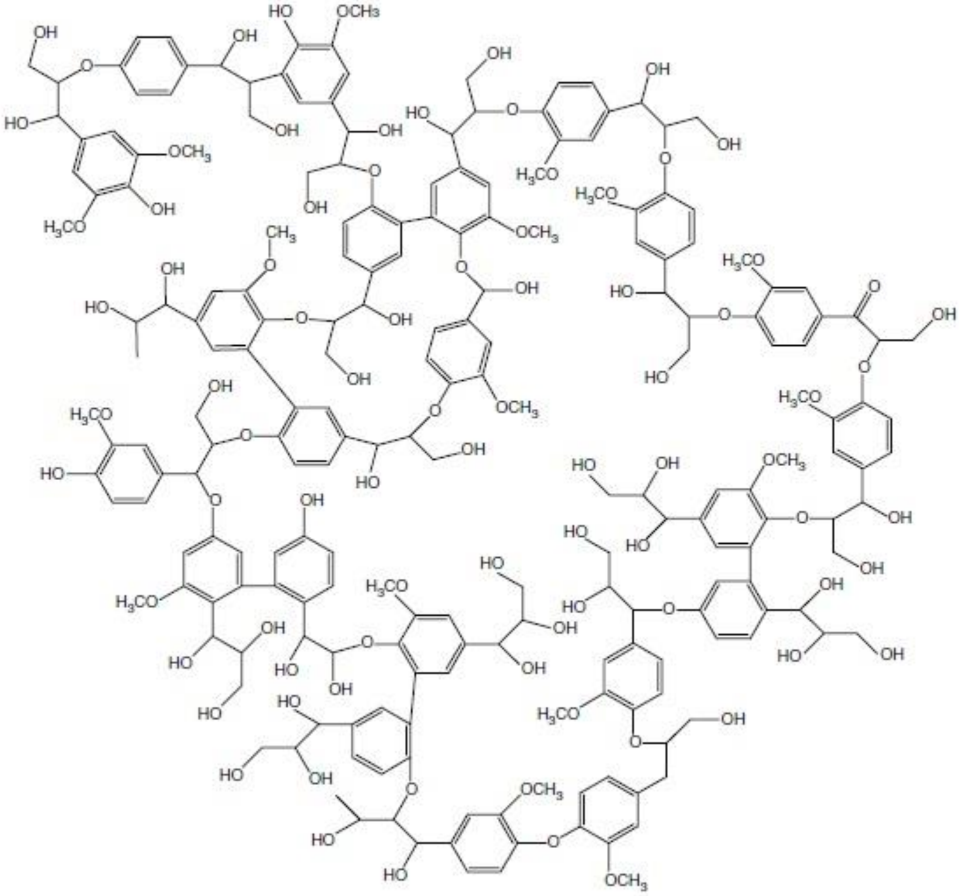

Fig. 1-9 A representative molecular structure of a softwood lignin (Hill 2006).

1.2.3.5 Extractives

The amount of extractives in wood varies from 0.5 to 20% by weight depending on the species. Extractives are a part of chemical constituents in the cell wall and they are complicated compositions of fats, phenols, rosin, resin acids, waxes, fatty acids, fatty alcohols terpenes, steroids, and various other minor organic compounds. The extractives content are generally less in hardwoods than in softwoods and they are mostly located in the heartwood of both hardwoods and softwoods. The extractives contribute to wood properties such as color, odor, and durability. The qualitative differences in extractive contents among wood species provide the basis of chemotaxonomy of woody (Hill 2006; Rowell 2013).

1.2.4 Moisture and wood

The amount of moisture content in freshly cut green wood can vary widely, in the range of 30-250%, depending on the age, species and growing conditions of the wood (Bousquet 2000). At the cellular level, moisture can exist in wood cells in three forms:

1. Free water, liquid filling the wood cell cavities.
2. Water vapor in the air of the cell cavities not totally filled by free water.
3. Bound water, vapor or liquid chemically bound the cellulose of the wood cell wall with hydrogen bonding.

In wood drying process, free water in the cell cavities leaves first due to it is only held by weaker capillary forces than the bound water. Then the bound water is released.

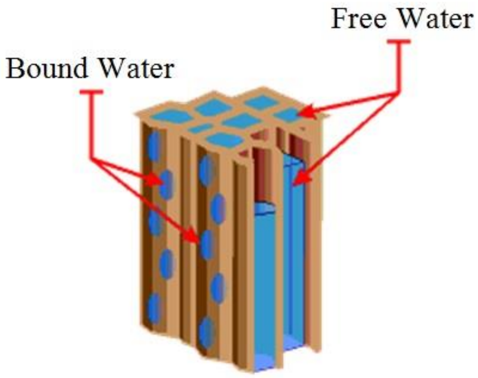

Fig. 1-10 Magnified wood section (Civil and Environmental Engineering).

The moisture content (MC) in wood is defined as the ratio of the mass of water in a wood piece and the mass of wood when no water is present Normally, MC is presented in percentage and calculated according to the following Equations (1-1) and (1-2).

On dry basis,

$$\text{Moisture content}\,(\%) = \frac{\text{Weight of water in wood}}{\text{Weight of total dried wood}}\,x100 \tag{1-1}$$

On wet basis,

$$\text{Moisture content}\,(\%) = \frac{\text{Weight of water in wood}}{\text{Weight of total dried wood and water}}\,x100 \tag{1-2}$$

1.2.4.1 Fiber Saturation Point

Fiber saturation point or FSP is occurred at the cell level. The hypothetical moisture condition of wood wherein the cell cavities are devoid of free water because all of the free water is removed but the cell walls are thoroughly saturated with bound water. The FSP is approximately 26-32% moisture content, depending on the species of wood (Dieste et al. 2010; Jalaludin et al. 2010; Skaar

1988). When the moisture in wood below its fiber saturation point state, wood will shrink as the cell walls lose moisture.

1.2.4.2 Equilibrium Moisture Content

Wood is hygroscopic material and its moisture content is directly related to the relative humidity and temperature in the surrounding air. The equilibrium moisture content (EMC) of wood occurs when wood reached an equilibrium condition with its surroundings and is neither gaining nor losing moisture at a specific air temperature and relative moisture (Hill 2006). When wood is kept in air with high moisture (relative humidity), it will absorb moisture and swell. When exposed to dry air, it will release moisture and shrinks until reaching a balance with its surroundings (equilibrium state) (Sik et al. 2009). The conditions of temperature and relative humidity are the essential factors to define the lowest content of moisture that can be accomplished when wood is used outdoor.

1.2.4.3 Shrinkage and swelling (Dimensional Stability)

Changes in dimension of wood occur when environmental humidity varies. When moisture content of wood below fiber saturation point and the amount of shrinkage and swelling is corresponding to the amount of bound water gained or lost, shrinkage and swelling will occur. Generally, the dimensionally stability of wood is occurred moisture content in wood higher than the fiber saturation point. Since, the amount of bound water are investigated the volume of cell wall, below FSP, wood will shrink when the cell walls lose moisture and wood will swell when the cell walls gain moisture. The final moisture content that the wood attains is directly related to the degree of shrinkage. The shrinkage values were consistent with drying wood from moisture content greater than 30% to moisture content 12%. The shrinking or swelling can cause the wood defects such as splitting, checking, loosening and warping. Accordingly, need to realize the importance of the dimensional stability of wood before selecting a wood product to use in the large moisture variations environment.

Wood shrinks most in the tangential direction or in the annual growth rings direction about twice as much as across the radial direction and negligible along the grain (longitudinally). These three main directions combination effect can affect the shapes of wooden objects. The shrinkage related with various sections cut from a log is presented in Fig. 1-11 (Ross 2010).

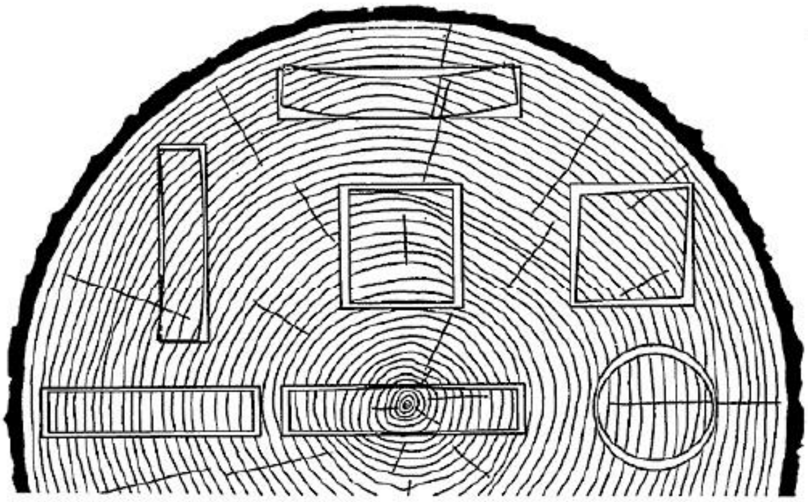

Fig. 1-11 Characterization of the distortion and shrinkage of square, flat and round pieces (affected by growth rings direction).

1.2.5 Rubberwood Processing

General step in rubberwood manufacture is displayed in Fig. 1-12. Rubberwood log is harvested (after its expiry from its rubber latex production) and transported to the wood processing manufacture. Because the freshly cut rubberwood is susceptible to degradation by mould and fungus due to its high contents of sugar and starch, it is impregnated with liquid chemical compound (borax-base chemical) under high pressure after it finishes sawmilling process of freshly cut rubberwood. All of impregnated woods will be left to conventional drying kiln to be dried to attain the required final moisture content. The conventional drying process performed at temperature in the range of 60-85°C for 7-12 days depending on thickness of the lumber and initial moisture content. This process will increase its durability and prevent cracking and splitting of surface. To ensure quality, dried rubberwood are appearance inspected for its defect before packing, storing and shipping to specific locations.

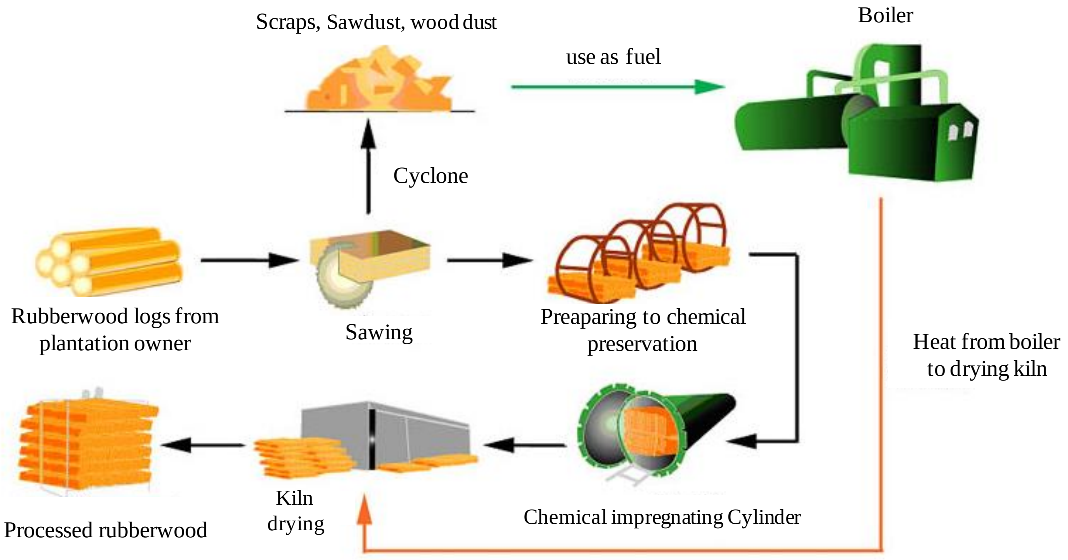

Fig. 1-12 Rubberwood processing in manufacture (Department of Industrial Works 2011).

1.2.6 Drying wood

Before the wood boards are used to make furniture, toys, equipment or any application, it must be dried to attain the required moisture content to increase the physical properties of the wood and especially improve its durability. Drying process can generally be classified into two major method; namely, ordinarily used procedures of air-drying and kiln-drying, and the specialized techniques using chemicals, solvents, vacuum system, solar energy, high frequency generators, etc. The suitable drying technique depends on size and species of wood. The moisture content of wood are reduced while drying to attain the desired final moisture content depending on its expected applications and also to avoid degrade (Bousquet 2000).

There are several advantages to dry wood as following:

- Product weight is reduce, shipping and handling costs also reduce because these costs based on the material weight.
- Kiln drying of wood is probably more appropriate than air drying when it is serious to:
    - shipping within a plan;
    - reduce drying costs in some situation because the air drying charge associated with storing and Other financial expenses;
    - accomplish a low moisture content (e.g., less than 12% to 15%).
- Minimize shrinking and swelling (dimensional instability) which occur as the wood changes in moisture content as seasonal changes in the relative humidity of the atmosphere.
- Suitably dried wood can certainly cut to exact dimensions and more easily work with machined.
- For fitted and fastened together with screws, nails, bolts, as well adhesives; parts of wood can be securely work.
- The deleterious effects of wood from uncontrolled drying such as warping, splitting, checking are widely eliminated.
- More effectively applied and maintained for paint, varnish and other finishes.
- Stain and decay resistance are improved if the wood is subsequently treated with preservatives or protected from excessive moisture adsorption.

1.2.7 Drying with Superheated steam

Superheated steam is a steam at a temperature greater than its boiling point at the absolute pressure where the temperature is determined, has been used for drying since the early 1900s and is known to have been used in industry at 1930s in Germany. Superheated steam drying relate to the application of superheated steam in a direct (convective) dryer instead of hot air, combustion, or flue gases as the drying medium supply heat for drying and to bring off the evaporated moisture. In the drying process, superheated steam will contact directly with product to be dried. Superheated steam drying has a number of important advantages over air drying. The evident benefit is that the dryer exhaust is steam, even though at lower specific enthalpy. The latent heat in the exhausted steam in the case of air drying is extremely expensive and difficult to recover. Some significant advantages of superheated steam are as follows (Mujumdar 2006):

- This technique can maximize the energy efficiency by recycling a main fraction of the exhaust steam. Thereby, this technique is usually performed in closed system to obtain high energy efficiency.
- In direct dryers, can be used superheated steam in stead of hot air. There is no oxygen in the system consequently it can be avoided oxidative or combustion reactions. Accordingly, it disposes the explosion hazards, risk of fire as well as obtains better quality product (such as color and some nutrients).
- Both constant and falling rate periods possibility effect to higher drying rates that depending on temperature of steam.
- Toxic or expensive organic liquids can consequently be recovered more conveniently than hot air drying.
- This process allows sterilization, pasteurization, and deodorization of products because the superheated steam process carried out with high temperature.

Superheated steam drying has gained an increasing interest in industrial applications for example food products, paper drying, as well as wood and biomaterials. At a very high operation temperature, temperature of wood is over the boiling point of water or 100°C, essentially enhances the flow of moisture inside wood (Bekhta P. and Niemz P. 2005).

1.2.7.1 Properties of superheated steam

Superheated steam occurs when steam has been obtained additional sensible heat to elevate its temperature level above the saturation temperature at a certain pressure. Although temperature is reduced, it will not lead to steam condensation on condition that the operation temperature is still higher than saturation temperature at the operation pressure, this phenomenon is different from saturated steam. Any moisture that is evaporated from the material does not need to be exhausted, but instead becomes part of the drying medium, therefore the drying medium is recycled in this process and also provided sensible heat is added. Drying medium is the key differences between superheated steam and conventional air drying. There are three obvious stages of superheated steam drying process:

In the first stage, preheating and condensation takes place, superheated steam is brought in direct contact with the product to be dried. The temperature of product material is increased to the boiling condition of water at processing pressure by allowing the product a part of its sensible heat. If this stage is not enough sensible heat in the superheated steam, may occur some condensation on the product or in the drying room.

The constant rate stage (second stage), the external resistance to water vapor exclusion from the surface of products is higher than the internal resistance to moisture diffusion. The hot air drying rate depends on the convective of heat transfer from the air to the product surface and water diffusion from the product surface to the air across the moisture boundary layer of product surrounding. In superheated steam drying, there is no water diffusive resistance across the boundary layer and water only moves by bulk flow. Moreover, the heat transfer coefficient of superheated steam is larger and water evaporation into superheated steam is higher than into dry air except when temperature of superheated steam attain to the saturation level. Under the same conditions, period of this stage for superheated steam take longer than hot air drying.

The third stage, the falling rate, during this stage, the drying rate decreases and the temperature of product increases. In this stage, the resistance of internal moisture transport is higher than the external resistance. Since temperature of product is greater, the superheated steam drying rate is larger than rate of hot air drying, and lead to greater moisture diffusion in the product. Additionally, casehardening or skinning may not occur thereby eliminating a possible obstacle intensive drying and the product is probably to be more porous also.

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1.2.8 Thermal modification of wood

Thermal modification of wood used to improve properties of wood such as decay resistance and dimensional stability, generally carry out in a temperature range of 180–260°C. Many techniques of thermally treatment of wood have been developed and commercialized in the past decade.

1.2.8.1 ThermoWood process (Finland)

Base on production capacity, among manufacturing technologies of wood, ThermoWood is the most extensively used in Europe. Two standard treatment types of ThermoWood are Thermo-S and Thermo-D, based on the durability and purpose applications. The ThermoWood process can divide into three main phases (International Thermowood Association 2003):

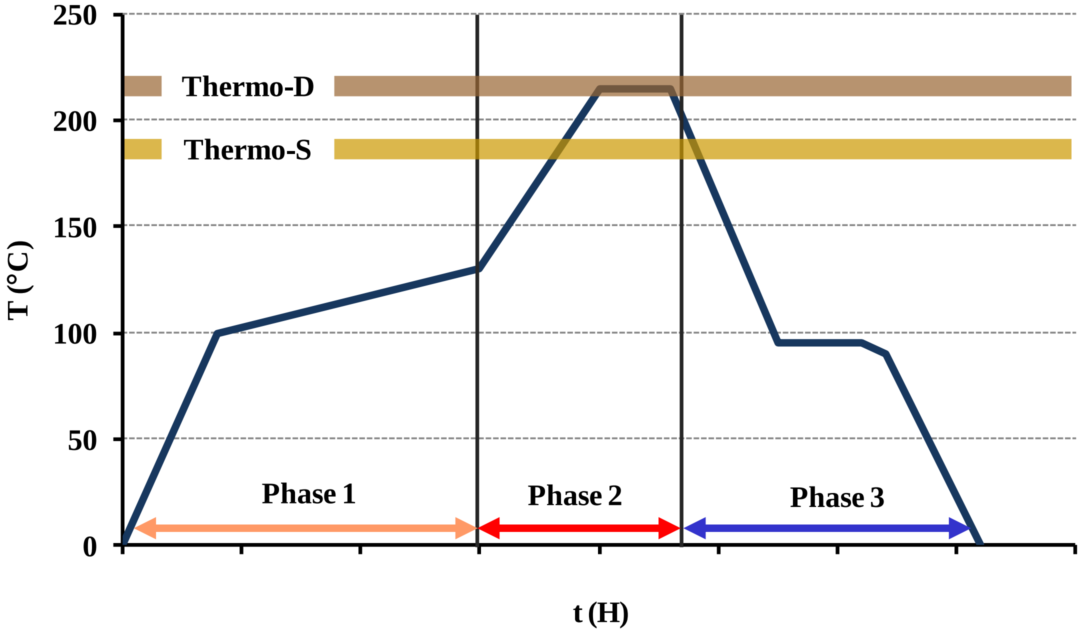


Fig. 1-13 Diagram of the ThermoWood production process.

Phase 1 (Temperature increase and high-temperature drying): The kiln temperature is increased speedily to about 100ºC. Then, the temperature is increased steadily to 130°C, during which time the high-temperature drying occurs and the moisture content in the wood reduces to nearly zero.

Phase 2 (Heat treatment): The kiln temperature is raised to about 185°C and 215°C. When attain the aim point, then maintain that temperature for two to three hours (depends on product's application).

Phase 3 (Cooling and moisture): Final stage, the temperature is lowered with water spray systems. When 80ºC–90ºC is reached re-moisturising occur allowing the moisture content of wood rise to a practicable level of 4-7%.

1.2.8.2 Plato-Process (Netherlands)

The plato process generally consists of two stages with an intermediate drying operation. The first stage, green or air dried wood is heated under pressure (saturated steam conditions) between 160 to 190°C. Then the heated wood is dried in conventional kiln to and subsequently heat again with superheated steam at atmospheric conditions to temperatures in range 170°C and 190°C. The process duration is depending on the species, shape and thickness, of wood etc., and applys a thermolysis step for 4-5 hours followed by an intermediate drying step for 3-5 days and a final is curing step for 14-16 hours (Militz and Tjeerdsma 2000).

1.2.8.3 Rectification process (France)

The rectification process uses nitrogen as heating media. Dry wood (moisture content of about 12%) is treated with this method in an oven at temperatures of 200 to 240°C and in a nitrogen atmosphere (below 2% oxygen) (Militz 2002).

1.2.8.4 OHT – Process (oil-heat treatment, Germany)

The hot oil process is operated in a closed vessel. After the wood is loaded into the vessel, hot oil with temperature about 180°C to 220°C is pumped into the system and keep this process temperature for 2-4 hours. For heating up and cooling down additional time is importance depending on the dimensions of wood. Crude vegetable oil is used to be the heating medium. This thermal treatment process serves for a fast and equal heat transfer to the wood and the same conditions all over the whole vessel; also oil serves as a perfect separation of oxygen from wood (Militz 2002).

1.2.9 Microstructure and physical changes of wood after heat treatment

Several chemical and physical properties of wood are altered after thermal modification. The extent of the change in wood properties during thermal treatment depends on the method of thermal modification, wood species and its characteristic properties, initial moisture content of wood, the surrounding atmosphere, as well as temperature and duration time of treatment process. Usually temperature factor is considered the most influential on various wood properties. The properties modification is mostly caused by thermal degradation of hemicelluloses.

The color changes can be used as an indicator of conversion. The wood appearance is characterized by color which occurred from the chemical substances (cellulose, hemicelluloses, lignin and extractives). After thermal treatment, the wood becomes in darker color, and its color is affected mainly by the color of the extractives, which make up a small percentage of the wood’s structure. Aldehydes and phenols are produced when wood is treated with high temperatures level, contributing to the formation of colored compounds in consequence of the chemical reactions that take place (Aydemir et al. 2010).

