

Development of particleboard made from sweet sorghum bagasse and citric acid

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Chapter 1

General introduction

1.1. Current status of forest and agricultural resources in the production of wood-based composites

The consumption of wood-based composites continues to increase with the expansion of the world population (FAO, 2009). On the other hand, forest area that provides wood raw material for wood-based composite products such as particleboard has been decreasing due to deforestation (Nath and Mwchahary, 2012). The food and agriculture organization (FAO) (2016) reported that net forest losses in 2000-2010 were about 7 million hectares per year in tropical countries, while net gain in agricultural land was 6 million hectares per year. The greatest net loss of forests and net gain in agricultural land over the period was in low-income countries, where rural populations are growing.

Large-scale commercial agriculture accounts for about 40% of deforestation in the tropics and subtropics, local subsistence agriculture for 33%, infrastructure for 10%, urban expansion for 10% and mining for 7%. However, there are significant regional variations. For example, commercial agriculture accounts for almost 70% of deforestation in Latin America, but only one-third in Africa, where small-scale agriculture is a more significant driver of deforestation. Globally, utilization of agriculture for human life has been generating abundant residues, as shown in Table 1.1.

Table 1.1 Residues (straw, stalk and shell) of the main agricultural crops in 1983 (Strehler and Stutzle, 1987).

(1,000 ton)

Product	Africa	Asia	Latin America	North America	Europe	Former USSR	Oceania	World
Wheat	12,047	229,085	27,195	124,970	167,970	98,800	24,538	684,605
Rice	12,015	606,476	23,586	11,929	2,743	10	921	657,680
Barley	4,398	19,182	1,482	28,651	95,342	5,460	7,271	161,786
Rye	15	2,720	210	13	23,835	14,700	13	41,506
Oats	354	1,562	1,452	13,460	20,864	2,100	2,135	41,927
Millet	12,470	27,392	190	-	42	3,080	42	43,216
Sorghum	12,603	30,502	22,793	41,083	770	280	2,639	110,670
Maize	22,201	100,157	51,742	218,437	60,264	13,000	549	466,350
Peanut	3832	13,384	846	2,196	24	2	60	20,800
Root crops	54,989	146,142	25,775	14,017	64,353	51,180	1,672	358,128
Sugar	9,592	48,835	64,746	25,250	49	-	4,226	152,698
Oilseed	8,910	80,196	15,968	30,690	22,046	26,802	1,180	185,792
Legumes	8,314	50,700	41,100	78,075	7040	10,867	938	197,034
Cocoa	624	10,104	787	498	-	-	902	12,915
Total	162,364	1,366,893	277,872	589,269	465,342	226,281	47,086	3,135,107

Table 1.2 Chemical properties of various non-wood lignocellulose from agricultural resources (Hurter, 1988).

Non-wood lignocellulose source	Cross & Bevan Cellulose (%)	α -Cellulose (%)	Lignin (%)	Pentosans (%)	Ash (%)	Silica (%)
Bast Fibers						
Jute	57-58	39-42	21-26	18-21	0.5-1	<1
Kenaf-bast	45-57	31-39	7.5-9.5	16-23	2-5.5	-
Kenaf-core		34	17.5	19.3	2.5	-
Textile flax tow	76-79	50-68	10-15	6-17	2-5	<1
Leaf fibers						
Abaca	78	61	9	17	1	<1
Sisal	55-73	43-56	8-9	21-24	0.6-1	<1
Stalk Fibers						
Sugarcane bagasse	49-62	32-44	19-24	27-32	1.5-5	0.7-3
Bamboo	57-66	26-43	21-31	15-26	1.7-5	1.5-3
Sorghum	44-46	27-35	13-15	23-27	5.8	-
Cereal straw						
Barley	47-48	31-34	14-15	24-29	5-7	3-6
Oat	44-53	31-37	16-19	27-38	6-8	4-7
Rice	43-49	28-36	12-16	23-28	15-20	9-14
Wheat	49-54	29-35	16-21	26-32	4-9	3-7
Grasses						
Esparto	50-54	33-38	17-19	27-32	6-8	2-3
Sabai	54-57	-	17-22	18-24	5-7	3-4
Switchgrass	-	43	34-36	22-24	1.5-2	-
Reeds						
Phragmites mmunis	57	45	22	20	3	2
Coniferous (Softwood)	53-62	40-45	26-34	7-14	1	<1
Decduous (hardwood)	54-61	38-49	23-30	19-26	1	<1

In general, the density of non-wood lignocellulose from agricultural resources is very low, which makes them extremely bulky. The storage, collection, and transportation of these materials require special attention. High compaction ratio and transport cost are among the restrictions for utilization of bulk density materials. Basically, the structural, physical, and chemical characteristics of the non-wood lignocellulose are different from those of wood. However, sugarcane bagasse, cereal straws, and corn stalks are quite similar to hardwood as the fiber fraction. In addition, they are more heterogeneous and contain a large proportion of very thin-walled and fine epidermal cells in a wide range of dimensions (Hurter, 1997). Moreover, the moisture content of most agricultural residues is high, some residues such as bagasse are fired with 40–60 wt% moisture (Clarke, 1988). Most agricultural residues have low bulk densities. For example, the bulk densities of rice husks and soy hull are 0.08 g/cm³ to 0.14 g/cm³ (Mansaray and Ghaly, 1997) and 0.22 g/cm³ (Cardosa *et al.*, 2013), respectively. Table 1.2 shows the chemical properties of some common non-wood lignocellulose from agricultural resources. Such of the non-wood lignocelluloses are usually characterized by lower lignin and higher pentosan/hemicelluloses contents than softwood. Chemical composition varies between plants, and within different parts of the same plants. Geographic location, age, climate, and soil conditions affect the chemical composition of plants (Rowell *et al.*, 1997; Morison *et al.*, 1999; Neto *et al.*, 1996; Nishimura *et al.*, 2002; Ohtani *et al.*, 2001). Stalk fibers are closer to hardwoods than softwood in chemical properties, with the major difference being the higher ash and silica contents.

Non-wood lignocellulose from agricultural resources have been considered for use as a raw material of wood-based composite products (Muller *et al.*, 2012; Ndazi *et al.*, 2006). These

resources are abundantly available in many countries, including as residues (Rowell *et al.*, 1997). Various non-wood lignocellulose have been used as the raw materials of particleboard, including wheat-cereal straws (Mo *et al.*, 2001; Wang and Sun, 2002; Cheng *et al.*, 2004; Sain and Phantapulakkal, 2006), rice husks (Leiva *et al.*, 2007), tobacco (Ntalos and Grigoiou, 2002), kenaf (Xu *et al.*, 2005; Kalaycroglu and Nemli, 2006), bamboo (Hiziroglu *et al.*, 2005; Sudin and Swamy, 2006), bagasse (Widyorini *et al.*, 2005; Liao *et al.*, 2016), sunflower stalks (Nemli, 2003), oil palm (Khalil *et al.*, 2007), cotton carpel (Alma *et al.*, 2005) and sorghum bagasse (Iswanto *et al.*, 2014; Khazaeian *et al.*, 2015).

In any sustainable development, there must be a long-term guaranteed supply of resources. To insure a continuous supply, management of agricultural land should be proactively designed for both sustainable agriculture and the promotion of healthy ecosystems.

1.2. Current status and characteristics of sweet sorghum and bagasse

1.2.1. Current situation of sweet sorghum

Sweet sorghum (*Sorghum bicolor* (L.) Moench) is a multifunctional crop used for energy, food, feed, and fiber; it has been planted throughout the world (Almoderas *et al.*, 2009). In Indonesia, sweet sorghum is considered one of the most common multi-purpose crops (Kamal *et al.*, 2014). For renewable energy in particular, sweet sorghum is a one of the most promising crops for energy resources, due to the fact that its stalk can produce juice that contains high sugar content (Almoderas *et al.*, 2008b). Generally, sweet sorghum can produce 54 – 69 stalks t/ha (Almoderas *et al.*, 2008b). In addition, Kim and Dale (2004) reported that annual global production and average yield of dry sweet sorghum were about 53 teragrams (Tg) and 1.2 dry

megagrams (Mg) ha⁻¹, respectively. They also mentioned that about 6% of global annual production of sweet sorghum is wasted.

1.2.2. Characteristic of sweet sorghum

In additions to rapid growth, high sugar accumulation (Almoderas and Sepahi 1996), and biomass production potential (Almoderas *et al.*, 1994), sweet sorghum has wide adaptability (Reddy *et al.*, 2005). Sweet sorghum is well adapted to the sub-tropical and temperate regions of the world, and is water efficient. Sweet sorghum has many positive characteristics, such as a drought resistance (Tesso *et al.*, 2005), water-lodging tolerance, and salinity resistance (Almoderas *et al.* 2007, 2008a). Moreover, sweet sorghum is a C4 crop with high photosynthetic efficiency; hence, sweet sorghum will play an important role in promoting the agricultural development of production, livestock husbandry (Fazaeli *et al.*, 2006), energy sources (Nahvi *et al.*, 1994a,b), refining sugar, paper making, etc.

Carbohydrates of sweet sorghum is classified to the non-structural, such as sugar and starch, and structural, such as cellulose, hemicellulose, and pectin substances (Anglani, 1998). Actually, two parts of sweet sorghum are usually used in processes, the grain and the stalk. Sweet sorghum stalks are composed of pith and bark, which are present in approximately equal amounts on a dry basis; pith accounts for 65% of the stem on a fresh-matter basis, and bark for 35% (Billa *et al.*, 1997). The bulk density of sweet sorghum bagasse is 0.24 g/cm³ (Cardoso *et al.*, 2013). Moreover, sweet sorghum bagasse is mainly composed of 34–44% cellulose, 25–27% hemicellulose, and 18–20% lignin (Ballesteros *et al.*, 2003; Kim and Day 2011, Sipos *et al.*, 2009).

1.2.3. Utilization of sweet sorghum bagasse

Bagasse as a byproduct of juice extraction from the stalk of sweet sorghum, and can be used for ethanol production or animal feed (Jafarinia *et al.*, 2005), silage (Linden, Henk and Murphy, 1987) and bio-pellets (Theerarattananoon, 2011). However, the production of ethanol from sweet sorghum bagasse is not feasible economically in recent years (Drapcho *et al.*, 2008). Bio-pellets, animal feed, and silage productions from sweet sorghum bagasse are economically feasible, but could not maintain carbon dioxide neutrality (Mohanty *et al.*, 2002) because these utilization of sweet sorghum bagasse can't keep carbon stock for longterm. Therefore, utilization of sweet sorghum bagasse as a raw material for particleboard manufacture is an effective way to reuse this material. Recently, some researcher investigated the manufacturing of particleboards using sorghum bagasse and a synthetic resin, such as urea formaldehyde (UF) resin (Iswanto *et al.*, 2014; and Khazaeian *et al.*, 2015). Their studies demonstrated that the mechanical properties of these boards satisfied the JIS (Japanese Industrial Standard) and EN (European Norm) requirements. However, the boards had poor dimensional stability. The physical properties of these boards were improved by using phenol formaldehyde (PF) resin and polymeric 4,4'-methylenediphenyl isocyanate (pMDI) (Iswanto *et al.*, 2014).

Generally, conventional synthetic resin adhesives are composed of assorted chemical substances derived from fossil resources. However, their use will be inescapably restricted in the future due to decreases in the stock of fossil resources. Hence, the development of natural adhesive using bio-resources, i.e., lignin, tannin, proteins, and polysaccharides (Pizzi, 2006), and ligno-cellulose nanofiber (LCNF) (Kojima *et al.*, 2006) has been investigated. Nevertheless, the use of chemical substances derived from fossil resources was necessary to obtain good bondability (Yang, 2006; El Mansouri, 2007; Krug, 2010; Hoong, 2011). However, conventional

natural adhesives contain harmful chemical substances, i.e., various organic solvents and aldehyde compounds that cause environmental pollution and damage health (Shebe, 2013). Considering these problems, research should be focused on obtaining an excellent bonding performance using a natural adhesive without the addition of harmful chemical substances. Nowadays, citric acid has been observed as a wood-based natural adhesive in manufacturing of wood-based molding (Umemura *et al.*, 2012a, 2012b).

1.3. Current status and characteristic of citric acid and its utilization

1.3.1. Current status of citric acid

World production of citric acid in 2004 was about 1.4 million tons, as estimated by the Business Communication Co. (BCC) in a recent study of fermentation markets (Soccol *et al.*, 2006). Production capacity and consumption was largely in China, Western Europe and the United States (Soccol *et al.*, 2006). China was estimated to account for at least half of global production capacity, while Western Europe and the United States combined accounted for about a third. Thus, Western Europe, the United States, and China combined are estimated to account for 65–70% of global citric acid consumption (Soccol *et al.*, 2006).

1.3.2. Characteristic of citric acid

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is an organic polycarboxylic acid containing three carboxyl groups. It occurs in citrus fruits such as lemon and limes, and is commercially produced by fermenting glucose, or glucose and sucrose-containing materials (Abou-Zeid *et al.*, 1984; Tsao *et al.*, 1999).

Based on the thermal decomposition of citric acid as reported by Barbooti and Al-Sammerrai (1986), citric acid melts at 153 °C and dehydrates to give aconitic acid on heating to 175 °C. Further heating results in the formation of methyl maleic acid. The solubility of citric acid in water at 20 °C is about 57 wt% (Dalman, 1937).

1.3.3. Utilization of citric acid

Citric acid is widely used in food, beverages and pharmaceuticals, due to its general recognition as safe with a pleasant taste, high water solubility, and chelating and buffering properties (Soccol *et al.*, 2006). In addition, citric acid has been researched as a crosslinking agent for wood (Bogoslav *et al.*, 2009; Vukusic *et al.*, 2006), plant fiber (Ghosh, 1995), paper (Yang, 1996), starch (Reddy, 2010), and bio-based elastomers (Tran, 2009). Recently, citric acid is also being used as a wood-based natural adhesive in the research of manufacture of wood-based molding (Umemura *et al.*, 2012a, 2012b). In case of the manufacturing of particleboard from wood, citric acid was used with sucrose as the adhesive (Umemura *et al.*, 2013; 2014). They found that the physical properties of particleboard bonded with 20 wt% of the adhesive content under citric acid to sucrose ratio of 100/0 wt% were inferior. Furthermore, they discovered that the physical properties was improved using the citric acid to sucrose ratio of 25/75 wt%. This mean that, sucrose as a disaccharide contributed in improving bondability of the particleboard. Furthermore, citric acid was used also as natural adhesive in the manufacturing of particleboard from bamboo (Widyorini *et al.*, 2016) and low density particleboard from bagasse (Liao *et al.*, 2016). In those previous report of particleboard bonded with citric acid and sucrose, the raw materials were dried to remove excess moisture after sprayed by the adhesive. However, they did not observe the effect of non-drying and pre drying of particle on physical properties, formaldehyde emission, and biological durability against termite and decay of the particleboard.

Based on the chemical composition of sweet sorghum as mentioned above, sweet sorghum contained higher hemicellulose than wood. Generally, hemicellulose composed of polysaccharide and it was hydrolyzed easily by acid and heat treatment. Hemicellulose reacted effectively with citric acid to form chemical linkages that contributed to the good bondability (Liao *et al.*, 2016).

1.4. Objectives

Sweet sorghum bagasse as a non-wood lignocellulose material that contain high hemicellulose is a promising substitute wood material for the manufacture of particleboard. The high content of hemicellulose probably would make sweet sorghum bagasse react effectively with citric acid as a natural adhesive, hence the particleboard made from sweet sorghum bagasse bonded with citric acid would have good bondability. Therefore, the objective of this study is to utilize sweet sorghum bagasse in the manufacturing of environmentally friendly particleboard bonded with citric acid. The effect of the manufacturing conditions of particleboard such as pre-treatment of particles before hot pressing condition, citric acid contents, pressing temperature and time, and adding sucrose in adhesion system on physical properties of particleboard were investigated. In addition, wet bending test type B, brittleness, screw holding power, Charpy impact strength, formaldehyde emission, and biological durability against termite and decay were observed.

The present thesis consists of four chapters;

1. Chapter 1 is a literature review of the current status of forest and agricultural resources in the production of wood-based composites, as well as the current situation, characteristics, and utilization of sweet sorghum bagasse and citric acid.

2. Chapter 2 describes the pre-treatment of particles before pressing and effective citric acid content in the manufacture of particleboard. Particles sprayed with adhesive were pre-dried to observe the effect of moisture content on the physical properties of the particleboards. Moreover, we evaluated the effect of citric acid content on the physical properties of the particleboards. The bonding mechanism underlying the production of the particleboards was investigated using Fourier transform infrared (FT-IR) spectroscopy.
3. Chapter 3 demonstrates the hot-pressing conditions in the manufacture of particleboard. We first investigated the effect of pressing-temperature optimization on the manufacture of particleboard. Based on the effective pressing temperature, we then considered the effect of pressing time on particleboard manufacturing. In optimizing these conditions, the effects of pressing temperature and time on physical properties of particleboard were inspected. Furthermore, wet bending (WB), screw-holding power (SH), biological durability and formaldehyde emission of particleboard under effective pressing temperature and time were evaluated. In addition, the effect of pressing temperature and time in the formation of ester linkages on adhesion system were analyzed using FT-IR.
4. Chapter 4 deals with the effect of added sucrose on the physical properties of particleboard. We investigated the influence of the ratio of citric acid to sucrose on the physical properties of particleboard. Moreover, brittleness, Charpy impact strength, screw holding power (SH), FT-IR of particleboard, and thermal properties of sweet sorghum bagasse particles sprayed with solutions of citric acid and sucrose are discussed.

Chapter 2

Effect of pre-drying treatment and citric acid content on particleboard properties

2.1. Introduction

Commonly, sweet sorghum stalk contained high hemicellulose and had low bulk density as mentioned in Chapter 1. Those characteristic of sweet sorghum, especially its hemicellulose content had good benefit for the manufacture of particleboard using citric acid as natural adhesive. Therefore, in Chapter 2, the chemical compositions and bulk density of sweet sorghum bagasse that used for the manufacture of particleboard were observed.

As reviewed in Chapter 1, the particles that sprayed by 20 wt% of citric acid-based adhesive content with the concentration of 59 wt%, were dried to reduce the moisture content. (Widyorini *et al.*, 2016; Liao *et al.*, 2016; Umemura *et al.*, 2013; 2014). However, the effect of moisture content of the particles that had been dried on physical properties of particleboard did not observe in those previous research. Generally, moisture content of the particles is an extremely critical factor that influence the physical properties of particleboard.

In this chapter, the particles that had been sprayed with adhesive were pre-dried to observe the effect of the moisture content of the particles on the physical properties of the particleboards. Additionally, the effect of the citric acid content on the physical properties of the particleboards was evaluated. The bonding mechanism underlying the production of the particleboards was investigated using Fourier Transform Infrared spectroscopy (FT-IR). In addition, chemical composition and bulk density of sweet sorghum bagasse were observed.

2.2. Materials and methods

2.2.1. Preparation of materials

Sweet sorghum (*Sorghum bicolor* (L). Moench) bagasse from squeezed sorghum stalks was obtained from a research field at the Innovation Center of the Indonesian Institute of Sciences. The outer bark of the sorghum stalk was removed by hand, after which a chipper and a knife-ring flaker machine were used to produce particles. The particles were screened using a sieving machine to obtain particles of uniform sizes, and the particles remaining between aperture sizes of 0.9 and 5.9 mm were used as the raw material. The particles were dried in an oven at 80 °C for 12 h to obtain a moisture content of less than 4%. Citric acid (anhydrous) of extra purity grade was purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and was used without further purification. Citric acid was dissolved in water at a concentration of 59 wt%, and this solution was used as the adhesive. No other chemical compounds were used. The pH and viscosity of the solution at 20 °C were 0.3 and 30 mPa·s, respectively. PF resin (B-1370 type) and pMDI (B-1605 type) from Oshika Co., Ltd. (Tokyo, Japan) were used as reference adhesives.

2.2.2. Chemical composition analysis of sweet sorghum bagasse

Based on the method that Han and Rowell (1997) used to prepare samples for analysis of the lignocellulose chemical composition, the oven-dried particles (105 °C, 24 h) were ground into a powder using a grinder, and the particles that passed through a 40-mesh sieve and were by retained by a 60-mesh sieve were obtained using a high-speed vibrating sample mill (Iida sieve shaker, Iida Seisakusho Co., Ltd.). These particles were extracted by refluxing in a toluene:ethanol (2:1/v:v) solution for 6 h (Han and Rowell, 1997). The holocellulose and lignin contents were determined using the methods of Wise and Klason, respectively. The α -cellulose content was determined by extracting the holocellulose using a solution of 17.5% NaOH. Finally,

the hemicellulose content was determined by subtracting the α -cellulose content from the holocellulose content. All of the chemical component analyses were performed in triplicate. The holocellulose, lignin, α -cellulose, and hemicellulose contents were determined based on the chemical component analysis of lignocellulose in Widyorini *et al.* (2005). The ash content of the particles was determined by incinerating oven-dried samples at 600 °C for 4 h (Rabemanolontsoa *et al.*, 2011).

For analysis of the sugar content, 2 g of bagasse powder was extracted in 500 mL of boiling water for 1 h to obtain the water-soluble sugar (Li *et al.*, 2013). After filtration through an IG3 glass filter, the extracted liquor was used to determine the sugar content using high-performance liquid chromatography (HPLC). Samples were prepared for HPLC analysis as follows: at a specified reaction time, 60 μ L of the reaction medium was thoroughly mixed with 60 μ L of distilled water, and the mixture was filtered through a 0.45- μ m filter (Miyata and Miyafuji, 2014). The filtrates were analyzed under the following conditions: column, Shodex sugar KS-80; flow rate, 1 ml/min; eluent, distilled water; detector, RID; and column temperature, 80 °C.

2.2.3. Bulk density measurement of sweet sorghum bagasse particles

The bulk density of particles dried at 105 °C for 24 h was determined by calculating the ratio of the mass to the volume occupied (Cardoso *et al.*, 2013; Ominiya and Olorunnisola, 2014). First, a 50-mL graduated cylinder was weighed. Particles were added to a 50-mL graduated cylinder until they reached the 50-ml mark, and the cylinder was then reweighed. The difference between the mass of the filled graduated cylinder and the mass of the empty graduated cylinder was divided by the volume occupied by the sorghum bagasse particles to obtain the bulk density.

2.2.4. Manufacture of particleboards

The citric acid solution was sprayed onto dried particles to achieve various citric acid contents, i.e., 0, 5, 10, 20 and 30 wt%. To obtain boards containing 0 wt% citric acid, dried particles that were not sprayed with a citric acid solution were directly shaped into a mat, and the mat was pressed using a hot-pressing machine; this board was used as a control in this study. Additionally, particles that had been sprayed with adhesive were prepared under the following two conditions: (a) wet particles that had been sprayed with adhesive were used directly to form mats and were called non-dried particles or type (a) particles; (b) wet particles that had been sprayed with adhesive were dried at 80 °C for 12 h to reach a moisture content of 3-14% and were called pre-dried particles or type (b) particles. The moisture content of these two types of particles were determined and are shown in Table 2.1. Subsequently, these particles were formed into mats using a forming box. The mats of particles were pressed using a hot-pressing machine under the conditions described in a previous report of Umemura *et al.* (2014), i.e., 200 °C for 10 min.

The particleboard size and target density were 300 x 300 x 9 mm and 0.8 g/cm³, respectively. A 9-mm thick bar was used to control the board thickness during the hot-pressing process. In addition, particleboards without pre-drying treatment of particles and bonded using a 12 wt% content of PF resin and an 8 wt% content of pMDI resin with a size and target density of each these particleboards similar to those of the particleboards bonded using citric acid were manufactured as references. Both the PF resin and pMDI were diluted by acetone of 20 and 10 wt%, respectively, to reduce the viscosity of these adhesives. The pressing temperature and time were 200 °C and 6 min, respectively, for the particleboard bonded using PF and were 180 °C and 8 min, respectively, for the particleboard bonded using pMDI. The conditions of resin content,

pressing temperature and time of each particleboard bonded with PF and pMDI were set up based on the normal protocol of PF and pMDI application for particleboard.

Table 2.1 Moisture content of the particles before undergoing the hot-pressing process.

