岐阜大学機関リポジトリ
Gifu University Institutional Repository

The Effect of Wood Flour Characteristics by Different Filler Fabrication Treatment on the Mechanical Properties of Wood Plastic Composites

メタデータ	言語: English 出版者: 公開日: 2022-06-23 キーワード (Ja): キーワード (En): 作成者: ARIF DELVIAWAN メールアドレス: 所属:
URL	http://hdl.handle.net/20.500.12099/82783

The Effect of Wood Flour Characteristics by Different Filler Fabrication Treatment on the Mechanical Properties of Wood Plastic Composites

(解繊処理の異なる木粉の性状が混練型 WPC の機械的特性に及ぼす影響)

2021

The United Graduate School of Agricultural Science,
Gifu University
Science of Biological Resources
(Shizuoka University)

ARIF DELVIAWAN

The Effect of Wood Flour Characteristics by Different Filler Fabrication Treatment on the Mechanical Properties of Wood Plastic Composites

(解繊処理の異なる木粉の性状が混練型 WPC の機械的特性に及ぼす影響)

ARIF DELVIAWAN

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background

Wood plastic composite (WPC) is a common term referring to composite wood-based materials and polymers (Gardner *et al*., 2015) prepared under specific heat and pressure conditions (Rahman *et al.*, 2013) by various production techniques (Najafi *et al.*, 2011). Table 1 shows the number of reported studies on the WPC theme, in the last three decades, according to the Web of Science database. An increase in research interest on WPC theme is evident. In 1991 only 6 studies were available and increased up to 2005. A sharp increase in WPC theme is noticeable from the beginning of 2010 up to the present. This indicates that the WPC field has good prospects and indeed has many advantages such as better thermal and acoustic isolation, better durability, and lower maintenance requirement than other wood-based materials (Garcia *et al.*, 2009).

Table 1. The numbers of reported studies in the WPC theme in the last three decades (*source:* Web of Science database).

Year	**1991**	**1995**	**2000**	**2005**	**2010**	**2015**	**2020**
Number of studies	6	12	20	37	148	196	280

According to Schwarzkopf and Burnard (2016), the application of WPC can be classified into five categories (see Table 2). Those categories including, among others construction, automotive, furniture, highway materials, consumer goods, and other WPC applications. One of the largest commercial applications for WPC is exterior use, followed by automotive interior substrates, furniture, packaging, housing (English and Falk, 1996),

and cladding applications (Friedrich and Luible, 2016). The most abundant profiles made from WPC are board or lumber used in outdoor decking applications (Gardner *et al.*, 2015).

Table 2. Common applications of WPC and their product categories.

No.	WPC products	Category of WPC products
1.	Decking (boards and tiles), exterior siding, flooring, door, and frames of window	Construction and outdoors
2.	Gardening furniture, landscape materials, and fencing	Garden/yard and outdoors
3.	Engine components, storage (trims in trunks, shelves for spare tires) and automotive interior door trims	Automotive parts
4.	Furniture and parts of furniture	Housing and interior
5.	Packaging, components of games, household electronics, toys, tableware, and other devices	Consumer goods, interior, and outdoor

The difficulty of waste decomposition can present a serious problem for the worldwide environment. Thus, significant efforts are needed to reduce the accumulation of waste and increase its use value. Using recycled materials and other fibers in the manufacturing of WPC could be a solution. Sawdust from wood processing industries, bagasse, rice hull (agro-waste), and recycled plastic can be used as raw materials for WPC. Beside improving the use value, using sawdust for the manufacturing of WPC could help minimize waste (Rahman *et al.*, 2013). The advantages of agro-wastes such as bagasse and rice straw are renewable, low-cost materials and easy availability (Naguib *et al.*, 2015). The mechanical properties of WPC could be enhanced by adding a coupling agent (Isa *et al.*, 2013; Martins *et al.*, 2017).

This coupling agent would improve the interface compatibility between non-polar plastic and polar sawdust by providing a chemical interaction between both (Animpong *et al.*, 2017).