The anatomical structure of wood is affected by heat treatment and depended on the species of wood as well as the technique process and conditions applied. Generally, softwood species are highly sensitive to tangential cracks in the latewood section, particularly wood with narrow annual rings and/or an abrupt transition between earlywood and latewood. Investigation in radial crack, mostly found in wood structure with impermeable such as Norway spruce, affected by huge stresses occurred in the structure of wood during heat treatment. Epithelial cells around resin canals and parenchyma cells in the rays of treated pine sapwood are some damaged but in the heartwood portion has not been found this case. Hardwood species, such as poplar and beech, are importantly sensitve to collaps of the vessels and some deformation of the libriform fibres directly near the vessels. Thermal-treated birch and beech wood indicated radial cracks close to the rays. . In the softwood and hardwood species after thermal treatment, there is observation that the cell walls perpendicular to the fiber direction damaged leading to ruptures in transverse. This resulting in sudden fractures of treated wood as noticed in the test of bending, which can bring about highly many failure behavior after impact or mechanical stress. Decomposition of some thermal-treated softwood and hardwood species (small cracks between tracheids) was remarked after thermal treatment. Thermal treatment did not result in damage to the ray parenchyma pit membranes, bordered pits and large window pit membranes; the margo fibrils present without damage (Boonstra 2008).

1.2.9.1 Chemical changes of wood due to heat treatment

Cellulose, hemicelluloses and lignin, the main components of the wood cell wall, have differences in the thermal stability. These chemical constituent undergo degradation that affects the performance of wood when wood is reached to elevate temperatures. The extent of these changes depends on the heat and duration exposure conditions.

Hemicelluloses are less thermally stable than cellulose and lignin. They are the first component to be degraded caused by heat treatment (temperature from 160°C to 260°C) due to their low molecular weight and branching structure permits rapid degradation compared to the other components. The degradation of hemicelluloses starts by deacetylation, and acetic acid is released which acts as a depolymerization catalyst that further enhances polysaccharide decomposition (Fengel and Wegener 1989; Gunduz et al. 2010; Percin et al. 2016; Tjeerdsma et al. 1998). Acetyl group in hemicelluloses is a key factor in the thermal degradation. This compound is thermal unstable substances and result in the formation of acetic acid, consequently acid-catalyzed degradation of the polysaccharides is occurred. The release of acetyl groups from larch galactoglucomannans has been revealed to increase the thermal stability of the deacetylated hemicelluloses Loss of hemicelluloses causes an increase in crystallinity of wood, excluding those changes associated with degradation/rearrangement of the amorphous cellulose content (Hill 2006).

At higher temperatures, cellulose degrades more slowly than the hemicelluloses because of its crystalline structure which increasing the wood’s thermal stability. The crystalline cellulose degradation takes place particularly in a high temperature range from 300°C to 340°C (Hill 2006). Moreover, high temperature treatment was found to increase significantly the crystallinity of wood cellulose, to and to reduce hydroxyl groups from amorphous regions of cellulose and hemicelluloses. Consequently, dimensional stability and hygroscopicity of wood are improved (Sik et al. 2010). For lignin component, it degrades slower than cellulose and hemicellulose components; it is classified as the most stable component against thermal degradation.

The loss of polysaccharide substance on heating results in an increase in the lignin content of the wood. Commonly, lignin is the most stable polymeric material of the cell wall polymers against thermal degradation. Nevertheless, the degradation of lignin can occur after thermal modification in early stages of treatment, which the modification in lignin strongly depend on treatment temperature and process duration (Hill 2006). During the thermal treatment, bonds between phenylpropane units are partially broken. Aryl ether bonds between syringyl units break more easily than bonds between guaiacyl units. Thermochemical reactions are more ordinary for allylic side chains than aryl-alkyl ether bonds. The longer the autohydrolysis time is, the more condensation reactions take place. Both b-ketone and conjugated carboxylic acid groups are obtained as products from condensation reaction. As the temperature exceeds 200°C, lignin begins to decrease its mass; the b-aryl ether bonds start to break. At high temperatures, lignin’s methoxy content decreases and some of lingnin’s non-condensed units are transformed into diphenylmethane-type units. Consequently, diphenylmethane-type condensation is the most common reaction at temperature in the range of 120-220ºC. This reaction has an important effect on properties of lignin in thermal treatment, such as color, reactivity, and dissolution (International Thermowood Association 2003).

The extractive influence the color of heat treated wood. During thermal treatment, extractive tend to move toward the surface of wood and some extractive volatilize and it is the most volatile compounds withdraw from the wood while others are degraded. The emission profile of volatile organic compound (VOC) from heat-treated wood is used to determine the loss of volatile extractives during thermal treatment (Hill 2006).

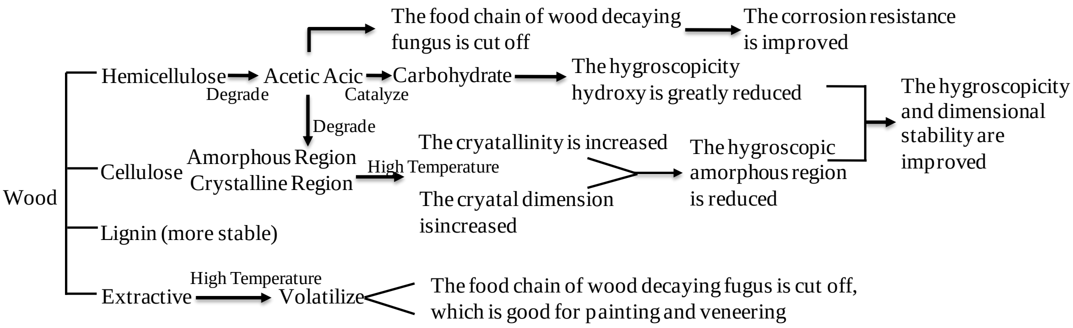


Fig. 1-14 Mechanism for thermally modified wood (Anhui Forwood Drying Equipment Co., Ltd. 2018).

The mechanism for thermally modified wood, as indicated by Liyang Forwood Wood Drying Equipment Co., Ltd. in China (Anhui Forwood Drying Equipment Co., Ltd.), is presented in Fig. 1-14. The company implements a heating process from 160-230°C, or commonly from 180-212°C to improve the quality of wood, lower the hygroscopicity of wood, improve the dimensional stability, corrosion resistance and weather fastness for the wood. An example drying schedule presented by the manufacturer showed a gradual temperature increase from 60°C to 190°C in about 25 hours, a holding period at 190°°C about 5 hours, a gradual decreasing period back to 100°C of about 20 hours, and a sharp decreasing period to 60°C in about 8 hours. From Fig. 1-14, the effect of heat treatment effectively changes the hemicelluloses wood structure into acetic acid and carbohydrate with low hygroscopicity. In addition, thermal treatment effectively increases the crystalline region in the wood cellulose while reducing the hygroscopic amorphous region. Other benefits claimed by the manufacturers include corrosion resistance, a more stable lignin region, and cutting off the food chain for wood decaying fungus.

1.2.10 Sorption in wood

Wood is a hygroscopic material, which means it naturally gains and loss water to equilibrate with its surrounding. Sorption isotherm of moisture in wood is characterized by the sigmoidal, which describes the relationship between the equilibrium moisture content (EMC) of wood and the relative humidity (RH) at a fixed temperature. Nevertheless, the sigmoid relationship is not unique to wood. Other material may exhibit different characteristic sorption isotherms. The sorption behaviors of wood have been discussed extensively in the literature, and many theoretical models have been acquired to describe this process. The classic sigmoidal shape of a sorption or desorption isotherm is deconvoluted into a monomolecular water layer and a multilayer component. The monolayer is related with the early sorption site (OH group), therefore it is probable to verify accessible hydroxyl group content of the wood. While polylayer constitutive where the cell wall bound water molecules are less closely associated with ith the fixed cell wall hydroxyl groups (Hill 2006). The Hailwood and Horrobin (H-H) model is a sorption model has been ordinarily used to describe the sigmoidal adsorption isotherm in wood science field

1.2.10.1 Hailwood-Horrobin Model

To describe the sorption isotherm on plant-based materials, including wood, the Hailwood and Horrobin (H-H) model (Hailwood and Horrobin 1946) is usually used. A physical representation of the H-H model is shown as Fig. 1-15. The H-H model originally developed and applied to elucidate for the sorption isotherm of cotton, then this model has been extensively applied examine the sorption behavior of wood (Siau 1984; Skaar 1972).

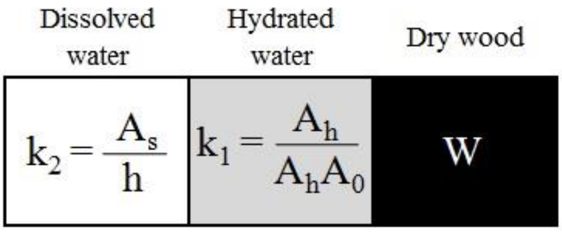


Fig. 1-15 Physical representation of the H-H model (Dieste et al. 2010).

It is assumed that molecules of water vapor are attracted to a surface. The water present in the wood cell wall are considered by the H-H model that can exist in two states; called monolayer water (water of hydration corresponding to water molecules which are hydrogen bonded to the hydroxyl groups of cell wall) and polylayer water (dissolved water or solid solution corresponding to water molecules that are located within the micropores of cell wall but that are less constrained). Then, three chemical constituents are appeared in the wood cell wall; unhydrated (dry) wood, hydrate wood (chemisorbed water) and dissolved water (polylayer water), serve as an ideal solution (Hailwood and Horrobin 1946). If the number of moles of unhydrated wood, hydrated wood (thus the moles of hydration number, presuming one mole of water of hydration per mole of hydrated wood), and dissolved water are specified as X_0, X_h, and X_s, respectively. The terms the molecular weight of polymer per mole of water sorption sites (i.e. accessible hydroxyl groups) are possible used to examine the molecular weight (W) of the wood cell wall polymers. According to H-H theory, the molecular weight per sorption site can be estimated, if we know the mole numbers of sorption sites per weight (gram) of dry wood. The total number of moles of the three species is $X_0 + X_h + X_s$. Since this solution is presumed as an ideal solution, therefore the activities A_0, A_h, and A_s of these three species are equal to their mole fractions in the solution, or

Unhydrated; $$A_0 = \frac{X_0}{(X_0 + X_h + X_s)} \qquad (1\text{-}3)$$

Hydrated;
$$A_h = \frac{X_h}{(X_0 + X_h + X_s)} \tag{1-4}$$

Solution;
$$A_s = \frac{X_s}{(X_0 + X_h + X_s)} \tag{1-5}$$

When an equilibrium condition of the three constituents are attained as form as below:

$$A_0 + A_s \overset{k_1}{\rightleftarrows} A_h$$

The equilibrium constant k$_1$, is prescribed as the proportion of the activity Ah of the hydrate (reaction product) against the products of the activities of two reactants, unhydrated wood and dissolved water.

Consequently

$$k_1 = \frac{A_h}{(A_0 A_s)} = \frac{X_h}{(X_0 A_s)} \tag{1-6}$$

Or

$$X_h = k_1 X_0 A_s \tag{1-7}$$

Furthermore, when an equilibrium state between the relative vapor pressure in the atmosphere (h) and the dissolved water are reached as form as below:

$$h \overset{k_2}{\rightleftarrows} A_s$$

Thus

$$k_2 = \frac{A_s}{h} \tag{1-8}$$

Or

$$A_s = k_2h \tag{1-9}$$

The ratio $X_h/(X_h + X_0)$ provides the moles X_h of hydrated wood, and of water of hydration, per mole of dry wood, because this is equal to $X_h + X_0$. Then, merging equations (1-7) and (1-8) gives:

$$\frac{X_h}{X_h + X_0} = \frac{k_1X_0k_2h}{k_1X_0k_2h + X_0} = \frac{k_1k_2h}{k_1k_2h + 1} \tag{1-10}$$

The ratio Xs / (Xh + Xo) presents the number of moles of dissolved water per mole of dry wood. This is acquired by inverting equation (1-5) and rearranging, then inverted and combined with equation (1-8).

$$\frac{(X_h + X_0)}{X_s} = \frac{1}{A_s} - 1 = \frac{1 - A_s}{A_s} \tag{1-11}$$

$$\frac{X_s}{X_h + X_0} = \frac{k_2h}{1 - k_2h} \tag{1-12}$$

The sum of equations (1-10) and (1-12) is obtained the total number of water moles in the wood polymer per dry wood. According to The grams of water divided by the water molecular weight of (18) are equivalent to the moles of water, grams of dry wood divided by the wood molecular weight per mole of sorption sites are equivalent to the moles of dry wood. Thus:

$$\frac{X_h}{X_h + X_0} + \frac{X_s}{X_h + X_0} = \frac{\left[\left(\frac{\text{hydrated water, g}}{18}\right) + \left(\frac{\text{dissolvedd water, g}}{18}\right)\right]}{\left(\frac{\text{dry wood, g}}{W}\right)} \tag{1-13}$$

$$\frac{X_h + X_s}{X_h + X_0} = \left(\frac{W}{18}\right) \times \frac{[(\text{hydrated water, g}) + (\text{dissolvedd water, g})]}{(\text{dry wood, g})} \tag{1-14}$$

$$\frac{X_h + X_s}{X_h + X_0} = \left(\frac{W}{18}\right) \times (m_h + m_s) = \left(\frac{W}{18}\right) \times m \tag{1-15}$$

Where m is total fractional moisture content (m = m_h + m_s), W is the apparent molecular weight of the wood per mole of sorption or hydration sites, m_h and m_s are the moisture contents corresponding to the hydrated and dissolved water, respectively, all based on the dry weight of wood. Equation (1-16) can be rearranged after combining with equations (1-10) and (1-12) to give.

$$m = m_h + m_s = \left(\frac{W}{18}\right)\left(\frac{k_1 k_2 h}{1 + k_1 k_2 h} + \frac{k_2 h}{1 - k_2 h}\right) \tag{1-16}$$

If relative humidity H = 100h, and %moisture content M = 100m:

$$M = M_h + M_s = \left(\frac{1800}{W}\right)\left(\frac{k_1 k_2 H}{1 + k_1 k_2 H}\right) + \left(\frac{1800}{W}\right)\left(\frac{k_2 H}{100 - k_2 H}\right) \tag{1-17}$$

The term 18/W is equivalent to m_1, the moisture content corresponding to complete hydration of all of the available sorption sites in the wood.

Since term 18/W is equivalent to the fractional moisture content, m_1, when single molecule of water on each available sorption site, so:

$$m_1 = \frac{18}{W}\left(\frac{g}{g}\right) = \left(\frac{1800}{W}\right)(\%) \tag{1-18}$$

The two equilibrium constants k_1, k_2, together with W (or m_1) in equations (1-16) and (1-17), determine the sorption isotherm. Likewise, they determine the magnitude of water of hydration (M_h) and water of solution (M_s), the total moisture content M at any vapor activity H, at any vapor activity H. Equation (1-17) can be rearranged into:

$$\frac{H}{M} = \left(\frac{1800}{W}\right)\left(\frac{(100 + k_1k_2H)(100 - k_2H)}{k_2(100 + k_1k_2H) + k_1k_2(100 - k_2H)}\right) \tag{1-19}$$

$$\frac{H}{M} = \left(\frac{W}{18}\right)\left(\frac{1}{k_2(k_1 + 1)}\right) + \left(\frac{W(k_1 - 1)H}{1800(k_1 + 1)}\right) - \left(\frac{W}{180000}\right)\left(\frac{k_1k_2H^2}{k_1 + 1}\right) \tag{1-20}$$

Rewriting equation (1-20) in a simple empirical equation which:

$$\frac{H}{M} = A + BH - CH^2 \tag{1-21}$$

Where

$$A = \left(\frac{W}{18}\right)\left(\frac{1}{k_2(k_1 + 1)}\right) \tag{1-22}$$

$$B = \left(\frac{W}{1800}\right)\left(\frac{k_1 - 1}{k_1 + 1}\right) \tag{1-23}$$

$$C = \left(\frac{W}{180000}\right)\left(\frac{k_1k_2}{k_1 + 1}\right) \tag{1-24}$$

Thus the H-H sorption theory can estimate the relationship of parabolic between the proportion H/M and H. Then fitting the second order polynomial parameters to calculate empirical parameters (A, B and C). And it is capable to calculate the three fundamental constants k_1, k_2 and W, as well as M_h and M_s.

$$k_1 = 1 + \frac{B^2 + B\sqrt{B^2 + 4AC}}{2AC} \qquad (1\text{-}25)$$

$$k_2 = \frac{50\left(-B + \sqrt{B^2 + 4AC}\right)}{A} \qquad (1\text{-}26)$$

$$W = 1800\sqrt{B^2 + 4AC} \qquad (1\text{-}27)$$

1.2.11 Biological degradation of wood

Wood is degraded by several biological threat agents such as bacteria, moulds, blue stain, insects, termites, as well as wood rotting fungi (i.e. soft-, white and brown rots), if there are availability for the appropriate environmental conditions. The significant food source in wood is the carbohydrates such as sugars and hemicelluloses (Rowell 2013).

According to a natural material, wood is susceptible to fungal degradation and the rate of degradation is dependent on the wood species and the micro-organisms involved. Wood decay fungi are micro-organisms that the wood is consumed when the adequate conditions are available (source of nutrients, moisture, oxygen as well as heat and proper pH). The best method to protection fungal attack is to improve the wood to be a moisture resistance material. Wood-destroying fungi are divided into three main classes; brown rot, white rot and soft rot types.

Food or nutrients is the wood organic constituent (hemicellulose, cellulose, and lignin), which is destroyed by the fungus (Rowell 2013). For the other major factors (moisture, oxygen and heat), fungal spores growth on the surface and form microscopic tubes or tiny filaments known as hyphae. One potential approach to protection wood is to use its extractives which improve fungal resistance. Because heartwood has significantly more extractives than softwood, heartwood is more resistant to fungal attack than softwood (Tsoumis 1991).

The optimum combination of moisture and weather provide proper fungal growth conditions. These factors are considered simultaneously because the void space in wood which are filled with either air or water. Decay fungi require a moisture content of wood at least 20% to start any growth, and upper moisture contents (above 29%) are adequate condition for fungal attack. However, if very large quantities of water substitute air from wood, lack of oxygen necessity for life-sustaining of fungus is occurred, and it will slow or prevent degradation from decay fungi (Tsoumis 1991).

The effects of heat on fungal growth in wood depend on many factors, especially on the air temperature. The most favorable temperature for the growth of fungi is in the range of 20°C and 30°C. In the case of pH factor, appropriate pH for fungal development ranges between 4.5 and 5.5. Concurrently with the tendency to form more acidic products in wood by growth of them due to their metabolism (Tsoumis 1991).

Subterranean termites are some of the most common type of termites that infest homes. The colony of them is divided into three different functional castes (reproductives, workers, and soldiers). These termites closely associated with the soil, where they typically build their main underground nest, therefore “subterranean termites” is the name. They can penetrate narrow tunnels through the soil to reach water and food. Soil acts as a source of moisture that is essential factor in survival of subterranean termites. Termites generally prefer attack the softer earlywood than the harder latewood. The essential food of subterranean termites is cellulose acquired from wood and other plant tissues (Rowell 2013).

1.3 Review of Literatures

Wood from rubber tree (*Hevea brasiliensis Muell*. Arg.) is a significant raw material available in South-East Asia, including Thailand. It has been utilized in an extensive variety of products such as furniture, toys, playground equipment, etc. However, this wood species is low strength, high hygroscopicity, low durability and less dimensional stability (Umar et al. 2016). Hence, modification by thermal treatments has been suggested as an eco-friendly alternative method to improve wood properties (especially dimensional stability, biological durability, and hygroscopicity) avoiding the use of toxic chemical preservatives (Calonego et al. 2010; Gündüz et al. 2008a; Percin et al. 2016; Schneid et al. 2014)

An important characteristic of rubberwood is its hygroscopicity. Generally, wood, is hygroscopic material, responding to humidity because of its hydrophilic cell-wall polymers (cellulose, hemicellulose and lignin). These cell-wall polymers contain hydroxyl groups, which attract water and hold it by hydrogen bonding (Chauhan et al. 2001). When wood is kept in air with high moisture (relative humidity), it will absorb moisture and swell. When exposed to dry air, it will release moisture and shrinks until reaching a balance with its surroundings (equilibrium state) (Sik et al. 2010). Usually, water in wood appears in two forms: free water and bound water. Free water is found in liquid and vapor state in cell lumens and other voids in the wood. Free water is held only by weak capillary forces and cannot cause changes in physical properties (i.e. swelling or shrinking), because the cell-wall is saturated by bound water. Bound water or hygroscopic water is found in the cell-wall and is bound to the cell-wall polymers with hydrogen bonds (Siau 1984). As the free water is released, the cell cavities can become empty; however, the cell-walls retain the bound water. The moisture content reaches the fiber saturation point (FSP) during equilibration at 100% RH (Dieste et al. 2010).

Superheated steam technology has been proposed and applied to various industrial fields such as foods, agricultural materials as well as wood products. Previously, (Yamsaengsung and Tabtiang 2011) compared the drying time and mechanical properties of the rubberwood using hybrid superheated steam and hot air to conventional drying, they found that the drying time of hybrid system was reduced more than 60% and mechanical properties of the rubberwood after hybrid superheated steam drying were improved from those of control cases. Furthermore, (Yamsaengsung and Sattho 2008) reported that the superheated steam can reduce stress and eliminate cracking during superheated steam vacuum drying of rubberwood. Besides, drying time was less than 20 hours and the mechanical properties of wood were improved. (Bao and Zhou 2017) conducted a study which analyzed Chinese cedar (*Cryptomeria fortunei*) wood after conventional and superheated steam drying. The findings indicated that wood samples after superheated steam drying had lower hygroscopicity and improved dimensional stability. Previously, (Gawron et al. 2011) reported that heat treatment of the beech wood in superheated steam at 220°C for 10 h reduced hemicelluloses content to almost 90% from the untreated baseline.

Three fairly similar heat treatments have been developed in Europe in the recent years: Retiwood, developed in France, Thermowood®, developed in Finland by VTT, and Plato®wood developed in The Netherlands (Esteves et al. 2013). These processes autoclave the treated wood, submitting it to heat and pressure, including water vapor or nitrogen to control drying in a treatment process ranging from 24 to 48 hours at temperatures ranging from 180 to 230°C depending on the species of wood. The FSP of wood is also influenced by heat treatment. (Jalaludin et al. 2010) and (Bal 2015) pointed out that the FSP of heat-treated wood was below that of the control samples. This property was affected because the hygroscopic constituents of wood (hemicelluloses) were degraded; leading to the loss of sorption sites (Olek et al. 2012). Sik et al. (2010) found wood crystallinity of rubberwood increased after high temperature drying (100°C to 150°C), reflecting the loss of hemicellulose and the presence of fewer water/hydrogen bonding sites within the cell wall. This resulted in a reduction in hygroscopicity and sorption capacity for rubberwood dried at 130°C, compared to conventional drying 60°C.

Thermal treatment also improves the natural decay resistance of wood due to changes in the chemical composition of wood, especially reduced hemicelluloses that would be available food to fungi (Calonego et al. 2010). Moreover, an increase of the treatment temperature changed the color into a darker shade, caused by decreased content of hemicelluloses, especially the pentosans.