Citric acid content (wt%)	Moisture content (%)		
	Control (non-sprayed particles)	Type (a) (non-drying sprayed particle)	Type (b) (pre-drying sprayed particle)
0	2.53 (0.47)		
5		8.02 (1.41)	3.65 (0.74)
10		13.97 (0.91)	6.79 (0.61)
20		16.88 (0.86)	10.75 (0.21)
30		20.95 (0.71)	13.50 (0.32)

Values in parentheses are standard deviation (SD)

2.2.5. Evaluation of the physical properties

After conditioning for 1 week at a room temperature of 20 °C and a relative humidity of approximately 60 %, the boards were tested according to the Japanese Industrial Standards for particleboards (JIS A 5908, 2003). The bending properties of the boards, i.e., the modulus of rupture (MOR) and the modulus of elasticity (MOE), were evaluated by conducting a three-point bending test on a 200 x 30 x 9 mm specimen of each board under dry conditions. The loading speed and effective span were 10 mm/min and 150 mm, respectively. The internal bonding (IB) strength was investigated using a 50 x 50 x 9 mm specimen of each board. The thickness swelling (TS) and water absorption (WA) values of each board after water immersion at 20 °C

for 24 h were measured for specimens of the same size as those used for the IB test. Subsequently, the pH values of the solutions in which the water-immersion treatment was performed were measured.

Furthermore, after the TS test was performed, the specimens were subjected to a cyclic aging treatment (drying at 105 °C for 10 h, warm-water immersion at 70 °C for 24 h, drying at 105 °C for 10 h, immersion in boiling water for 4 h, and drying at 105 °C for 10 h). The thickness and weight changes of the specimens that occurred throughout the treatment were determined. Each experiment was performed in five replications, and the average values and standard deviations were calculated. The MOR, MOE, and IB values of the boards shown in the figures are values that were corrected for each target density based on regression lines between the actual values of the mechanical properties and the specimen densities.

2.2.6. Statistical analysis

Data for each test were statistically analyzed. The analysis of variance was used to evaluate the significance in difference between factors and levels. Comparison of the means was done by using Duncan post hoc test to identify which groups were significantly different from other groups at 95% confidence level. The standard deviation were also calculated from the data and are shown as error bars in each corresponding figure.

2.2.7. Fourier Transform Infrared Spectroscopy (FT-IR)

The edge of an original board and a board given the cyclic aging treatment were scratched to obtain particles. The particles were ground into a powder, and the powder obtained was dried in a vacuum drying oven at 60 °C for 12 h. Infrared (IR) spectral data were obtained with a FT-IR

spectrophotometer (FT-IR-4200; JASCO Corporation, Tokyo, Japan) using the KBr disk method and were recorded with an average of 16 scans at a resolution of 4 cm⁻¹.

2.3. Results and discussion

2.3.1. Chemical composition and bulk density

Table 2.2 Chemical components of sweet sorghum bagasse particles.

Chemical Composition	Content (% dry weight)
Cellulose	34.87 (1.09)
Hemicellulose	33.95 (3.59)
Lignin	23.02 (1.29)
Extractive	2.87 (1.62)
Ash	4.20 (0.12)

Values in parentheses are standard deviations (SD)

Based on the results of the chemical component analyses, shown in Table 2.2, particles of sweet sorghum bagasse had cellulose and hemicellulose contents similar to those of other agricultural plants that are commonly used as raw materials to produce particleboard, such as kenaf core, sugarcane bagasse, wheat stalk, rice stalk, and bamboo (Han and Rowell, 1997). Furthermore, the hemicellulose content was higher than that of hardwood and softwood, even though the cellulose content was slightly lower than that of those two types of wood (Fengal and Wenger, 1989). The hemicellulose content of sweet sorghum bagasse determined in this study was higher than that of sweet sorghum bagasse specimens obtained from a different location (Almodares and Hadi, 2009).

In addition, the particles contained water-soluble sugar, as shown in Table 2.3. The water-soluble sugar content of the particles was lower than that of sweet sorghum stalks (7 – 12% weight basis) prior to squeezing, as reported by Almodares and Hadi (2009). The low sugar

content was due to most of the water-soluble sugar having been removed when the sweet sorghum stalks were squeezed to obtain their juice. In fact, the total sugar content of sweet sorghum juice is low (11.8 wt%), as reported by Kim and Day (2010).

The bulk density of particles dried at 105 °C for 24 h was 0.125 g/cm³ (SD = 0.005). This value was similar to the bulk density of other agricultural plants that used as a raw material of particleboard, i.e., kenaf core chips (0.118 g/cm³) (Grigoriu *et al.*, 2000), bamboo chips (0.20 g/cm³) (Papadopoulos *et al.*, 2004), and flax chips (0.09 g/cm³) (Papadopoulos and Hague, 2003). Generally, low bulk density of raw material was easier than the high bulk density of materials to obtain desired particleboard density.

Table 2.3 Sugar composition of dried sweet sorghum bagasse particles.

Sugar component	Content (% dry weight)
Glucose	0.75
Fructose	2.5
Sucrose	0.25

2.3.2. Mechanical properties

Figure 2.1 shows the relationship between the citric acid contents and the bending properties of type (a) and (b) particleboards. Irrespective of the type of board, the MOR and MOE values increased as the citric acid content was increased from 0 to 20 wt% and then slightly decreased. The maximum average MOR and MOE values of type (b) particleboards were 21.80 MPa and 5.27 GPa at 20 wt% citric acid, respectively.

The MOR values of both type (a) and (b) particleboards bonded using a citric acid content of 20 wt% were comparable to the values required (≥ 18 MPa) for the 18 type of JIS A 5908 (2003).

The MOE values of those boards were slightly higher than those of the particleboards bonded using PF or pMDI resin. These MOE values were not significantly different ($p < 0.05$).

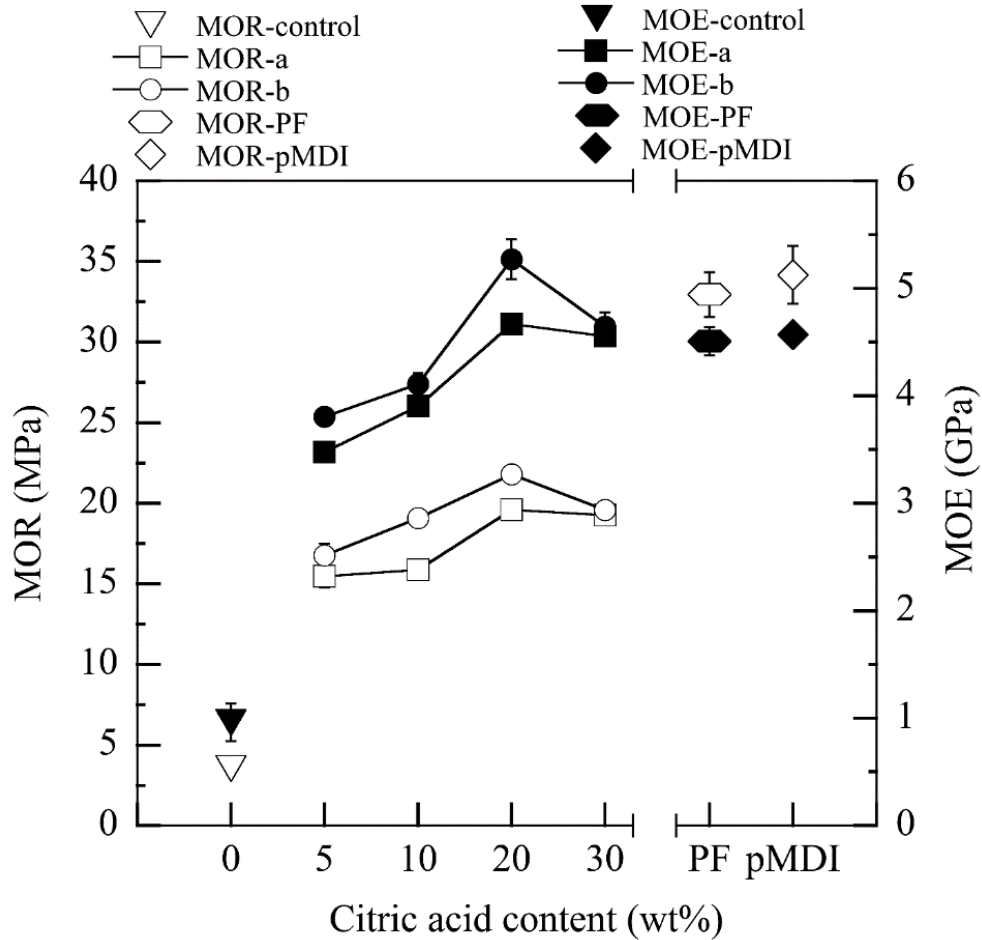


Fig. 2.1 Relationship between the citric acid content and the bending properties of type (a) and (b) particleboards. Error bars indicate the standard deviations.

Figure 2.2 shows the relationship between the citric acid content and the IB strength of type (a) and (b) particleboards. The IB strengths of both type (a) and (b) particleboards increased linearly with increasing citric acid content. Furthermore, type (b) boards bonded with 30 wt% citric acid had a significantly higher IB strength than did the type (a) boards produced using the same citric acid content.

The IB strength of type (b) particleboards bonded with 30 wt% citric acid was approximately 30 and two times greater than those of board bonded with 0 and 5 wt% citric acid, respectively. Furthermore, the IB strength of type (b) boards bonded with 30 wt% citric acid was slightly higher than that of boards bonded with 20 wt% citric acid. In addition, the IB strength of the type (b) particleboards bonded using 20 and 30 wt% citric acid were slightly higher than that of particleboard bonded with PF resin and slightly lower than that of particleboard bonded with pMDI. The IB strengths of both type (a) and (b) particleboards bonded with citric acid at 5 – 30 wt% satisfied the requirement (≥ 0.3 MPa) of the 18 type JIS A 5908 (2003).

The discovered trends of the effect of citric acid content on mechanical properties can be elucidated as follows: the mechanical properties were determined by bondability among particles and the strength of the particles themselves. Citric acid would react with the functional group of the particles under high temperature, and improve the bondability of particleboard. Therefore, the mechanical properties of particleboard increased when citric acid content increased from 0% to 20 wt%. However, the amount of particles would be reduced with the increasing of citric acid content when a particleboard density was fixed, hence the mechanical properties was decreased. This mean that the mechanical properties of the particleboard decreased with extra increase in citric acid content more than 20 wt%.

The mechanical properties of type (b) particleboard being superior to those of type (a) particleboard can be explained by the moisture content of the particles used to produce them. The moisture content of type (b) particles was lower than that of type (a) particles, as shown in Table 2.1. It is known that excessive moisture inhibited the strong interaction between adhesive and lignocellulose materials, thus lowering the bondability of these materials (Kelly, 1977). Maloney (1977), Halligan and Schniewind (1974) and Ndazi *et al.* (2006) reported that using particles

with a high moisture content resulted in particleboards with inferior mechanical properties due to the poor adhesion between the adhesive and the particles. Water formed the steam when water boils and if heated further more than 100 °C, it become superheated steam (Taylor *et al.*, 2012). The steam as a water in the gas phase contain much amount of free-hydroxyl group. Based on the previous research, high moisture content of the particles without pre-drying (type (a)) would produce much amount of steam hence condensation reaction between carboxyl groups of citric acid and hydroxyl groups of sweet sorghum bagasse was not generate effectively. Thus, the bondability of the particleboard type (a) was low. As a result, mechanical properties of the particleboard type (a) were lower than those of particleboard type (b).

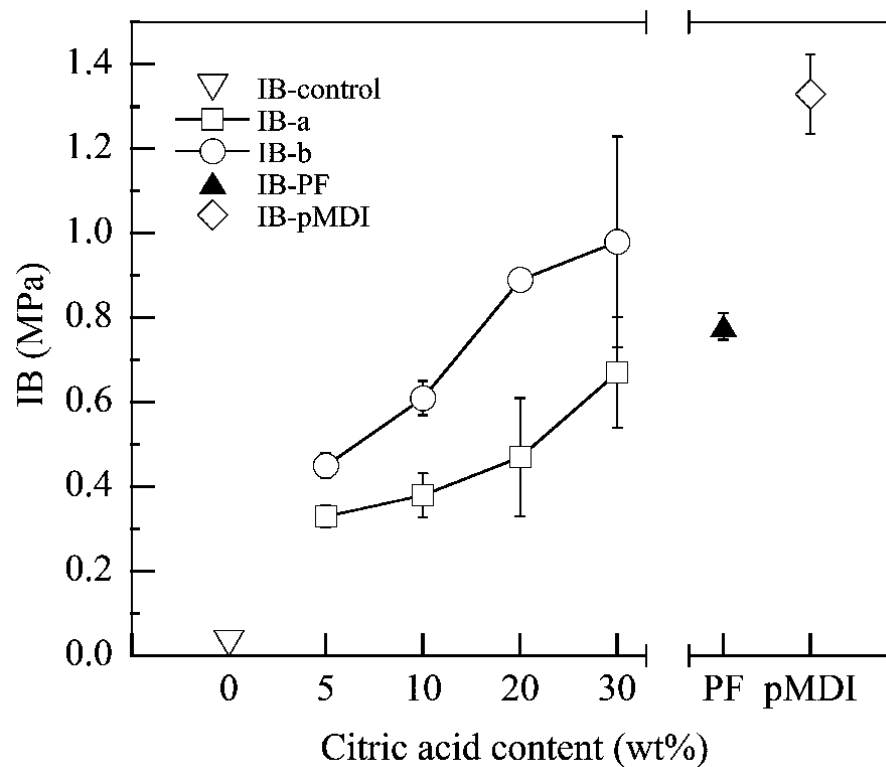


Fig. 2.2 Relationship between the citric acid content and the IB strength of type (a) and (b) particleboards. Error bars indicate the standard deviations.

Based on the best mechanical properties of particleboard in this chapter, the pre-drying of particles was suitable pre-treatment of particles before hot pressing to obtain good mechanical properties. In addition, 20 wt% of citric acid content was suitable level of citric acid content to gain excellent mechanical properties. Moreover, the sweet sorghum bagasse particleboard under suitable conditions of pre-treatment of particles and citric acid content had higher mechanical properties than those of the wood particleboard under same conditions of pre-drying of particles and bonded with 20 wt% of citric acid only as reported in previous research (Umemura *et al.*, 2013). This phenomena was happened seem to be high hemicellulose content of sweet sorghum bagasse gave more effective reaction of citric acid and particles. Generally, hemicellulose was decomposed easily by acid and heat, and then produced oligosaccharide that have rich hydroxyl group. Therefore, we expected that the citric acid interact effectively with sweet sorghum bagasse particles. Consequently, this reaction contributed to a good bondability of the sweet sorghum bagasse particleboard.

2.3.3. Dimensional stability

Figure 2.3 shows the effect of the citric acid content on the TS and WA values of type (a) and (b) particleboards. The TS values of both type (a) and (b) boards decreased with increasing citric acid content. The TS values of the type (a) boards bonded with 20 and 30 wt% citric acid were approximately one-eighth and one-twelfth that of boards bonded with 0 wt% citric acid, respectively. The TS values of type (b) boards bonded with 20 and 30 wt% citric acid were approximately one-eighteenth that of boards bonded with 0 wt% citric acid. The principal factors affecting the TS value of particleboards are the type of adhesives used and the resin content and compressibility of the boards (Kelly, 1977). In this study, the density of the boards was constant, regardless of the resin content, which indicates that the amount of particles in the boards

decreased when the citric acid content was increased. The decrease in the amount of particles leads to the compressed particles having a decreased reaction force and results in a decreased TS value (Kelly, 1977).

Type (b) particleboards bonded with 30 wt% citric acid had a lower TS value (9.02 %) than that (13.45 %) of type (a) particleboards with the same citric acid content. This result indicates that the pre-drying treatment performed after spraying the particles with adhesive improved the TS value of the particleboard. Moreover, the TS value of type (b) particleboards bonded with 20 and 30 wt% citric acid complied with the requirement (≤ 12 %) 18 type of JIS A 5908 (2003). In addition, the TS values of those boards were approximately half than those of particleboards bonded with PF (20.6 %) or pMDI (23.1 %) resin. This result indicated that particleboards bonded with citric acid had a good level of dimensional stability.

The WA value of the boards decreased with increasing citric acid content. Both type (a) and (b) boards bonded with 30 wt% citric acid had WA values that were one-quarter those of boards bonded with 0 wt% citric acid. This result indicates that citric acid inhibited water absorption by the boards during the water-immersion treatment. As a result, the water resistance of the boards would increase. However, the WA value (61.75 %) of type (b) boards bonded with 30 wt% citric acid was higher than those of boards bonded with PF (51.24 %) or pMDI (35.26 %) resin.

The pH values of the water solutions after the TS tests were evaluated. As shown in Table 2.4, the pH values of the leached water with CA-bonded board ranged from 3.30 to 5.40. Furthermore, the pH values of the leached water with CA-bonded board type (a) boards bonded with 20 and 30 wt% citric acid were significantly lower ($p < 0.05$) than those of the type (b) boards with similar citric acid contents. This result indicates that the type (a) boards released a greater amount of acidic compounds, including unreacted citric acid, into the water than did the type (b) boards.

The range of pH values observed was similar to that of wood (pH 3.75 – 6.05) (Hon and Minemura, 2010).

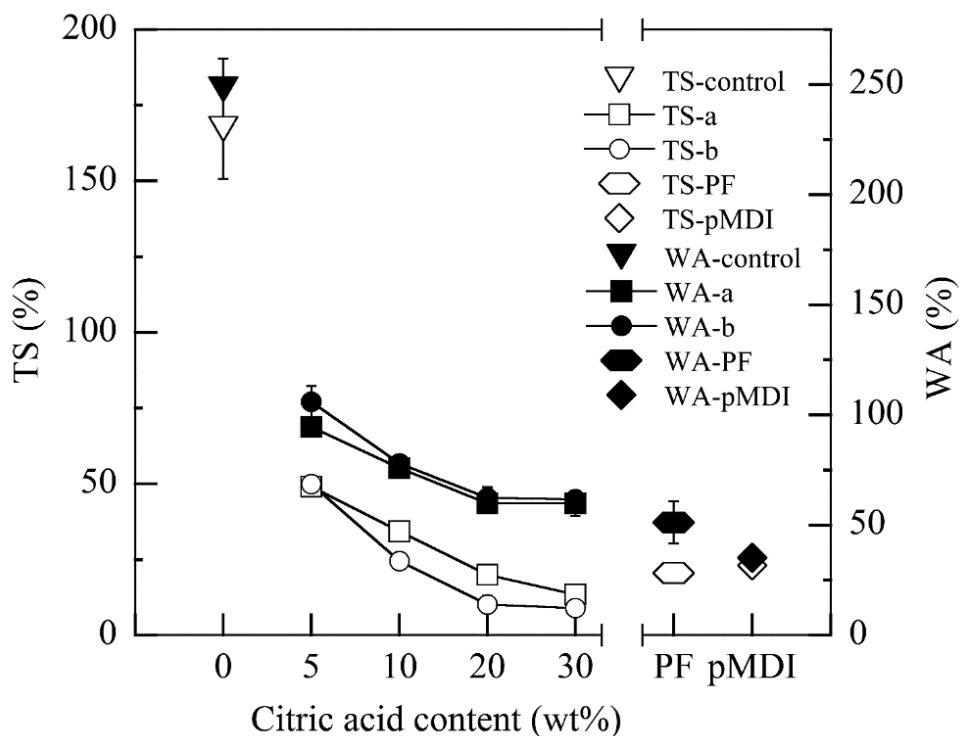


Fig. 2.3 Effect of the citric acid content on the TS and WA values of type (a) and (b) particleboards. Error bars indicate the standard deviations.

The changes in the thickness of type (a) and (b) boards are shown in Fig. 2.4 and 2.5, respectively. The thickness change of type (a) boards at each stage of the cyclic aging treatment was decreased with increasing citric acid content as shown in Fig. 2.4. The original shape of those particleboards was maintained throughout the stages of the cyclic aging treatment, except for that of the particleboard bonded with 0 wt% citric acid. This particleboard decomposed while being boiled in water for 4 h. The results indicate that boards bonded with a high citric acid content had good dimensional stability. The type (b) particleboards exhibited a thickness-change trend similar to that of the type (a) particleboards, as shown in Figure 2.5.

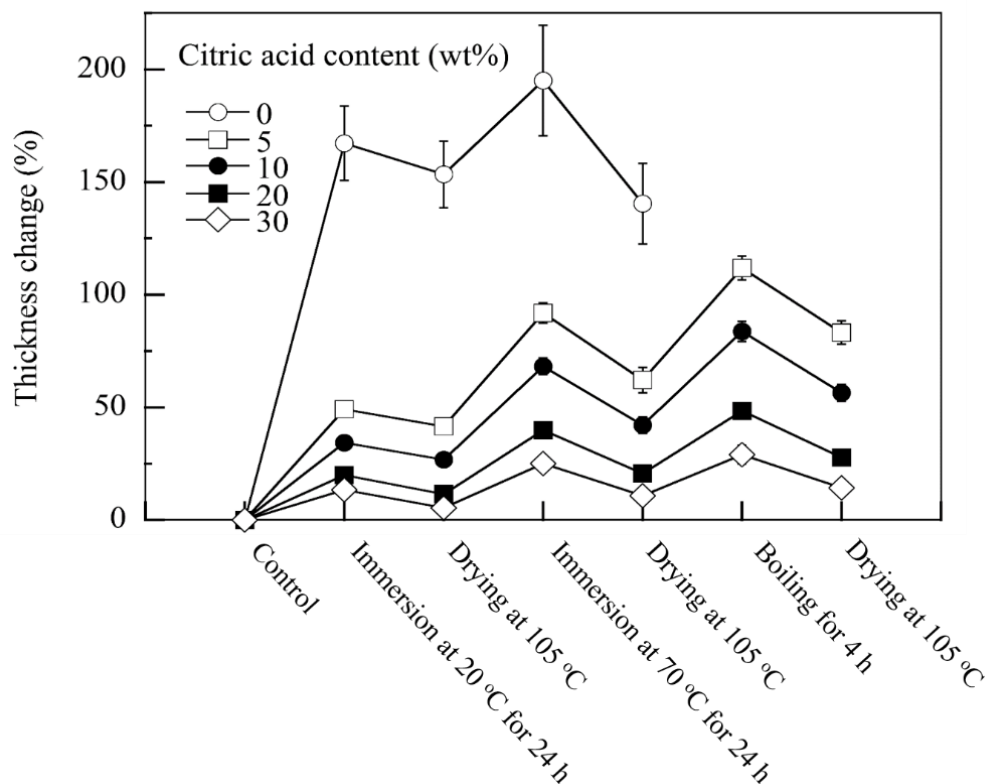


Fig. 2.4 Thickness change during cyclic aging treatment of type (a) particleboards. Error bars indicate the standard deviations.

Table 2.4 pH of the solution after water-immersion treatment at 20 °C for 24 h.

Citric acid content (wt%)	pH		
	Control (non-sprayed particles)	Type (a) (non-drying sprayed particle)	Type (b) (pre-drying sprayed particle)
0	7.0 (0.01)		
5		5.0 (0.10)	5.2 (0.15)
10		4.4 (0.11)	5.4 (0.14)
20		3.5 (0.21)	4.7 (0.08)
30		3.3 (0.12)	4.3 (0.10)

Values in parentheses are standard deviations (SD)

The thickness-change values of type (b) boards bonded with 20 and 30 wt% citric acid after being boiled in water for 4 h were 19.1 and 12.6 %, respectively, which were lower than those of type (a) boards, i.e., 48.5 and 29 %, respectively. In addition, the thickness-change values of type (b) boards were lower than those of boards bonded with PF (32.8 %) or pMDI (47.1 %). This result indicates that the drying treatment applied to the particles after spraying them with adhesive was an effective method for obtaining boards with good dimensional stability.

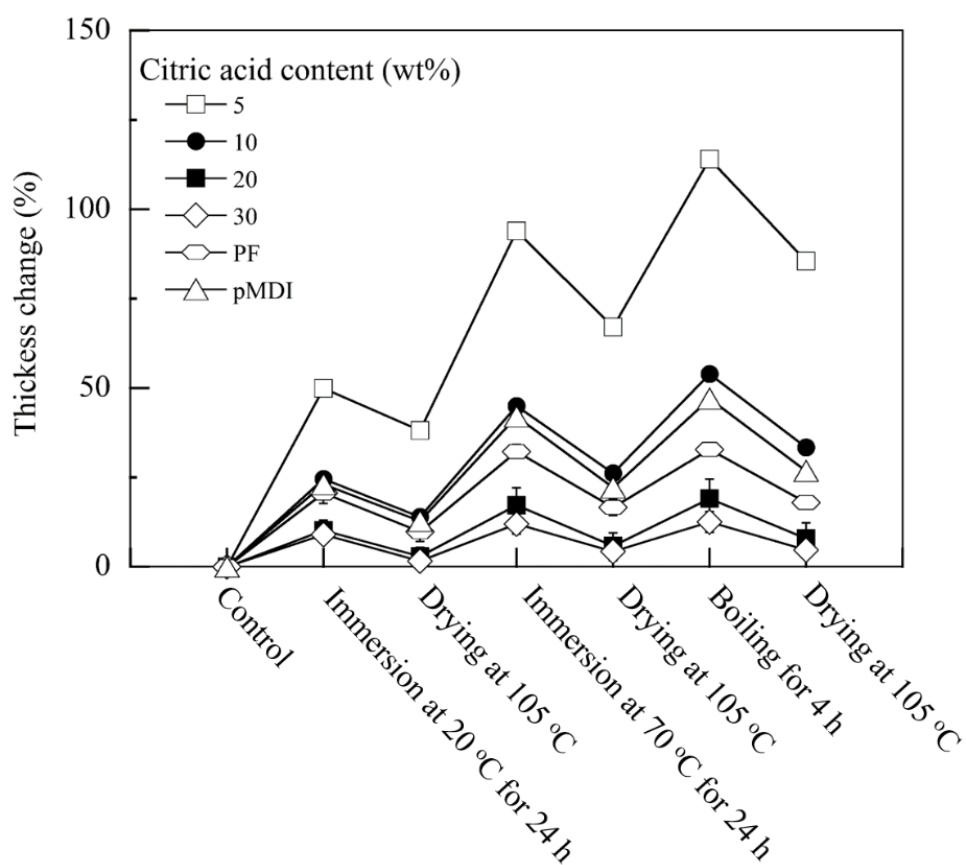


Fig. 2.5 Thickness change during cyclic aging treatment of type (b) particleboards. Error bars indicate the standard deviations.