In the study by (Percin et al. 2016), compression strength parallel to grain and hardness of wood increased with heat treatment at 150°C, and at 175°C for 1, 3 or 5 h, from those of untreated samples. However, thermal treatment at temperatures up to 200°C degraded the mechanical properties of beech wood. For rubberwood, Sik et al. (2009) observed that compression strength parallel to grain and hardness tend to increase with drying temperature in the range from 100 to 150°C from those achieved at conventional temperature (60°C)

(Kačíková et al. 2013) found an increase degree of cellulose crystallinity for Norway spruce wood subjected to thermal treatment at 113-271°C, caused by the degradation of hemicelluloses and less ordered cellulose. Thermal treatment also improves the natural decay resistance of wood due to changes in the chemical composition of wood, especially reduced hemicelluloses that would be available food to fungi (Calonego et al. 2010). Moreover, an increase of the treatment temperature changed the color into a darker shade, caused by decreased content of hemicelluloses, especially the pentosans.

(Akyildiz and Ates 2008) found that the equilibrium moisture content (EMC) of oak, chestnut, calabrian pine, and black pine decreased with the temperature (130°C, 180°C and 230°C) and time (2 and 8 h) of heat treatment. Similaly, (Majka et al. 2016) discovered that the EMC of the treated wood can decrease by up to 50% due to heat treatment at 240°C for 5 h. Likewise, (Olek et al. 2012) investigated the effects of heat treatment at 180°C and 220°C on hygroscopicity of poplar and European beech wood. The heat treatment substantially decreased the EMC of wood and the active sorption sites of wood treated at 220°C were reduced to about a third of the initial number of sites. Furthermore, Sik et al. (2010) dried rubberwood from its green condition (at 130°C) and found that the EMC of dried rubberwood (at 60% RH and at 90% RH, at 30°C) was below that of conventionally dried rubberwood.

An adsorption isotherm is measured by determining the EMC of wood at various RHs, but at a fixed temperature. Hailwood-Horrobin (H-H) theory of sorption was used here to fit the isotherm of wood, considering wood material a polymer. This theory assumes that the water sorbed exists in two forms; namely; water of hydration and dissolution water; in the cell-walls. The hydration water or monolayer water corresponds to water hydrogen bonded to the cell-wall OH groups. The dissolved water or polylayer corresponds to water in less constrained state, but however situated within the micropores of cell-wall (Hailwood and Horrobin 1946). (Ohmae et al. 2009) analyzed water adsorption of heated bamboo using the H-H model and found that the amount of hydroxyl groups (water adsorption ability) in bamboo decreased with heat treatment at 200°C for 2 to 5 h. Moreover, (Obataya et al. 2000) studied the effects of heat treatment at 140°C -200°C for 8 h on the hygroscopicity of hinoki wood, finding that the EMC (at 25°C and 100% RH) and the amount of available adsorption sites (estimated from the H-H model) were reduced. Furthermore,(Li et al. 2017) applied the H-H theory to evaluate the hygroscopicity of modified poplar wood treated at 170°C and 210°C for 3 h. They reported that the monolayer moisture content of wood decreased with heat treatment temperature.

1.4 Objectives

- To study mechanical and physical properties of rubberwood after superheated steam treatment at various conditions.
- To determine the optimum treatment process using high temperature superheated steam base on mechanical properties and effectiveness in increasing the product’s resistant to fungal and termite attack.

CHAPTER 2

Research Methodology

2.1 Materials

Rubberwood (Hevea brasiliensis) flat-sawn board (see Fig. 2-1) that is generally used for making furniture, with dimensions approximately 110 cm long x 10.5 cm wide x 2 cm thick, were obtained from a manufacturer of rough sawn rubberwood, in Songkhla province, Thailand.

The samples were pre-dried to an average 10±2% moisture content on dry basis, prior to the superheated steam treatments. The conventional drying process performed in an industrial-scale operation used temperature in the range of 60-85°C and steam was also sprayed into the kiln for a short period as kiln schedule. This process usually takes 7 to 12 days to attain the required final moisture content of a product (varying from 6 to 16% d.b.) depending on its intended applications.

Fig. 2-1 Rubberwood (*Hevea brasiliensis*) flat-sawn board

2.2 Experimental Setup

Fig. 2-2 demonstrates the experimental setup schematic diagram. A 1.5 m^3, 2kW electrical chamber was started up by heating its air temperature from 32°C (room temperature) to 140, 150, or 160°C. The saturated steam at 100°C and 1 bar was fed into the closed-loop hot air circulation driven by the top centrifugal blower. The temperature of the mixed atmosphere (hot air + superheated steam) decreased by approx. 10 to 20°C from its set point on feeding steam at 100°C and 1 bar into the chamber. The temperature then increased back to its set-point within 30 min. At the steady state, the temperature of superheated steam was controlled at the set point; the rubberwood boards were then fed into the chamber. During treatment, the moisture evaporated from wood and excess steam were released to ambient air.

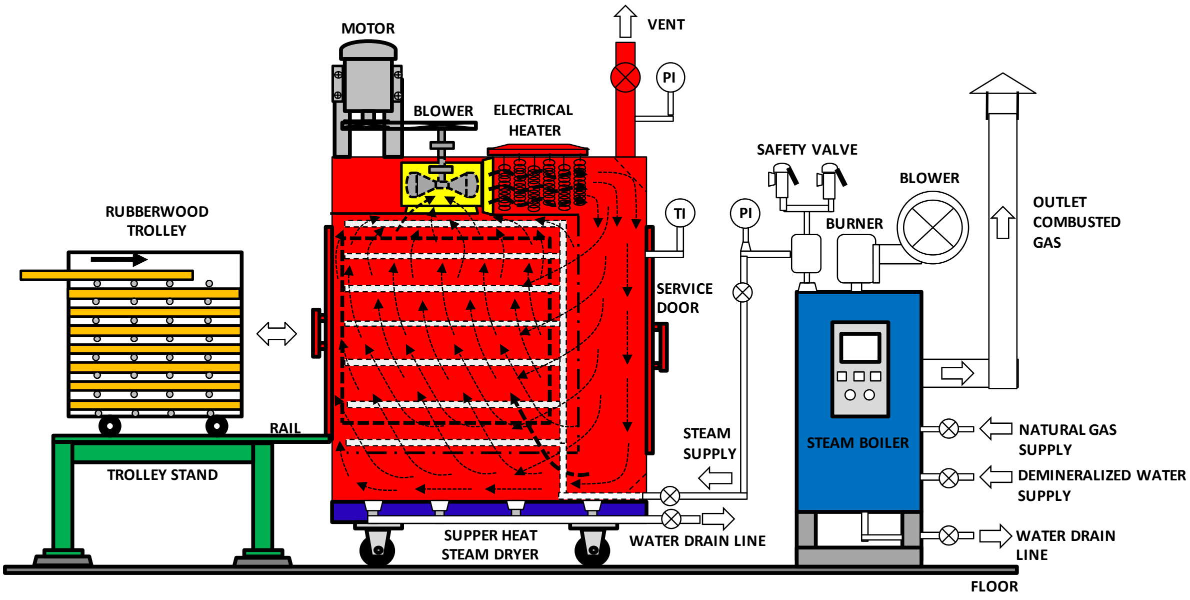


Fig. 2-2 Schematic of a pilot scale high temperature dryer using superheated steam (1.5 m^3).

Fig. 2-3 Actual equipment setup.

2.3 The treatment with superheated steam

The superheated steam heat treatment experiments were conducted in the Pilot-Scale Superheated Steam treatment chamber. Three temperatures (140, 150, and 160°C±1°C) and three durations (1, 2, and 3 h) under atmospheric pressure and in the presence of air were applied to the wood boards.

2.4 Properties of Rubberwood

2.4.1 Mechanical Properties

Four methods were carried out for evaluating mechanical properties of rubberwood samples by Universal Testing Machine (Amsler, Germany) with 4000 kgf capacity at Department of Civil Engineering at Prince of Songkla University. In this study, the testing of mechanical properties of wood includes the following:

Compressive strength parallel-to-grain (ISO 3787 1976). Test samples were prepared in the dimensions of 15 mm x 15 mm x 60 mm. Load was applied to the sample in the parallel to grain direction until it was damaged.

Hardness (ISO 3350 1975). Test samples were prepared in the dimensions of 50 mm x 50 mm x 70 mm. To determine the load required to embed an 11.28 mm (0.444") diameter steel ball to one-half its depth into the wood sample by using the modified Janka hardness test.

Impact strength (ASTM D143 2000 p. 143). Test samples were prepared in the dimensions of 20 mm x 20 mm x 300 mm. A specific weight hammer was dropped upon a beam from successively increasing height until rupture occurred or the beam deflected 152 mm (6 inches) or more.

Tensile Strength perpendicular to grain (ISO 3346 1975). Test samples were prepared in the dimensions of 20 mm x 20 mm x 70 mm with V shapes of both ends. The test sample was inserted into the claw grips of the machine then applied loading on the sample in the perpendicular-to-grain direction unitil it was broken.

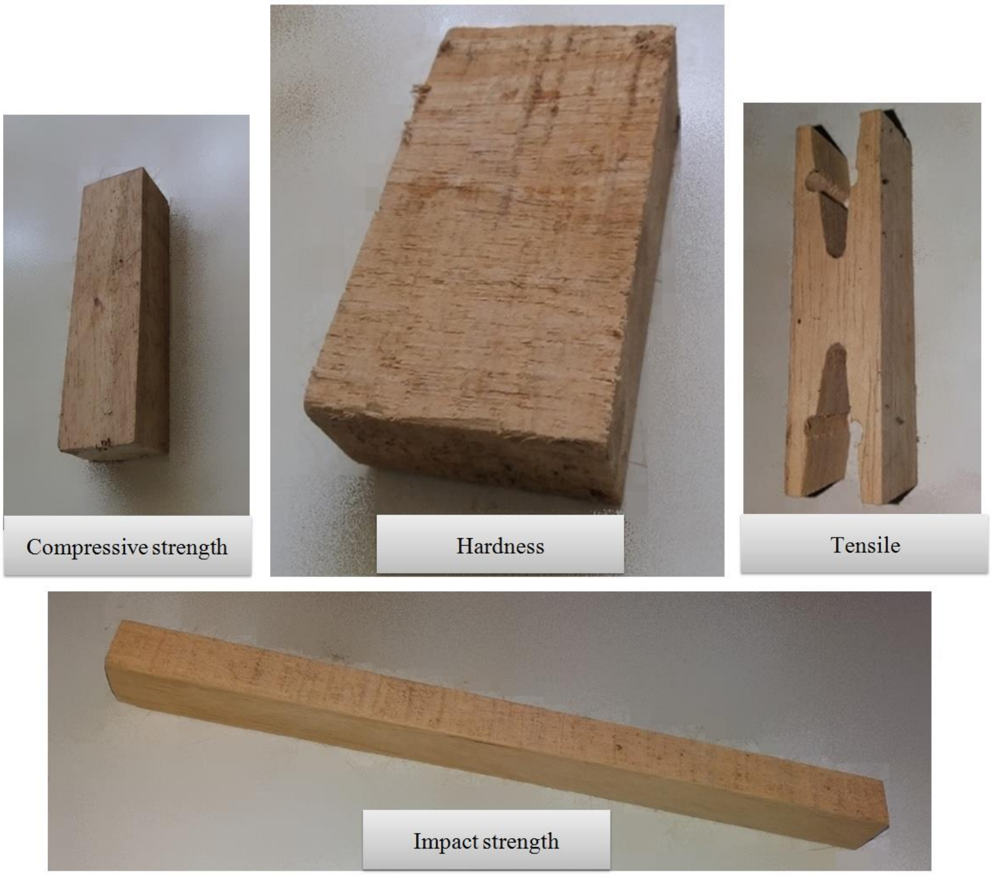


Fig. 2-4 The specimens of rubberwood for mechanical tests.

2.4.2 Moisture sorption isotherms

After treatment, rubberwood specimens were cut into 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) from treated and untreated control boards, and were carefully smoothed with sandpaper to remove loosely adhering fibers.

Table 2-1 Selected salt solutions and their corresponding relative humidities at 30°C (Greenspan 1977).

Salt	**RH (%)**
LiCl: Lithium chloride	11
$MgCl_2.6H_2O$: Magnesium chloride	32
K_2CO_3: Potassium carbonate	43
$Mg(NO_3)_2.6H_2O$: Magnesium nitrate	51
NaCl: Sodium chloride	75
KNO_3: Potassium nitrate	92

The relative humidity (RH) of air was controlled as explained by (Stamm 1964). The specific salts used for the tests and the corresponding relative humidities are listed in Table 2-1. Each RH values prevail at equilibrium with the saturated salt solutions, where excess salt in solid state must be maintained to assure saturation. The specimens were placed on a mesh platform above a salt solution in a glass chamber, with three wood samples per container (**Fig. 2-5**). The containers were kept at 30±2°C room temperature (Chauhan et al. 2001).

Fig. 2-5 Experimental apparatus for the sorption isotherms measurement.

Each sample was weighed on an electrical balance (OHAUS) with a precision of 0.001 g, continuing adsorption until constant weight. The equilibrium moisture content (EMC) was calculated from

$$M = \frac{M_e - M_d}{M_d} \times 100 \tag{2-1}$$

where M is the equilibrium moisture content on dry basis (%), M_e is the mass of the specimen at equilibrium (g), and M_d is the mass of specimen (g) after oven-drying at 103±2°C for 24 h. The Hailwood and Horrobin theory was used to analyze the results of experiment. Because the Hailwood-Horrobin model can be applied at any RH level, the absorption parameters were determined from the moisture contents at all six relative humidities used.

2.4.2.1 Isotherm model fit and adsorption properties

In the (Hailwood and Horrobin 1946) theory, the total amount of adsorbed water is separated into monolayer and polylayer components. The equation of model as follows:

$$M = M_h + M_s = \frac{1800}{W}\left(\frac{k_1 k_2 H}{1 + k_1 k_2 H}\right) + \frac{1800}{W}\left(\frac{k_2 H}{100 - k_2 H}\right) \qquad (2\text{-}2)$$

Here M is the equilibrium moisture content of wood at a specific relative humidity (H), Mh and Ms are the moisture contents in monolayer (relating to hydration water) and in polylayer (relating to dissolved water), respectively, W is the molecular weight of dry wood per mole of sorption sites, and correspondingly 1/W indicates the density of sorption sites, k_1 is the equilibrium constant of hydrate formation from dissolved water and dry wood, and k_2 is the equilibrium constant between dissolved water and external vapor pressure.

Equation (2-2) can be rearranged to parabolic form by plotting the ratio of relative humidity to wood moisture content at equilibrium (H/M) against the relative humidity (%H), as follows:

$$\frac{H}{M} = A + BH - CH^2 \qquad (2\text{-}3)$$

where H(%) is relative humidity, M(%) is the equilibrium moisture content, and A, B, and C are the fitting parameters (Skaar 1988). The values of A, B, C, k_1, k_2 and W can be calculated applying the equations below:

$$A = \frac{W}{18}\left[\frac{1}{k_2(k_1+1)}\right] \tag{2-4}$$

$$B = \left(\frac{W}{1800}\right)\left[\frac{k_1-1}{k_1+1}\right] \tag{2-5}$$

$$C = \left(\frac{W}{180000}\right)\left[\frac{k_1k_2}{k_1+1}\right] \tag{2-6}$$

$$k_1 = 1+\frac{B^2+B\sqrt{B^2+4AC}}{2AC} \tag{2-7}$$

$$k_2 = \frac{50\left(-B+\sqrt{B^2+4AC}\right)}{A} \tag{2-8}$$

$$W = 1800\sqrt{B^2+4AC} \tag{2-9}$$

2.4.3 Color measurements

Color evaluations of all specimens were performed on the surface of the rubberwood samples before and after superheated steam treatment by a color analyzer (ColorFlex EZ spectrophotometer, Hunter Associates Laboratory, Inc., USA) (Fig. 2-6). This instrument equipped with a light source in the visible spectrum with wavelength range from approximately 400 to 700 nm. The color was measured in the three-dimensional colorimetric system L*a*b* or in CIELab*.

Fig. 2-6 ColorFlex EZ spectrophotometer (Hunter Associates Laboratory, USA).

The coordinate L* defines a lightness-darkness axis (from zero – black to 100 – white), a* and b* define a redness–greenness axis and a yellowness–blueness axis, respectively. A positive number of a* indicates the amount of redness, and a negative value indicates greenness of a specimen. Likewise, a positive b* indicates yellow, and a negative value indicates blue. Furthermore, the total color change (ΔE) between treated and the controls (without treatment) was calculated using equation (2-10).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2-10}$$

where ΔL*, Δa*, and Δb* are the differences in the lightness, green-redness-greenness, and yellowness-blueness, respectively, between the color of a treated and untreated specimens.

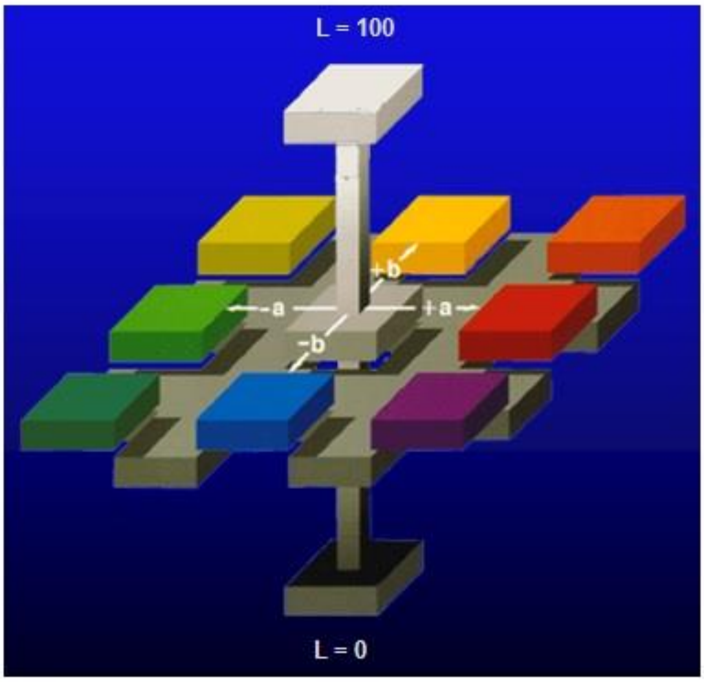


Fig. 2-7 CIELab* color space (HunterLab 2013).

2.4.4 Resistance to fungal test

The tests were carried out according to the American Society for Testing and Materials standard method (ASTM D-1413 2007 p. 1413). The superheated steam treated and untreated sample were cut to dimensions approximately 25.4 mm x 25.4 mm x 6.4 cm (longitudinal x tangential x radial), with five replicates for untreated and each treated rubberwood. Feeder strips (30x30x5 mm) of rubberwood were prepared and inoculated with the white-rot decay fungus (*Trametes versicolor*) until the wood surface was entirely covered with the mycelium. Each of decay containers consisting of a 300-mL container half filled with garden soil, were sterilized for 30 min at 121°C. After filling the containers with distilled water, a feeder strip was added. The untreated and treated samples were sterilized at 121°C for 20 min. The sample weight before exposure (W_1) was recorded. Then, the samples were placed in the decay containers with the cross-section face of the feeder strip facing down. The each set of decay container were incubated in the condition of 80±5% relative humidity and 25±2°C for 12 weeks. After the end of exposure, the test samples then were removed, carefully cleaned by brushing off any soil and mycelium. The samples were dried at 103±2°C once again until constant weight was achieved (W_2). The percentage of weight loss was determined using equation below:

$$WL_f = \frac{W_1 - W_2}{W_1} x100 \tag{2-11}$$

where WL_f is weight loss from fungus test (%), W_1 is oven-dried weight of the specimen before exposure to the termites (g), and W_2 is oven-dried weight of the specimen after exposure to the fungus (g).

Fig. 2-8 Fungal decay test

2.4.5 Resistance to subterranean termite (Coptotermes gestroi) test

The experiment for termite resistance was conducted according to the American Society for Testing and Materials standard method (ASTM D3345-08

1999). The superheated steam treated and untreated sample were cut to dimensions approximately 25.4 mm x 25.4 mm x 6.4 mm (longitudinal x tangential x radial), with five replicates for untreated and each treated rubberwood. Subterranean termites (*Coptotermes gestroi*) were collected from a wood building in Nakhon Si Thammarat, Thailand. Each oven-dried sample was placed in a clean plastic box with 200 g sand, 8.5 mL deionised water and 1.50±0.05 g subterranean termites. The plastic boxes were concealed with black papers and then stored in a room at 25±2°C and 80% RH for 4 weeks. After the end of test period, samples were then removed, carefully cleaned. The percentage of weight loss was determined using equation below:

$$WL_t = \frac{W_3 - W_4}{W_3} x100 \tag{2-12}$$

where WL_t is weight loss from termite test (%), W_3 is oven-dried weight of the specimen before exposure to the termites (g), and W_4 is oven-dried weight of the specimen after exposure to the termites (g).

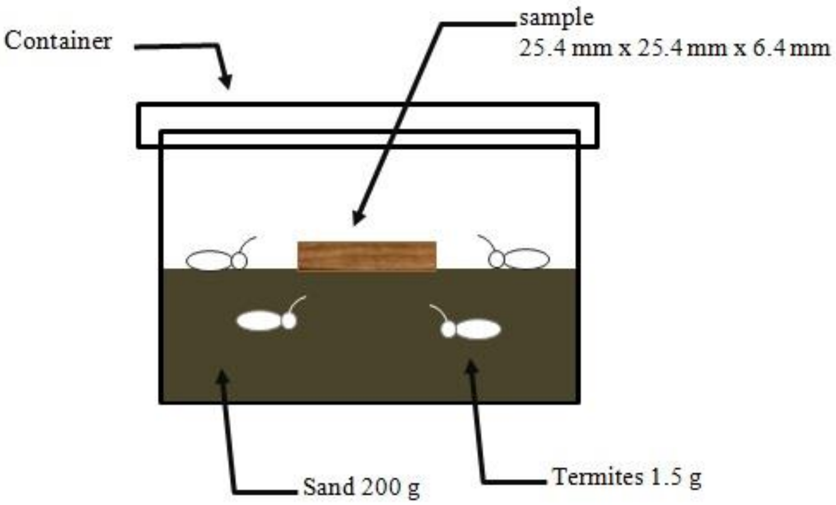


Fig. 2-9 Schematic of resistance to subterranean termite test

2.4.6 Fourier Transform Infrared Spectroscopy (FT-IR) analyses

Fourier transform-infrared spectroscopy (FT-IR) spectra of the wood surface were recorded with a Fourier Transform Infrared Spectrometer (EQUINOX 55, Bruker, Germany) (Fig. 2-10). The analyses were performed using KBr pellet technique. The spectra were from 4000 to 400 cm−1 at a spectral resolution of 4 cm−1, and 64 scans were used. The technique allows assigning the structure of substances by the interpretation of the frequencies of functional groups and is appropriate to detect the chemical modifications of raw material and mixtures.

Fig. 2-10 Fourier Transform Infrared Spectrometer (EQUINOX 55, Bruker, Germany).

2.4.7 Scanning electron microscope (SEM) analysis

The surface the wood sample was also examined using scanning electron microscope, SEM (JSM-5800LV, JEOL, Japan) (Fig. 2-11). Micrograph images were taken from the tangential section of the control and heat treated samples at a temperature of 140°C-160°C for 3 hours with size of 1 cm by 1 cm. These dried specimens were mounted on the aluminum stub and coated with gold in a sputter coater prior to viewing with a scanning electron microscope. The images were then analyzed the surface area of starch particles on the wood surface by using a freely available software ImageJ version 1.52a (National Institutes of Health, Bethesda, Maryland, USA). See procedure of using scanned image and ImageJ software to estimate the particle size in Appendix C.

Fig. 2-11 scanning electron microscope (JSM-5800 LV, JEOL).

2.5 Statistical Analysis

The statistical analysis was conducted by using SPSS® (version 17) (Software International Inc., Chicago, IL, USA). All experiments were carried out at least in triplicate and reported the mean values with standard deviations. Analysis of variance (ANOVA) is used to analyze the data of this experiment. Test of Duncan's multiple range was applied to determine the multiple comparisons of the mean values which were considered at 95% confidence level ($p<0.05$).

CHAPTER 3

Result and Discussions

3.1 Mechanical Properties

Some mechanical properties of treated and untreated (conventional drying from manufacture) samples of the same board are compared with reference values (Theppaya 1998; Yamsaengsung and Tabtiang 2011) as shown in Table 3-1. Since the pre-dried (untreated) samples used in this investigation had substantially higher mechanical properties compared to the reference, the percentage change in the mechanical properties between the untreated and treated samples were determined to serve as an indication for improvement in the mechanical properties of the rubberwood. The data revealed that mechanical properties of the samples were improved after superheated steam treatment. Most of the mechanical properties for treated samples were significantly higher than the untreated samples and the reference values. For example, in the case of samples treated at 160°C for 3 h, the compression parallel-to-grain, hardness, tensile strength perpendicular-to-grain and impact strength increased by 14.37%, 13.46%, 7.58 and 28.36%, respectively, compared to the untreated sample of each condition.

In the case of previous results (hybrid drying) (Yamsaengsung and Tabtiang 2011), the hardness increased by 9.10% according to the reference data (Theppaya 1998). Therefore the percentage increase between treated and untreated sample were higher than that between the hybrid and reference values. Furthermore, when considering the compression strength parallel-to-grain of the treated woods at 140°C, 150°C and 160°C for 3 h, it was found that the percentage increase of each set of samples were 9.77%, 9.14% and 14.38%, respectively. These results are consistent with the prior report by (Percin et al. 2016). They also found that there is a significant temperature effect on the compression parallel-to-grain occurred between the beech woods treated at 150°C and 175°C for 3 h. Finally, from the Table 3-1, the data revealed that there were no significant difference ($p<0.05$) between treated and untreated samples from 1 to 3 hours at all three temperatures of tensile strength perpendicular-to-grain and impact strength.

In addition, this study has attempted to observe the effects of superheated steam treatment on some mechanical properties of samples at higher temperature (170-180°C for 1-3 h). The results showed that the compression parallel-to-grain and the hardness of treated wood were still higher than untreated wood for all treatment conditions. However, regarding impact strength, it was found the samples treated at temperatures higher than 160°C had become brittle.

Table 3-1 Mechanical properties of superheated steam treated pre-dried rubberwood.

Wood Conditions		Properties							
		Compression Parallel to grain (MPa)		Hardness (kN)		Tensile Strength (MPa)		Impact test (kg-m)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Superheated steam treatment	**140°C/1H**	76.51 (3.20)^{a}	89.76 (7.78)^{bcd}	8.40 (1.25)^{ab}	8.91 (0.83)^{abcd}	3.27 (0.44)^{a}	3.73 (0.65)^{abc}	1.74 (0.28)^{ghij}	1.84 (0.38)^{ghij}
	140°C/2H	87.01 (5.45)^{bc}	91.28 (3.89)^{bcdea}	9.95 (1.30)^{cdefg}	10.80 (0.72)^{efghijk}	4.07 (0.93)^{abcd}	4.20 (0.69)^{bcd}	1.69 (0.47)^{ghi}	1.96 (0.53)^{hij}
	140°C/3H	90.54 (10.42)^{bcde}	99.39 (8.11)^{efgh}	11.78 (1.22)^{hijkl}	12.13 (1.68)^{jkl}	5.24 (1.42)^{ef}	5.48 (0.97)^{f}	1.59 (0.56)^{fghi}	1.70 (0.47)^{ghi}
	150°C/1H	97.86 (8.23)^{defgh}	104.76 (3.97)^{ghi}	11.58 (0.56)^{hijkl}	12.70 (0.91)^{l}	4.75 (0.28)^{def}	5.10 (0.63)^{ef}	1.37 (0.31)^{cdefgh}	1.42 (0.34)^{defgh}
	150°C/2H	101.79 (11.99)^{fghi}	106.39 (5.76)^{hi}	7.93 (0.71)^{a}	8.53 (0.43)^{abc}	4.12 (0.81)^{bcd}	4.84 (0.88)^{def}	2.06 (0.31)^{ij}	2.29 (0.51)^{j}
	150°C/3H	86.18 (11.48)^{b}	94.05 (6.85)^{bcdef}	10.20 (2.62)^{defgh}	11.24 (2.93)^{fghijkl}	4.50 (0.71)^{cde}	4.83 (0.41)^{def}	1.59 (0.55)^{fghi}	1.80 (0.50)^{ghij}
	160°C/1H	91.84 (15.75)^{bcde}	94.41 (11.06)^{bcdef}	9.59 (1.50)^{bcde}	10.59 (1.70)^{efghij}	4.78 (0.68)^{def}	4.86 (0.56)^{def}	1.52 (0.56)^{efghi}	1.73 (0.70)^{ghij}
	160°C/2H	86.40 (13.72)^{b}	94.06 (6.41)^{bcdef}	9.01 (0.53)^{abcd}	9.71 (0.88)^{bcdef}	3.54 (0.54)^{ab}	3.67 (0.62)^{ab}	1.94 (0.79)^{ghij}	1.51 (0.43)^{efghi}
	160°C/3H	96.16 (6.77)^{cdefg}	109.98 (7.75)^{i}	10.18 (1.12)^{defgh}	11.55 (1.72)^{ghijkl}	3.30 (1.05)^{a}	3.55 (1.05)^{ab}	1.34 (0.56)^{bcdefg}	1.72 (0.32)^{ghij}

Table 3-1 Mechanical properties of superheated steam treated pre-dried rubberwood. (Continued).

Wood Conditions		**Properties**							
		Compression Parallel to grain (MPa)		**Hardness (kN)**		**Tensile Strength (MPa)**		**Impact test (kg-m)**	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Superheated steam treatment	**170°C/1H**	78.52 (8.96)^{abc}	99.25 (9.23)^{fghi}	10.75 (1.22)^{efghijk}	12.33 (1.70)^{kl}	-	-	0.96 (0.49)^{abcde}	0.82 (0.43)^{abc}
	170°C/2H	72.89 (10.31)^{a}	95.85 (13.06)^{defghi}	10.62 (1.42)^{efghij}	11.90 (1.49)^{ijkl}	-	-	0.81 (0.25)^{abc}	0.77 (0.21)^{ab}
	170°C/3H	75.18 (13.94)^{a}	88.82 (14.05)^{def}	10.76 (2.18)^{efghijk}	11.67 (2.76)^{hijkl}	-	-	0.96 (0.14)^{abcde}	0.90 (0.26)^{abcd}
	180°C/1H	74.59 (9.18)^{a}	90.40 (13.25)^{def}	10.43 (1.81)^{defghi}	10.87 (1.42)^{efghijk}	-	-	1.37 (0.56)^{cdefgh}	1.00 (0.38)^{abcdef}
	180°C/2H	72.84 (9.38)^{a}	89.38 (7.48)^{def}	8.97 (0.56)^{abcd}	10.16 (0.89)^{defgh}	-	-	1.53 (0.46)^{efghi}	1.09 (0.53)^{abcdef}
	180°C/3H	73.80 (19.20)^{a}	91.15 (14.47)^{defg}	10.36 (1.32)^{defghi}	10.91 (1.21)^{efgk}	-	-	0.66 (0.24)^{a}	0.75 (0.29)^{a}
***Hybrid** (Yamsaengsung and Tabtiang 2011)		39.93	-	5.69	-	-	-	-	-
Ref. (Theppaya 1998)		46.88	-	5.22	-	2.75	-	-	-

Values in parenthesis are the standard deviation (n =10) and values in the same column of both untreated and treated with different superscripts mean that the values are significantly different ($p<0.05$). *Hybrid: Superheated steam at 105–107°C and hot air at 80°C

3.2 Moisture sorption isotherms

Table 3-1 present the effects of various superheated steam conditions on the equilibrium moisture content (EMC) of pre-dried rubberwood at each relative humidity (RH) level. It is observed that the EMC of treated wood at any RH was below that of untreated control samples, indicating that the hygroscopicity of wood was reduced consistently by the treatments.

Furthermore, when compared to the control samples at 75% RH (the average relative humidity in Thailand) (Thai Meteorological Department n.d.), the decreasing EMC of 3 hours treated rubberwood were found to be 5.62, 9.64 and 13.05% respectively, for 140°C, 150°C and 160°C. Similarly, at 92% RH (during the wet season), the EMC of 140°C, 150°C and 160°C for 3 hours were decreased by 11.00, 19.44 and 22.02% compared to the controls, respectively. Moreover, the change of the EMC in the treated samples according to control samples at 92% relative humidity was more significant. These results are consistent with the prior report by Gündüz et al. (2008b) for Uludag fir wood treated at 170, 190, and 210°C for 4, 8, and 12 hours.

Table 3-2 Average values of EMCs at various levels of RH for untreated and treated rubberwood samples

Treatment conditions		**RH (%)**					
T (°C)	**Time (h)**	**11**	**32**	**43**	**51**	**75**	**92**
Control	**-**	3.63^{h} (0.01)	6.36^{h} (0.07)	7.18^{d} (0.06)	8.08^{f} (0.06)	11.43^{d} (0.05)	22.07^{h} (0.01)
140	**1**	3.28^{g} (0.06)	5.61^{g} (0.03)	6.39^{c} (0.09)	7.16^{e} (0.10)	11.32^{d} (0.05)	21.04^{g} (0.02)
	2	2.72^{f} (0.02)	4.99^{f} (0.10)	5.80^{b} (0.12)	6.40^{d} (0.39)	10.86^{c} (0.13)	19.80^{f} (0.17)
	3	2.62^{ef} (0.01)	4.74^{e} (0.09)	5.80^{b} (0.29)	6.32^{cd} (0.33)	10.79^{c} (0.28)	19.64^{f} (0.42)
150	**1**	2.60^{def} (0.21)	4.63^{de} (0.17)	5.21^{a} (0.00)	6.45^{d} (0.13)	10.74^{c} (0.02)	18.90^{e} (0.20)
	2	2.51^{cde} (0.06)	4.52^{d} (0.10)	5.15^{a} (0.02)	6.27^{cd} (0.01)	10.72^{c} (0.02)	18.38^{d} (0.11)
	3	2.44^{bcd} (0.04)	4.37^{c} (0.06)	5.12^{a} (0.01)	6.07^{bc} (0.03)	10.33^{b} (0.07)	17.78^{bc} (0.52)
160	**1**	2.41^{bc} (0.08)	4.56^{d} (0.07)	5.14^{a} (0.12)	5.89^{b} (0.01)	10.37^{b} (0.3)	18.14^{cd} (0.36)
	2	2.32^{ab} (0.15)	4.18^{b} (0.04)	5.04^{a} (0.04)	5.51^{a} (0.03)	10.05^{a} (0.11)	17.38^{ab} (0.06)
	3	2.22^{a} (0.04)	3.93^{a} (0.00)	5.01^{a} (0.01)	5.37^{a} (0.01)	9.94^{a} (0.02)	17.21^{a} (0.05)

Values in parenthesis are the standard deviation and values in the same column with different superscripts mean that the values are significantly different ($p<0.05$).

Table 3-3 Fitted and constant parameters calculated from the Hailwood–Horrobin adsorption isotherm of rubberwood

Treatment conditions		**A**	**B**	**C**	**R^2**	**k_1**	**k_2**	**W**
T (°C)	**Time (h)**							
Control	**-**	0.923	0.192	0.002	0.934	25.357	0.852	373.199
140	**1**	1.078	0.216	0.002	0.982	24.247	0.861	421.468
	2	1.711	0.223	0.002	0.983	16.015	0.869	455.275
	3	1.928	0.221	0.002	0.989	14.201	0.870	458.691
150	**1**	1.938	0.231	0.002	0.983	14.619	0.875	476.655
	2	2.104	0.231	0.002	0.985	13.553	0.873	481.215
	3	2.195	0.234	0.002	0.995	13.287	0.869	490.388
160	**1**	2.101	0.238	0.002	0.980	13.970	0.873	494.462
	2	2.221	0.252	0.002	0.983	13.899	0.879	523.306
	3	2.492	0.253	0.002	0.979	12.580	0.875	532.996

A low k_1 suggests a reduction in the activity of hydrated wood concerning both the activities of dry wood and dissolved water. It was found that the k_1 values of the treated rubberwood were decreased by the more severe treatment conditions. This result is consistent with those previously reported by (Murata et al. 2013), (Mantanis and Papadopoulos 2010) , and (Jalaludin et al. 2011).

The constant k_2 represents the activity between dissolved water and vapor pressure in the cell-wall, as defined above. According to (Okoh and Skaar 1980) this value should be similar if it has the activity in the same way as liquid water. From the model fitting of the various conditions used, there were no distinct differences in the k_2 values that vary from 0.852 to 0.879. However, the k_2 values were a bit higher with all treatments compared with the control, indicating that the dissolved water had lower activity than liquid water (Okoh and Skaar 1980).

In estimates based on the H-H model, the molecular weight of dry cell-wall per mole of moisture sorption sites (W) revealed differences between treatments. The wood treated at 160°C for 3 hours had the highest W at 533, more than 42% above untreated wood. The increase in this parameter confirms decreased number of active adsorption sites. This indicates that hydroxyl group adsorption sites in treated wood had decreased, and consequently the wood treated at 160°C for 3 hours was the least hygroscopic.

The adsorption isotherm was divided into M_h component, characteristic of chemical-sorption on a surface where a monolayer is formed, and M_s component, for dissolved water in wood corresponding to multilayer sorption (Skaar 1972). These partial isotherms for monolayer and polylayer from the H-H fits to the data are plotted in Fig. 3-1 and Fig. 3-2. The plots reveal that after rubberwood was treated with superheated steam, the hygroscopicity was reduced for both monolayer and polylayer adsorption. The largest decrease in M_h was 32-45% in the case of 160°C for 3 hours treatment, followed by 31-41% in the case of 160°C for 2 hours treatment, and the smallest 11-12% decrease was for the treatment at 140°C for an hour, relative to untreated control across the whole isotherm. The considerable decrease in M_h confirms the reduction in accessible OH groups in the cell-walls, that are required for primary adsorption. The reduction in Ms of treated rubberwood was consistent with the Mh results, in that the largest decrease was 15-27% with 160°C treatment for 3 hours, and the smallest decrease was with 140°C treatment for 1 hour. The decreased Ms presumably indicates reduced capacity of cell-wall expansion from increased matrix stiffness and increased lignin cross-linking (Jalaludin et al. 2010).

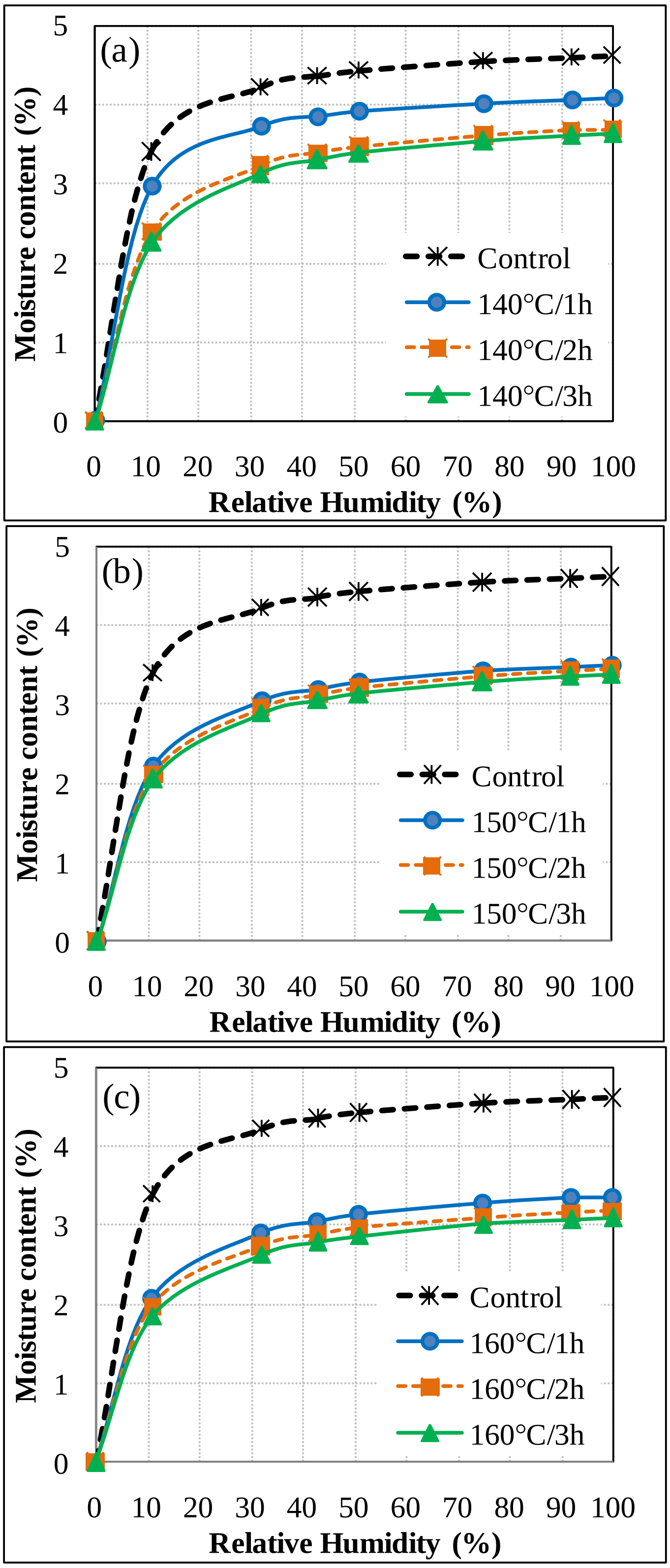


Fig. 3-1 Monolayer moisture content (M_h) using the H-H model.

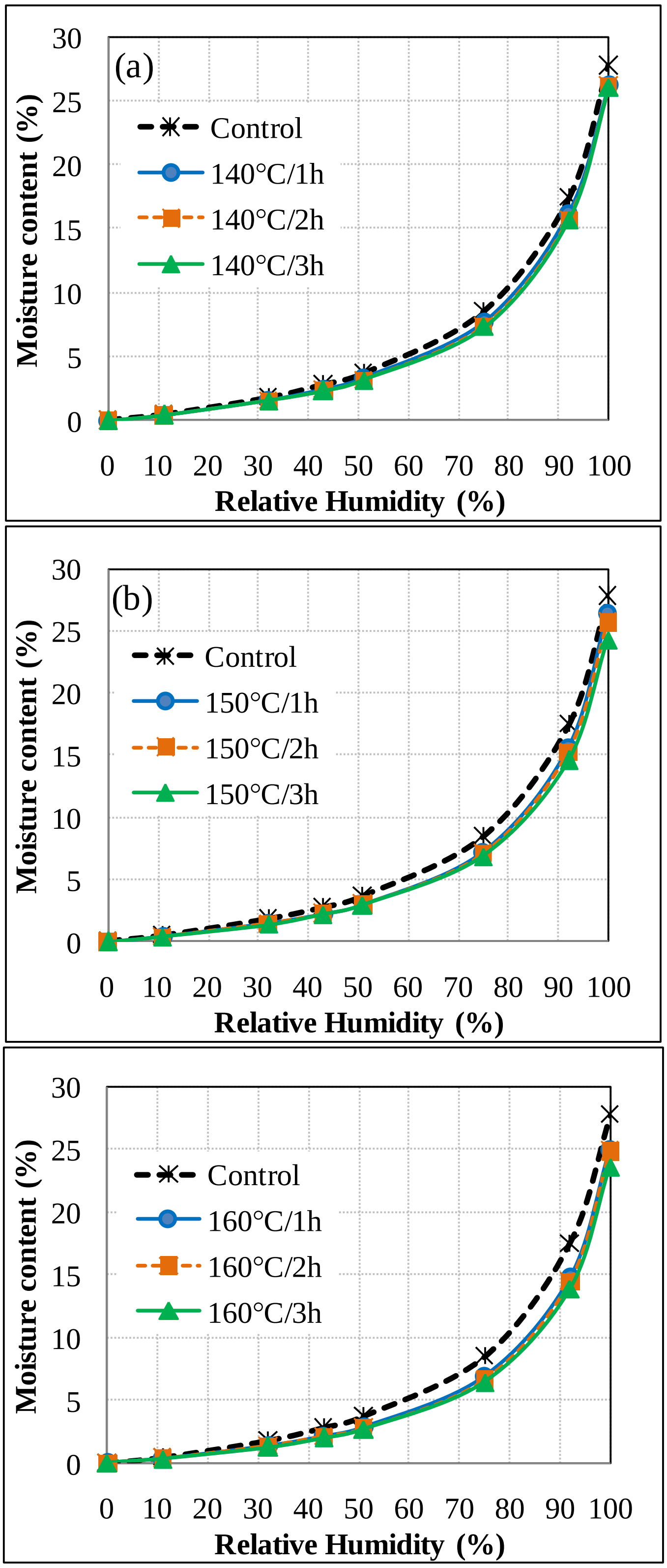


Fig. 3-2 Polylayer moisture content (M_s) using the H-H model.

The fiber saturation point (FSP) was estimated from the fitted isotherm models at 100%RH, and are summarized in **Table 3-4**. The corresponding values of M_h and M_s were decreased by the more severe treatments.

Table 3-4 The estimated value of Mh, Ms and FSP corresponding at 100%RH.