Figures 2.6 and 2.7 show the weight changes of type (a) and (b) particleboards, respectively. Figure 2.6 demonstrates that the weight change of the boards decreased with increasing citric acid content. This result indicates that the increasing citric acid content increasingly inhibited water absorption. The weight changes of the boards due to the subsequent warm-water immersion treatment were greater than those due to the first water-immersion treatment. This phenomenon is caused by the decreased water resistance of the adhesive and by water penetration into the boards. With the subsequent drying treatment, the weight of the boards changed by approximately -7 to -20 %.

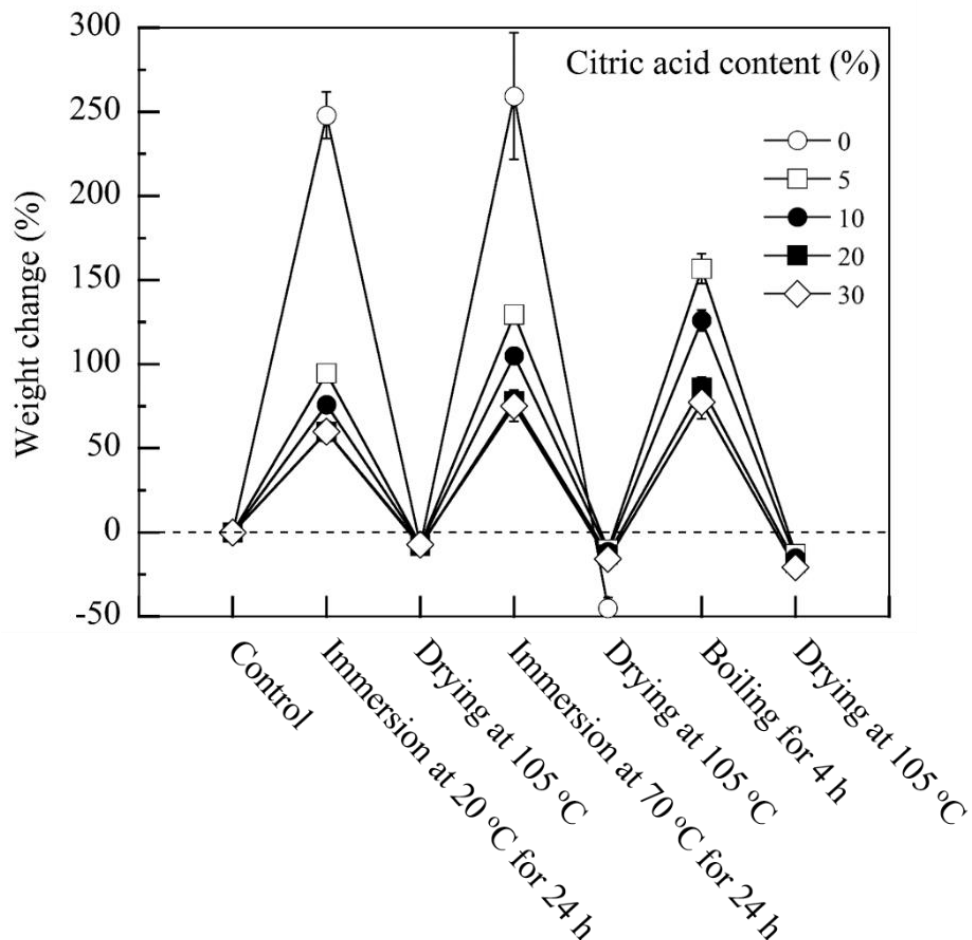


Fig. 2.6 Weight change in a cyclic aging treatment of type (a) particleboards. Error bars indicate the standard deviations.

Figure 2.7 demonstrates that the degree of weight change of type (b) particleboards followed a trend similar to that of type (a) particleboards, as explained above. However, the weight changes of the type (b) boards due to each drying treatment were approximately – 5 to – 16 %. These values were slightly lower than those of the type (a) particleboards. This result indicates that the type (a) boards contained greater amounts of water-soluble compounds, such as unreacted citric acid and that those compounds were released from the boards during the hot-water treatment.

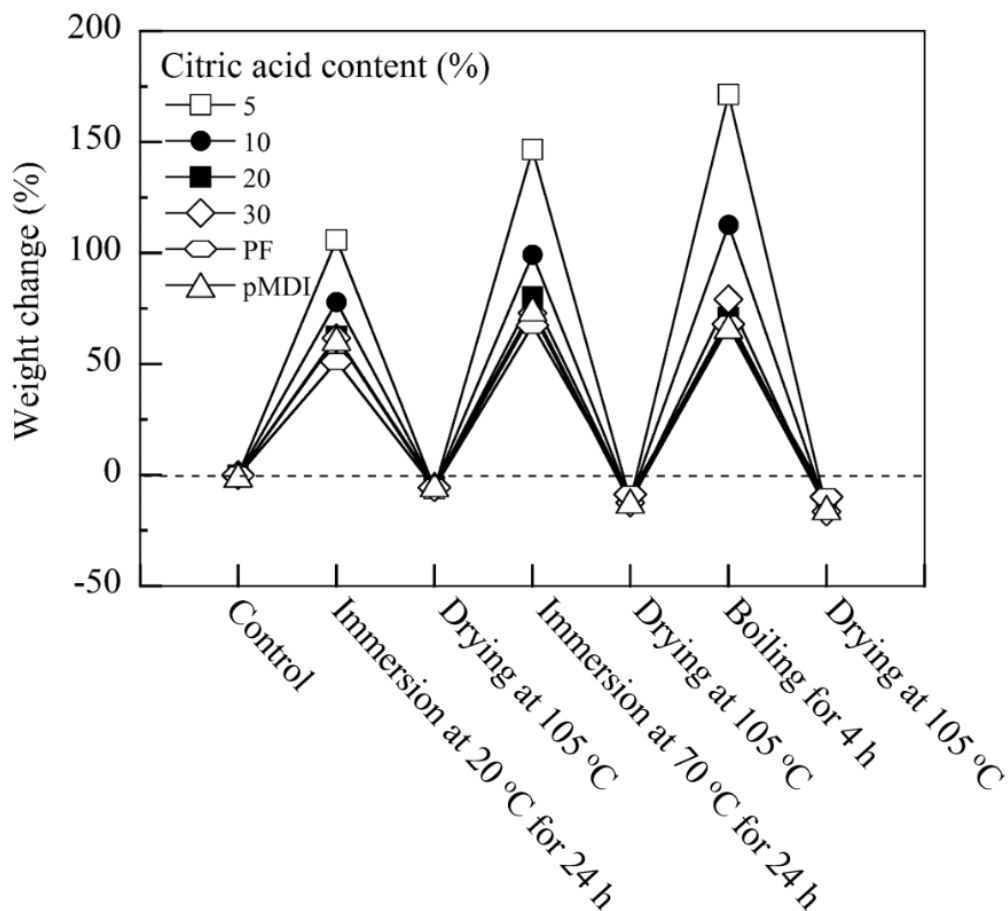


Fig. 2.7 Weight change in a cyclic aging treatment of type (b) particleboards. Error bars indicate the standard deviations.

The founded trends of dimensional stability of particleboard in this chapter can be explained as follows: dimensional stability was improved means TS, WA, thickness and weight changes

decreased with the increasing of citric acid content. The reason was that the amount of chemical linkages that generated from the interaction between citric acid and sweet sorghum bagasse particles increased with the increasing of citric acid content, weakening the expansion of the particles, eliminating the hygroscopicity of sweet sorghum bagasse particles, which contributed to the decrease of TS, WA, thickness and weight change of particleboard. Dimensional stability of particleboard using non-pre drying of particles (particleboard type (a)) was lower than that of particleboard using pre drying of particles (particleboard type (b)) because high moisture content of non-pre drying of particles interfered reaction between citric acid and the particles during hot pressing, hence the expansion of the particles becoming strong and the hygroscopicity of the particles did not eliminate. Therefore, pre drying of the particles was effective pretreatment method to enhance dimensional stability of the particleboard.

2.3.4. Bonding mechanism

Based on the results obtained, the bonding mechanisms of type (b) boards with various citric acid contents were investigated using FT-IR spectroscopy. The infrared (IR) spectra of the boards are shown in Fig. 2.8. The intensity of the peak at approximately 1721 cm^{-1} increased with increasing citric acid content. This peak is typically ascribed to C=O stretching due to carboxyl groups and/or C=O ester groups (Yang *et al.*, 1996 and Zagar *et al.*, 2003). Changes in intensity were also found in the peak at approximately 1200 cm^{-1} , which was assigned to the C-O stretch in esters. According to the results shown in Fig. 2.7, the boards contained water-soluble substances; therefore, it was necessary to examine the chemical structure of boards that lacked water-soluble substances. The IR spectra of boards that had been subjected to the cyclic aging treatment are shown in Fig. 2.9, which demonstrate that the intensities of the absorption peaks at approximately 1721 and 1200 cm^{-1} slightly increased with increasing citric acid content,

indicating that citric acid reacted with the hydroxyl groups of sorghum bagasse particles to form ester linkages. In addition, the intensities of the absorption peaks at around 1721 cm^{-1} of type (b) particleboard (3) was higher than that of type (a) particleboard under suitable condition of citric acid content (20 wt%) as shown in Fig. 2.10. This indicates that the pre-drying of particles was suitable method to lead effective reaction between carboxyl groups of citric acid and hydroxyl groups of sweet sorghum bagasse, and formed ester linkages. Consequently, the formation of ester linkages would result in good adhesiveness and impart excellent physical properties to the boards. The possible reaction between citric acid and sweet sorghum bagasse was shown in Fig. 2.11.

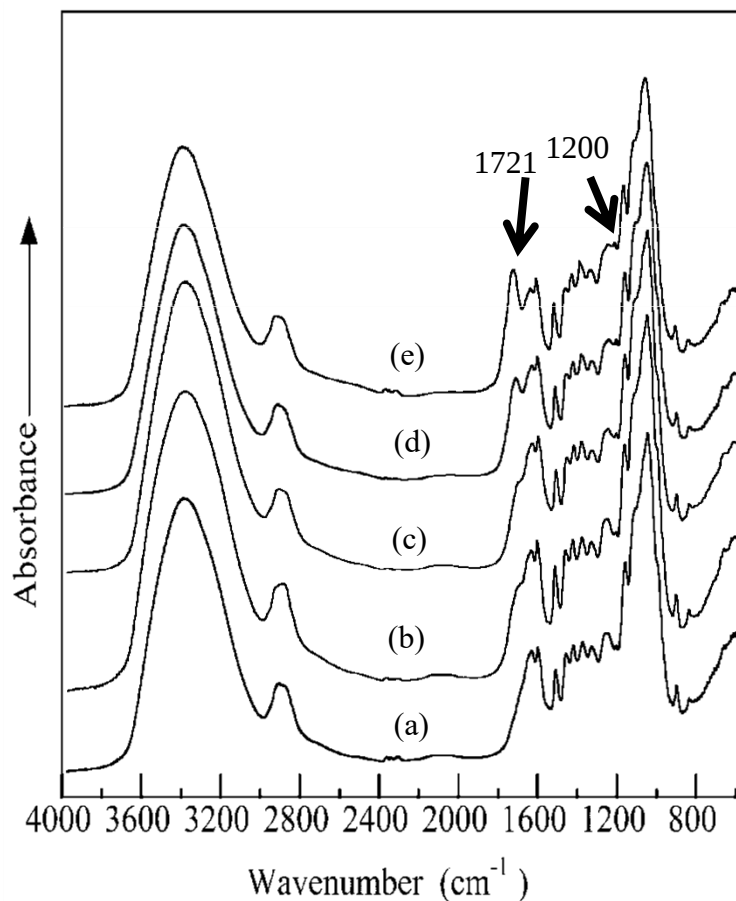


Fig. 2.8 FT-IR of sweet sorghum bagasse type (b) particleboards bonded with citric acid at 0 (a), 5 (b), 10 (c), 20 (d), 30 (e) wt% before undergoing the cyclic aging treatment.

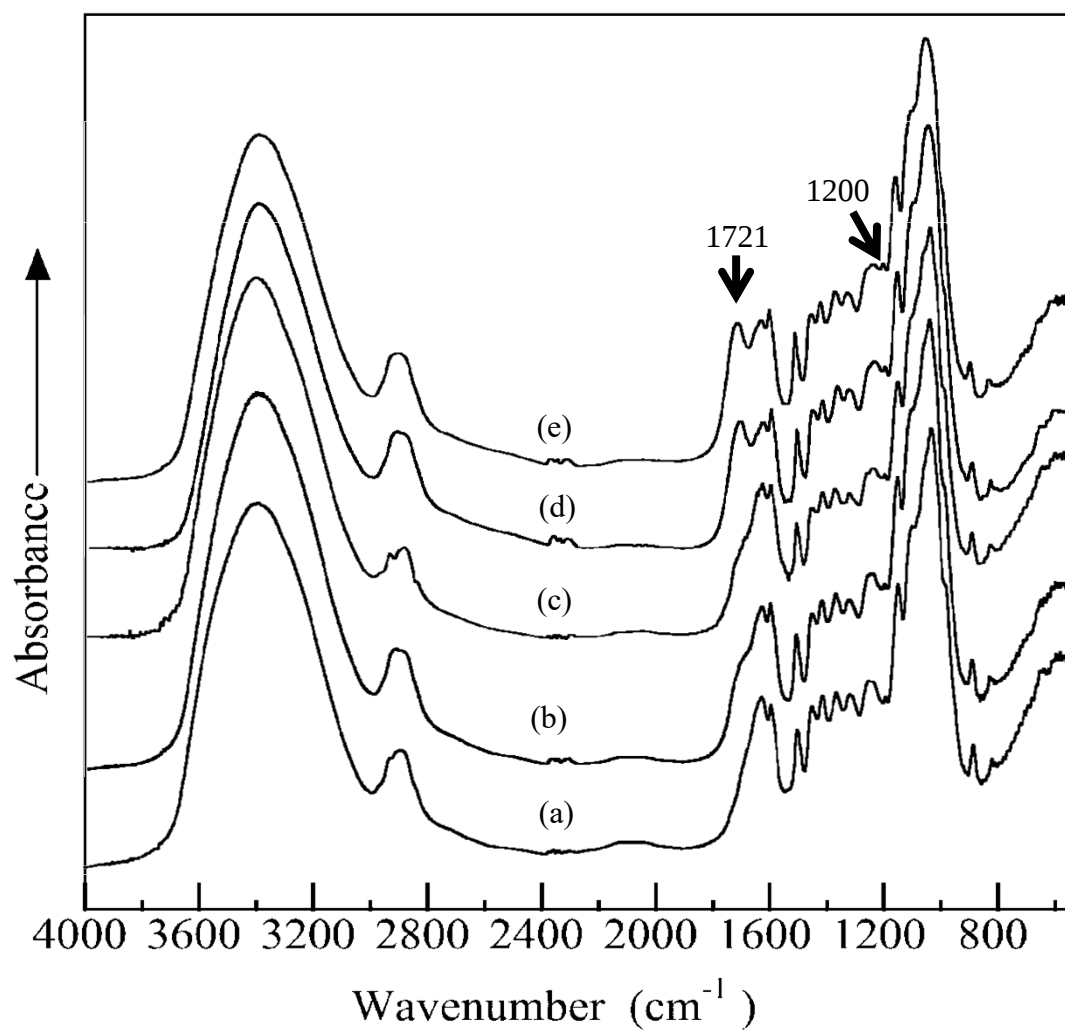


Fig. 2.9 FT-IR of sweet sorghum bagasse type (b) particleboards bonded with citric acid at 0 (a), 5 (b), 10 (c), 20 (d), 30 (e) wt% that had undergone the cyclic aging treatment.

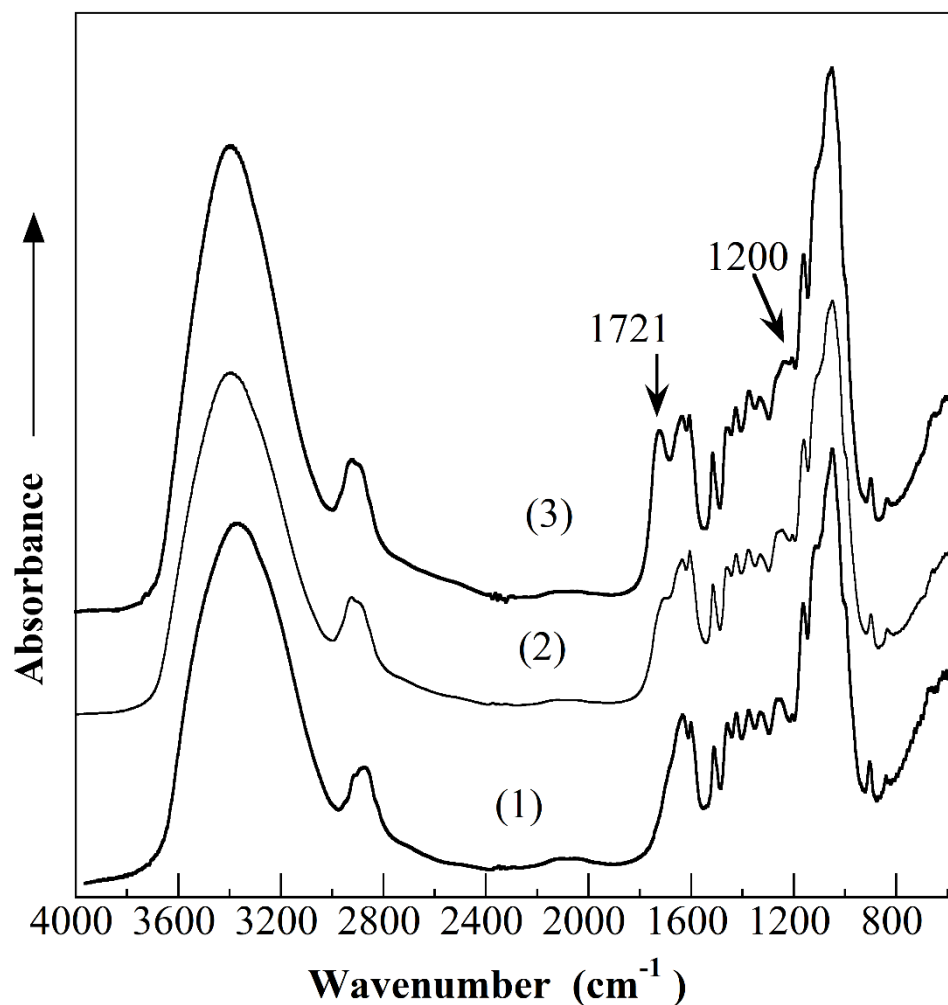


Fig. 2.10 FT-IR of particleboard after undergone the cyclic aging treatment; (1) particleboard bonded with 0 wt% of citric acid content; (2) particleboard using non-drying of particles and (3) particleboard using pre-drying of particles under suitable citric acid content of 20 wt%.

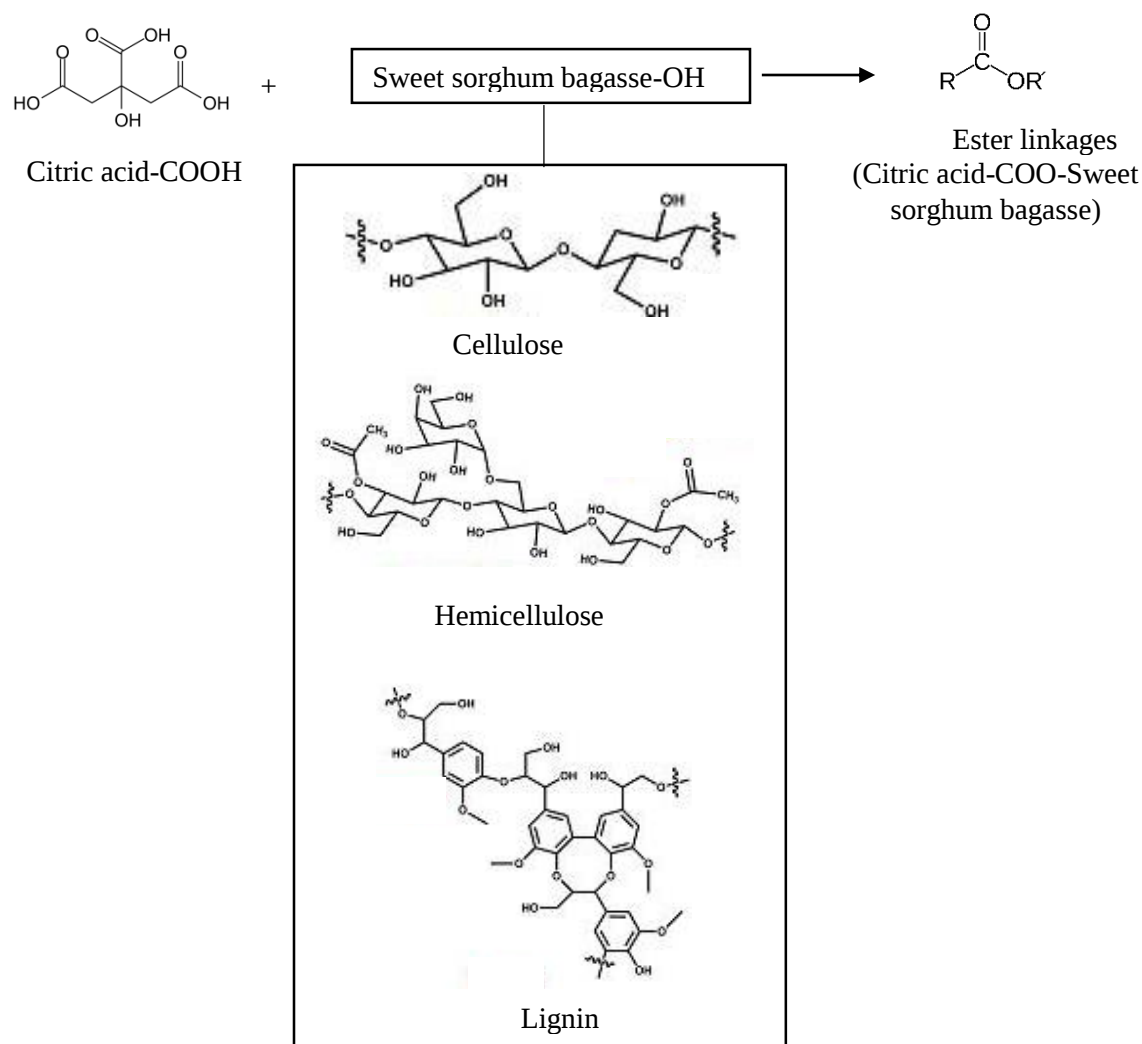


Fig. 2.11 Possibility reaction between citric acid and sweet sorghum bagasse.

2.4. Summary

The effects of the citric acid content and the pre-drying treatment of particles that had been sprayed with adhesive on the physical properties of sweet sorghum bagasse particleboard were investigated. The mechanical properties and water resistance of the particleboards were enhanced by increasing the citric acid content and applying the pre-drying treatment to the particles after

spraying them with adhesive. Based on the results obtained in this chapter, the boards prepared using pre-dried particles (type (b)) and bonded with 20 and 30 wt% citric acid had the best mechanical properties and water-resistance level. Furthermore, the bending strength, IB strength and TS values of those boards satisfied the requirement of the 18 type of JIS A 5908 standard. In addition, the mechanical properties of the boards prepared using type (b) particles and bonded with 20 and 30 wt% citric acid were comparable to those of the boards bonded with PF resin or pMDI.