Treatment conditions		**M_h (%)**	**M_s (%)**	**FSP (%)**
T (°C)	**Time (h)**			
Control	**-**	4.61	27.83	32.44
140	**1**	4.08	26.37	30.45
	2	3.69	26.21	29.90
	3	3.63	26.15	29.78
150	**1**	3.50	26.44	29.94
	2	3.45	25.72	29.17
	3	3.38	24.34	27.71
160	**1**	3.36	25.09	28.45
	2	3.18	24.89	28.07
	3	3.10	23.63	26.72

The values for M_h, M_s and FSP were 4.61%, 27.83% and 32.44%, respectively, for the untreated control rubberwood samples. After superheated steam treatment, the largest reduction in M_h, M_s and FSP was 32.8%, 15.1% and 17.6%, respectively. These values were obtained at treatment of 160°C for 3 h. Moreover, the more severe treatment conditions gave the largest decreases. Similar results have been provided by (Jalaludin et al. 2010) for acacia and sesendok wood species.

3.3 Color Changes

The color difference of the treated wood increased with the treatment temperature and duration (Table 3-5). It was found that L* value decrease with increasing treatment temperature and duration. The largest reduction L* was observed for rubberwood treated at 160°C for 3 h. However, there were no significant difference ($p<0.05$) of L* between treated and untreated samples from each condition. Moreover, the redness (a*) and the yellowness (b*) values of the treated rubberwood samples were increased with increasing treatment temperature and duration compared to the untreated control samples and these results consistent with (Gunduz et al. 2010) who found L* values decreased, but a* and b* value of Uludag fir wood increased after heat treatment.

The total color change of the wood surface (ΔE^*) were increased with increasing treatment temperature and duration. The increase in the color difference of wood samples after treatment at varying condition are caused by a decrease in hemicelluloses content and this observation is consistent with previous studies (Gunduz et al. 2010). However, at temperatures from 140-160°C, the total color changes were not significantly different and the greatest color differences occurred at 160°C for 3 h treatment condition.

Furthermore, this study has attempted to observe the effects of superheated steam treatment on color changes of samples at higher temperature (170-180°C for 1-3 h) and found that these temperature levels tend to be consistent with the aforementioned conditions (140-160°C). Results indicated that the highest reduction in L* of treated samples was obtained with the treatment at 180°C for 3 h. However, at temperatures from 140-170°C, the total color change was not significant, while the largest change occurred with 180°C for 3 h treatment.

Table 3-5 Changes in color properties of the heat-treated rubberwood.

Treatment Conditions		**Color Properties**						
		L*		**a***		**b***		
T (°C)	**Time (H)**	**Untreated**	**Treated**	**Untreated**	**Treated**	**Untreated**	**Treated**	**ΔE***
140	**1**	68.68 (2.22)^{bcde}	66.90 (1.27)^{abcde}	8.09 (0.38)^{ab}	9.48 (1.25)^{abcde}	22.24 (1.05)^{a}	23.08 (1.78)^{a}	3.45 (2.01)^{ab}
	2	70.43 (2.82)^{de}	68.76 (3.11)^{bcde}	7.64 (1.14)^{a}	8.47 (1.12)^{abc}	23.17 (0.76)^{a}	25.47 (0.60)^{cd}	3.13 (0.59)^{a}
	3	68.85 (2.51)^{bcde}	66.55 (2.36)^{abcde}	9.06 (0.38)^{abcd}	9.23 (1.08)^{abcd}	23.53 (1.79)^{a}	25.41 (0.94)^{cd}	3.60 (0.88)^{ab}
150	**1**	71.40 (1.73)^{e}	69.46 (2.72)^{cde}	8.47 (0.53)^{abc}	7.86 (1.43)^{ab}	25.31 (0.84)^{c}	25.56 (0.40)^{cde}	2.57 (0.89)^{a}
	2	67.77 (2.74)^{abcde}	64.30 (2.79)^{abc}	9.16 (1.48)^{abcd}	9.56 (0.88)^{abcde}	23.73 (1.33)^{ab}	25.00 (0.39)^{bc}	4.26 (1.52)^{ab}
	3	67.66 (2.53)^{abcde}	63.98 (2.59)^{abc}	9.80 (1.38)^{bcde}	11.49 (1.61)^{e}	25.87 (0.33)^{cde}	26.30 (0.45)^{cde}	4.12 (1.27)^{ab}
160	**1**	63.59 (8.02)^{ab}	62.41 (6.50)^{a}	11.04 (2.86)^{de}	10.96 (2.42)^{de}	25.54 (0.97)^{cde}	26.10 (0.60)^{cde}	3.44 (1.57)^{ab}
	2	65.12 (4.41)^{abcd}	62.26 (3.76)^{a}	10.34 (1.63)^{cde}	11.37 (1.18)^{e}	26.04 (0.66)^{cde}	27.13 (1.29)^{e}	3.57 (1.34)^{ab}
	3	68.05 (4.53)^{bcde}	63.27 (3.17)^{ab}	9.57 (1.39)^{abcde}	11.01 (1.16)^{de}	25.60 (1.64)^{cde}	26.98 (1.57)^{de}	5.42 (2.25)^{b}

Table 3-5 Changes in color properties of the heat-treated rubberwood (Continued)

Treatment Conditions		**Color Properties**						**ΔE***
		L*		**a***		**b***		
T (°C)	**Time (H)**	**Untreated**	**Treated**	**Untreated**	**Treated**	**Untreated**	**Treated**	
170	**1**	66.82 (5.00)^{efghi}	64.88 (2.08)^{defgh}	9.51 (1.69) ^{abcdefg}	9.86 (1.31)^{abcdefghi}	25.51 (0.54)^{defg}	26.23 (1.10)^{defghi}	3.93 (1.99)^{ab}
	2	61.81 (3.85)^{bcde}	60.55 (2.73)^{abcd}	11.28 (1.32)^{efghi}	12.10 (1.12)^{hi}	25.68 (0.49)^{defgh}	28.26 (0.77)^{j}	3.94 (2.04)^{ab}
	3	62.00 (3.80)^{bcdef}	57.55 (4.86)^{ab}	11.82 (2.26)^{ghi}	12.07 (1.95)^{hi}	25.95 (0.48)^{defghi}	27.06 (0.94)^{ghij}	5.78 (2.15)^{bc}
180	**1**	65.60 (6.51)^{defghi}	61.62 (5.90)^{bcde}	9.98 (2.05)^{abcdefghi}	10.81 (2.05)^{defghi}	25.42 (0.74)^{de}	26.19 (1.50)^{defghi}	4.34 (2.20)^{ab}
	2	65.39 (2.85)^{defghi}	58.69 (2.89)^{abc}	10.07 (0.95)^{bcdefghi}	11.08 (1.05)^{efghi}	25.22 (1.10)^{d}	26.03 (0.89)^{defghi}	6.89(1.92)^{cd}
	3	63.95 (4.73)^{cdefg}	55.98 (5.59)^{a}	10.83 (2.58)^{defghi}	12.20 (1.47)^{i}	26.89 (0.61)^{efghij}	27.35 (1.15)^{ij}	8.26 (2.67)^{d}

Values in parenthesis are the standard deviation and values in the untreated and treated column with different superscripts mean that the values are significantly different ($p<0.05$).

3.4 Fungal Resistance

The mean weight loss percentages of treated and untreated rubberwood samples in soil block laboratory decay against white rot decay fungus (*Trametes versicolor*) after 12 weeks are given in Fig. 3-3 and the fungal mycelium growth covering on rubberwood specimens are shown in **Fig. 3-4**. The data revealed that the resistance of wood against this fungus was improved. The weight loss in untreated rubberwood was 15.18% and 4.00-11.68% for treated rubberwood. Moreover, there was a significant effect of all treatment condition on the susceptibility of the rubberwood relative with untreated wood. The weight loss to decay fungus were decreased by the more severe treatment conditions and could reach values up to 73.7% found in the treated wood at 160°C for 3 hours compared to untreated samples. These results are consistent with (Calonego et al. 2010). They also found the durability against the decay fungus *P. sanguineus* of thermally-treated *Eucalyptus grandis* wood was increased after thermal treatment with temperatures between 180 and 220 °C.

Furthermore, the results suggest that the treatment temperature played more important role in the improvement of decay resistance than the treatment duration. The wood is more decay resistance after thermal treatment because there were changes in chemical constituent of wood, reduction in the equilibrium moisture content and availability of food (hemicelluloses) to fungi and there is a cross-linking between lignin and the polymer from the thermally degraded cellulose (Calonego et al. 2010).

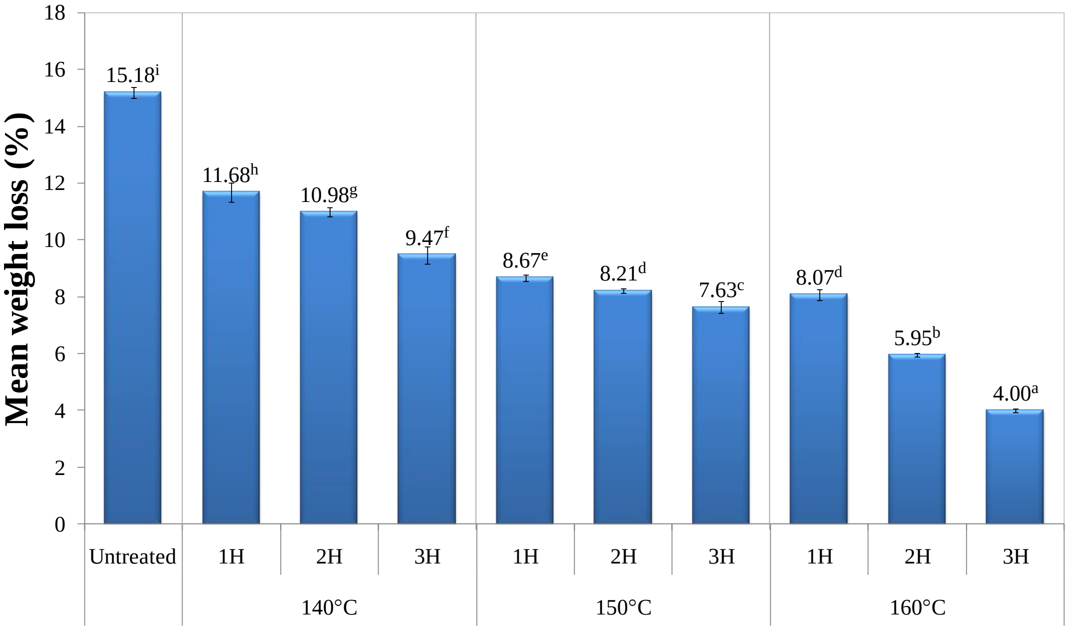


Fig. 3-3 Mean Weight loss percentages of untreated and treated rubberwood samples subjected to white rot decay fungus

(Superscript letters indicate significant differences ($P < 0.05$) between groups)

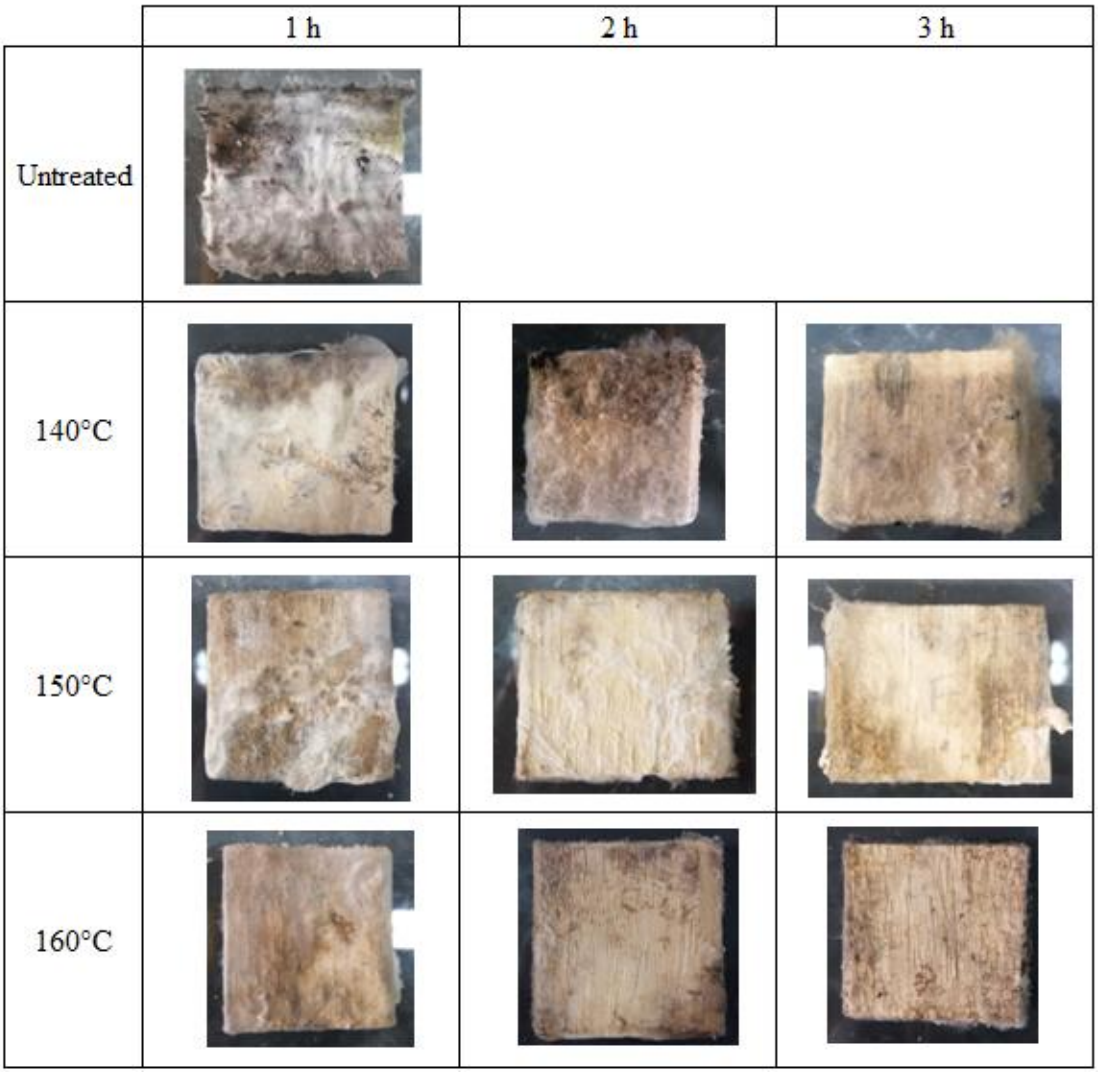


Fig. 3-4 Rubberwood specimens after 12 weeks of exposure the white-rot fungus.

3.5 Termite Resistance

Fig. 3-5 shows the mean weight losses of treated rubberwood compared to its controls after four weeks of exposure to subterranean termites (*Coptotermes gestroi*). The results showed that superheated steam treatment improved rubberwood resistance against subterranean termites. Mean weight losses were 7.78-19.94% for treated samples at 140-160°C for 1-3 h treatment, compared to 20.50% for untreated ones. Treatment temperature levels from 140 to 160°C also played more significant effect on the mass loss. This result are consistent with (Manalo and Garcia 2012). They investigated the effects of heat treatment (140–200°C for 30–120 min.) on the resistance of *Dendrocalamus asper* and found improvement in resistance against subterranean termites varies with different temperature levels holding periods and their interactions.

Moreover, Treatment temperature had a highly significant effect on the mass loss ($p < 0.05$) and also interactions between temperature and duration were significant ($p < 0.05$) except between 150°C for 1 and 2 h. Exposure of the rubberwood samples to highest temperature and duration level (160°C for 3 h) achieved the greatest of termite resistance as the lowest of weight loss.

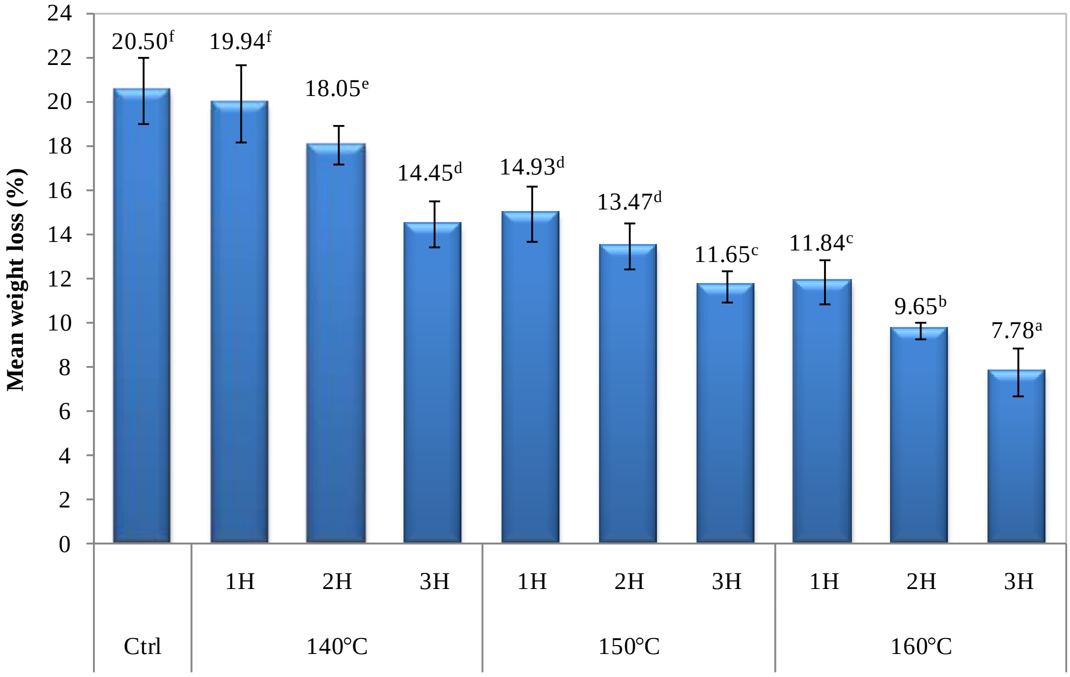


Fig. 3-5 Mean Weight loss percentages of untreated and treated rubberwood samples subjected to termite attack

(Superscript letters indicate significant differences ($P < 0.05$) between groups)

	1 h	2 h	3 h
Untreated			
140°C			
150°C			
160°C			

Fig. 3-6 Rubberwood specimens after 4 weeks of exposure the subterranean termites.

3.6 Fourier Transform Infrared Spectroscopy (FT-IR)

The change in cell-wall components in heat treated and untreated wood were analyzed by FT-IR spectroscopy. FT-IR spectra of the untreated and heat-treated rubberwood samples were taken between the wavelengths of 4000 and 800 cm^{-1} as Fig. 3-7 and the assignment of IR bands is presented in Table 3-6. The intensity of the band around 1425 cm^{-1}, CH_2 bending in cellulose, slightly shifted to higher wavelength in treated sample, especially in the samples treated at temperatures higher than 160°C. This result is consistent with the research findings of (Lionetto et al. 2012).

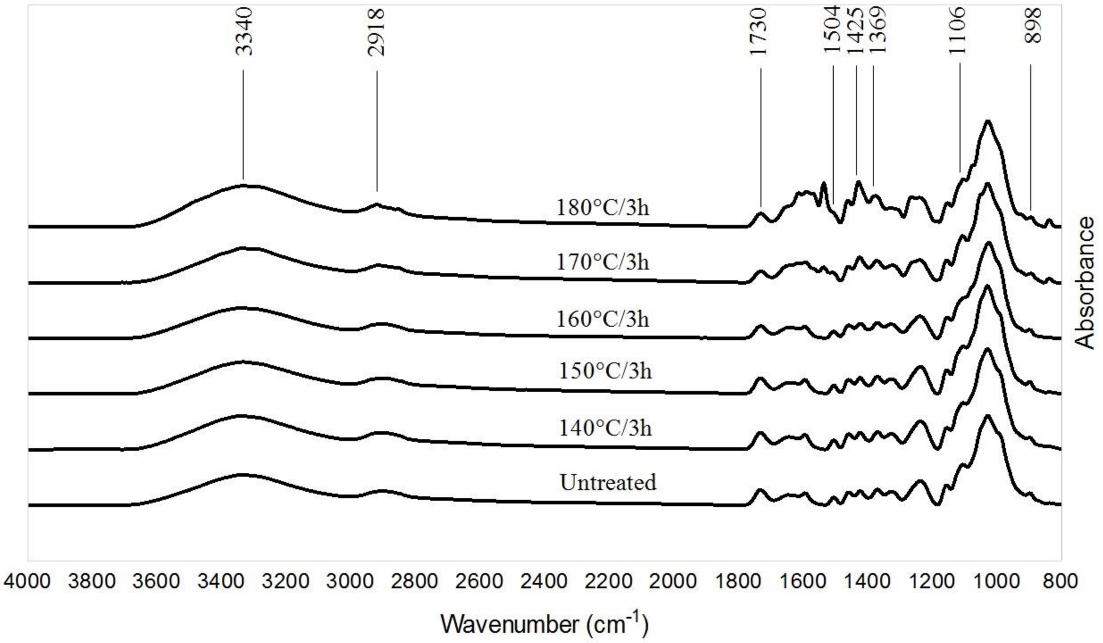


Fig. 3-7 FTIR spectra of untreated and treated rubberwood samples at 140-160 ºC for 3 h.

The band around 1504 cm^{-1}, for C=C stretching in aromatic skeleton (lignin), was not obviously changed in the samples heat treated at 140 to 160°C for 3 h from that for untreated sample, this result is consistent with (Akgül et al. 2006). However, this band was clearly reduced by treatments at 170 and 180°C for 3 h due to the condensation reactions and splitting of the aliphatic side chains in the lignin (Özgenç et al. 2018). Moreover, there was no distinct effect from any treatment at the band around 1106 cm-1 (asymmetric bridge C-O-C stretching in cellulose). This result is consistent with (Ates et al. 2009).

Table 3-6 FTIR Absorption Peak Location and Assignment of untreated and treated rubberwood.

Wavenumber (cm^{-1})	Functional group and Assignment
3340	OH stretching in hydroxyl groups (Fabiyi and Ogunleye 2015)
2918	C-H stretching in methyl and methalene groups (Fabiyi and Ogunleye 2015)
1730	attributed to the carboxyl- and ester groups, nonconjugated aldehyde (Aydemir et al. 2011)
1504	C=C Stretching of aromatic skeleton (Lignin) (Liu et al. 2015)
1425	CH_2 bending (Cellulose) (Lionetto et al. 2012)
1369	CH_2 deformation vibration (Cellulose, Hemicellulose) (Fabiyi and Ogunleye 2015)
1106	asymmetric bridge C-O-C stretching for cellulose (Ates et al. 2009)
898	C_1-H bending of anomeric carbon (Cellulose) (Ates et al. 2009)

The heat treatment changed chemical composition of wood with hemicellulose the first component to be affected from 160-260°C (Esteves et al. 2013). Here its peak around 1730 cm^{-1} (attributed to the carboxyl- and ester groups, nonconjugated aldehyde) decreased with treatments at 160, 170 and 180°C from that for untreated samples. This result agrees with Esteves et al. (2013), who studied the FT-IR spectra of heat treated eucalyptus and pine wood, found that the band around 1730 cm^{-1} decreased initially at 170-180°C for 2-24 h due to the breaking of acetyl or acetoxy groups in xylan. Furthermore, the absorption by treated samples also decreased around 3340 cm^{-1} (OH stretching). This confirms that the number of hydroxyl groups was decreased by the treatments.

Table 3-7 Relative crystallinity index of cellulose for untreated and treated (140-180ºC for 3 h) rubberwood samples.

Superheated steam treatment temperature	**Crystallinity**	
	I1425/I898	**I1369/I2918**
Untreated	1.182	1.140
140°C	1.409	1.056
150°C	1.338	1.137
160°C	1.688	1.105
170°C	2.721	1.252
180°C	4.560	1.384

The ratio of peak intensities at 1425 and 897 cm^{-1} (I1425/I898) and the similar ratio I1369/I2918 in FT-IR spectra of the wood samples were used to estimate the crystallinity of cellulose in wood samples (Fabiyi and Ogunleye 2015). The results in Table 3-7 reveal that the I1425/I898 ratio for cellulose in rubberwood samples ranged from 1.182 to 4.560, and the I1369/I2918 ratio ranged from 1.056 to 1.384. According to these results, it was stated that the relative crystallinity was affected from superheated steam treatment in rubberwood samples. In a previous study, the degree of cellulose crystallinity in spruce and beech wood samples also increased with thermal modification at 150 and 180°C for 6 and 10 h due to the degradation of hemicelluloses and amorphous cellulose (Yildiz and Gümüşkaya 2007). In this study, the relative crystallinity increased with temperature, for superheated steam treatment with 3 h duration, compared to untreated sample and the largest values were found in the samples treated at 180°C for 3 h. The results indicate that the superheated steam treatment reduced accessible OH groups, and this should decrease the water adsorption by treated wood.

3.7 Scanning electron microscope (SEM) analysis

SEM micrographs for the untreated and treated rubberwood samples at 140, 150, 160, 170 and 180°C for 3 hours are shown in Fig. 3-8 (a)-(f), respectively. With reference to circle or oval shapes observed by Gunduz et al. (2016) as starch grains, Fig. 3-8 indicates that the numbers of starch grains (or granules) were decreased with increasing temperature. The data in Table 3-8 also confirm this result. ImageJ software was used to analyze coverage of starch particles on the wood, as a function of the total SEM photo area. The data revealed that the coverage by starch particles decreased consistently with treatment temperature, and the lowest coverage (0.963%) was obtained with treatment at 180°C for 3 h.

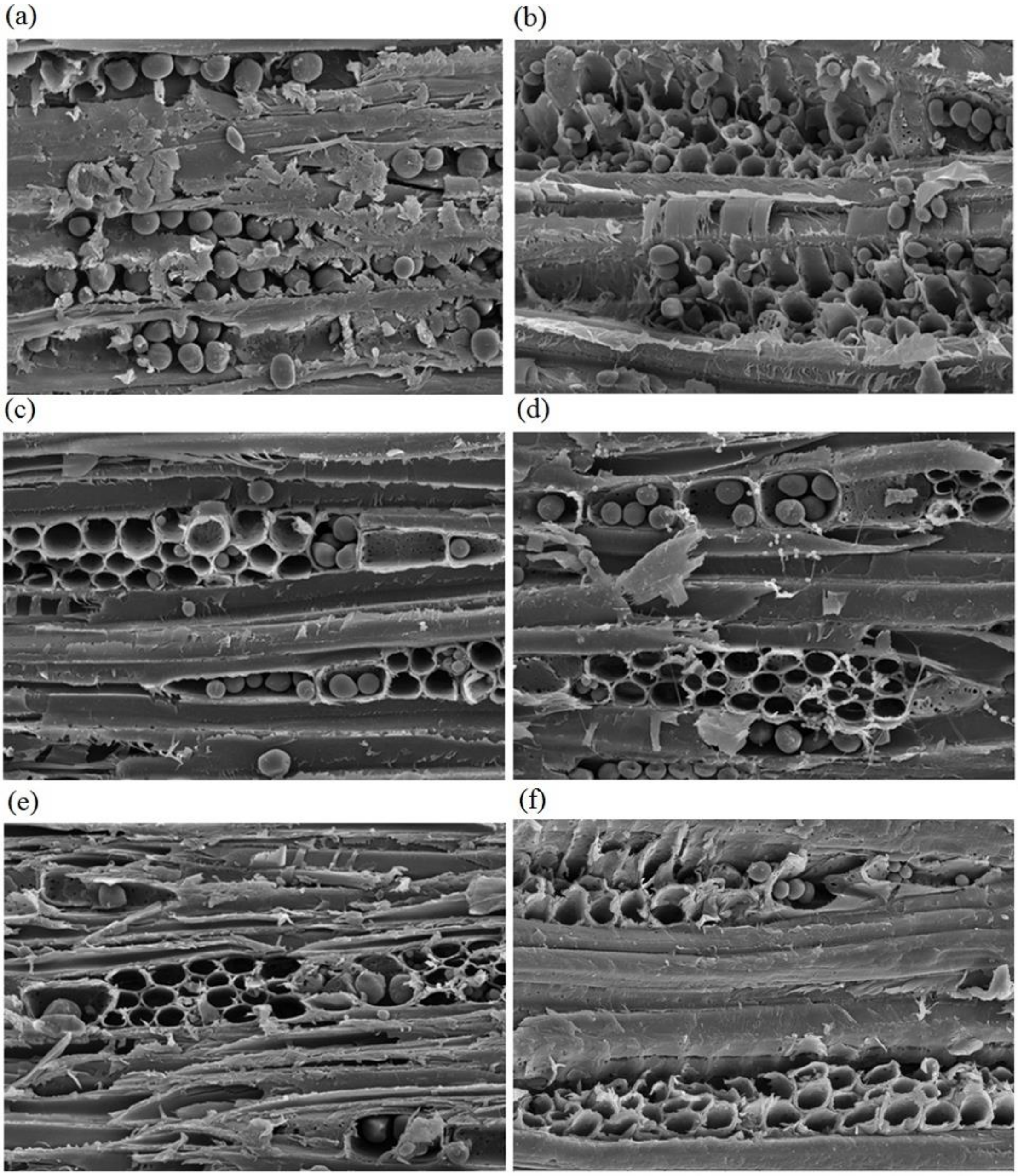


Fig. 3-8 SEM images (magnification x500) of the tangential sections of untreated and treated wood show spherical starch grains in the cell; (a) untreated, (b) 140°C for 3 h, (c) 150°C for 3 h, (d) 160°C for 3 h, 170°C for 3 h, and (e) 180°C for 3 h.

Table 3-8 Area coverage of starch particles in SEM photos for untreated and treated (140-180ºC for 3 h) rubberwood samples (analyzed using ImageJ).

Treatment condition	Area of starch particles/surface area (%)
Untreated	14.953
140°C	5.583
150°C	3.695
160°C	4.266
170°C	2.492
180°C	0.963

CHAPTER 4

Conclusions and Suggestions

4.1 Conclusions

1) The effect of superheated steam treatment on the mechanical properties of rubberwood

The superheated steam treatment conditions were able to improve the mechanical properties given as the percentage increase relative to the untreated samples. The largest increase of hardness and impact strength was found in the treated samples at 160°C for 3 h increased by 13.46% and 33.33% respectively, compared to the untreated sample of each condition. In the case of compress and tensile strength properties, the largest increase were found in the treated samples at 140°C for 1 h and 150°C for 2 h increased by 17.32% and 17.48 respectively, compared to the untreated sample.

2) The effect of superheated steam treatment on the moisture adsorption of rubberwood

In this study, superheated steam treatment of rubberwood in different temperatures and durations caused changes in adsorption isotherms, mechanical properties and color, when compared with untreated (pre-dried) rubberwood. The adsorption isotherms were examined by using the Hailwood-Horrobin theory. The wood heat-treated at 160°C for 3 hours had the smallest monolayer and polylayer adsorptions and the most reduced availability of adsorption sites among the treatments tested. The results indicate that the equilibrium moisture content of heat-treated rubberwood mainly decrease due to the loss of available sorption sites.

3) The effect of superheated steam treatment on the color change of rubberwood

The color coordinates L*, a* and b* of the treated samples changed, meaning that the color of the wood surface was altered. The superheated steam treatment of rubberwood caused to treated wood become darker, reddish and yellowish. The most intense total color changes occurred in 160°C for 3 h.

4) The effect of superheated steam treatment on the resistance to fungal and subterranean termite test of rubberwood

For treatment temperatures between 140 and 160°C, and duration 1-3 hours, the weight loss reduced as the treatment temperature and duration increased and the decay resistance of wood against both fungus and termite was improved. The weight loss could reach values up to 62.0% for termite attack and 73.6% for decay fungus found in 160°C for 3 h compared to untreated samples.

5) The effect of superheated steam treatment on the surface and cell-wall components of rubberwood

After analyzed cell-wall components of the heat treated wood by FTIR spectroscopy, it was concluded that the hydroxyl groups of rubberwood samples decreased and crystallinity increased after superheated steam treatment at 140°C, 150°C and 160°C for 3 hours. As a result, moisture adsorption ability of wood reduced. Moreover, SEM micrographs show that the starch particles decreased consistently with increasing in treatment temperature.

4.2 Suggestions

1) For the rubberwood boards using in the research should be obtained from the same source to get more accurate results.

2) The arrangement of rubberwood boards, all experiments must be kept the same position on the rack inside the drying chamber.

3) Improving the efficiency of drying chamber to operate with higher temperature range.

4) Water for generate steam should be used demineralized water to avoid the effects of contamination.

5) Further study might explore to use of higher temperature and different duration.

6) Scale-up of industrial scale can be furthermore developed in two models as below,

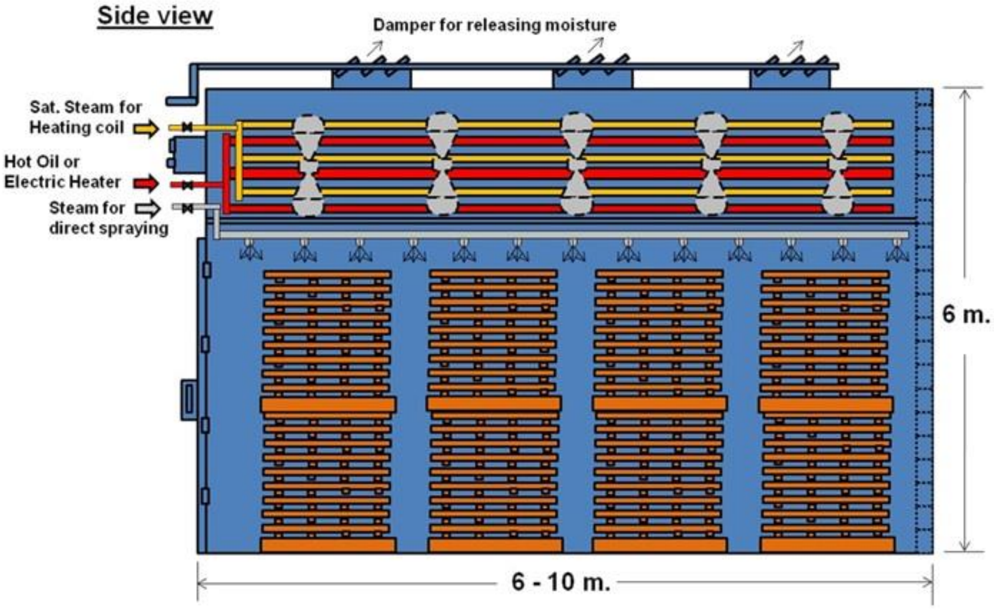
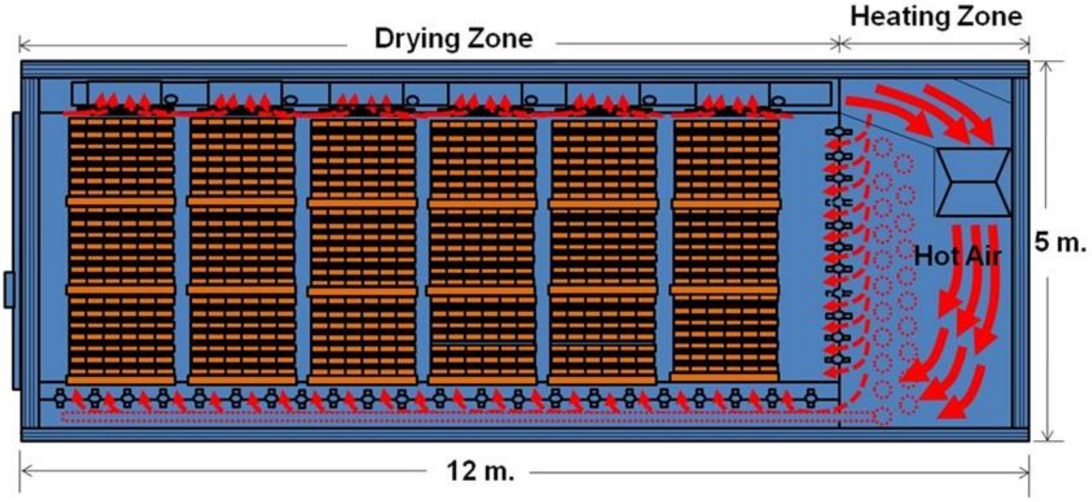


Fig. 4-1 Model 1: Modified original drying room (Refractory Brick).

Side view



Front view

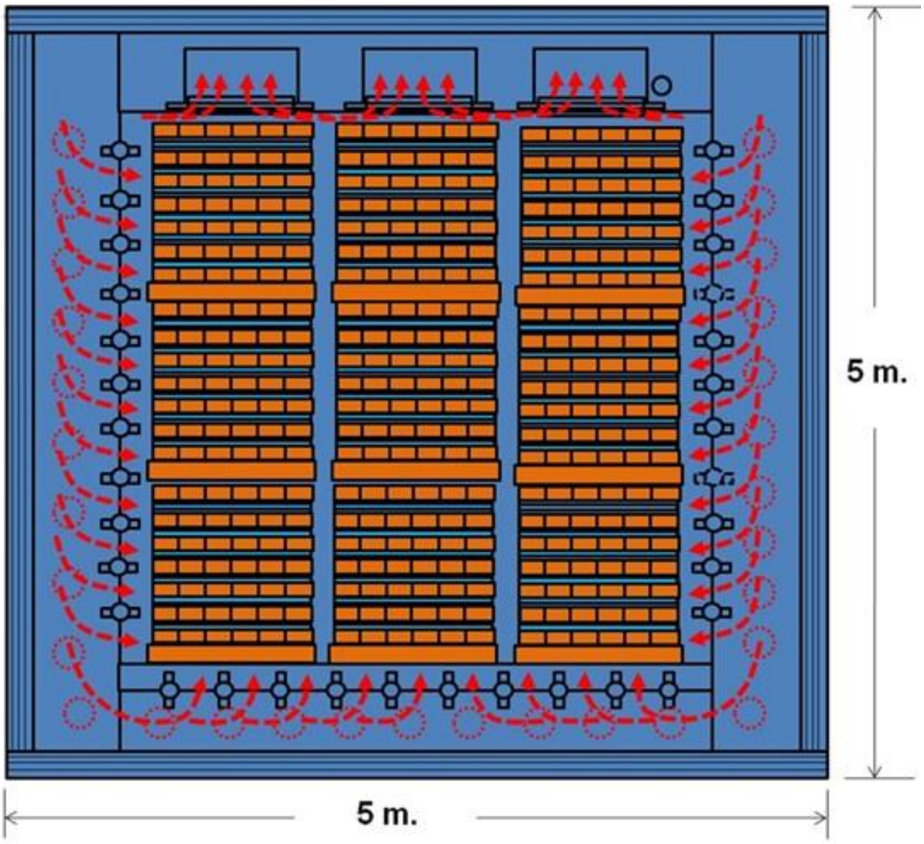


Fig. 4-2 Model 2: New concept of drying room (Insulated Wall).

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APPENDIX A

Experiment data

APPENDIX A1

Data of mechanical properties

Table A- 1 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 140°C for 1 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	80.86	9120	2.00	2.91	97.73	8679	2.10	3.77
2	78.74	8434	1.90	4.14	95.55	9218	1.90	3.45
3	72.76	7698	2.00	3.48	83.61	7993	2.40	4.74
4	77.17	6649	1.25	2.99	99.22	7845	1.60	3.33
5	73.97	10444	1.70	3.33	85.84	10052	1.60	4.87
6	79.61	8042	2.00	3.70	89.83	9620	1.70	4.23
7	76.73	6737	1.25	3.27	88.69	9807	1.80	3.23
8	70.49	9807	1.70	2.89	98.67	8483	2.30	3.33
9	77.14	9169	1.80	2.66	78.39	7894	1.10	3.12
10	77.65	7845	1.75	3.33	80.02	9464	1.85	3.23

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-2 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 140°C for 2 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	93.47	11670	1.80	3.22	94.68	11180	2.20	4.34
2	85.64	10395	1.50	3.24	87.94	11033	1.55	2.92
3	77.72	9856	2.20	2.57	97.65	11817	2.35	5.13
4	86.58	10886	1.30	4.82	88.32	10689	1.75	4.94
5	82.20	7894	1.50	4.96	87.22	9660	2.00	4.70
6	87.19	8973	1.65	5.10	86.48	10444	1.85	4.47
7	81.01	11376	1.00	3.26	91.06	9758	1.10	3.58
8	92.62	8091	1.60	4.72	91.81	11768	1.65	4.01
9	91.76	9709	1.60	4.82	96.17	10787	2.00	3.50
10	91.91	10640	2.70	3.96	91.50	10886	3.10	4.37

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-3 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 140°C for 3 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	87.72	10101	0.80	2.97	93.27	11082	2.20	5.17
2	87.06	10837	2.40	4.32	96.43	10297	2.45	4.58
3	80.00	11719	1.10	4.64	95.47	12798	2.20	4.42
4	103.12	11621	1.20	6.89	91.04	11523	1.40	5.79
5	69.72	13141	1.80	3.23	92.76	12013	1.45	4.91
6	98.88	13288	2.00	6.44	111.02	15053	2.00	6.17
7	86.42	12798	1.40	6.78	112.78	14857	1.05	5.53
8	97.91	11082	2.30	6.32	107.16	12209	1.40	6.96
9	94.00	10199	1.85	5.55	93.15	10935	1.50	6.94
10	100.61	13043	1.00	5.24	100.85	10493	1.30	4.35

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-4 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 150°C for 1 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	109.61	11768	1.50	4.39	101.51	11523	1.30	5.72
2	102.87	12504	1.60	5.21	104.06	13092	1.40	5.67
3	94.58	11572	1.20	4.44	101.98	11719	1.60	4.20
4	102.74	11621	1.30	4.59	103.48	13190	1.40	5.46
5	96.13	10787	0.90	4.82	105.20	12798	0.90	4.73
6	102.96	11229	1.10	4.57	104.68	13896	0.95	5.71
7	84.12	11033	1.00	4.99	104.55	12160	1.20	4.62
8	103.35	12455	1.60	4.70	110.20	14122	1.80	4.11
9	85.05	11278	1.70	5.12	112.61	11768	1.80	5.32
10	97.21	11523	1.80	4.68	99.28	12749	1.85	5.49

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-5 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 150°C for 2 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	118.98	8042	2.40	5.28	106.49	8728	1.80	5.46
2	101.18	7306	1.90	3.05	102.66	8483	2.40	3.52
3	110.11	7012	2.10	4.87	106.16	7698	2.40	4.93
4	116.11	7993	1.50	4.61	109.91	8581	1.70	5.58
5	85.68	9022	2.50	3.88	100.53	8777	3.00	6.20
6	97.28	8189	2.00	2.73	102.73	8875	1.80	3.36
7	108.46	7502	2.40	3.83	105.01	8826	3.10	4.86
8	99.17	7796	2.00	4.70	121.02	7796	2.60	5.20
9	98.75	9120	1.80	4.47	103.42	8630	1.80	4.77
10	82.21	7306	2.00	3.77	105.96	8875	2.30	4.56

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-6 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 150°C for 3 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	74.09	7600	2.30	5.15	92.45	9660	1.90	4.66
2	85.74	7404	1.40	5.05	91.42	8238	1.80	5.19
3	90.36	13533	1.70	4.23	98.56	15250	1.50	4.01
4	79.68	14220	1.30	5.41	81.77	14710	1.30	5.47
5	66.72	9071	0.50	3.27	91.05	10542	1.10	4.57
6	99.68	9365	1.10	3.60	97.14	9022	1.20	4.91
7	105.47	13141	1.40	4.79	95.22	14416	2.50	5.11
8	88.97	9120	2.15	4.72	108.67	8434	2.45	4.68
9	89.89	7453	2.00	3.92	92.62	13730	2.10	4.63
10	81.17	11082	2.00	4.88	91.63	8385	2.10	5.09

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-7 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 160°C for 1 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	107.52	7404	1.00	5.66	93.57	8581	1.25	5.36
2	109.15	7306	1.00	5.51	97.37	8434	1.35	5.75
3	62.59	10640	1.50	4.98	110.94	12209	1.75	5.02
4	96.16	10689	2.00	5.27	91.52	11915	2.30	4.26
5	67.78	10591	2.00	4.24	96.78	11817	2.95	3.91
6	102.84	10935	2.50	3.62	79.22	10591	1.90	4.42
7	92.52	10542	1.10	3.90	101.73	12259	1.60	5.26
8	84.96	9709	1.00	4.73	73.98	9415	0.70	5.11
9	98.37	7698	1.10	4.77	104.54	8434	1.00	4.89
10	96.47	10395	2.00	5.13	94.41	12209	2.50	4.61

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-8 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 160°C for 2 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	99.16	8042	1.40	3.44	97.49	9052	1.40	2.39
2	95.96	8826	0.45	2.91	95.67	8581	1.65	4.09
3	94.93	9120	1.75	3.03	95.54	10493	1.25	4.17
4	92.47	9415	1.90	2.68	91.00	10935	1.20	4.01
5	93.40	9513	1.10	3.27	100.76	9856	0.65	4.17
6	61.39	9120	2.60	3.87	102.46	9267	1.50	4.01
7	63.85	8336	2.50	4.01	90.51	8924	2.00	3.89
8	87.94	9022	2.80	4.16	98.67	10984	1.45	3.39
9	79.03	8875	2.90	4.00	83.34	10052	2.00	2.79
10	95.88	9807	2.00	4.00	85.15	8924	2.00	3.75

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

Table A-9 Data of mechanical properties of the untreated and superheated steam treated rubberwood at 160°C for 3 h.