The TS values of the former boards were lower than those of the boards bonded with PF resin or pMDI. This result indicates that the boards prepared using type (b) particles and bonded with 20 and 30 wt% citric acid had good dimensional stability. Moreover, high hemicellulose content of sweet sorghum bagasse affected to give an effective reaction between citric acid and sweet sorghum bagasse particles, hence physical properties of the sweet sorghum bagasse particleboard were better than the wood particleboard bonded with citric acid only. FT-IR analysis of the particleboards demonstrated that citric acid had reacted with the sweet sorghum bagasse particles to form ester linkages. As a result, particleboards with excellent physical properties were obtained.

Chapter 3

Influences of pressing temperature and time on particleboard properties

3.1. Introduction

Particleboards made from sweet sorghum bagasse and citric acid were successfully manufactured under suitable conditions of pretreatment of particles and citric acid content as reported in Chapter 2. The good physical properties of particleboards were obtained by using pre-drying of particles and 20 wt% of citric acid content as mentioned in Chapter 2. However, the particleboards were manufactured at one condition of press temperature and time i.e. 200 °C and 10 min, respectively. The pressing operation is obviously an extremely critical step in particleboard production. Some of press conditions such as press temperature and time are the most significant pressing conditions affecting the properties of particleboard (Kelly, 1997). In addition, more details properties of particleboard were necessary to know in wider application of particleboard such as wet bending properties, screw-holding power, biological durability, and formaldehyde emission.

The durability of wood-based composite is one of their most important properties when are used in residential construction. In the previous study of Norita *et al.* (2008), they investigated the quantitative relationship between the wet-bending-A test and the Wet-bending-B test as mentioned in JIS A 5908 (2003) to know durability of wood-based composite. Susceptibility of wood to biological attack have restricted wood products from many potential markets (Rowell *et al.*, 1988). With implementation of the 1990 Clean Air Act, formaldehyde emissions and hazardous air pollutants (HAPs) arising during the hot-pressing of particleboard manufacturers. The adhesives and the wood itself contain volatile compounds such as formladehyde, which may

be emitted during manufacturing (Jiang *et al.*, 2002). Additionally, thermal degradation of the wood may contribute to formaldehyde emission during manufacturing (Jiang *et al.*, 2002).

Therefore, in Chapter 3, the effects of pressing temperature and time on the physical properties of particleboards were investigated. Furthermore, wet bending (WB), screw-holding power (SH), biological durability and formaldehyde emission of particleboard under effective pressing temperature and time were evaluated.

3.2. Materials and Methods

3.2.1. Preparation of materials

The raw materials and the preparation were same as mentioned in Chapter 2.

3.2.2. Manufacture of particleboards

Based on the results of Chapter 2, 20 wt% citric acid (CA) was sprayed onto particles and then dried at 80 °C for 12 h to reach a moisture content of about 10%. Subsequently, the particles were formed into mats as same as in Chapter 2. The mat of particles was pressed using a hot-pressing machine under various temperature and time conditions, i.e., 140–220 °C, and 2–15 min, respectively. Furthermore, the detail process of manufacture of particleboard as similar as in Chapter 2.

3.2.3. Measurement of mat temperature

The temperature of mat during hot pressing was measured with a thermocouple sensor (Type T/copper-constantan) and a data logger (HIOKI 8420-51 memory Hi Logger) (HIOKI E. E. Corporation, Nagano, Japan). The thermocouple sensor was installed at each layer of mat (i.e.,

face, core, and back layer) and connected to the data logger (HIOKI 8420-51 memory Hi Logger) (HIOKI E. E. Corporation, Nagano, Japan). Measurement of the change in mat temperature was initiated when the platen pressure reach the mat surface.

3.2.4. Evaluation of the physical properties

The particleboards were tested after being conditioned as same as in Chapter 2. The procedure of cutting sample specimen from each particleboard as same as in Chapter 2. The dry-bending strength of particleboards, i.e., the modulus of rupture (MOR) and the modulus of elasticity (MOE), internal bonding (IB) strength, and the thickness swelling (TS) and water absorption (WA) of particleboard were evaluated as explained detail in Chapter 2. All physical properties of particleboards were tested according to JIS A 5908 (2003) as same as in Chapter 2.

Subsequently, bending strength test B under wet conditions and screw holding (SH) power test of particleboard under the effective condition of hot pressing temperature and time were also evaluated according to JIS A 5908 (2003). The size of wet-bending strength specimen as same as dry-bending strength as mentioned in Chapter 2. The SH specimen of 50 × 100 mm was drilled by drill of 2 mm in diameter to make holes of about 3 mm deep in the two center positions of board cross section. The distance of each hole was 25 mm from the edge side as a mentioned in JIS A 5908 (2003). Screws used for SH test were 2.7 mm in diameter and 16 mm in length. The screws were inserted into the hole to a depth of 9 mm, leaving 7 mm of shank free for loading grip. The depth of inserting screw into the hole is modification method of JIS that the requirement of the screw depth is approximately 11mm. The pulling-out load speed was about 2 mm/min.

Each experiment was performed in five replications, and the average values and standard deviations were calculated. The MOR, MOE, and IB values of particleboards shown in the figures are values that were corrected for each target density based on regression lines between the actual values of the mechanical properties and the specimen densities.

3.2.5. Termite and decay resistance tests

Termite and decay resistance of particleboard manufactured under effective pressing condition, and each particleboard bonded with PF and pMDI were evaluated. The size of specimens for each test of termite and decay resistance were $20 \times 20 \times 9$ mm. Five specimens per board type such as particleboard bonded using CA, PF, pMDI were assayed against termites and decays.

In the termite resistance test, the specimens were exposed to the subterranean termite *Coptotermes formosanus* Shiraki, according to the Japan Wood Protection Association standard (JWPAS-TE (2011)). The containers used for the termite test were acrylic cylinders (80 mm in diameter, 60 mm in height), the lower ends of which were sealed with a 5-mm thick hard dental plaster (New Plastone, GC Corp.). Test specimen were set at the center of the plaster bottom of the test container on a plastic mesh. A total of 150 worker termites and 15 soldiers collected from a laboratory termite colony at Deterioration Organisms Laboratory, Research Institute for Sustainable Humanosphere (RISH), Kyoto University, were introduced into each test container. Small sapwood blocks ($20 \times 20 \times 9$ (mm)) of sugi (*Cryptomeria japonica* (Thunb. Ex L.f.) D. Don) were used as a control. The assembled containers were placed on damp cotton pads to supply water to the specimens, and left at 28 °C and >85% relative humidity (RH) in darkness for 3 weeks. The mass loss of the specimens as a result of termite attack was calculated based on the difference between initial and final oven dry weights of the specimens after cleaning off the

debris from termite attack. Termite mortality was calculated based on the number of dead workers termites divided by initial total worker termites (150).

In the decay resistance tests, a monoculture decay test was carried out with the brown-rot fungus (*Fomitopsis palustris* (Berk. Et Curt) Gilbn. & Ryv. (FFPRI 0507), and the white-rot fungus (*Trametes versicolor* (L.:Fr.) Pilat. (FFPRI 1030), according to the JWPAS-FE (2011). A 100-ml aliquot of liquid medium containing 1.5% malt extract, 0.3% peptone, and 4% glucose was inoculated with stock culture of either *T. versicolor* or *F. palustris*. The incubation of inoculated liquid medium was conducted with a shaker (120 rpm) at 26 °C for 10 days. A 250-g medium of sea sand in a glass jar was permeated with 80-85 ml of nutrient solution containing 4% glucose, 0.3% peptone, and 1.5% malt extract for *T. versicolor*; half as much of each component was used for *F. palustris*. About 3-4 ml of these liquid fungal stock cultures were used in inoculating the jars. The oven-dry weight of board specimens was measured, and specimens were then sterilized with gaseous ethylene oxide. When the mycelium had fully covered the medium in the glass jars, three specimens were placed on top of the growing mycelium. A plastic mesh spacer was used for *F. palustris*, but not for *T. versicolor*. Small sapwood blocks (20 × 20 × 9 mm) of sugi wood (*Cryptomeria japonica* (Thunb. Ex L.f.) D. Don) were used as a control. The test jars were then incubated at 27 °C and for 12 weeks. Nine replicates were tested for each decay fungus for each board type. The extent of the fungal attack was expressed as the average mass loss (percent) calculated from oven-dry weights of nine specimens before and after the decay procedure.

3.2.6. Formaldehyde emission

The formaldehyde emission of 150 × 50 mm specimens were measured by desiccator method outlined in the JIS A 1460 (2001). Ten replicates were tested, for a total surface board area of

approximately 1800 cm². The specimens were placed in a desiccator containing a vessel with water. The formaldehyde released from the specimens at 20 °C over 24 h was absorbed by the water solution. This solution was first thoroughly mixed before measurement. Detail procedures of formaldehyde emission measurement in the JIS A 1460 (2001) had been obeyed. The absorbance of formaldehyde emission in the water solution was measured at 412 nm of wavelength against water as a control using a spectrophotometer (Spectrophotometer AE-350) (Erma Inc. Tokyo, Japan).

The slope of the calibration curve on the standard solution of formaldehyde was carried out by measuring the wavelength absorbance of the formaldehyde standard solution using a spectrophotometer with various quantities of formaldehyde standard solution (i.e., 0–3 mg). The graphs of the correlation between the quantity of formaldehyde and the absorbance was then determined to obtain the slope by the least squares regression line method. The concentration of formaldehyde from the test piece absorbed into the water in the glass crystallizing dish inside the desiccator was calculated using the following the formula from the JIS A 1460 (2001):

$$G = F \times (A_d - A_b) \times (1800/S)$$

Where, G : concentration of formaldehyde from the test piece (mg/l)

A_d : absorbance of solution inside desiccator containing the test piece

A_b : absorbance of background formaldehyde (blank test)

F : slope of the calibration curve of the standard formaldehyde solution (mg/l)

S : surface area of test piece (cm²)

3.2.7. Statistical analysis

The experimental design for physical properties evaluation, formaldehyde emission test, and termite and decay resistance test were completely randomized design. The data were analyzed

using analysis of variance. The standard deviation were also computed from the data and are shown as error bars in each corresponding figure.

3.2.8. Fourier Transform Infrared Spectroscopy (FT-IR)

The powders for FT-IR analysis of particleboards were prepared as same as in Chapter 2. The running method of FT-IR analysis was explained in Chapter 2. As a control, the infrared spectra of sweet sorghum bagasse particles were also measured.

3.3. Results and Discussion

3.3.1. Effect of pressing temperature

The influence of pressing temperature on the physical properties of particleboard were observed under a pressing time of 10 min. Fig. 3.1 shows the relationship between pressing temperature and the bending properties (MOR and MOE) of the particleboards. The bending properties increased with increasing of pressing temperature from 140–200 °C, and then decreased at 220 °C. This indicated that a pressing temperature of 200 °C is the effective temperature in terms of bending properties in this research of chapter 3. Decreasing of the MOR at 220 °C might be due to material degradation and lead to embrittlement of surface layer (Yang *et al.*, 2014). Actually, chemical component of lignocellulose material including sweet sorghum bagasse such as hemicellulose decompose at 220 – 315 °C (Yang, 2007) and citric acid degrade around over 220 °C (Barbooti, 1986). The maximum average MOR and MOE values of particleboards were 21.8 MPa and 5.3 GPa at 200 °C pressing temperature, respectively. Those values were about 1.5 times or more high than those of board manufactured at 140 °C. The MOR

value of particleboards manufactured at 180 and 200 °C were higher than the requirement values (≥ 18 MPa) of 18 type JIS A 5908 (2003).

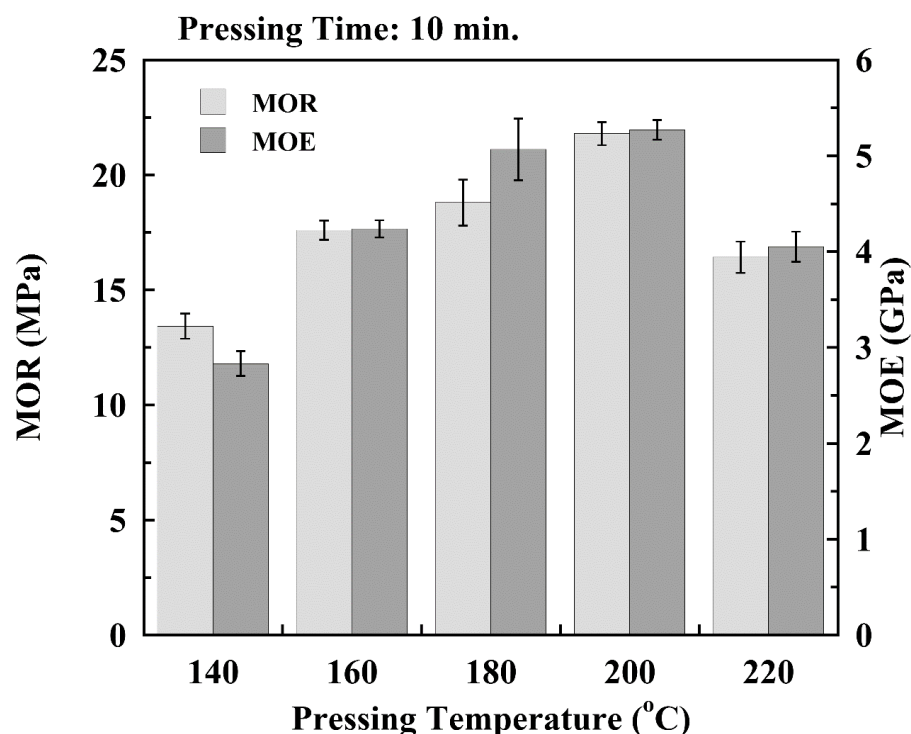


Fig. 3.1 Relationship between pressing temperature and bending properties of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Table 3.1 shows MOR, MOE, SH power, and formaldehyde emission of particleboard bonded with CA under effective hot pressing condition (i.e. 200 °C of pressing temperature and 10 min of pressing time), and for particleboards bonded with PF resin and pMDI. As can be seen in the table, MOR (21.8 MPa) of the board bonded with CA was lower than those of boards bonded with PF (32.9 MPa) and pMDI (34.1 MPa), while the MOE (5.2 GPa) of the CA boards was higher with that of those bonded with synthetic resins (PF [4.5 GPa]; pMDI [4.6 GPa]). However, those MOE values were not significantly different ($p > 0.05$). In a previous report, Azeredo *et al.*

(2015) reported that the tensile strength of wheat straw hemicellulose film decreased and its modulus of elasticity increased as the CA content increased up to 20 wt%, due to the citric acid acting as a flexible cross linker. Based on those findings, our results might have also been caused by the citric acid acting as cross-linking agent. The acid causes the material to seem stiff and brittle hence the elasticity was improved and the strength of particleboard decreased.

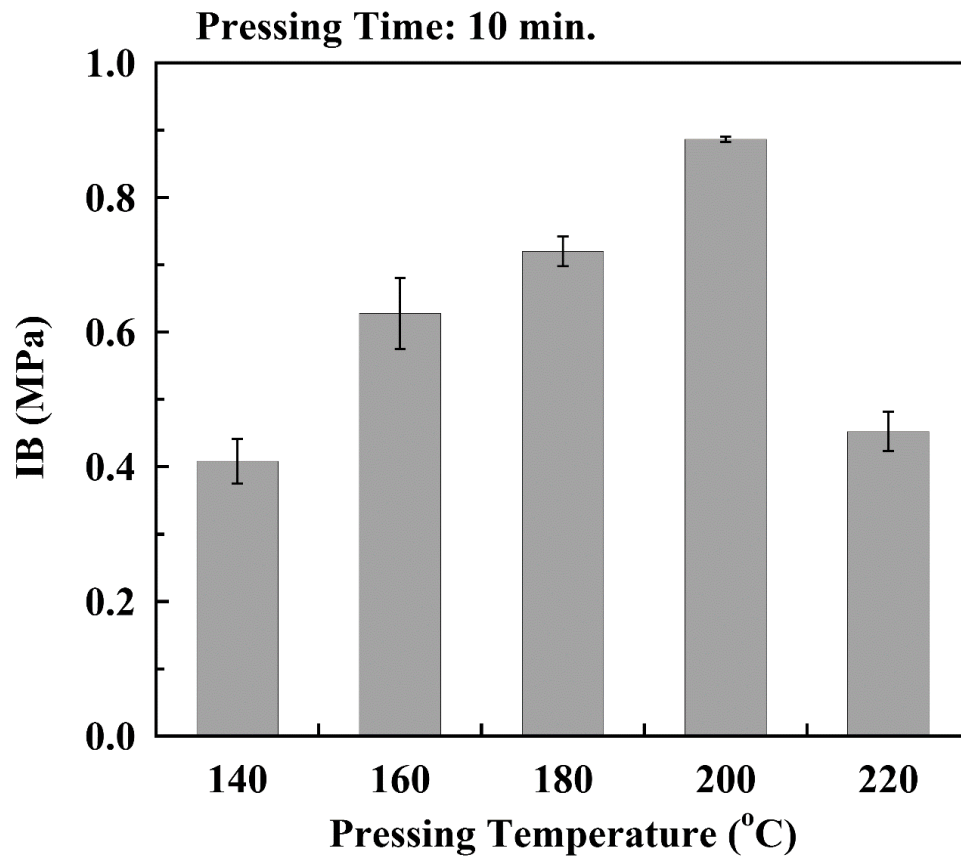


Fig. 3.2 Relationship between pressing temperature and IB strength of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Figure 3.2 shows the relationship between pressing temperature and the IB strength of particleboards. IB strength increased gradually when boards were manufactured at 140–200 °C,

while it decreased sharply in those manufactured at 220 °C. The IB value of the board manufactured at 200 °C was double that of boards manufactured at 140 and 220 °C. Theoretically, the IB strength is affected by the adhesiveness of the core layer (Roffael and Rauch, 1972). According to this general theory, and the melting point of CA (~150 °C), the board manufactured at 200 °C might have reached an effective temperature of more than 150 °C in the core layer during hot pressing. Hence, the citric acid melted, and could have easily formed linkages with the sweet sorghum bagasse component to obtain good adhesiveness.

On the other hand, the IB strength of the board decreased at a higher pressing temperature of 220 °C. A previous study by Yang *et al.* (2007) found that the hemicellulose decomposed at 220-315 °C. In addition, the added CA as acid compound would be promote the degradation of hemicellulose (Liao *et al.*, 2016). According to those studies, the decreasing of IB strength at high temperature more than 200 °C appeared to have been caused by the degradation and decomposition of some components such as hemicellulose. The formation of its volatile components then proceeded, and as a result, these components interfered with the adhesiveness of the core layer. This means that a pressing temperature of 200 °C was likely to be the effective temperature for obtaining good IB strength. Furthermore, all of the boards met the requirement (≥ 0.3 MPa) of type 18 JIS A 5908 (2003). In addition, the IB value of the board under effective pressing temperature as shown in Table 3.1 was higher than that of those bonded with PF resin, and lower than that of boards bonded with pMDI.

Figure 3.3 shows the TS and WA of particleboards manufactured at different pressing temperatures. TS and WA values declined considerably up to 200 °C, and then decreased slightly. The TS of boards manufactured at high pressing temperatures of 200 and 220 °C satisfied the requirement ($\leq 12\%$) of type 18 JIS A 5908 (2003). Previous research has reported that the cross-

linking between CA and wood powder in wood-based molding at higher pressing temperatures of 200 and 220 °C might occur effectively than at temperatures less than 180 °C (Umemura *et al.*, 2012). Hence, cross-linking between CA and sweet sorghum bagasse particles would also be improved. Accordingly, a pressing temperature of 200 °C or higher was necessary to obtain good dimensional stability.

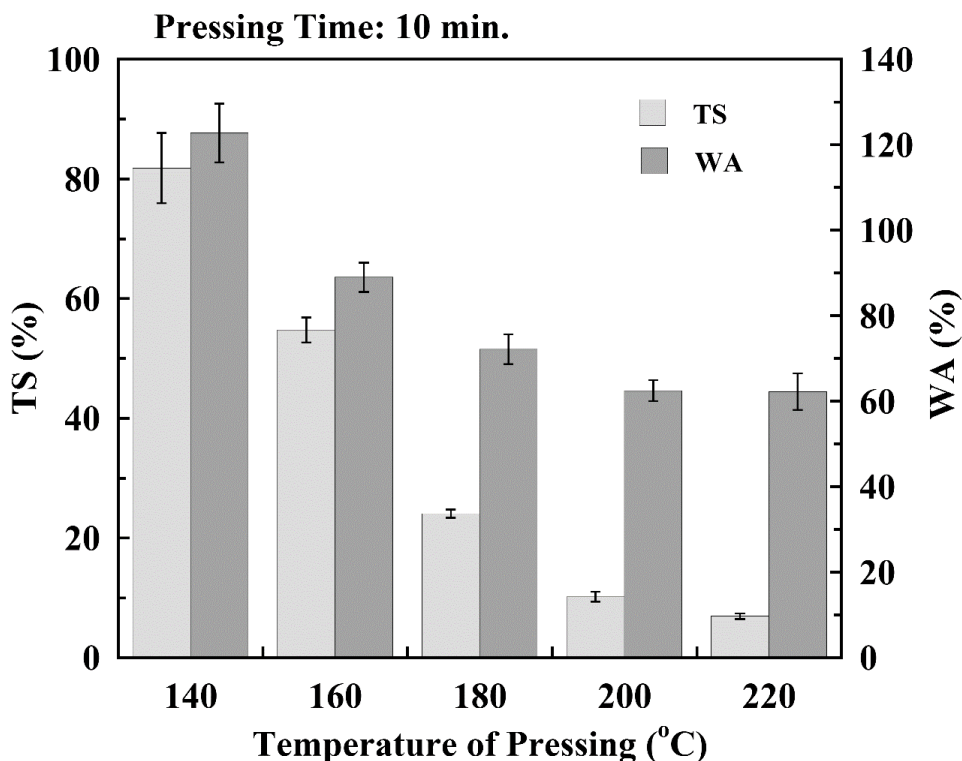


Fig. 3.3 Effect of pressing temperature on TS and WA of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Furthermore, the TS of those boards were lower than that of boards bonded using PF and pMDI, as shown in Table 3.1. Xu *et al.* (2009) pointed out that particleboard made from sugarcane bagasse bonded with PF and pMDI had inferior dimensional stability because sugarcane bagasse is composed of sucrose-rich pith and a lignocellulose rind, as well as

quantitative non-fiber substances that easily absorbed water. In addition, Hosseinaei *et al.* (2012) reported that the high hemicellulose of wood flour affected the water absorption of composite board. Considering those studies, the high hemicellulose content of sweet sorghum bagasse (Kusumah *et al.*, 2016) might have affected the high TS of boards bonded with PF and pMDI. Therefore, citric acid was effective adhesive in the manufacturing of particleboard made from sweet sorghum bagasse that contained high hemicellulose. Based on the results shown in Figs. 3.1, 3.2, and 3.3, the suitable pressing temperature of particleboard manufactured from sweet sorghum bagasse and CA was 200 °C.

3.3.2. Effect of pressing time

The effects of pressing time on physical properties of particleboard were investigated under a pressing temperature of 200 °C. Figure 3.4 shows the bending properties of particleboard with different pressing time. The MOR and MOE increased gradually from 2 to 10 min and then decreased slightly at 15 min. This means that 10 min is an effective pressing time to obtain good bending properties. The reason for the slight decrease of the bending properties at 15 min due to degradation of material and adhesive by receiving more heat energy during hot pressing at a fixed temperature. As explained above, the degradation of raw material components and adhesive lead to embrittlement of surface layer (Yang *et al.*, 2014). Generally, the bending properties of particleboard were influenced by bondability among particles and the strength of the particles themselves. Except for the board manufactured at 2 min, all of the boards had MOR satisfied the requirement (≥ 18 MPa) of 18 type JIS A 5908 (2003).

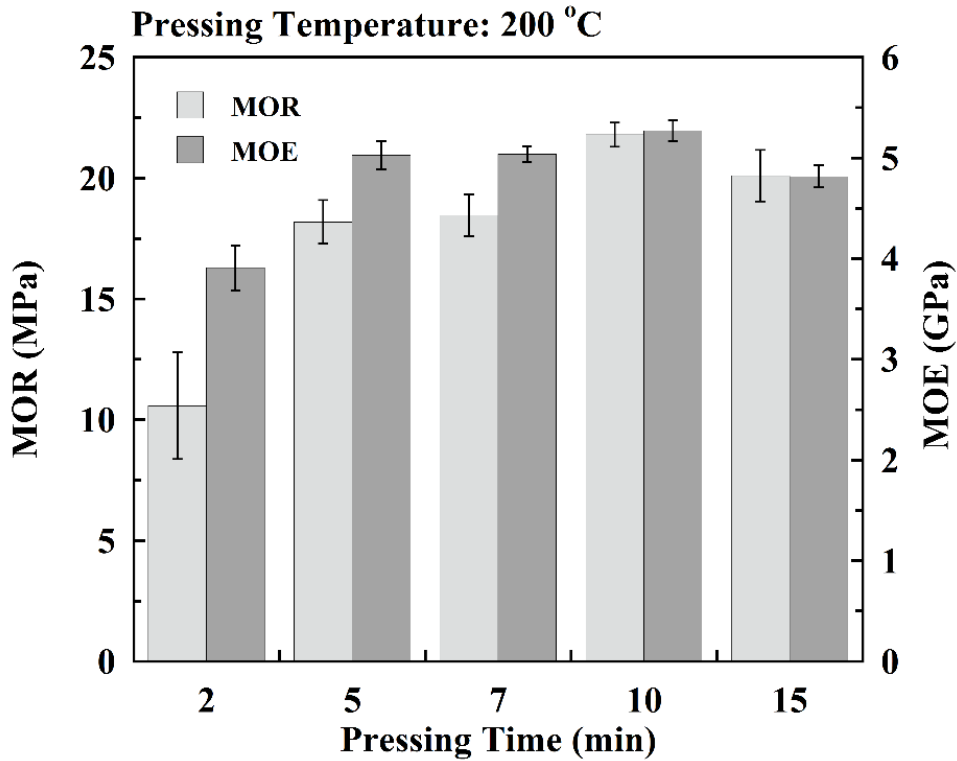


Fig. 3.4 Relationship between pressing time and bending properties of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Relationship between the IB strength and pressing time is showed in Fig. 3.5. The IB strength of the boards increased greatly with increasing of pressing time from 2 to 10 min and then decreased slightly at 15 min. The IB value of the board with 2 min pressing time was extremely lower value. Based on the temperature of each layer of the board during hot pressing as shown in Fig. 3.6, the increasing temperature in the core layer of particleboard was slower than that in the surface layers. The temperature at core layer for 2 min pressing reached less than target temperature of 200 °C i.e. around 150 °C, hence the reaction of citric acid did not enough at core layer. Consequently, the adhesiveness at core layer was poor. However, the temperature at core layer for pressing time more than 5 min was closed to the target temperature and reached about

200 °C at 10 min. Because of that, the IB strength of the board increased significantly from 2 to 5 min and then increased gradually until 10 min. It means that the pressing time of 10 min was needed to obtain good adhesiveness in all layer of particleboard. Furthermore, excluding the board manufactured for 2 min, all of the boards had higher IB strength than the requirement (≥ 0.3 MPa) of 18 type JIS A 5908 (2003).

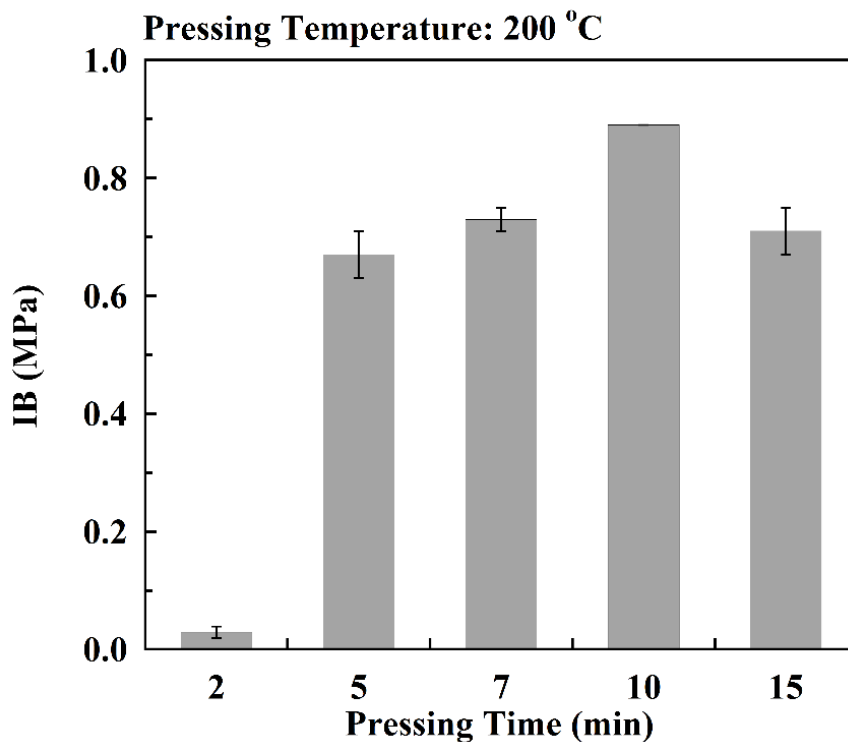


Fig. 3.5 Relationship between pressing time and IB strength of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

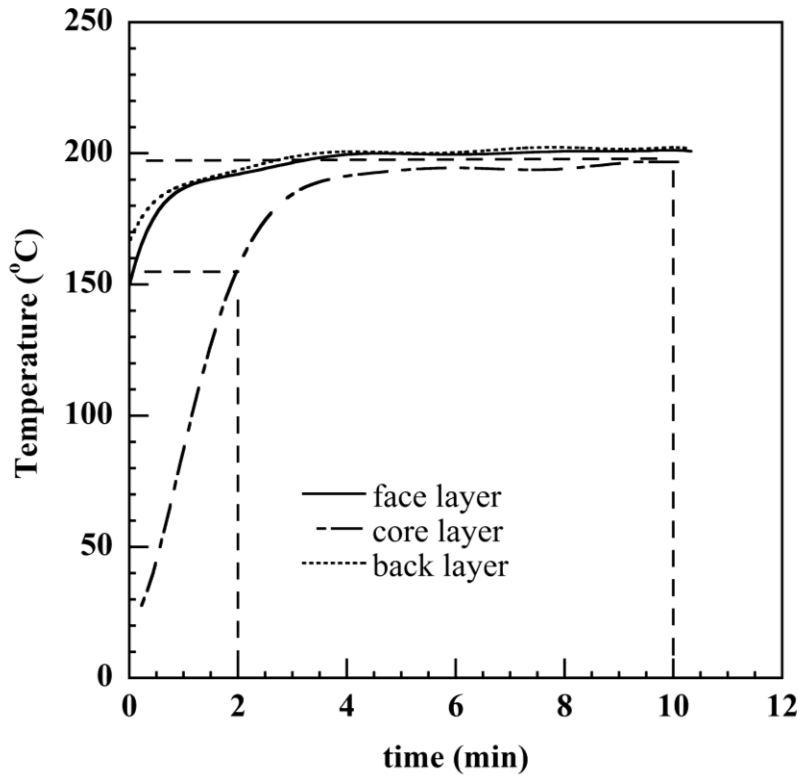


Fig. 3.6 Temperature of each layer of particleboard during hot pressing.

Figure 3.7 shows the effect of pressing time on TS and WA of particleboard. The board with 2 min pressing time had the highest TS and WA values and then decreased sharply at 5 min pressing time followed with slight decreasing of those values at 5-15 min. TS values of the board with 10 and 15 min pressing time were 10.2% and 9.5%, respectively. Those values were not significantly different ($p > 0.05$) and were about one-five lower than TS of the board with 2 min pressing time. The TS values of the boards with 10 min pressing time or longer satisfied the requirement ($\leq 12\%$) of 18 type JIS A 5908 (2003). Therefore, the pressing time of 10 min or longer was required to attain good dimensional stability of the board. Theoretically, a good inter-particle bonding is a one of influence factor that affected excellent dimensional stability of

particleboard. A good inter-particle bonding was determined by effective reaction of adhesive or the adhesive cured completely and uniformly in all parts of particleboard during hot pressing. In this chapter, the suitable pressing time of 10 min is required to generate the effective reaction of citric acid that contributed to a good inter-particle bonding. The adhesive cured uniformly in all parts of particleboard during hot pressing can be accomplished by increasing the pressing time at a constant temperature. Therefore, the increasing of pressing time from 2 to 15 min would generate effective reaction between citric acid and particles and it cured uniformly. As a result, TS and WA of particleboards decreased with increasing of pressing time as shown in Fig. 3.7.

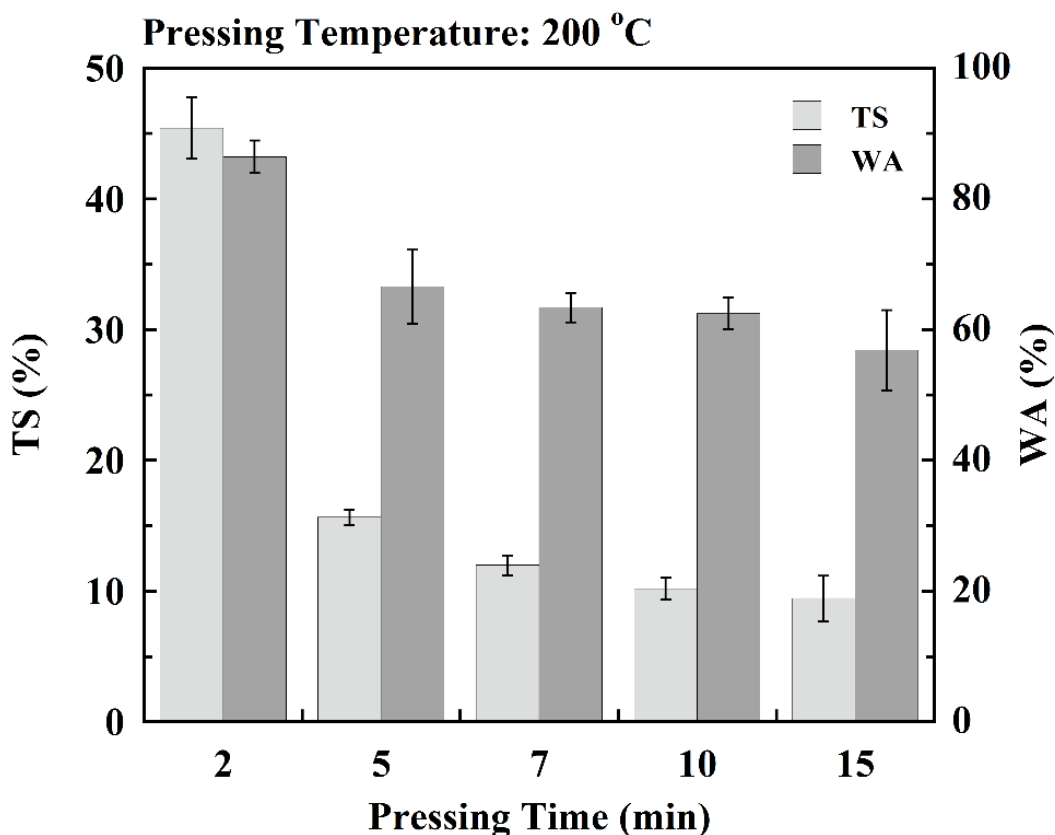


Fig. 3.7 Effect of pressing time on TS and WA of particleboards bonded with 20 wt% citric acid content. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Table 3.1 MOR, MOE, screw holding (SH), IB, TS and formaldeyde emission of sweet sorghum bagasse particleboard bonded with citric acid, PF, and pMDI.

Particleboard Type	MOR (MPa)		MOE (GPa)		IB (MPa)	TS (%)	SH (N)	Formaldehyde emission (mg/L)
	Dry-test	Wet-test	Dry-test	Wet-test				
CA	21.8 (0.39)	7.7 (0.39)	5.2 (0.19)	1.8 (0.10)	0.89 (0.01)	10.1 (2.89)	348 (10.96)	0.00 (0.0000)
PF	32.9 (1.38)	14.6 (1.19)	4.5 (0.13)	1.4 (0.00)	0.78 (0.03)	20.6 (2.89)	652 (37.16)	0.01 (0.0004)
pMDI	34.1 (1.80)	11.3 (0.34)	4.6 (0.06)	1.6 (0.10)	1.33 (0.09)	23.1 (1.65)	858 (54.78)	0.00 (0.0000)

Values in parentheses are standard deviation

CA (Citric Acid) is particleboard bonded with 20 wt% citric acid content in optimum of pressing temperature (200 °C) and time (10 min); PF (Phenol Formaldehyde) is particleboard bonded with 12 wt% PF resin with the pressing condition of 200 °C for 6 min; pMDI (polymeric 4,4'-methylenediphenyl isocyanate) is particleboard bonded with 8 wt% pMDI with the pressing condition of 180 °C for 8 min; MOR (Modulus of Rupture) and MOE (Modulus of Elasticity) are bending properties of particleboard; IB (Internal Bond) is internal bonding strength of particleboard; TS (Thickness Swelling) is swelling of thickness of particleboard after imersion of sample in the 20 °C of water for 24 h; SH (Screw Holding) is screw holding power of particleboard.

3.3.3. The other properties under suitable conditions of the manufacturing

Based on the results above, the suitable of pressing temperature and time were 200 °C and 10 min, respectively. Moreover, in the previous research results of Chapter 2, we found the effectiveness of pre-drying treatment of particle before hot pressing and citric acid content of 20 wt%. According to those effective manufacturing condition, bending strength under wet condition, SH power, formaldehyde emission, the resistance of termite and decay were investigated. Considering further application of the particleboard (i.e. exterior or interior) for construction material, the information of those particleboard properties are necessary.

The results are shown in Table 3.1. As with dry-bending strength, the wet-MOR of CA boards was lower than that of boards bonded with PF and pMDI. However, the wet-MOE of boards was higher than those of boards bonded with PF and pMDI. The wet-MOR value of the board under effective conditions satisfied the requirement (≥ 6.5 MPa) of 13 type JIS A 5908 (2003). SH of the board was lower than those of boards bonded with PF and pMDI, probably because the CA made particles brittle (Feng *et al.*, 2014). Gambhir and Jamwal (2014) reported that brittle particles absorbed very little energy. This means that boards bonded with CA seemed to result in weak holding power for screws. The SH value of the board bonded with CA did not met the requirement (≥ 500 MPa) of 18 type, but satisfied the requirement (≥ 300 N) of 8 type JIS A 5908 (2003). As to the formaldehyde emission test, the board bonded with CA did not emit formaldehyde like the boards bonded with pMDI and PF. The formaldehyde emission value was lower than the F**** criteria (< 0.4 mg/L) of lowest formaldehyde emission of 18 type JIS A 5908 (2003). Thus, particleboard bonded with CA are safe for human health in its application.

The mass losses in the specimens by termite attack are shown in Table 3.2. The board bonded with CA contributed to higher termite mortality and a lower degree of mass loss than the controls,

and was almost similar to those bonded with PF and pMDI. This indicated that chemicals derived from CA probably show inhibitory properties against termite. In a previous study, Indrayani *et al.* (2015) also mentioned that the chemical composition of CA in MDF may act as an effective inhibitor against termite. Moreover, Papadopoulos *et al.* (2008) found that wood modified with carboxylic acid anhydrides such as acetic acid anhydride showed the greatest resistance against termite. They mentioned that the good resistance against termite because the substitution of hydrophilic hydroxyl groups of wood with hydrophobic acetyl groups of acetic anhydride made the moisture content of acetylated-wood decreased, or due to the cell wall being bulked by adduct, or by combination of these phenomena. The previous research (Papadopoulos *et al.*, 2008) mentioned also that termites seek water and are attracted to condition that might also be favorable for growth of decay and mould fungi. Evidence also proposes that they are attracted to wood decayed by certain brown rot fungi (Kartal *et al.*, 2003). Based on those previous research, the reaction between carboxyl groups of citric acid and hydroxyl groups of sweet sorghum bagasse likely to be the particleboard had less moisture content and also the cell wall of sweet sorghum bagasse being bulked by the chemical linkages that generated from the reaction. Therefore, the particleboard had good termite resistant.

The mass losses of specimens during the 12-week fungal decay tests are also presented in Table 3.2. The mass losses of the boards bonded with CA exposed to the brown-rot fungus were quite similar to those of boards bonded with PF and pMDI. However, the mass losses of boards bonded with CA and exposed to the white-rot fungus were higher than those of boards bonded with PF. On the other hand, they were lower than those of the board bonded with pMDI. In addition, the degree of mass losses of boards bonded with CA was much lower than that of solid wood specimens (*Cryptomeria japonica* (Thunb. Ex L.f.) D. Don).

Table 3.2 Termite and decay resistance of sweet sorghum bagasse particleboard bonded with citric acid, PF and pMDI.

Biological-Durability Testing	Specimen Type			
	CA	PF	pMDI	Control
Termite resistance				
Termite mortality (%)	42.8 (4.1)	46.4 (9.4)	37.9 (2.1)	24.73 (5.84)
Mass loss (%)	5.9 (0.36)	3.92 (0.28)	5.91 (0.9)	13.57 (2.35)
Decay resistance				
Mass loss of the specimen expose to:				
Brown-rot fungus (%)	5.34 (1.36)	5.79 (2.83)	4.54 (0.63)	10.23 (4.77)
White-rot fungus (%)	21.63 (11.72)	9.09 (0.78)	31.02 (5.41)	37.49 (6.05)

Values in parentheses are standard deviation

CA (Citric Acid) is particleboard bonded with 20 wt% citric acid content in optimum of pressing temperature (200 °C) and time (10 min); PF (Phenol Formaldehyde) is particleboard bonded with 12 wt% PF resin with the pressing condition of 200 °C for 6 min; pMDI (polymeric 4,4'-methylenediphenyl isocyanate) is particleboard bonded with 8 wt% pMDI with the pressing condition of 180 °C for 8 min; control is sugi (*Cryptomeria japonica* (Thunb. Ex L.f.) D. Don) wood specimen.

In a previous study, Despot *et al.* (2008) demonstrated that wood modified by CA had the greatest protection against decay. They also mentioned that the enhancement of decay resistance in wood modified by CA was exclusively the result of the cross-linking of CA and hydroxyl groups of the wood components. Based on their previous study, the board bonded with CA in this chapter had good durability against decay due to high hemicellulose content of sweet sorghum bagasse that contributed to the much amount of hydroxyl groups react with CA and generated cross-linking. Thus, the hygroscopicity of sweet sorghum bagasse was eliminated by existing of the cross-linking, hence the particleboard less absorbed the moisture from the environment. As a results, the fungus or decay could not growth well in the particleboard.

Based on the results of this study, boards bonded with CA manufactured at effective conditions of hot pressing had some advantages: i.e., good bending properties, high IB strength, good dimensional stability, good biological durability and low formaldehyde emission. However, they also had low MOR and SH power. Therefore, improvements of MOR and SH power were required in further research.

3.3.4. Changes of chemical structure

Changes in chemical structure of the boards bonded with CA manufactured at several pressing temperatures and times were measured by FT-IR. The results are shown in Figures 8 and 9. Particles collected from the particleboard were divided into two conditions as follows: (I) original particleboard specimen, and (II) particleboard specimens after cyclic aging treatment to remove unreacted CA.

Figure 3. 8 (I) shows that an absorption peak definitely appeared at approximately 1721 cm^{-1} in the board manufactured at $140\text{ }^{\circ}\text{C}$ (b) to $220\text{ }^{\circ}\text{C}$ (f). This peak is basically assigned to C=O stretching derived from the carboxyl group and/or the C=O ester group (Yang *et al.*, 1996; Žagar *et al.*, 2003). However, the peak decreased with increasing pressing temperature from $140\text{ }^{\circ}\text{C}$ (b) to $220\text{ }^{\circ}\text{C}$ (f). A small shoulder peak was also recognized around 1200 cm^{-1} . This peak is ascribed to C-O stretching of formed ester bonds (Hassan *et al.*, 2000; Bagheri *et al.*, 2014; Groen *et al.*, 2001; Rhim *et al.*, 2004). Conversely, in Fig. 3.8 (II), the absorbance intensity of the peak at approximately 1721 cm^{-1} increased with increasing pressing temperature. Furthermore, the absorbance intensity of the peaks at around 1721 cm^{-1} of the board manufactured at $140\text{ }^{\circ}\text{C}$ (b) and $160\text{ }^{\circ}\text{C}$ (c) after boiling treatment (Fig. 3.8 (II)) was lower than that of boards before boiling treatment (Fig. 3.8 (I)).

Table 3.3 shows that the pH values of the boards manufactured at low temperature were lower than those of boards manufactured at high temperature. This means that the unreacted CA from the boards manufactured at low temperature was largely released into the water after the boiling treatment. Because of that, the peaks of the boards manufactured at low temperature decreased after boiling treatment. Considering that the melting point and boiling point of CA is about 150 °C and 170 °C, respectively, CA reacted effectively with the hydroxyl groups of sweet sorghum bagasse at high temperature. Based on those results, we conclude that the low physical properties of the boards manufactured at low temperature would be affected by the low reactivity of CA.

Table 3.3 pH value of the water after TS test of particleboard bonded with citric acid.

	Type of Particleboard									
	Based on Pressing temperature (°C)					Based on Pressing time (min)				
	CA140	CA160	CA180	CA200	CA220	CA2	CA5	CA7	CA10	CA15
pH	2.83	2.91	3.31	4.48	5.51	3.05	3.88	4.27	4.48	5.104
	(0.01)	(0.02)	(0.06)	(0.04)	(0.10)	(0.05)	(0.19)	(0.24)	(0.04)	(0.08)

Values in parentheses are standard deviation

CA (Citric Acid) is particleboard bonded with 20 wt% citric acid content; 140, 160, 180, 200, and 220 are pressing temperature; 2, 5, 7, 10, 15 are pressing time; TS (Thickness Swelling) is swelling of thickness of particleboard after immersion of sample in the 20 °C of water for 24 h

In Figure 3.9 (I), the absorbance intensity of the peaks at around 1721 cm⁻¹ decreased with increasing pressing time. However, those peaks increased with increasing pressing time in the particleboard after cyclic aging treatments as shown in Fig 3.9 (II). The small peak at around 1200 cm⁻¹ can also be observed in the figures. From Figs 3.9 (I) and (II), the peaks at around 1721 cm⁻¹ of specimen (b) and (c) were decreased after boiling treatment. In Table 3.3, the pH of boards manufactured at short pressing time was lower than that of boards manufactured at long

pressing time. Consequently, the unreacted CA of the boards manufactured at short pressing time would release into the water under boiling treatment. This means that the boards manufactured at short pressing time contained an abundance of unreacted CA. These results support the low physical properties found for the boards manufactured at short pressing time.

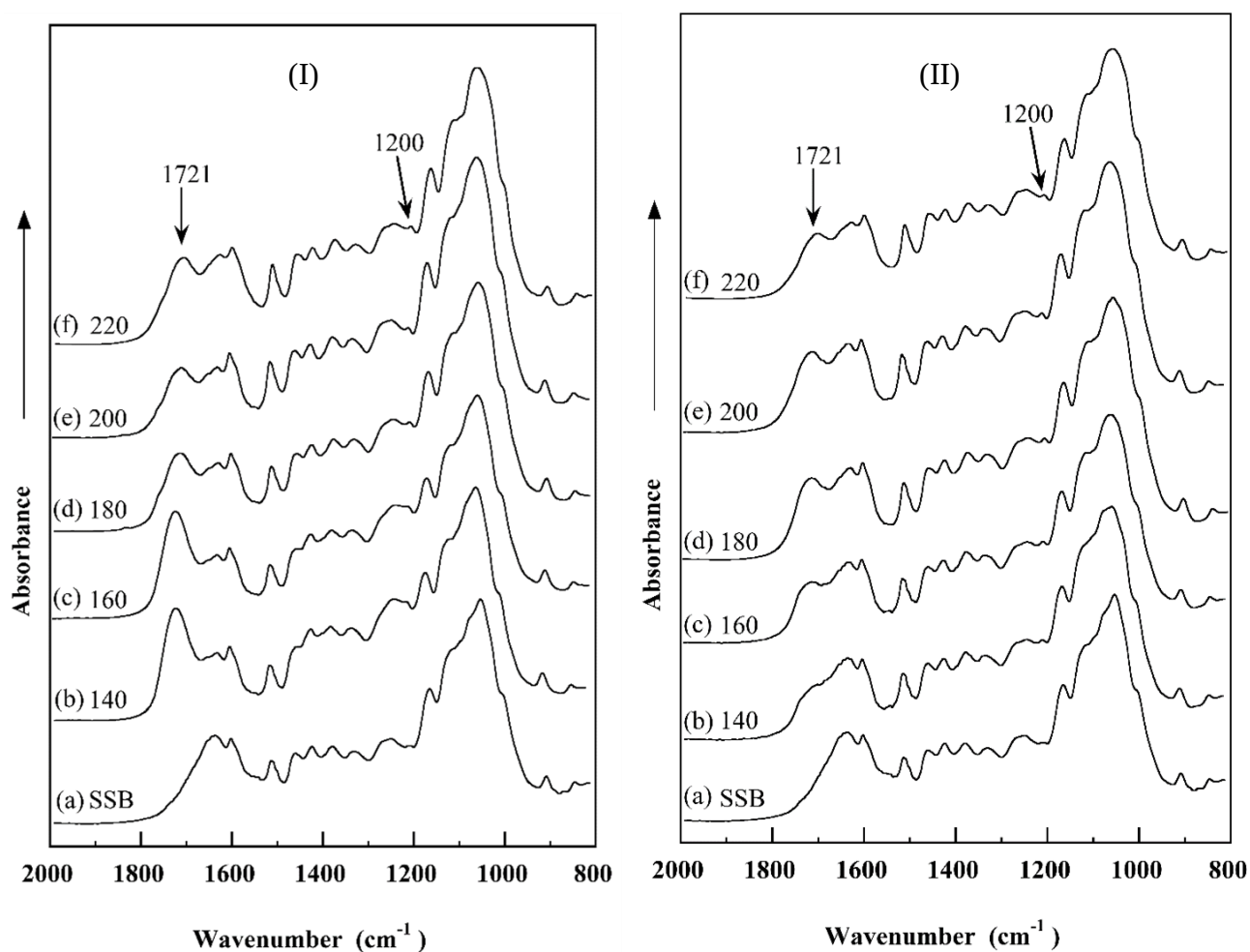


Fig. 3.8 Fourier transform infrared spectra of original particle of sweet sorghum bagasse (SSB) (a), sweet sorghum bagasse particleboard bonded with 20 wt% citric acid under pressing temperature of 140 (b), 160 (c), 180 (d), 200 (e), and 220 (f) °C before (I) and after (II) cyclic aging treatment.