Sample No.	Untreated				Treated			
	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)	CP (MPa)	HN (N)	IP (Kg-m)	TS (MPa)
1	100.22	9022	0.60	4.75	114.40	9660	1.45	4.88
2	105.02	10886	1.00	4.94	117.61	13190	1.40	5.65
3	97.68	12357	1.40	2.55	103.70	12602	1.45	2.60
4	96.55	10542	2.30	1.83	100.68	12896	2.30	2.71
5	92.54	9071	2.00	2.44	100.57	12308	2.10	3.75
6	106.57	9169	1.40	2.76	119.92	8679	1.45	2.41
7	90.97	9807	1.90	3.12	112.29	12994	2.00	2.87
8	87.78	9218	1.00	3.22	114.39	10542	1.75	3.55
9	97.73	11327	1.00	3.00	100.43	9660	1.80	4.01
10	86.49	10346	0.80	4.40	115.80	12994	1.50	3.10

Where CP is Compression Parallel to grain, HN is Hardness, IP is Transverse impact test (Total energy absorbed) and TS is Tensile Strength.

APPENDIX A2

Data of EMCs

Table A-10 Data of EMC at various levels of RH for untreated and treated rubberwood samples at 140°C for 1-3 h.

RH (%)	Sample No.	Untreated sample	Treatment Duration (H)		
			1	2	3
11	1	3.623	3.214	2.742	2.624
	2	3.647	3.310	2.705	2.612
	3	3.620	3.317	2.702	2.633
32	1	6.326	5.636	5.088	4.838
	2	6.309	5.598	4.893	4.676
	3	6.430	5.583	5.000	4.708
43	1	7.207	6.430	5.715	5.683
	2	7.216	6.287	5.749	5.578
	3	7.108	6.450	5.940	6.130
51	1	8.088	7.047	5.981	6.467
	2	8.010	7.235	6.746	6.558
	3	8.130	7.208	6.474	5.945

Table A-10 Data of EMC at various levels of RH for untreated and treated rubberwood samples at 140°C for 1-3 h. (Continued)

RH (%)	Sample No.	Untreated sample	Treatment Duration (H)		
			1	2	3
75	1	11.421	11.274	11.008	10.952
	2	11.391	11.368	10.825	10.956
	3	11.485	11.317	10.758	10.463
92	1	22.075	21.064	19.688	20.080
	2	22.063	21.025	19.712	19.609
	3	22.057	21.060	19.990	19.238

Table A-11 Data of EMC at various levels of RH for untreated and treated rubberwood samples at 150°C for 1-3 h.

RH (%)	Sample No.	Treatment Duration (H)		
		1	2	3
11	1	2.512	2.585	2.410
	2	2.451	2.492	2.483
	3	2.839	2.464	2.430
32	1	4.434	4.412	4.307
	2	4.752	4.530	4.368
	3	4.717	4.621	4.429
43	1	5.214	5.138	5.114
	2	5.218	5.142	5.132
	3	5.210	5.181	5.123
51	1	6.314	6.254	6.062
	2	6.471	6.283	6.100
	3	6.568	6.271	6.051
75	1	10.721	10.728	10.292
	2	10.739	10.744	10.277
	3	10.761	10.710	10.409
92	1	19.120	18.397	17.822
	2	18.723	18.475	18.274
	3	18.871	18.260	17.230

Table A-12 Data of EMC at various levels of RH for untreated and treated rubberwood samples at 160°C for 1-3 h.

RH (%)	Sample No.	Treatment Duration (H)		
		1	2	3
11	1	2.351	2.495	2.228
	2	2.509	2.209	2.258
	3	2.380	2.249	2.171
32	1	4.606	4.135	3.927
	2	4.601	4.215	3.927
	3	4.485	4.176	3.924
43	1	5.252	5.056	4.998
	2	5.012	4.996	5.012
	3	5.166	5.080	5.020
51	1	5.870	5.486	5.376
	2	5.897	5.495	5.364
	3	5.894	5.540	5.384
75	1	10.061	9.941	9.940
	2	10.652	10.055	9.959
	3	10.402	10.161	9.921
92	1	17.937	17.367	17.155
	2	18.556	17.444	17.223
	3	17.918	17.332	17.242

APPENDIX A3

Data of color properties

Table A-13 Data of color properties of the untreated and superheated steam treated rubberwood at 140°C.

Time (H)	Sample No.	Untreated			treated			ΔE*
		L*	a*	b*	L*	a*	b*	
1	1	71.08	7.97	23.75	65.53	9.80	25.13	6.01
	2	72.48	7.50	22.99	68.23	9.21	25.28	5.12
	3	62.16	12.47	24.77	59.49	12.97	25.17	2.75
	4	70.43	7.68	24.56	69.47	9.19	27.00	3.03
	5	71.96	9.11	25.63	68.04	7.48	25.18	4.26
2	1	66.44	8.10	25.07	60.86	9.64	24.80	5.79
	2	68.80	8.74	25.24	67.26	8.86	26.44	1.95
	3	66.49	9.26	24.81	65.66	10.24	27.10	2.63
	4	68.21	9.02	24.64	61.22	11.41	26.87	7.71
	5	67.19	9.68	24.99	59.73	11.85	27.35	8.12
3	1	66.60	10.84	25.99	63.55	11.92	27.09	3.42
	2	69.31	9.65	25.54	58.59	13.22	26.75	11.36
	3	66.45	10.83	25.80	60.35	12.42	26.12	6.31
	4	64.99	11.45	25.41	61.32	12.42	26.41	3.92
	5	67.27	6.53	24.26	53.29	12.81	25.43	15.38

Table A-14 Data of color properties of the untreated and superheated steam treated rubberwood at 150°C.

Time (H)	Sample No.	Untreated			treated			ΔE*
		L*	a*	b*	L*	a*	b*	
1	1	73.14	7.99	25.06	72.00	8.16	1.64	1.64
	2	70.19	9.21	25.18	68.46	10.01	1.94	1.94
	3	72.14	8.30	26.51	69.13	7.66	3.25	3.25
	4	72.52	8.03	24.22	72.11	6.05	2.28	2.28
	5	69.03	8.82	25.60	65.58	7.43	3.74	3.74
2	1	67.25	8.18	21.84	61.99	8.70	5.91	5.91
	2	68.24	8.85	23.30	64.51	10.71	4.45	4.45
	3	71.29	7.41	23.71	66.86	10.13	5.51	5.51
	4	68.42	10.60	24.34	67.16	8.71	2.43	2.43
	5	63.67	10.76	25.46	60.98	9.57	2.99	2.99
3	1	70.57	8.59	26.03	66.10	10.69	4.94	4.94
	2	69.74	9.06	25.33	66.79	10.09	3.27	3.27
	3	66.20	10.60	25.84	61.10	13.60	5.96	5.96
	4	64.39	11.85	26.21	61.54	12.84	3.09	3.09
	5	67.42	8.90	25.94	64.35	10.25	3.36	3.36

Table A-15 Data of color properties of the untreated and superheated steam treated rubberwood at 160°C.

Time (H)	Sample No.	Untreated			treated			ΔE*
		L*	a*	b*	L*	a*	b*	
1	1	52.24	14.65	24.82	52.51	14.65	25.77	0.99
	2	61.93	10.92	24.52	59.30	11.92	25.38	2.94
	3	70.50	9.37	25.90	66.43	9.94	25.95	4.11
	4	61.19	12.90	26.98	65.38	9.99	26.48	5.12
	5	72.08	7.37	25.49	68.43	8.32	26.91	4.03
2	1	67.40	9.29	25.66	62.75	10.20	26.24	4.77
	2	62.16	12.34	26.80	60.93	12.65	28.04	1.77
	3	64.59	9.93	25.10	61.69	12.29	27.87	4.66
	4	71.34	8.45	26.25	68.12	10.08	28.20	4.10
	5	60.12	11.69	26.37	57.80	11.61	25.30	2.56
3	1	62.11	10.97	24.43	58.82	12.01	27.23	4.45
	2	68.24	9.68	27.16	65.58	10.62	27.94	2.93
	3	65.16	10.82	27.37	61.10	12.46	28.56	4.54
	4	71.61	8.69	23.64	66.19	10.15	26.71	6.40
	5	73.12	7.71	25.39	64.65	9.84	24.48	8.78

APPENDIX A4

Data of weight losses from decay

Table A-16 Data of weight losses of the untreated rubberwood samples after exposure to the white-rot decay fungus for 12 weeks.

Sample No.	W_1 (g)	W_2 (g)	$\%WL_t$
1	6.779	5.736	15.386
2	6.177	5.257	14.894
3	6.735	5.718	15.100
4	5.515	4.677	15.195
5	5.339	4.521	15.321

Where W_1 is oven-dried weight of the specimen before exposure to the fungus, W_2 is oven-dried weight of the specimen after exposure to the fungus (g) and WL_f is weight loss from fungus decay test.

Table A-17 Data of weight losses of the untreated rubberwood samples after exposure to the termite for four weeks.

	No-choice test			Choice test		
Sample No.	W_3 (g)	W_4 (g)	$\%WL_t$	W_3 (g)	W_4 (g)	$\%WL_t$
1	4.426	3.411	22.933	4.948	3.719	24.838
2	4.879	3.956	18.918	4.276	3.273	23.457
3	4.026	3.229	19.796	5.008	3.966	20.807
4	5.284	4.187	20.761	5.079	4.062	20.024
5	5.424	4.334	20.096	5.559	4.363	21.515

Where W_3 is oven-dried weight of the specimen before exposure to the termites, W_4 is oven-dried weight of the specimen after exposure to the termites (g) and WL_t is weight loss from termite test.

Table A-18 Data of weight losses of the superheated steam rubberwood samples after exposure to the white-rot decay fungus for 12 weeks.

T (°C)	Sample No.	Treatment duration (H)								
		1			2			3		
		W_1 (g)	W_2 (g)	%WL_f	W_1 (g)	W_2 (g)	%WL_f	W_1 (g)	W_2 (g)	%WL_f
140	1	5.431	4.820	11.250	5.233	4.654	11.064	6.523	5.885	9.781
	2	6.243	5.523	11.533	4.806	4.280	10.945	5.966	5.417	9.202
	3	7.166	6.336	11.582	5.841	5.210	10.803	5.979	5.426	9.249
	4	7.531	6.635	11.897	6.314	5.628	10.865	5.959	5.407	9.263
	5	5.486	4.821	12.122	5.982	5.311	11.217	5.936	5.352	9.838
150	1	6.064	5.545	8.559	5.509	5.055	8.241	4.618	4.259	7.774
	2	6.562	5.986	8.778	5.674	5.208	8.213	4.920	4.554	7.439
	3	4.620	4.213	8.810	5.150	4.733	8.097	4.576	4.216	7.867
	4	5.039	4.603	8.653	5.328	4.887	8.277	4.813	4.444	7.667
	5	4.997	4.569	8.565	5.404	4.959	8.235	4.367	4.044	7.396
160	1	5.154	4.745	7.936	5.574	5.245	5.902	5.582	5.359	3.995
	2	5.566	5.128	7.869	5.552	5.219	5.998	6.783	6.518	3.907
	3	6.030	5.536	8.192	7.289	6.851	6.009	7.130	6.845	3.997
	4	5.815	5.348	8.031	6.076	5.719	5.876	6.472	6.211	4.033
	5	5.503	5.045	8.323	6.141	5.776	5.944	5.325	5.109	4.056

Where W_1 is oven-dried weight of the specimen before exposure to the fungus, W_2 is oven-dried weight of the specimen after exposure to the fungus (g) and WL_f is weight loss from fungus decay test.

Table A-19 Data of weight losses of the untreated and superheated steam treatment of rubberwood samples after exposure to the no-choice termite for four weeks.

T (°C)	Sample No.	Treatment duration (H)								
		1			2			3		
		W_3 (g)	W_4 (g)	$\%WL_t$	W_3 (g)	W_4 (g)	$\%WL_t$	W_3 (g)	W_4 (g)	$\%WL_t$
140	1	5.318	4.262	19.857	4.343	3.556	18.121	5.181	4.377	15.518
	2	4.267	3.494	18.116	3.671	2.960	19.368	5.028	4.335	13.783
	3	5.582	4.424	20.745	4.102	3.360	18.089	4.756	4.138	12.994
	4	4.463	3.637	18.508	4.487	3.692	17.718	4.679	3.992	14.683
	5	3.674	2.849	22.455	5.020	4.168	16.972	6.057	5.133	15.255
150	1	4.351	3.709	14.755	5.493	4.748	13.563	6.118	5.337	12.766
	2	4.662	3.928	15.744	3.916	3.320	15.220	3.911	3.467	11.353
	3	4.551	3.922	13.821	4.414	3.865	12.438	5.160	4.566	11.512
	4	4.838	4.034	16.618	4.533	3.933	13.236	5.587	4.980	10.865
	5	3.806	3.285	13.689	5.454	4.750	12.908	5.559	4.905	11.765
160	1	5.590	4.946	11.521	5.481	4.932	10.016	4.838	4.409	8.867
	2	5.827	5.120	12.133	6.138	5.536	9.808	4.591	4.186	8.822
	3	5.802	5.033	13.254	5.035	4.545	9.732	5.781	5.338	7.663
	4	4.822	4.249	11.883	4.797	4.334	9.652	4.951	4.609	6.908
	5	5.566	4.986	10.420	5.328	4.847	9.028	4.936	4.609	6.625

Where W_3 is oven-dried weight of the specimen before exposure to the termites, W_4 is oven-dried weight of the specimen after exposure to the termites (g) and WL_t is weight loss from termite test

APPENDIX A5

Data of moisture sorption properties

Table A-20 Hailwood-Horrobin (H-H) Data analysis

Temperature	Duration	RH (%)											
		11		32		43		51		75		92	
		M	H/M	M	H/M	M	H/M	M	H/M	M	H/M	M	H/M
Untreated		3.630	3.030	6.355	5.035	7.177	5.991	8.076	6.315	11.432	6.560	22.065	4.169
140°C	1H	3.280	3.353	5.606	5.708	6.389	6.730	7.163	7.119	11.320	6.626	21.050	4.371
	2H	2.716	4.050	4.994	6.408	5.801	7.412	6.400	7.969	10.864	6.904	19.797	4.647
	3H	2.623	4.193	4.740	6.750	5.797	7.418	6.324	8.065	10.790	6.951	19.642	4.684
150°C	1H	2.601	4.230	4.634	6.905	5.214	8.247	6.451	7.906	10.740	6.983	18.905	4.867
	2H	2.514	4.376	4.521	7.078	5.153	8.344	6.269	8.135	10.727	6.992	18.377	5.006
	3H	2.441	4.507	4.368	7.326	5.123	8.394	6.071	8.400	10.326	7.263	17.775	5.176

Table A-20 Hailwood-Horrobin (H-H) Data analysis (Continued)

Superheated steam treatment	Duration	RH (%)											
		11		32		43		51		75		92	
		M	H/M	M	H/M	M	H/M	M	H/M	M	H/M	M	H/M
160°C	1H	2.413	4.558	4.564	7.012	5.143	8.360	5.887	8.663	10.372	7.231	18.137	5.073
	2H	2.318	4.746	4.175	7.664	5.044	8.525	5.507	9.261	10.052	7.461	17.381	5.293
	3H	2.219	4.958	3.926	8.150	5.010	8.583	5.374	9.490	9.940	7.545	17.206	5.347

Where M is equilibrium moisture content (EMC, %), H is relative humidity (RH, %) and H/M is the ratio of RH versus EMC gives parabolic curves.

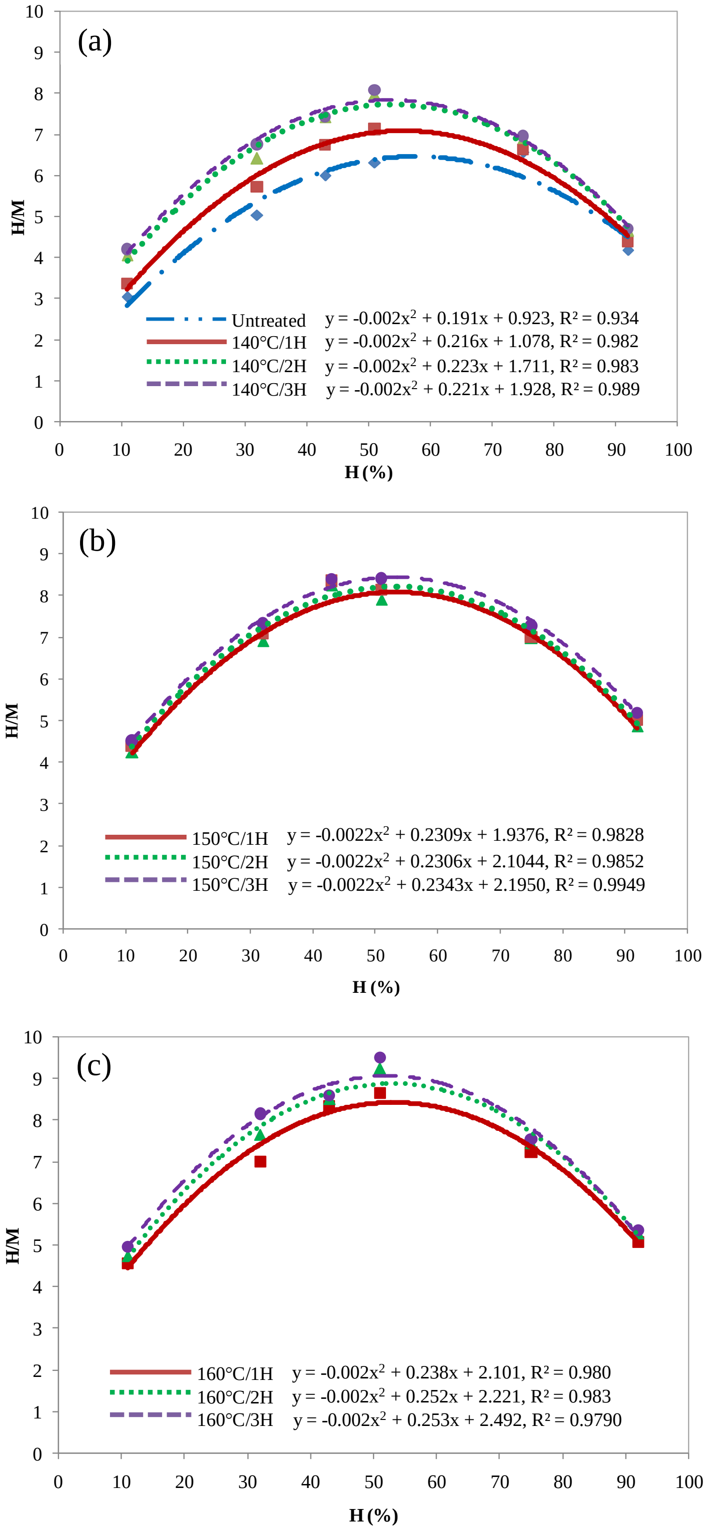


Fig. A-1 Parabola predicted by H-H theory of untreated and treated samples at different conditions.

Table A-21 Fitted and calculated empirical parameters from the Hailwood-Horribon adsorption isotherms.

Superheated steam treatment	**Duration**	**Empirical Equation**	**Empirical parameters**			
			A	**B**	**C**	**R^2**
Untreated		$y = -0.002x^2 + 0.192x + 0.923$	0.923	0.192	0.002	0.934
140°C	**1H**	$y = -0.002x^2 + 0.216x + 1.078$	1.078	0.216	0.002	0.982
	2H	$y = -0.002x^2 + 0.223x + 1.711$	1.711	0.223	0.002	0.983
	3H	$y = -0.002x^2 + 0.221x + 1.928$	1.928	0.221	0.002	0.989
150°C	**1H**	$y = -0.002x^2 + 0.231x + 1.938$	1.938	0.231	0.002	0.983
	2H	$y = -0.002x^2 + 0.231x + 2.104$	2.104	0.231	0.002	0.985
	3H	$y = -0.002x^2 + 0.234x + 2.195$	2.195	0.234	0.002	0.995

Table A-21 Fitted and calculated empirical parameters from the Hailwood-Horribon adsorption isotherms. (Continued)

Superheated steam treatment	**Duration**	**Empirical Equation**	**Empirical parameters**			
			A	**B**	**C**	**R^2**
160	**1H**	$y = -0.002x^2 + 0.238x + 2.101$	2.101	0.238	0.002	0.980
	2H	$y = -0.002x^2 + 0.252x + 2.221$	2.221	0.252	0.002	0.983
	3H	$y = -0.002x^2 + 0.253x + 2.492$	2.492	0.253	0.002	0.979

Table A-22 Calculated physical constants from empirical parameters of Hailwood-Horribon adsorption isotherms.