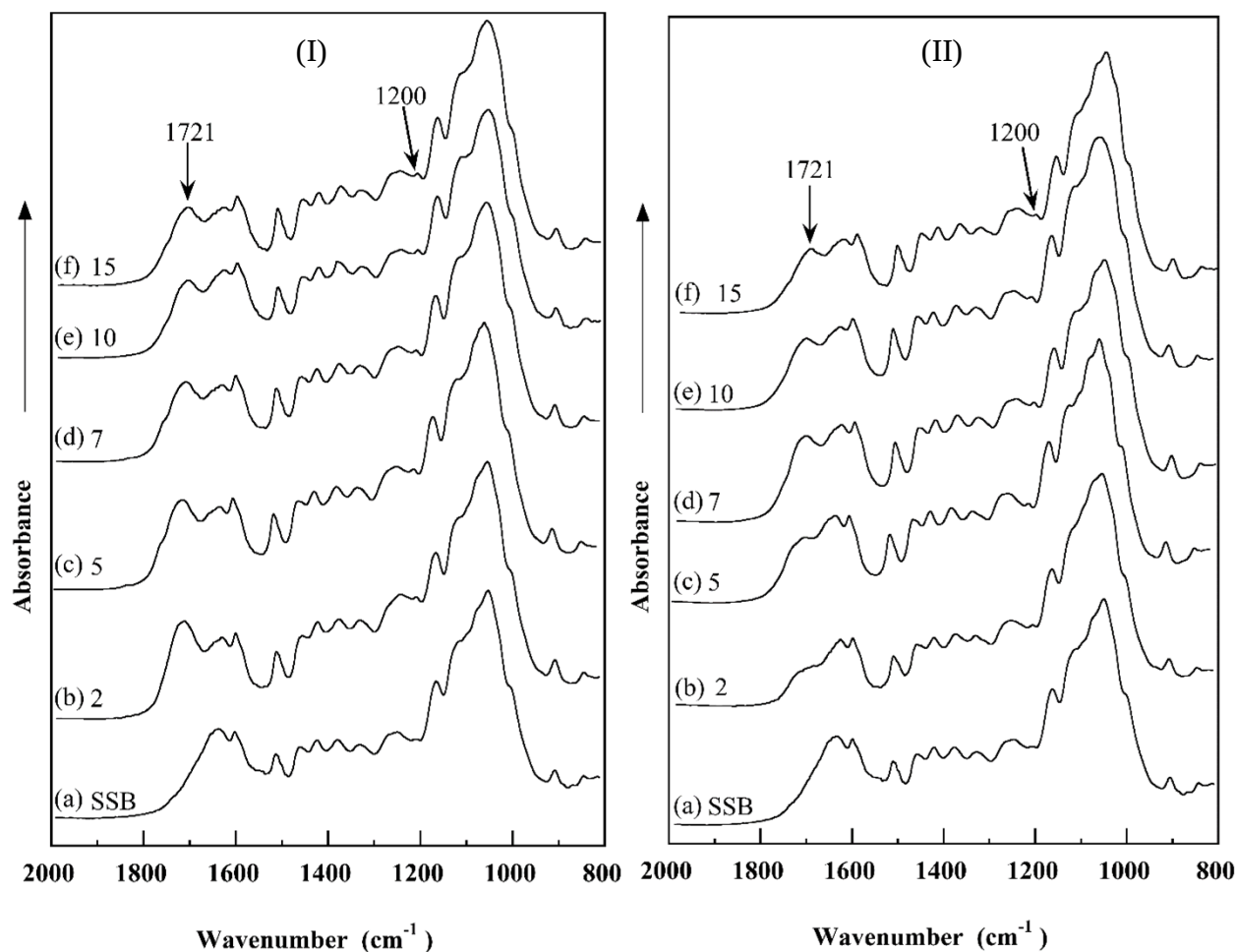


Fig. 3.9 Fourier transform infrared spectra of original particle of sweet sorghum bagasse (a), sweet sorghum bagasse particleboard bonded with 20 wt% citric acid (CA) under pressing times of 2 (b), 5 (c), 7 (d), 10 (e), and 15 (f) minutes before (I) and after (II) cyclic aging treatment.

According to the FT-IR results in both Figs. 3.8 (II) and 3.9 (II), high temperature and longtime of pressings were required to generate an effective reaction of CA with sweet sorghum bagasse particles.

3.4. Summary

The effects of the pressing temperature and time on the physical properties of sweet sorghum bagasse particleboard bonded with CA were investigated. The physical properties of CA boards improved with increasing pressing temperature at 140–200 °C, and decreased at 220 °C under pressing time of 10 min. Furthermore, the physical properties also increased when pressing time increased at 2–10 min, and decreased at 15 min under pressing temperature of 200 °C. Thus, effective pressing temperature and time were 200 °C and 10 min, respectively. The dry-MOR, IB strength, and TS of boards manufactured under suitable conditions of hot pressing satisfied the requirements of 18 type JIS A 5908 (2003). In addition, the Wet-MOR and SH power of boards satisfied the requirement of 13 and 8 types JIS A 5908 (2003), respectively. However, the wet-MOR and SH power of CA boards were lower than those of boards bonded using PF resin and pMDI. The boards bonded with CA had low formaldehyde emission, and effective biological durability against termite and fungus attack. Based on the infrared spectra, ester linkages appeared clearly in boards manufactured at 200 °C and 10 min. This means that those were the effective conditions under which the reaction between hydroxyl groups of sweet sorghum bagasse and carboxyl group of CA were activated to form ester linkages. As a result, characterization of particleboard was clarified.

Chapter 4

Improvement of the physical properties of particleboard by adding sucrose

4.1. Introduction

The suitable of manufacturing conditions of particleboard made from sweet sorghum bagasse and citric acid were obtained as reported in the Chapters 2 and 3. From those chapters, the particleboard made from sweet sorghum bagasse under suitable of manufacturing conditions i.e. pre-drying of particles, 20 wt% of citric acid content, and pressing temperature of 200 °C for 10 min had physical properties satisfied the requirement of 18 type JIS A 5908 (2003). In addition, the particleboard had good physical properties than the wood-particleboard (Umemura *et al.* 2013) and bamboo-particleboard (Widyorini *et al.* 2016) bonded with citric acid (CA) only. However, modulus of rupture (MOR) of the sweet sorghum bagasse particleboard was lower than that of particleboard bonded with PF (Kusumah *et al.*, 2017). Moreover, in previous chapter also showed that the screw holding (SH) of the sweet sorghum bagasse particleboard bonded with CA was lower than the requirement of 18 type JIS A 5908 (2003). Those phenomena were happened probably because the high content of CA as acidic compound affected the particleboard had high brittleness. Gambhir and Jamwal (2014) reported that the brittle particles absorbed very little energy. Moreover, Jonsson and Martin (2016) reported that amorphous polysaccharides was degraded easily by acidic compound. Degradation of amorphous polysaccharides compound is thought to become the main factor affecting brittleness of wood (Phuong *et al.*, 2007).

Previously, Umemura *et al.* (2013) and (2014) found that the CA to sucrose (SU) ratio of 25/75 wt% was suitable ratio to improve physical properties of particleboard. However, they did

not observe further SU ratios between 75 wt% to 100 wt% comprehensively. SU is a common disaccharide used as a condiment and food ingredient, the chemical characteristics of which are well researched. The heat derivatives of SU having hydroxyl group which it could react with carboxyl group of CA (Umemura *et al.* 2014). In this chapter, much amount of CA as acidic compound was reduced by adding SU to decrease brittleness of the particleboard and improve physical properties especially MOR and SH of the particleboard. Furthermore, the effect of adding sucrose on the physical properties of particleboard was investigated. In addition, formaldehyde emission, termite and decay resistance of the resulting particleboards, the thermal stability of sweet sorghum bagasse particles sprayed by CA-SU-based adhesive, and infrared spectra (IR) of the particleboard were observed.

4.2. Materials and methods

4.2.1. Preparation of materials

The sweet sorghum bagasse particles were prepared as same as in Chapters 2 and 3. CA and SU (anhydrous) of extra purity grade were used without further purification, those were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). CA and SU were dissolved in water at a concentration of 59 wt% under several weight ratios between CA and SU (CA : SU) as shown in Table 4.1, and those mixture solution were used as adhesives. The each pH and viscosity of the adhesive at 20 °C were measure by using pH meter and viscos meter, respectively.

Table 4.1 Viscosity and pH of mixture solution of CA and SU.

Type of particleboard	Mixture ratio of CA to SU (wt%)	Concentration (wt%)	Viscosity at 20 °C (mPa·s)	pH
A	100:0	59	30	0.30
B	75:25		21	0.55
C	50:50		22	1.00
D	25:75		25	1.25
E	20:80		50	1.26
F	15:85		50	1.36
G	10:90		60	1.55
H	0:100		70	2.77

4.2.2. Manufacture of particleboards

Based on the suitable of manufacturing conditions of particleboard as reported in Chapters 2 and 3, resin content, pressing temperature and time were decided i.e. 20 wt%, 200 °C, and 10 min, respectively. The SSB-particles were sprayed with the adhesive under several weight ratios between CA and SU, and then the particles were dried at 80 °C for 12 h to reach a moisture content of about 10%. Subsequently, the particles were formed into mats using a forming box as same as in Chapters 2 and 3. Particleboard size and target density that used in this chapter were same as mentioned in Chapters 2 and 3. The size of thick metal bar that used during the hot-pressing process to control the thickness of particleboard as the same size as used in chapter 2 and 3. Based on those ratios of CA and SU, types of particleboard were classified into 8 types as shown in Table 4.1.

4.2.3. Evaluation of the physical properties

The particleboards were tested after conditioning for 7 days under temperature and relative humidity as mentioned in Chapters 2 and 3. Each specimen for physical properties testing was cut as explained in Chapters 2 and 3. The bending properties, internal bonding (IB), screw holding (SH), and thickness swelling (TS) were evaluated according to JIS A 5908 (2003). In addition, the Charpy impact strength test was evaluated referring to JIS K 7111-1 (2006). The bending properties of the boards, i.e., the modulus of rupture (MOR) and the modulus of elasticity (MOE), were evaluated by using procedure as mentioned in Chapters II and III. Furthermore, the brittleness of particleboards were investigated by using load-deflection curve from bending test. The analyze method of brittleness referred to previous report of Phuong *et al.* (2007). The Charpy impact test was carried out using a digital impact tester DG-CD (Toyo Seiki Seisaku-sho, Ltd). A rectangular specimen of $80 \times 10 \times 9$ mm was prepared, and the impact strength in the flatwise direction was measured with un-notched sample.

The IB strength, TS, water absorption (WA), and SH were investigated using the same procedure as mentioned in Chapters 2 and 3. Furthermore, after the TS specimens of 50×50 mm were performed, the suitable type of particleboard specimens were subjected to a cyclic aging treatment (drying at $105\text{ }^{\circ}\text{C}$ for 10 h, warm-water immersion at $70\text{ }^{\circ}\text{C}$ for 24 h, drying at $105\text{ }^{\circ}\text{C}$ for 10 h, immersion in boiling water for 4 h, and drying at $105\text{ }^{\circ}\text{C}$ for 10 h). The thickness change of the specimens that occurred after each cyclic aging treatment were determined. Each experiment was performed in five replications, and the average values and standard deviations were calculated. The MOR, MOE, and IB values of the boards shown in the

figures are values that were corrected for each target density by using same method that mentioned in Chapters 2 and 3.

4.2.4. Formaldehyde emission

The formaldehyde emission of suitable types of particleboards was measured. The desiccator method was performed using the specimen according to JIS A 1460 (2001). The detail procedure of formaldehyde emission mentioned in Chapter 3.

4.2.5. Termite and decay resistance tests

Termite and decay resistance of suitable type, and the A type of particleboard were evaluated. The size of specimens for each test of termite and decay resistance were $20 \times 20 \times 9$ mm. Five specimens each particleboard type were assayed against termites and decays.

In the termite resistance test, the detail equipment, procedure of the test and calculation method of termite mortality and mass loss were explained in Chapter 3. A total of 150 worker termites and 15 soldiers collected from a laboratory termite colony at Department of Forest Product, Faculty of Forestry, Bogor Agricultural University (IPB), Indonesia, were introduced into each test container. Small wood blocks ($20 \times 20 \times 10$ mm) of akamatsu wood (*Pinus desiflora* Siebold and Zucc.) were used as a control. The mass loss of the specimens as a result of termite attack and termite mortality were calculated using the calculation methods as mentioned in Chapter 3.

In the decay resistance tests, the detail equipment, procedure of test and calculation method of mass loss were also explained in Chapter 3.

4.2.6. Statistical analysis

The detail explanation of the statistical analysis was described in Chapter 3.

4.2.7. Thermal analysis

The specimens which used in thermal analysis were SSB, CA, Su, CA-SU mixture solutions in various ratios as mentioned in Table 4.1, and SSB particles which is sprayed with CA-SU-based adhesive. The SSB particles which is sprayed with the adhesive were categorized into 8 types based on the ratio of citric acid to sucrose as mentioned in Table 4.1 i.e. type A to H. All specimens were dried at room temperature for one day, and pulverized into less than 150- μ m mesh. All of the specimens were dried by freeze drying for 1 h. The thermogravimetric analysis (TGA) was undertaken using a TGA 2050 (TA Instrument Japan). The powder was scanned from room temperature to 400 °C at a rate of 10 °C/min under nitrogen purging. The differential scanning calorimetry (DSC) measurement was carried out using a DSC2500 (TA Instruments, Tokyo, Japan). The powder was encapsulated in an aluminum pan and scanned from room temperature to 400 °C at a rate of 10 °C/min under nitrogen purging.

4.2.8. Fourier Transform Infrared Spectroscopy (FT-IR)

The detail procedure of FT-IR measurement of particleboard was explained in Chapter 2.

4.3. Results and discussion

4.3.1. Mechanical properties

Figure 4.1 shows the bending properties of particleboard under various ratio of citric acid and sucrose. The MOR and MOE values increased gradually as the SU ratio increased and extremely decreased at H type of particleboard.

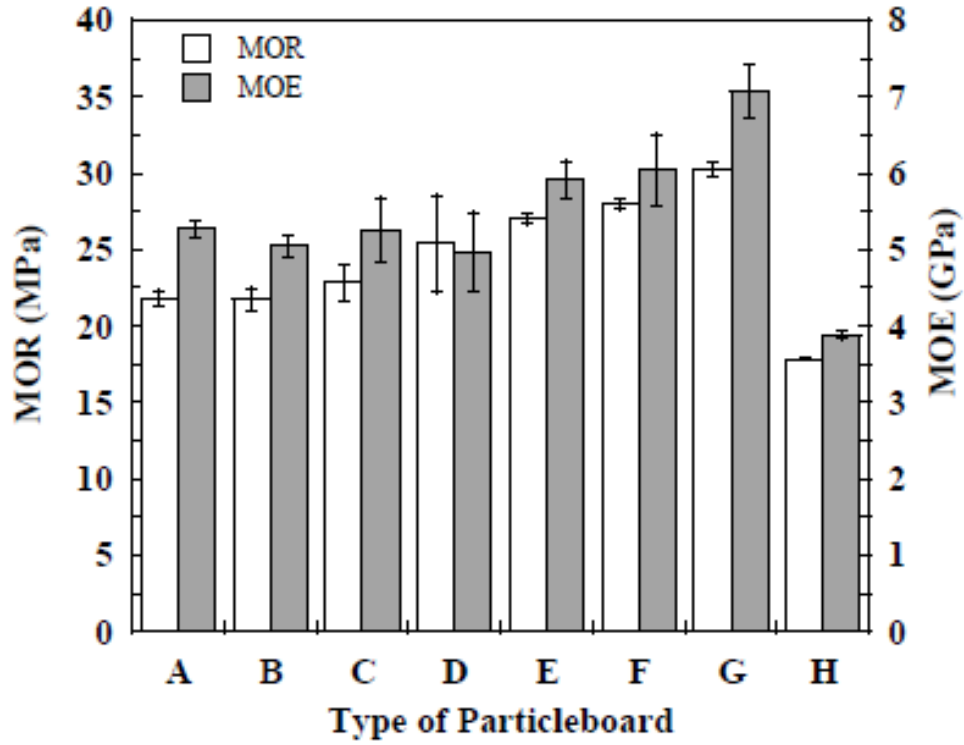


Fig. 4.1 Bending properties of particleboards bonded with 20 wt% CA-SU-based adhesive. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

The G type of particleboard had the highest MOR (30.22 MPa) and MOE (7.07 GPa) average values. The MOR value of G type of particleboard was comparable to the MOR of particleboard bonded with PF (32.9 MPa) (Kusumah *et al.*, 2017). Those phenomena indicated that the bending properties of particleboard was improved by adding SU. The reason was that the amount of citric acid reduced by adding sucrose, hence the brittleness of particleboard significantly decreased ($p < 0.05$) at CA to SU ratio of 10/90 wt% (G type particleboard) as shown in Fig. 4.2. As mentioned in the Chapter 3 that the high brittleness probably influenced low bending properties of the particleboard.

However, MOR of the particleboard bonded with sucrose only (H type) was lower than that of the G type particleboard. The reason was that the particleboard bonded with SU only had poor interaction between SU and sweet sorghum bagasse components as described in thermal analysis of this chapter. Therefore, the particleboard bonded with SU probably had low bondability than the particleboard bonded with CA-SU based adhesive. In general, bondability of the particleboard is a one of the important factor that affected the bending properties.

Except for type H particleboard, the MOR value of all the particleboards satisfied MOR requirement (≥ 18 MPa) of 18 type JIS A 5908 (2003).

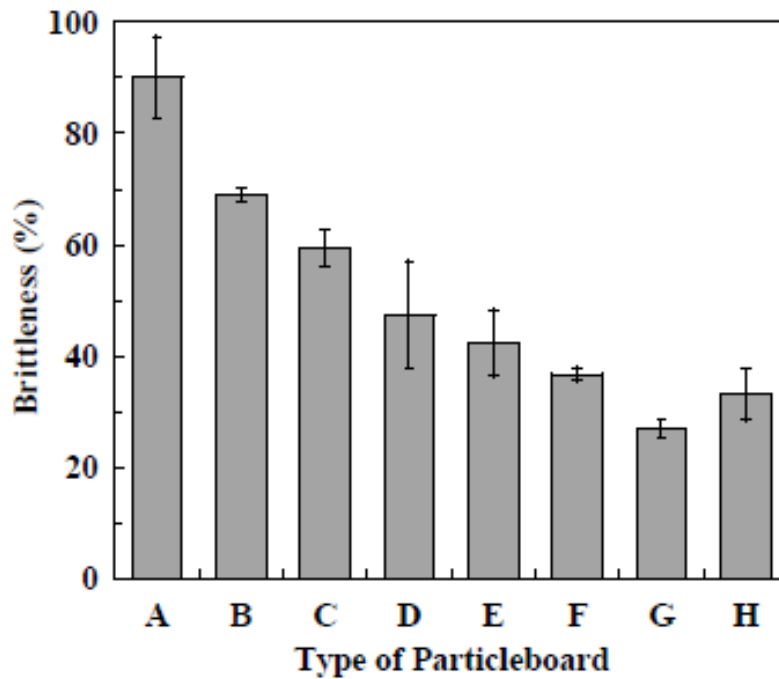


Fig. 4.2 Brittleness of particleboards bonded with 20 wt% CA-SU-based adhesive. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Furthermore, the load-deflection curve of static bending of particleboard was used for calculation the brittleness of particleboard. The results of the brittleness of particleboards under various ratio of CA and SU were shown in Fig. 4.2. In addition, brittleness of particleboard

bonded with PF was calculated by using its bending data in Chapter 3. In Figure 4.2, the brittleness of particleboards decreased significantly ($p < 0.05$) with increasing SU ratio. Moreover, brittleness of type G particleboard (27 %) was comparable with that of the particleboard bonded with PF (25 %). This means that the addition of sucrose has effectively decreased the brittleness of SSB-particleboard bonded with CA. The decreasing trend of the brittleness by calculation method using data of load-deflection curve of static bending was supported by the results of Charpy impact strength test as shown in Fig. 4.3. In this Figure shows that the Charpy impact strength of SSB-particleboard increased gradually with increasing SU ratio, as shown in A to E type of particleboards, and seem to be steadily until H type. Commonly, high value of Charpy impact strength showed low brittleness (Koehler, 1933). Therefore, based on the impact strength of SSB-particleboard, the brittleness of SSB-particleboard was reduced effectively by adding SU. In other words, the reducing of CA content in the 20 wt% resin content of adhesive by adding SU was effective method to reduce the brittleness that causes the lowering of bending properties of particleboard as mentioned in Chapter 3. The reason was that the reducing of the amount of citric acid by increasing sucrose ratio avoided degradation of the much amount of polysaccharides of sweet sorghum bagasse, hence the brittleness of particleboard would decreased.

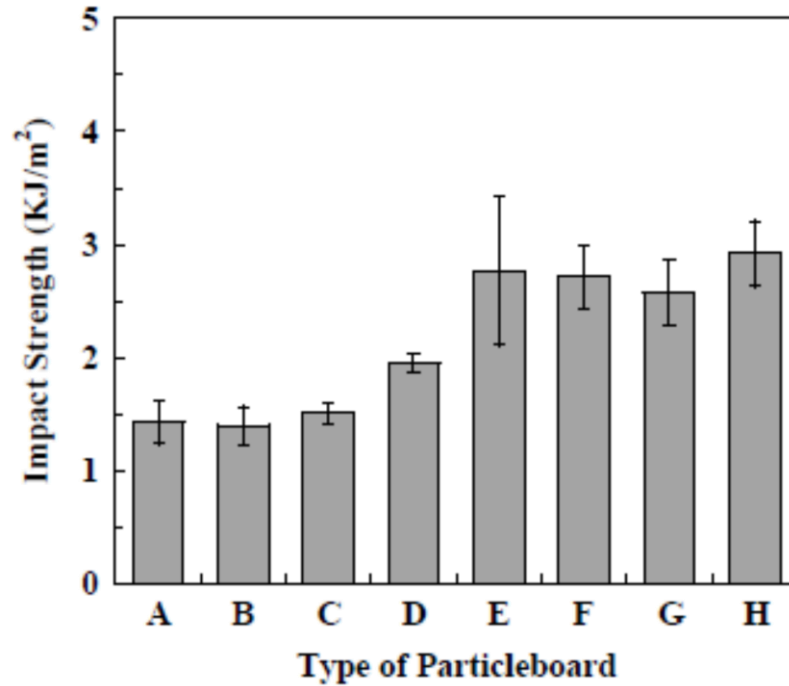


Fig. 4.3 Charpy impact strength of particleboards bonded with 20 wt% CA-SU-based adhesive.

Error bar indicates standard deviation. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

The IB values of the particleboard produced are shown in Fig. 4.4. The IB strengths of particleboards continuously increased until G type of particleboard with increasing sucrose ratio, and then decreased dramatically at H type of particleboard.

The IB strength of F and G types of particleboards were approximately 33% greater than that of A type of particleboard and two times higher than that of H type of particleboard. The addition of SU provided improvement of the bond strength between particles. Furthermore, the IB strengths of both F (1.15 MPa) and G (1.17 MPa) type of particleboards were quietly higher than that of particleboard bonded with PF (0.78 MPa) (Kusumah *et al.*, 2017). The IB strengths of all type of particleboard fulfilled the IB requirement (≥ 0.3 MPa) of 18 type JIS A 5908 (2003). It

was thought that SU was decomposed by citric acid and heat during hot pressing at high temperature of 200 °C, and then the caramelization was occurred. Furthermore, decomposition and caramelization of SU generated heated derivatives compounds of sucrose including monosaccharide and furan compound. The heated derivatives compound providing hydroxyl group that could react with carboxyl group of CA and forming ester linkages. Chai *et al.* (2003) reported in their previous report that hemicellulose was decomposed by heating treatment at 200 °C and it converted to heated derivatives compound of hemicellulose including oligosaccharides and glucuronic acid. Based on this previous research, the ester linkages in the particleboard of this study was probably also generated by the reaction between the heated derivatives compound of SU and hemicellulose. Consequently, the bondability of particleboard was strengthened by the chemical linkages. As a result, the internal bond strength of particleboard was increased.