Superheated steam treatment	**Duration**	**Physical constants**					
		k_1	**k_2**	**W**	**Mh (%)**	**Ms (%)**	**Mh+Ms (%)**
Untreated		25.357	0.852	373.199	4.610	27.826	32.436
140°C	**1H**	24.247	0.861	421.468	4.075	26.371	30.447
	2H	16.015	0.869	455.275	3.689	26.207	29.895
	3H	14.201	0.870	458.691	3.630	26.149	29.780
150°C	**1H**	14.619	0.875	476.655	3.503	26.437	29.939
	2H	13.553	0.873	481.215	3.449	25.724	29.173
	3H	13.287	0.869	490.388	3.378	24.335	27.713

Table A-22 Calculated physical constants from empirical parameters of Hailwood-Horribon adsorption isotherms. (Continued)

Superheated steam treatment	**Duration**	**Physical constants**					
		k_1	**k_2**	**W**	**Mh (%)**	**Ms (%)**	**Mh+Ms (%)**
160	**1H**	13.970	0.873	494.462	3.365	25.089	28.454
	2H	13.899	0.879	523.306	3.179	24.892	28.072
	3H	12.580	0.875	532.996	3.096	23.627	26.723

From Table A-21 and Table A-22; when parabolic relationship form is $\frac{H}{M} = A + BH - CH^2$,

$$k_1 = 1 + \frac{B_1 + B\sqrt{B^2 + 4AC}}{2AC},\ k_2 = \frac{50(-B + \sqrt{B^2 + 4AC}}{A},\ W = 1800\sqrt{B^2 + 4AC},$$

$$M_h = \frac{1800}{W}\left(\frac{k_1 k_2 H}{100 + k_1 k_2 H}\right) \text{ and } M_s = \frac{1800}{W}\left(\frac{k_2 H}{100 - k_2 H}\right)$$

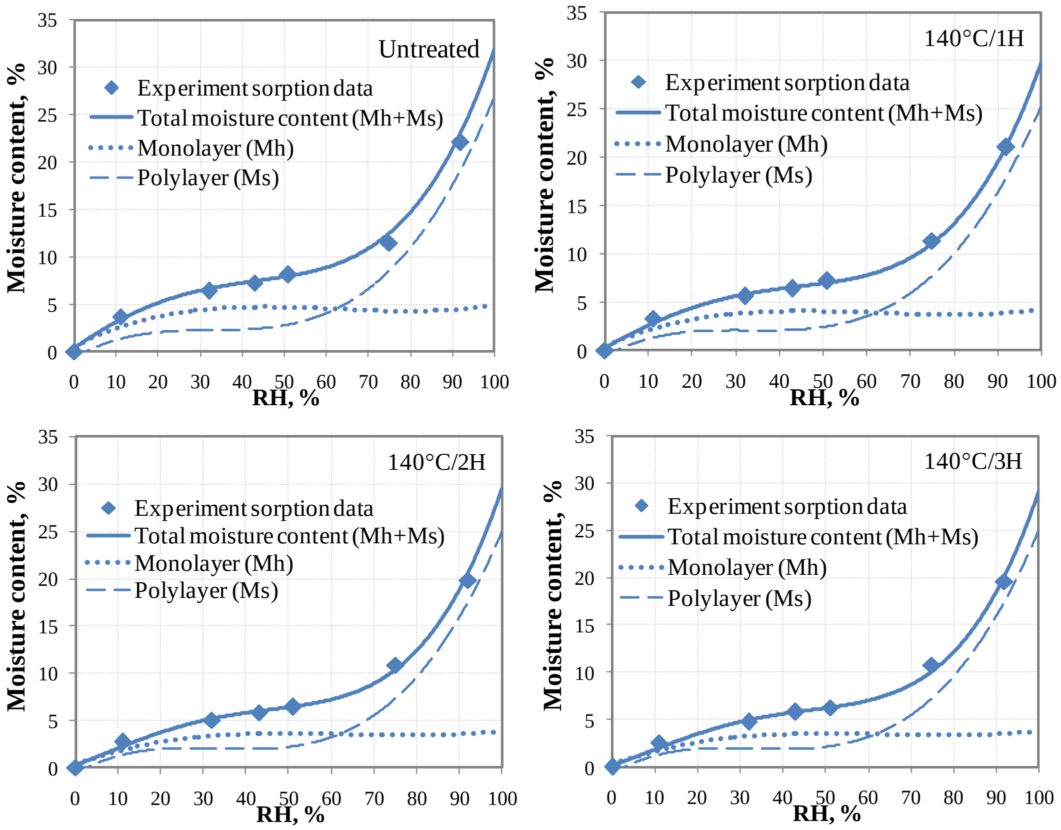


Fig. A-2 Water vapor adsorption experimental data with H-H theory of untreated and treated rubberwood samples at 140°C for 1-3 H.

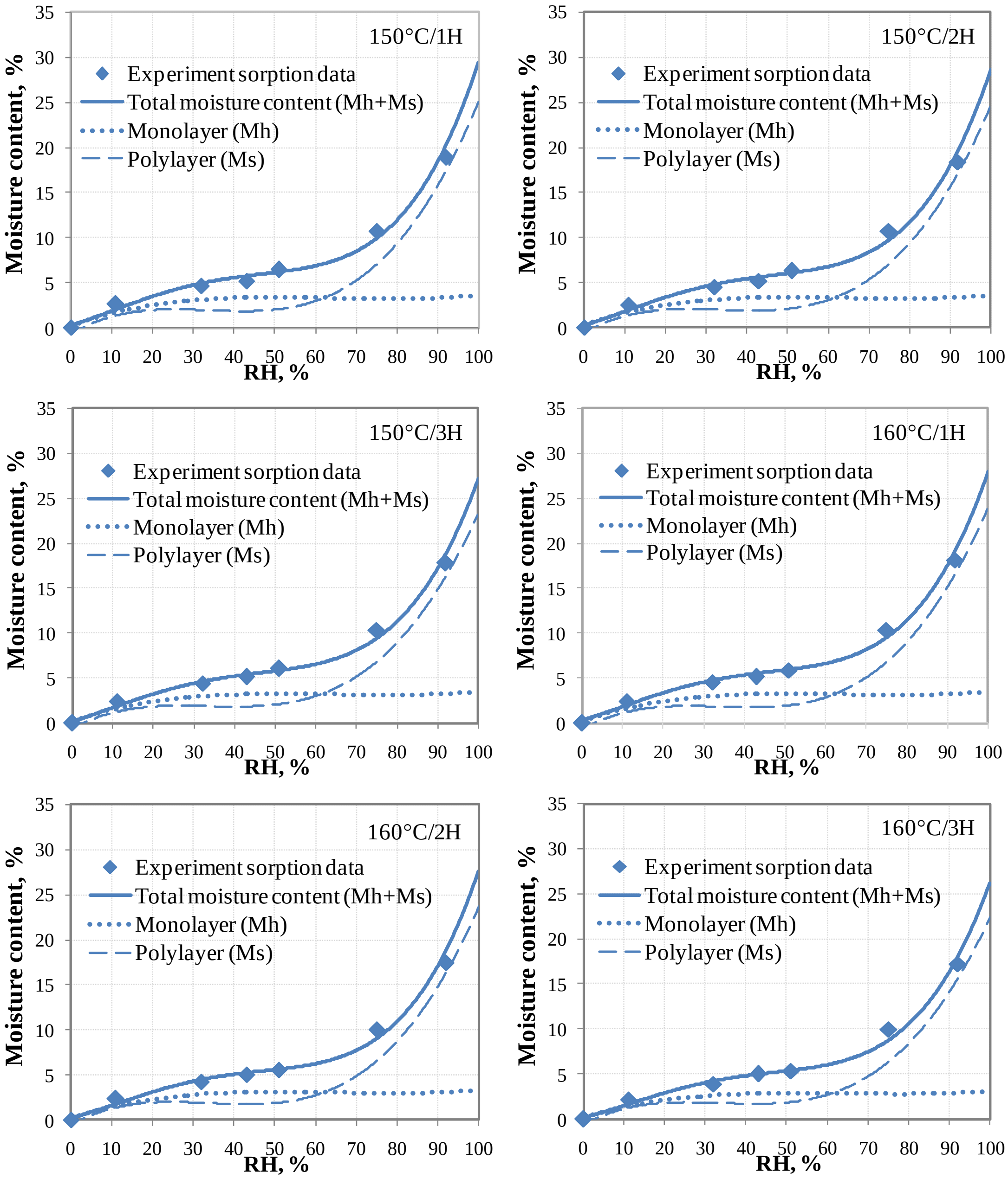


Fig. A-3 Water vapor adsorption experimental data with H-H theory of treated rubberwood samples at 150°C-160°C for 1-3 H.

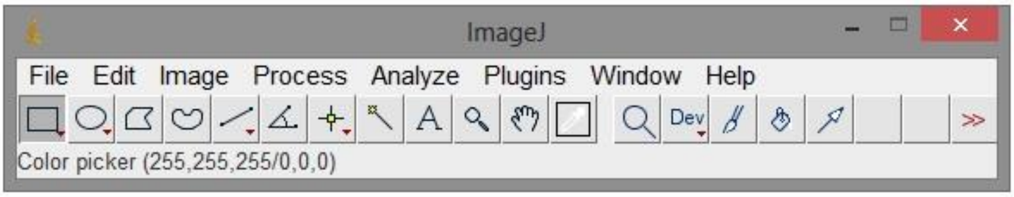
APPENDIX B

Starch grain analysis using ImageJ software

Starch grain analysis using ImageJ software

Procedure of using scanned image and ImageJ software to estimate the particle size:

1. Open the ImageJ software as Fig. B-1 ImageJ softwareand use the file menu to open an image as Fig. B-2 Open an image.



Color picker (255,255,255/0,0,0)

Fig. B-1 ImageJ software

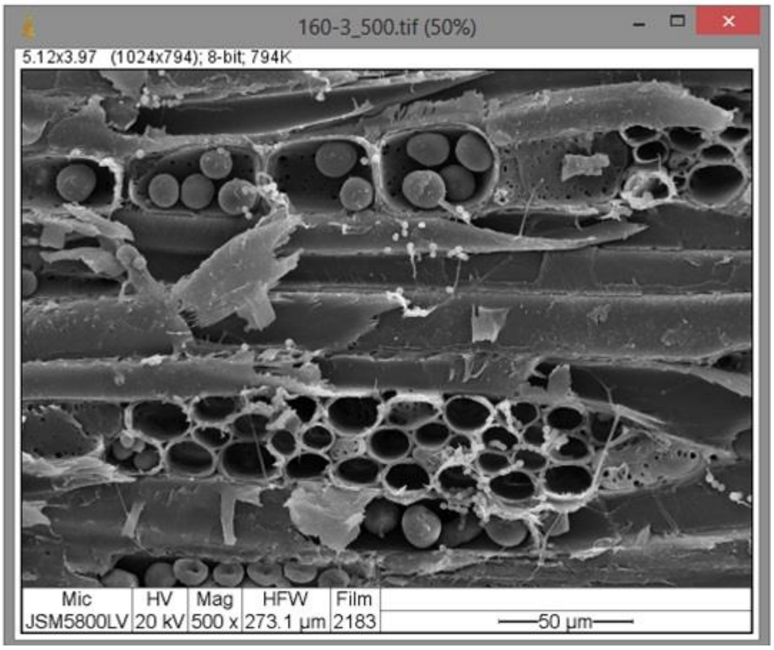
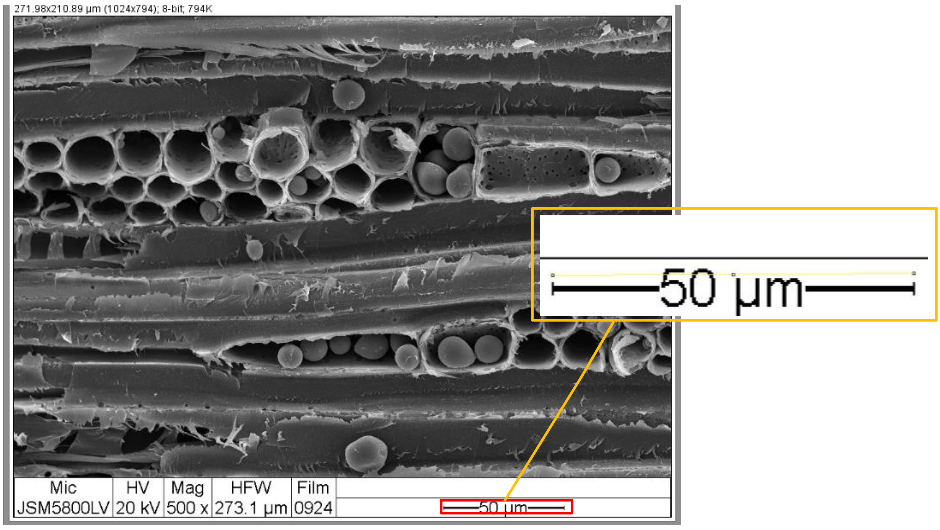


Fig. B-2 Open an image

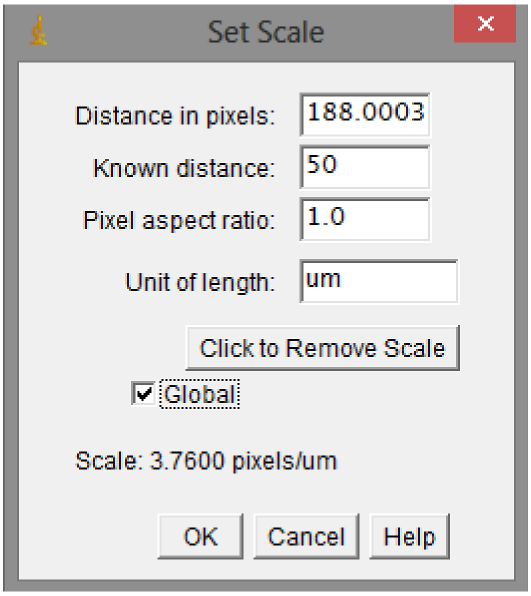
2. Define a known distance on image by selecting the straight line cursor on the toolbar, and then draw a line over the scale's line with the same dimension as precise as possible (Fig. B-3 draw a straight line to defines a known distance on image.).


271.98x210.89 µm (1024x794); 8-bit; 794K

Mic	HV	Mag	HFW	Film
JSM5800LV	20 kV	500 x	273.1 µm	0924

Fig. B-3 draw a straight line to defines a known distance on image.

3. Select 'Analyze' then 'Set Scale', the dialog box as Fig. B-4 Set the scale will open. Enter the 'Known distance' (50 µm in this case) without units and also define the units of length in the 'Unit of length' field (use um instead of µm as unit). Click on 'Global' then Click 'OK'.



Set Scale

Distance in pixels: 188.0003

Known distance: 50

Pixel aspect ratio: 1.0

Unit of length: um

☑ Global

Scale: 3.7600 pixels/um

Fig. B-4 Set the scale

4. Click the Zoom tool (the magnifying glass icon) to zoom in or out the image and use scrolling tool to select a starch grain of interest (Fig. B-5).

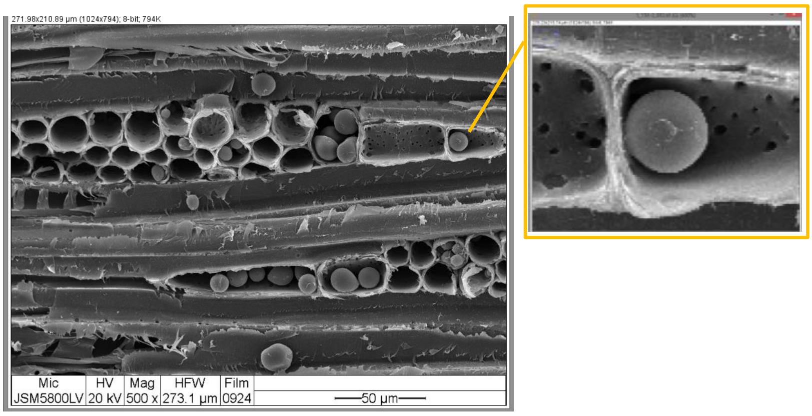
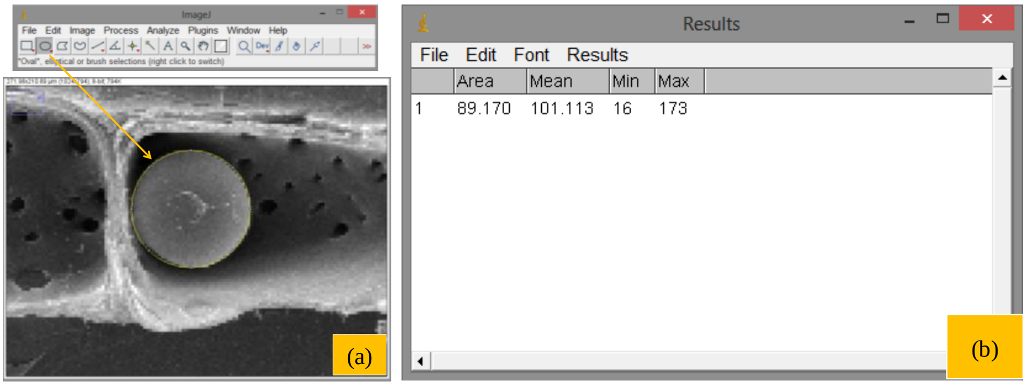


Fig. B-5 Select a point of interest

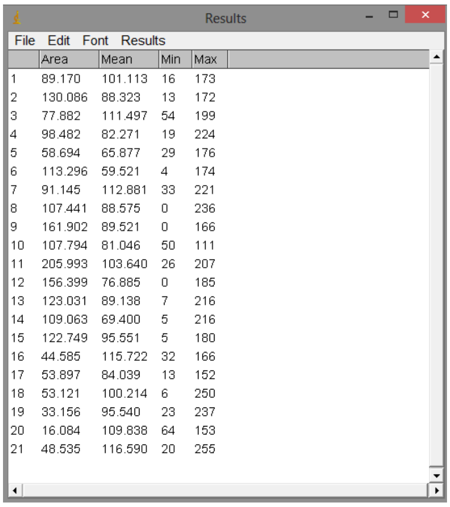
5. To measure each starch grain, select the oval or elliptical tool, click and drag to the desired size (Fig. B-6 (a)). To measure and record the properties of the region, go to 'Analyze' -> 'Measure' (or Ctrl+M). The results window will be opened asFig. B-6 (b).



	Area	Mean	Min	Max
1	89.170	101.113	16	173

Fig. B-6 (a) Measure each starch grain, (b) results table window.

6. Repeat step 5 until entire starch grain has been measured. The results table window look likes Fig. B-7.



	Area	Mean	Min	Max
1	89.170	101.113	16	173
2	130.086	88.323	13	172
3	77.882	111.497	54	199
4	98.482	82.271	19	224
5	58.694	65.877	29	176
6	113.296	59.521	4	174
7	91.145	112.881	33	221
8	107.441	88.575	0	236
9	161.902	89.521	0	166
10	107.794	81.046	50	111
11	205.993	103.640	26	207
12	156.399	76.885	0	185
13	123.031	89.138	7	216
14	109.063	69.400	5	216
15	122.749	95.551	5	180
16	44.585	115.722	32	166
17	53.897	84.039	13	152
18	53.121	100.214	6	250
19	33.156	95.540	23	237
20	16.084	109.838	64	153
21	48.535	116.590	20	255

Fig. B-7 Results table window of entire starch grain on an image.

APPENDIX C

Manuscripts for publication

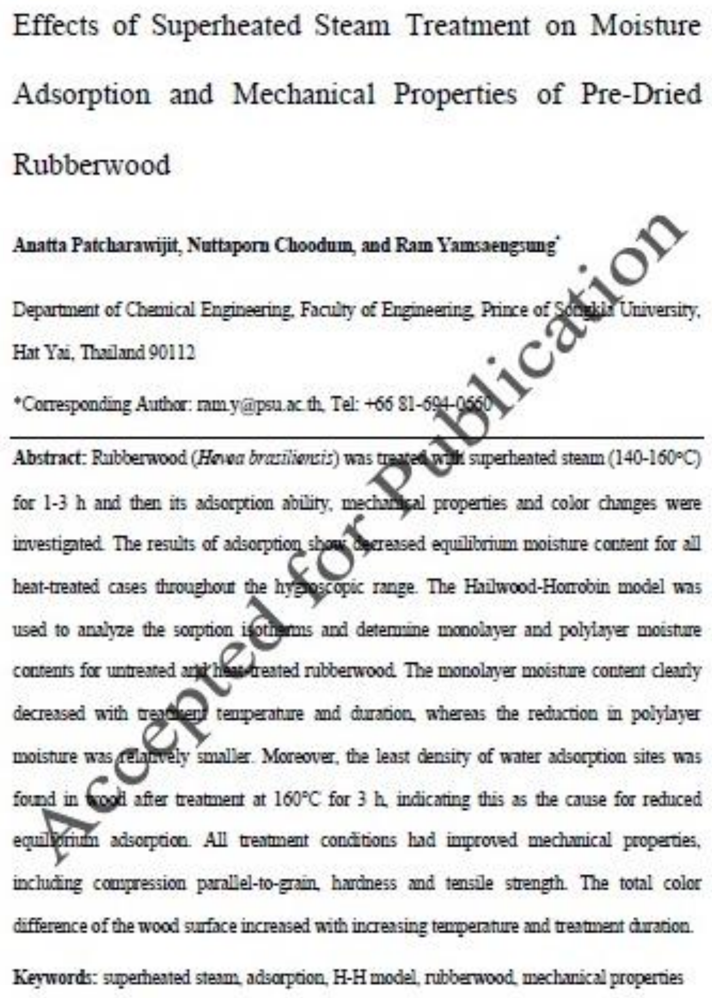
APPENDIX C1

Manuscript I

Title: Effects of Superheated Steam Treatment on Moisture Adsorption and Mechanical Properties of Pre-Dried Rubberwood

Journal Drying Technology

Status: Accepted (26 August 2018)



Effects of Superheated Steam Treatment on Moisture Adsorption and Mechanical Properties of Pre-Dried Rubberwood

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Abstract: Rubberwood (*Hevea brasiliensis*) was treated with superheated steam (140-160°C) for 1-3 h and then its adsorption ability, mechanical properties and color changes were investigated. The results of adsorption show decreased equilibrium moisture content for all heat-treated cases throughout the hygroscopic range. The Hailwood-Horrobin model was used to analyze the sorption isotherms and determine monolayer and polylayer moisture contents for untreated and heat-treated rubberwood. The monolayer moisture content clearly decreased with treatment temperature and duration, whereas the reduction in polylayer moisture was relatively smaller. Moreover, the least density of water adsorption sites was found in wood after treatment at 160°C for 3 h, indicating this as the cause for reduced equilibrium adsorption. All treatment conditions had improved mechanical properties, including compression parallel-to-grain, hardness and tensile strength. The total color difference of the wood surface increased with increasing temperature and treatment duration.

Keywords: superheated steam, adsorption, H-H model, rubberwood, mechanical properties

APPENDIX C2

Manuscript II

Title: Superheated steam treatment of rubberwood to enhance its mechanical, physiochemical, and biological properties

Journal Wood Material Science & Engineering

Status: Under review (19 November 2018)

Superheated steam treatment of rubberwood to enhance its mechanical, physiochemical, and biological properties

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Abstract

This research was aimed to investigate mechanical properties, color and cell-wall components changes, and durability of pre-dried rubberwood (*Hevea brasiliensis*) after superheated steam (SS) treatment. Wood samples were treated at different SS temperatures (140 to 180°C) for 1 to 3 h. The highest compression strength parallel-to-grain, hardness and impact strength were found for samples treated at 160°C for 3 h (30.7% higher than untreated), at 150°C for 1 h (26.6% higher than untreated) and at 150°C for 2 h (52.6% higher than untreated), respectively. The surface color after treatment was deeper than that of untreated wood. The number of accessible hydroxyl groups decreased and the relative cellulose crystallinity increased with SS temperature. Also, SEM micrographs of wood surface showed consistent decrease in starch particles with treatment temperature. Both decay and termite resistances of treated rubberwood improved with treatment temperature and time.

Keywords: Rubberwood, Superheated steam treatment, Mechanical properties, Cellulose

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- The Prince of Songkla University (PSU) Graduate School Research Fund
- The PSU-Ph.D. Scholarship from the Prince of Songkla University
- The Graduate of Engineering Scholarship from Faculty of Engineering, Prince of Songkla University

List of Publication and Proceeding

Patcharawijit, A., Yamsaengsung, R. (2014). The effect of high temperature superheated steam drying on the mechanical properties of rubberwood. The 4th TIChE International Conference, December, 2014, Chiang Mai Thailand.

Patcharawijit A., Choodum N., Yamsaengsung R. (in press). Effects of superheated steam treatment on moisture adsorption and mechanical properties of pre-dried rubberwood. Drying Technology.