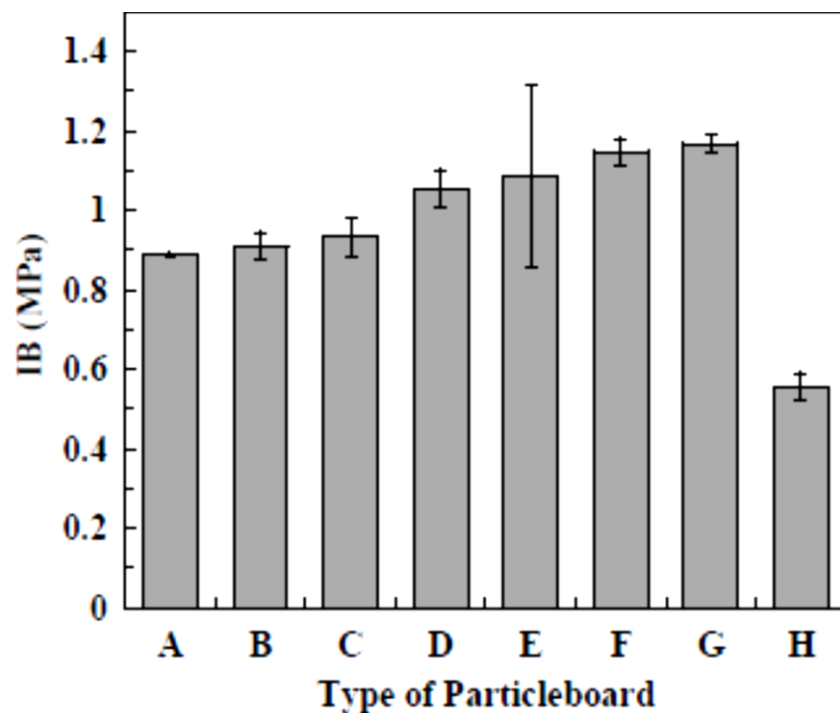


Fig. 4.4 Internal bonding (IB) of particleboards bonded with 20 wt% CA-SU-based adhesive.

Error bar indicates standard deviation. Number of replications are 5 (n = 5).

Judging from the results of bending properties, brittleness, impact strength, and IB as shown in Figs. 4.1 to 4.4, the suitable CA to SU ratios to obtain excellent mechanical properties of particleboard are 15/85 wt% and 10/90 wt% that used in the particleboard of F and G types, respectively. Based on the suitable ratios, the SH of the F and G type of particleboards were investigated. The SH values of both type F and G particleboards were 502 N and 525 N. Those SH value were about 50% higher than that of the particleboard bonded with CA only (348 N) as mentioned in chapter 3. In addition, the SH of both type of particleboards satisfied the SH requirement (≥ 500 N) of 18 type JIS A 5908 (2003). This means that addition SU has been improved effectively SH of particleboard. This phenomena would be due to the brittleness of particleboard was decreased with increasing SU ratio as shown in Fig. 2. In other words, the addition SU had resolved the low SH of particleboard due to the high content of CA affected the particle become brittle as mentioned in Chapter 3.

4.3.2. Dimensional stability

Figure 4.5 shows the TS and WA values of particleboards with different weight ratio of CA and SU. The TS values of particleboard increased slightly as SU ratio was increased as shown in the values of B to G types of particleboards, and then increased sharply when the particleboard only used SU (H type). However, the TS values of the C to G types of particleboards were not significantly different ($p > 0.05$). The TS range values of those type of particleboards were 11.3 % – 12 %. These means that the adding SU from middle to high ratio of SU did not affect to the increasing of TS. Those TS value were slightly higher than those of the A (10.2 %) and B (10.4 %) types particleboards. Moreover, TS of H type of particleboard (24.2 %) was two times higher than those of C to G types of particleboards. In other words, the H type of particleboard had low dimensional stability. Irrespective of H type of particleboard, the TS values of the particleboards

complied with the TS requirement ($\leq 12\%$) of 18 type JIS A 5908 (2003). In addition, the TS values of those particleboards (11.3 % - 12 %) were lower than those of particleboards bonded with PF (20.6 %) (Kusumah *et al.*, 2017). This result indicated that the additional of SU until G type still kept the particleboard had a good level of dimensional stability.

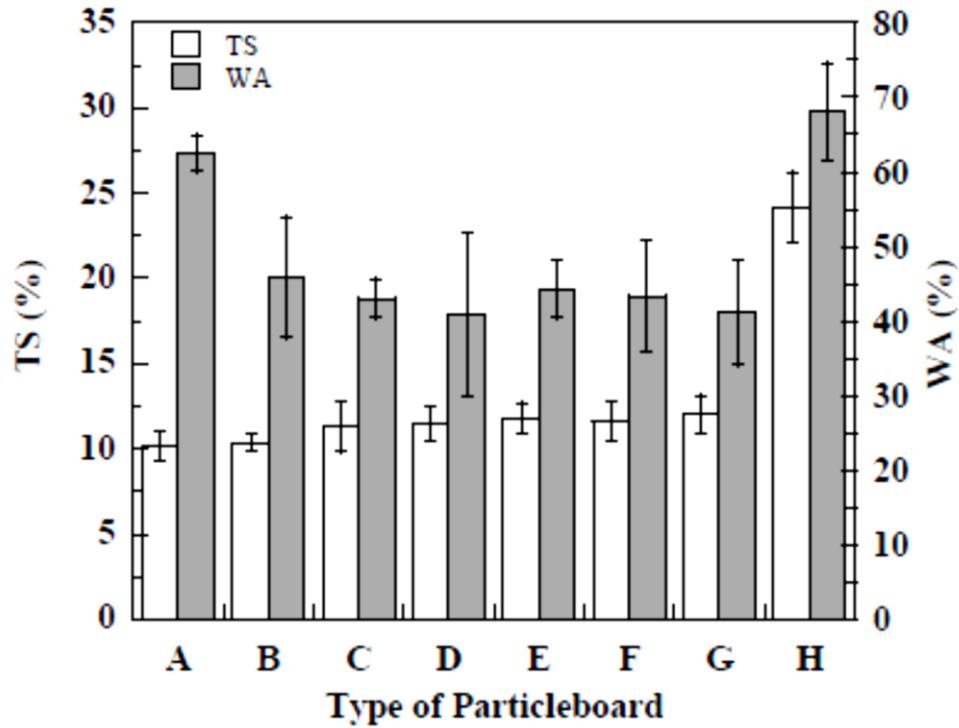


Fig. 4.5 Thickness swelling (TS) and water absorption (WA) of particleboards bonded with 20 wt% CA-SU-based adhesive. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

The WA values of B to G types of particleboards were significantly lower ($p < 0.05$) than that of A and H types of particleboards. It can be explained by the chemical reaction between CA, SU and sweet sorghum bagasse components that described previously in IB discussion. By this reaction, the ester linkages was generated, and then the hygroscopicity of particleboard was reduced. Therefore, the particleboard less absorbed water during water immersion test.

Moreover, the WA value (41.12 %) of G type of particleboard was lower than that of particleboards bonded with PF (51.24 %) (Kusumah *et al.*, 2017). Clarification of dimensional stability and water resistance of the particleboard in severe conditions were required as an approach of real condition. Therefore, the thickness change and weight change evaluation was continued by cyclic aging treatment.

Based on the results shown in Figure 4.5, the particleboards of F and G types were used as representative specimens of particleboard in the investigation of the thickness change. The thickness change of the A type of particleboard was also measured as a reference. Figure 6 shows the thickness change of A, F, and G types of particleboards in the cyclic accelerated aging treatment. The accelerated aging treatment led to a stepwise increase of thickness regardless of the kind of particleboard. The thickness change of the particleboard decreased when there was a decrease in the SU ratio. The thickness change of F (9.3%) and G (11.8%) types of particleboards were slightly higher than the A type of particleboard (7.9%). Based on the statistical analysis, the last thickness change value of the F type particleboard was not significantly different ($p > 0.05$) from the A type particleboard. Thus, the good dimensional stability of the particleboard was maintained with the addition of SU in the adhesion system even after severe treatment

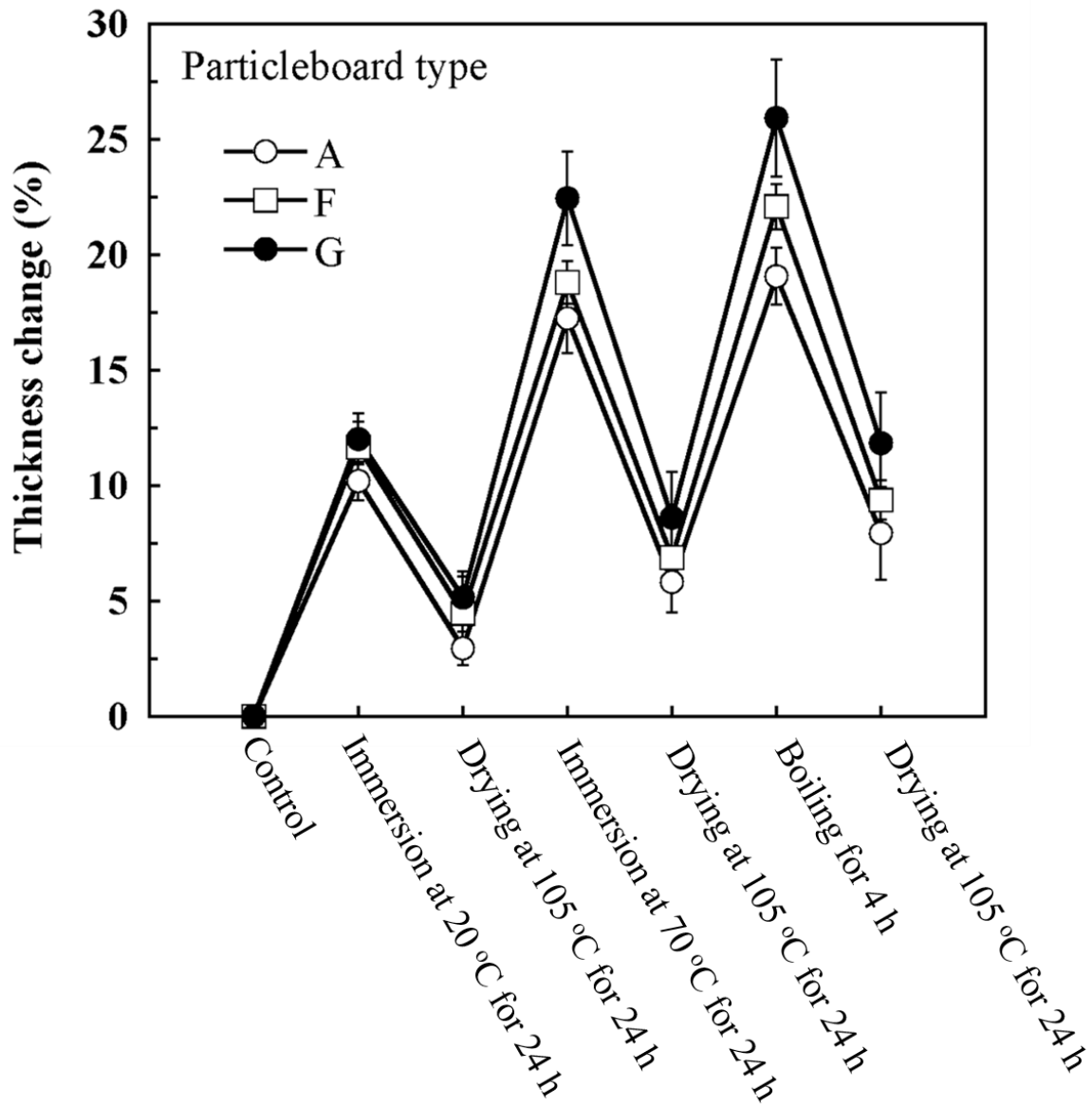


Fig. 4.6 Thickness change of particleboards bonded with 20 wt% CA-SU-based adhesive in cyclic accelerated aging treatment. Error bar indicates standard deviation. Number of replications are 5 ($n = 5$).

Figure 4.7 shows the weight change of type A, F, and G particleboards in cyclic accelerated aging treatment. Overall, the weight change increased gradually in each treatment. In the drying after the first treatment (immersion at 20 °C for 24 h), the weight decreases ranging from -2.3 to

-5.8 % were observed, indicating that some elution including adhesive happened. In the second treatment (immersion at 70 °C for 24 h), the weight increases of type F (53.1 %) and G (53.9 %) were about 34 % lower than that of type A.

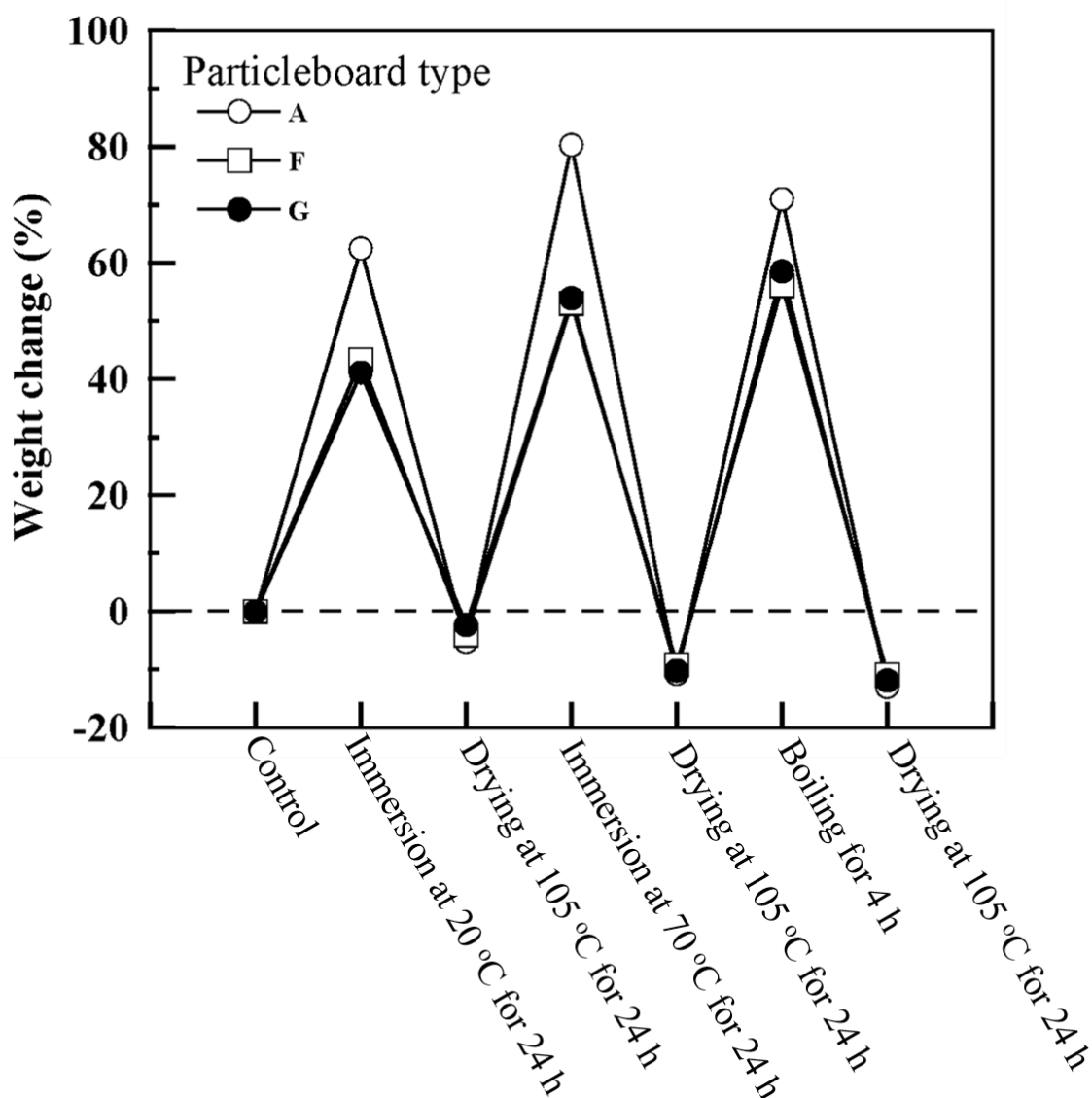


Fig. 4.7 Weight change of particleboards bonded with 20 wt% CA-SU-based adhesive in cyclic aging treatment. Error bar indicates standard deviation. Number of replications are 5 (n = 5).

The weight decreases of the particleboard after the second treatment were almost similar between each type of particleboard. In the third treatment (boiling for 4 h), the comprehensive weight change was the same as in the second treatment. In the last treatment of drying at 105 °C, the weight decreases of type F and G particleboards were comparable with that of the type A particleboard. This means that the addition of sucrose in adhesion system exhibited good water resistance of particleboard.

4.3.3. Formaldehyde emission, termite and decay resistance

Based on the previous report of Haworth and Jones (1944), SU would be converted to monosaccharides and generated aldehyde compound when SU was heated. Formaldehyde is the simplest of the aldehydes and it is one of the volatile organic compounds (VOCs) that has short- and long-term adverse health effects (Gminski *et al.*, 2011a; 2011b). Besides that, previous report of Waller and Curtis (2003) mentioned that paper treated with sucrose has low durability against termite and also high content of SU in cellular lumen of wood affected to decay resistance (Severo *et al.*, 2016). Therefore, the formaldehyde emission, termite and decay resistance of the particleboard were evaluated.

Judging from the results as shown in Figs. 4.1 to 4.7, we clarified that the suitable ratios of CA to SU were 15/85 wt% and 10/90 wt% that used in the manufacturing of F and G particleboards, respectively. Accordingly, the formaldehyde emission of the particleboards F and G types were attempted. Those particleboards types (0.00 mg/L) did not emit formaldehyde like the boards bonded with CA (0.00 mg/L), and PF (0.01 mg/L) as mentioned in chapter 3. The reason was that the monosaccharides reacted with CA, hence the aldehyde compound did not generate. The formaldehyde emission values were lower than the lowest formaldehyde emission

criteria (F****) (< 0.4 mg/L) of JIS A 5908 (2003). Thus, particleboards bonded with CA-SU based-adhesive are safe for human health.

According to the suitable ratios of CA to SU, the biological durability against termite and decay of particleboard F and G types were investigated. The results were shown in Table 4.2. The termite mortality in the F and G types of particleboards were comparable with that of A type, and particleboard bonded with PF (46.40 %) (Kusumah *et al.* 2017). Besides that, the mass losses of F and G types of particleboards were almost similar with that of A type and particleboard bonded with PF (3.92 %) (Kusumah *et al.*, 2017). This clarified that although much amount of SU was existed in adhesive, the particleboards still had good termite resistance. Previously, Tanaka *et al.* (2006) reported that the feeding termites with artificial diets containing glucose and cellobiose resulted in the disappearance of all protozoa. These protozoa and bacteria in termites (*C. formosanus*) play important roles in decomposition, digestion, and metabolism of diets. In addition, they showed in their reports that the survival ratio of termites (workers) feeding on only glucose was lower than that of termites feeding on wood powder and cellulose. Based on this previous report, the particleboard F and G types had good durability against termite even those particleboards content sucrose because it was decomposed by citric acid as acid compound and heating during hot pressing process, and then sucrose was converted to heated derivatives compounds including monosaccharide and furan compound. Furthermore, these heated derivatives compounds reacted with citric acid and then formed ester linkages.

Mass losses of F and G types after 3 months expose to white-rot fungus were almost similar with that of the A type. Moreover, those mass losses were higher than that of particleboard bonded with PF (9.09 %) as mentioned in Chapter 3. Some previous study (Hoareau *et al.*, 2006; Yalinkilic *et al.*, 1998) mentioned that the particleboards bonded with PF has good durability

against decay due to phenolic compound and formaldehyde. Furthermore, the mass losses of F and G types after expose to brown-rot fungus were comparable with that of the A type and particleboard bonded with PF (4.54 %) (Kusumah *et al.*, 2017). This indicates that the chemical derived from CA and SU probably show effective inhibitory against decay. In the previous study of Despot *et al.* (2008), it was mentioned that the improvement of decay resistance in wood modified by CA was definitely the result of the cross-linking of CA and hydroxyl groups of the wood components. In this study also, CA might act as cross-linking to hydroxyl groups of SSB components and SU, hence the particleboard has good decay resistance.

Table 4.2 Termite and decay resistance of A, F, G types of particleboard.

Biological-Durability Testing	Specimen Type			
	A type	F type	G type	Control
Termite resistance				
Termite mortality (%)	45.87 (1.10)	43.20 (2.33)	43.07 (2.14)	23.60 (4.46)
Mass loss (%)	4.33 (1.72)	5.27 (1.07)	5.45 (1.26)	13.43 (4.04)
Decay resistance				
Mass loss of the specimen expose to:				
Brown-rot fungus (%)	5.43 (1.36)	6.12 (1.2)	6.40 (0.9)	10.16 (2.05)
White-rot fungus (%)	21.63 (11.7)	23.27 (7.9)	23.42 (6.9)	30.15 (5.12)

Values in parentheses are standard deviation

A, F, and G types are particleboard bonded with 20 wt% resin content of CA-SU-based adhesive under A (100/0), F (15/85), and G (10/90) ratio of citric acid to sucrose; control is sugi (*Cryptomeria japonica* (Thunb. Ex L.f.) D. Don) wood specimen for decay test and akamatsu (*Pinus densiflora* Siebold and Zucc.) for termite test.

4.3.4. Thermal analysis

Based on the results of all specimens of DSC and TG analyses, the A and B type specimens showed similar behaviour in the DSC and TG curves; also, the C through G type specimens showed similar DSC and TG curves. Thus, Figs. 4.8 and 4.10 shows just the results of A, F, and H types as a representative of SSB particles sprayed with CA-SU mix solution. Figure 4.8 shows the DSCs of SSB, A, F, H types of particle specimens; Figure 4.9 show the DSCs of CA, SU, and CA-SU mix solution at a weight ratio of 15/85 (F) as references; Figure 4.10 shows the TGs of the particle specimens of A, F, and H types.

In Figure 4.8, first, the DSC curves of SSB particles show an endothermic peak at around 90 °C and also A, F, and H types show an endothermic peak at around 75 °C. This endothermic peak did not appear in the CA-SU mix solutions, or in CA and SU only. Hardly any weight loss of those particle specimens was recognized at that temperature, as shown in Fig. 4.10. A previous report by Mehrotra *et al.* (2010) mentioned that the endothermic peak at around 90 °C was the consequence of the weakening of the hydrogen bonds between carbohydrates. Therefore, the endothermic peaks of SSB, A, F, and G types of particle specimens were likely to be the weakening of the hydrogen bonds between carbohydrates. Further in Fig. 4.8, two endothermic peaks appeared clearly at around 150 °C to 200 °C in the A type particle specimen. The first endothermic peak at around 150 °C shows the melting point of CA (Barbooti and Al-Sammerrai 1986), the second endothermic peak at a temperature around 180 °C indicated decomposition of CA (Barbooti and Al-Sammerrai 1986). Meanwhile, those endothermic peaks appeared unclearly in the F type particle specimen; also, the endothermic peak at around 225 °C shown in the H type particle specimens, indicating the decomposition of SU (Gintner *et al.* 1989; Enggleston *et al.* 1996), did not appear in the the F type. These phenomena seem to suggest that

some interactions or reactions occurred between CA, SU, and SSB components in the F type particle specimen. In the DSC curve of the CA-SU mix compound shown in Fig. 4.9 the same phenomena occurred as in the F type. The DSC curve of CA-SU mix compound has two endothermic peaks at around 160 °C and 175 °C. Those endothermic peaks appeared at different temperatures from those of CA-only (157 °C) and SU-only. In addition, the endothermic peak at around 225 °C appeared in CA and SU as these compounds decomposed, but the peak did not appear in the CA-SU mix compound (F). It is likely that some interactions or reactions between CA and SU occurred. Therefore, in Fig. 4.10, the weight of the F type particle specimen especially at temperatures more than 200 °C was more moderately decreased than those of A and H type particle specimens, due to some interaction or reactions between the component CA, SU, and SSB components, occurring at low temperature around 150 °C to 200 °C as shown in DSC curve of the F type.

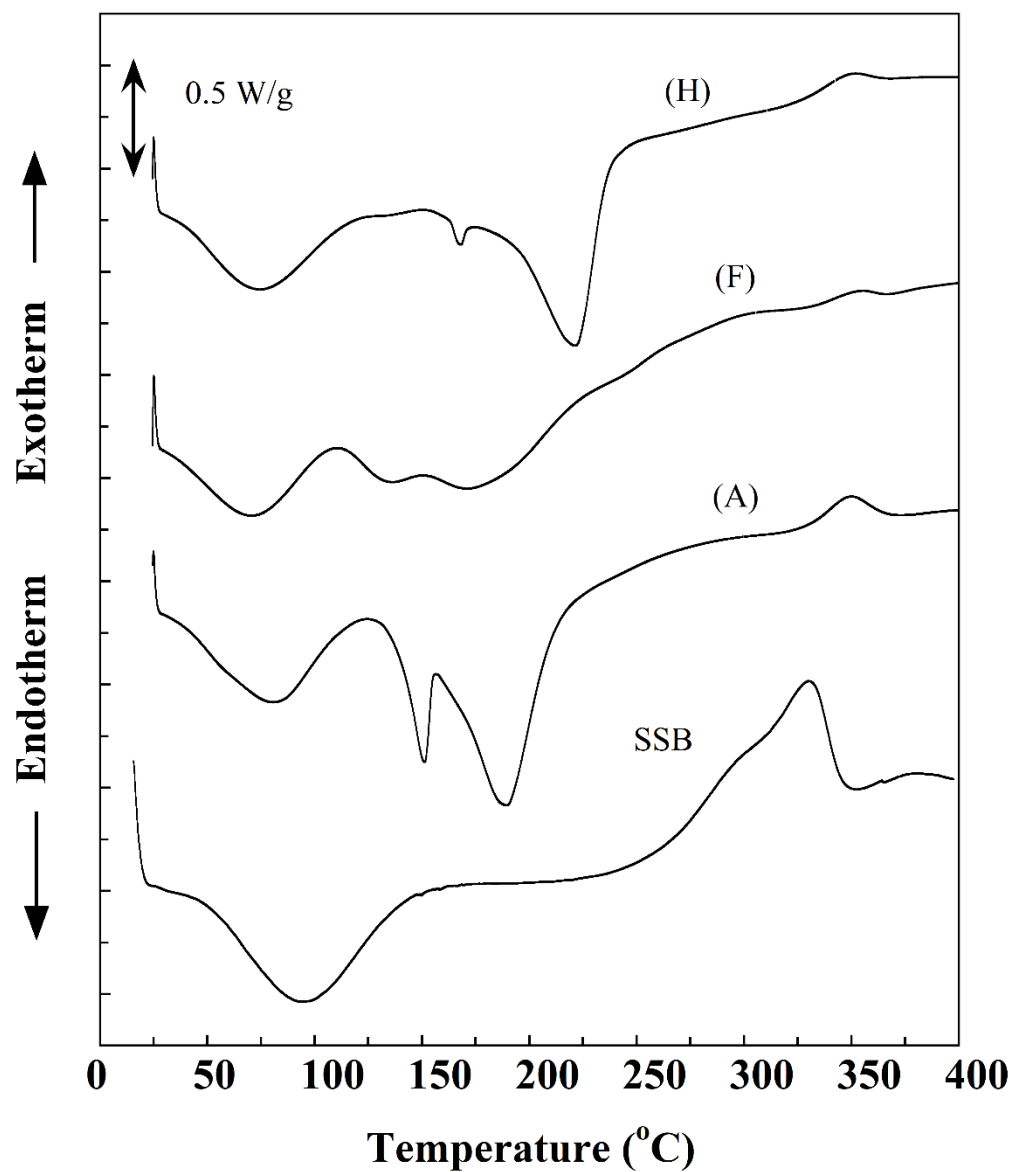


Fig. 4.8 Differential scanning calorimetry (DSC) of powder of original sweet sorghum bagasse (SSB), A, F, and H types of particles specimen.

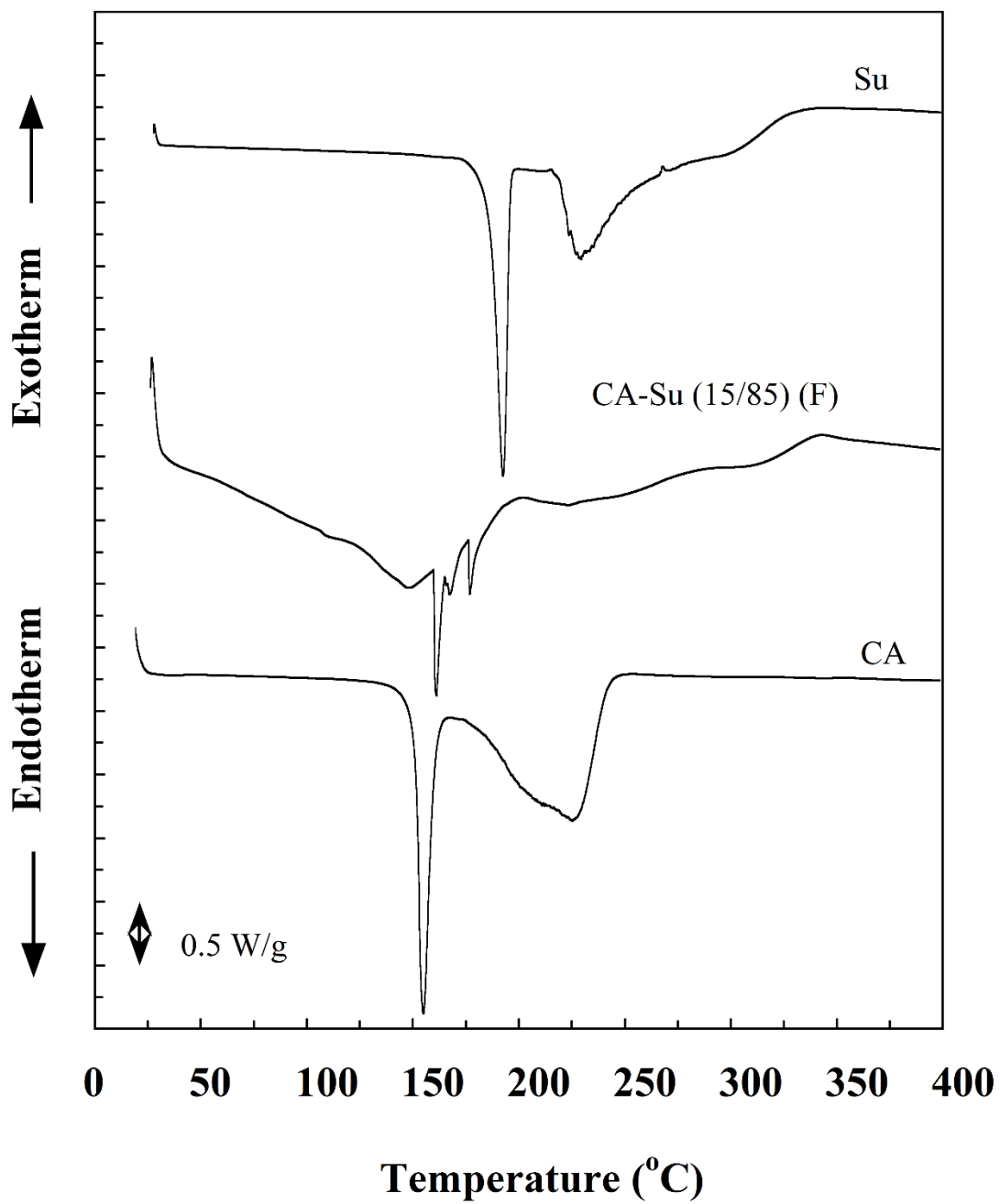


Fig. 4.9 Differential scanning calorimetry (DSC) of citric acid (CA), sucrose (SU), and CA-SU mix solution in weight ratio of 15/85 (F) as references.

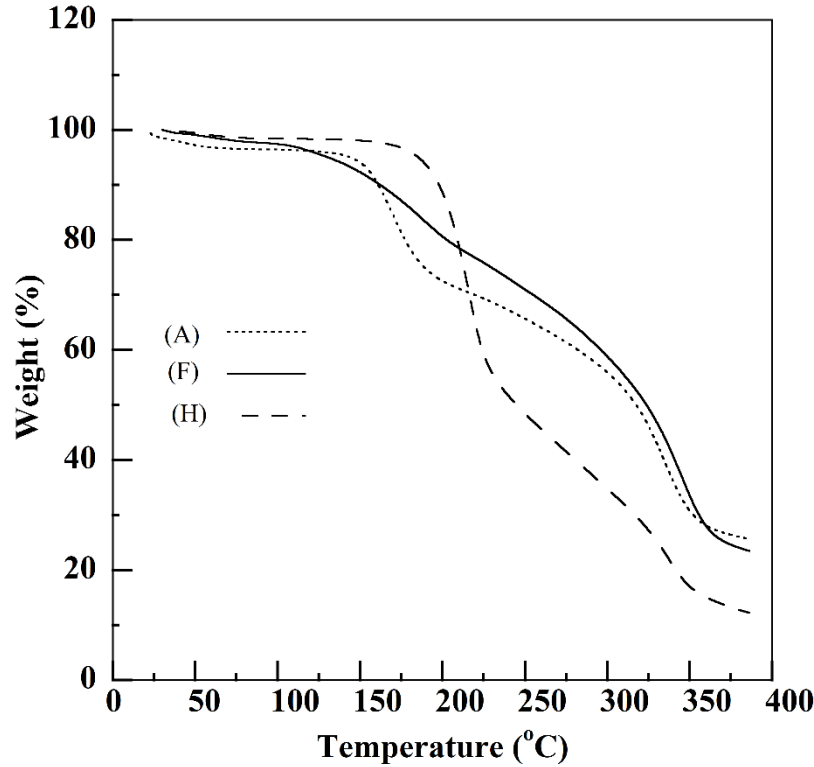


Fig. 4.10 Thermogravimetric (TG) of A, F, and H types of particles specimen.

4.3.5. Fourier Transform Infrared Spectroscopy (FT-IR)

The infrared (IR) spectra of F type particleboard was measured to clarify the chemical change of sweet sorghum bagasse particleboard. Powder as a specimen was collected from the particleboard after cyclic aging treatment to eliminate hot water soluble components. Figure 4.11 shows the results of IR spectra of sweet sorghum bagasse particles (SSB) and particleboard of F types after cyclic aging treatment. The absorption peak at approximately 1727 cm^{-1} appeared clearly in the (F) specimens. The peak at 1727 cm^{-1} is typically ascribed to C=O stretching due to carboxyl groups and/or C=O ester groups (Yang *et al.*, 1996 and Zagar *et al.*, 2003). In other absorbance intensity peak at 1245 cm^{-1} was observed obviously in the (F) type. This peak is related to the C=O stretching vibration band of ester groups (Aflori and Drobota 2015).

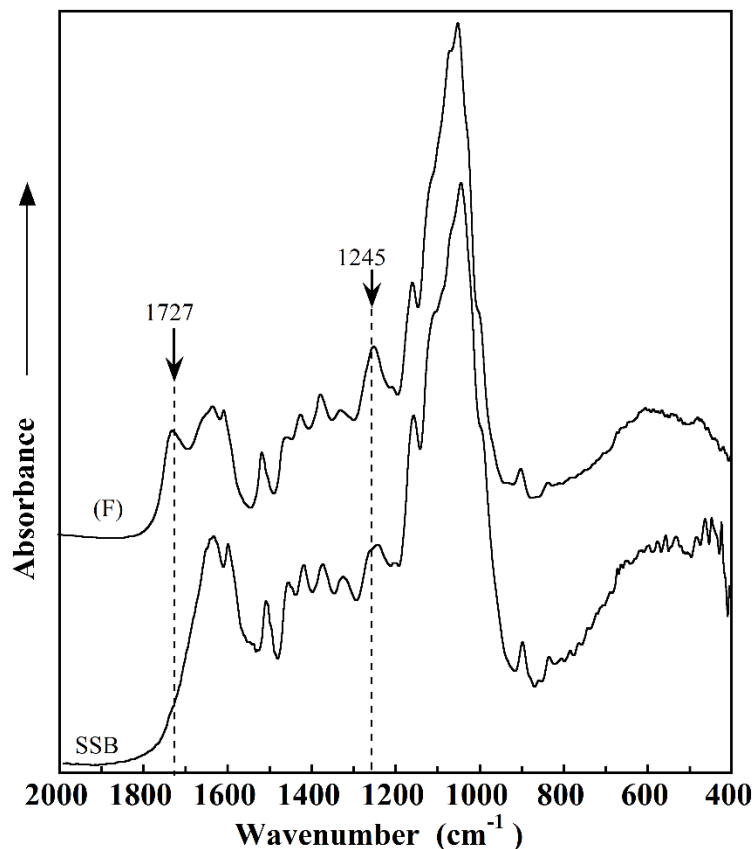


Fig. 4.11 FT-IR of sweet sorghum bagasse (SSB) and F type of particleboards after cyclic aging treatment.

Appearing ester groups in the IR spectra of (F) specimen indicated that the carboxyl groups of CA reacted with hydroxyl groups of sweet sorghum bagasse and SU, and then the ester linkages was formed. Kwok *et al.* (2010) reported that the sucrose was hydrolyzed by heating to the monosaccharides such as glucose and fructose in the mixtures of SU-CA solution, and those monosaccharides convert to 5-hydroxymethyl-2-furaldehyde (5-HMF) under heating or acidic condition. However, 5-HMF did not observe in the IR spectra of this chapter because small amount of sucrose contents in the particleboard. Therefore, the particleboard bonded with CA-SU-based adhesive seem to be that the particleboard had more ester linkages branch than that of particleboard bonded with CA only, due to carboxyl groups of CA react with each hydroxyl

groups of SU and sweet sorghum bagasse. In addition, the hemicellulose was decomposed by heating treatment at 200 °C and it converted to heated derivatives compound of hemicellulose including oligosaccharides and glucuronic acid (Chai *et al.*, 2003). Based on this previous report, the heated derivatives compounds of hemicellulose probably react with hydroxyl groups of SU and also formed ester linkages. Consequently, the formation of ester linkages would improve the adhesiveness. As a result, the physical properties of the particleboard was improved by adding the sucrose. The schematic of possible reaction between citric acid, sucrose and sweet sorghum bagasse components was shown in Fig. 4.12.

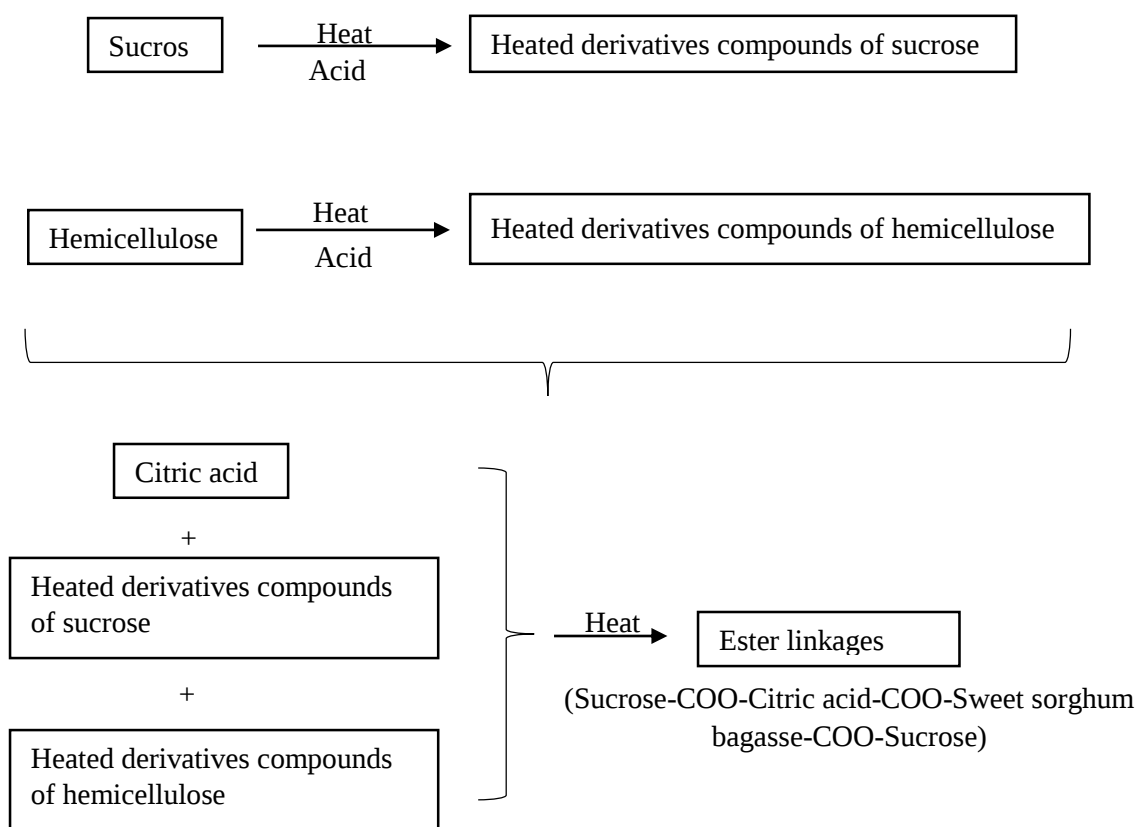


Fig. 4.12 Possibility reaction between citric acid, sucrose, and sweet sorghum bagasse.

4.4. Summary

Based on the results in this chapter, the particleboards bonded with the adhesives under 15/85 and 10/90 wt% ratio of CA to SU had higher mechanical properties, lower brittleness, and comparable dimensional stability than those of particleboards bonded with CA only and PF resin. The bending properties, IB strength, SH and TS values of those boards satisfied the requirement of 18 type JIS A 5908 (2003). The particleboards bonded with the adhesives under 15/85 and 10/90 wt% ratio of CA to SU had low formaldehyde emission, and satisfied 18 type of JIS A 5908 standard. The particleboard bonded with the adhesives under 15/85 and 10/90 wt% ratio of CA to SU had good termite and decay resistance as same as particleboard bonded with citric acid only. Thermal and FT-IR analysis demonstrated that citric acid reacted with the sucrose and sweet sorghum bagasse particles, and then the ester linkages was formed. Finally, the physical properties of particleboard were enhanced.

Conclusions

Generally, this study purposed to develop high performance of environmentally friendly particleboard made from sweet sorghum bagasse and citric acid. For this objective, the physical properties of the particleboard were investigated in various conditions of particleboard manufacturing such as pre-treatment of particles before hot pressing, citric acid contents, pressing temperature and time conditions, and addition sucrose in adhesion system. Therefore, the effective conditions of particleboard manufacturing were obtained. All these were discussed in the following chapters.

In Chapter 1, recent conditions of particleboard development from non-wood lignocellulose materials such as agriculture resources, natural-based adhesive development in manufacturing of particleboard, potential resources and characteristic of sweet sorghum, citric acid, and sucrose were discussed. Since the wood resources was restricted in its utilization as raw materials of particleboard, many researchers concerned to utilize agriculture plant as an alternative of non-wood lignocellulose materials such as wheat cereal straw, rice husks, tobacco, kenaf, bamboo, sugarcane bagasse, bamboo, sunflower stalks, oil palm trunk, cotton carpel, and sorghum bagasse, etc. As same as others agriculture resources, sweet sorghum bagasse has big potential to be used as raw materials of particleboard because it is widely cultivated as a multifunctional agriculture plant. In addition, sweet sorghum is one of the promising agriculture plant for energy resources because its stalk can produce a lots of juice that contain high sugar content, simple and economically maintenance of its plantation. Therefore, sweet sorghum will be planted widely around the world include Indonesia, and then the abundant of sweet sorghum bagasse as a waste of its utilization was generated. Thus, utilization of sweet sorghum bagasse as raw materials in the

manufacturing of particleboard is one of the effective utilization method of the waste. In recent years, manufacturing of particleboard from sweet sorghum bagasse was investigated. Unfortunately, the particleboard bonded with synthetic resins that contain harmful chemical agents from unsustainable resources i.e. petroleum resources. Moreover, the sweet sorghum bagasse particleboard bonded with synthetic resin had lower dimensional stability than the standard of particleboard. Based on the recent condition of natural adhesive development in manufacturing of wood particleboard, citric acid had high prospective to be used as environmentally friendly natural-based adhesive. According to the background in this study, the objective of this study is to develop high performance of environmentally friendly particleboard made from sweet sorghum bagasse and citric acid.

In Chapter 2, a pre-drying treatment of sprayed particles was performed to observe the effect of the pre-pressing moisture content of sprayed particles on the physical properties of the particleboards. In addition, the effect of the citric acid content on the physical properties of the particleboards was investigated. The boards were manufactured under the pressing conditions of 200 °C for 10 min. The citric acid content was varied in the range of 0 to 30 wt%. The board size and target density were 300 x 300 x 9 mm and 0.8 g/cm³, respectively. Particleboards manufactured using phenol formaldehyde (PF) resin and polymeric 4,4'-methylenediphenyl isocyanate (pMDI) were used as references. The physical properties of boards prepared using pre-dried particles were superior to those of the boards prepared using non-dried particles. The physical properties of boards were improved with increasing citric acid content up to 20 wt%. The physical properties of boards bonded with 20 wt% citric acid satisfied the requirement of the JIS A 5908 (2003) 18 type. In addition, the physical properties of the board were comparable to those of boards bonded using PF resin and pMDI. Infrared (IR) spectral analysis suggested the presence of ester linkages,

indicating that the carboxyl groups of citric acid had reacted with the hydroxyl groups of the sweet sorghum bagasse to give the boards good physical properties. Consequently, it was concluded that pre-drying treatment of the particles and a citric acid content of 20 wt% were effective in manufacturing particleboards composed of sweet sorghum bagasse and citric acid. In addition, the pressing temperature and time condition which used in this step was only one condition at high pressing temperature of 200 °C and long pressing time relatively for 10 min. Therefore, the several pressing temperatures and times of the particleboard manufacturing were used in the next chapter.

In Chapter 3, the effects of pressing temperature and time on physical properties such as dry-bending (DB), internal bond strength (IB), and thickness swelling (TS) of particleboard were investigated. Wet bending (WB), screw-holding power (SH), biological durability, and formaldehyde emission of particleboard manufactured under effective pressing temperature and time were also evaluated. The results showed that the effective pressing temperature and time were 200 °C and 10 min, respectively. It was clarified that DB, IB, and TS satisfied the type 18 requirements of the JIS A 5908 (2003), and its dimensional stability was comparable to those of particleboard bonded with PF and pMDI. However, the SH of particleboard did not satisfy type 18 of JIS. Particleboard manufactured under effective pressing conditions had good biological durability and low formaldehyde emission. Based on the results of infrared spectra (IR) measurement, the degree of ester linkages increased with increased pressing temperature and time. On the other hand, high content of citric acid i.e. 20 wt% seem to be probably the particleboard become brittle, hence MOR and screw holding power were lower than those of particleboard bonded with PF and or pMDI. Therefore, in Chapter 4, the improvement of those properties were observed by adding sucrose to the adhesion system in manufacturing of particleboard, hence the content of citric acid will be reduced.

In chapter 4, the effects of the ratio between citric acid (CA) and sucrose (SU) on the physical properties of the particleboards were investigated. Based on the effective conditions of particleboard manufacturing as discussed in Chapters 2 and 3, the particleboards were manufactured using pre-drying treatment particles before hot pressing and pressed under 200 °C for 10 min. Those particleboards were bonded with 20 wt% of CA-Su-based adhesive under several weight ratios of CA to SU. The mechanical properties of particleboards bonded with CA-SU based adhesive under 15/85 and 10/90 ratio of CA to Su were superior to those of the particleboard under other conditions of the ratio. In addition, the physical properties of the particleboard bonded with CA-SU based adhesive under 15/85 and 10/90 ratio of CA to SU were comparable to those of particleboard bonded using phenol formaldehyde (PF) resin and satisfied the requirement of the 18 type JIS A 5908 (2003). The brittleness of the particleboards were decreased effectively by adding sucrose. The low formaldehyde emission and good biological durability against termite and decay were obtained by particleboard under effective ratio of CA to Su. According to the results of thermal analysis and infrared spectra measurement, the ester linkages was generated by the reaction between CA, Su and SSB components.

In brief, development of particleboard using sweet sorghum bagasse, citric acid, and sucrose had some benefit values of environmental and technical aspects. Utilization of sweet sorghum bagasse in the manufacturing of particleboard could reserve the carbon for long term. In addition, citric acid as sustainable natural resources has well prospective to substitute petroleum resources for wood-based composite adhesive. Technically, the particleboard had good physical properties especially dimensional stability. Moreover, the particleboard is free from formaldehyde emission and good durability against termite and decay, hence the particleboard suitable for interior and exterior uses.

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