Wood flour is one of the most common natural fibers used in the thermoplastics industry and can be produced commercially from post-industrial sources, such as planer shavings and sawdust (Stark and Rowlands, 2003). Unused biomass resource such as forest thinning can be utilized as a filler of WPC (Isa *et al.*, 2014). However, for utilization of wood flour as a filler, several factors must be considered such as species and moisture content (Stark and Berger, 1997). These parameters could be controlled by an appropriate selection of the raw material in the manufacturing of WPC. The quality of the wood fiber as raw materials depends on factors such as the chemical nature of the surface, distribution of the particles, content of impurities, and their shape and porosity. One of the important parameters that influences the strength of WPC is the size and configuration of wood flour (Nourbakhsh *et al.*, 2010).

The characteristics of wood flour as a raw material are important in the manufacturing of WPC. The quality and functionality of WPC should be improved to meet the increasing public demand. Reducing the particle size of wood flour to get a smaller, and more uniform of size can be accomplished with a ball mill machine. Besides particle size reduction, ball mills are also widely used for mixing, dispersing, and blending. Grinding in a ball mill is affected by the point contact of ore particles and balls, and for a given time, any degree of fineness can be achieved (Wills and Napier-Munn, 2006). The wet ball milling process fibrillated the surface fibers of wood flour. The degree of fibrillation increased with increasing wet milling time (Isa *et al.*, 2014). Although various studies have been conducted, there are still unsolved factors such as the particle size distribution as a function of wet milling times and drying conditions. It is also necessary to consider the relationship between this factor and the mechanical properties of WPC.

1.2 Objective of the study

The objective of this study is to investigate the effect of wood flour characteristics by different filler fabrication treatment on the mechanical properties of WPC. Two kinds of parameter were evaluated in this research to know the influence on the mechanical properties of WPC. The first experimental item is wet milling time, which ranges for 0, 10, 20, 30, 40, 60, and 120 minutes of pulverization process. The second item is drying condition; heat drying and freezed-drying process. The tests to determine the mechanical properties such as bending, tensile, impact strength, and water resistance properties which would be affected by those parameters of milling time and drying conditions were conducted.

1.3 Structure of the dissertation

This dissertation consists of five chapters. Chapter 1 presents a general introduction, background and objectives of this study. This chapter also mentions the structure of the dissertation to be discussed in this study.

Chapter 2 covered the literature review of previous studies related to this research field. It is divided into four sections, i.e. the filler's material sources, the composition of raw materials, size and shapes of fillers, and chemical pretreatment. The filler's material sources introduced the wood-based filler, other natural fibers, and recycled materials that can be used on WPC manufacture. This chapter also explaines the composition of raw materials on the manufacturing of WPC, size and shapes of fillers as an effect of the applied process and chemical pretreatment that can be applied to improve the resistance of the composite product.

Chapter 3 described the materials that we used and the method that applied in this study. Wood flour of Japanese red pine (*Pinus densiflora*), Polypropylene (PP), and maleic anhydride-grafted PP (MAPP) were used as materials on the manufacturing of WPC. Wet milling was conducted with different time and two kinds of drying conditions were applied.

After drying, the wood flour and other materials combined to produce the WPC product. The chapter described the mechanical testing conducted to determine the effects of parameters on the properties of WPC.

Chapter 4 explained the results and discussion of the study. Percentage of dried wood flour and particle size distribution after ball mill, after re-fibrillation, and after screened were discussed at the beginning. The micro-structure of wood flour was investigated through a scanning electron microscope examination. Then the mechanical properties i.e., bending, tensile, impact strength, and water resistance properties were evaluated. The effect of wood flour characteristics by different filler fabrication treatment on the mechanical properties of WPC were analysed. Three sub-chapter was investigated; the first is the effect of drying conditions on the mechanical properties of WPC. The effects of wet milling time on each mechanical properties were analyzed as the second sub-chapter. The correlation between the intensity at any particle size and the mechanical properties were also calculated in this sub-chapter. And in the last sub-chapter, the mechanical properties of WPC made from smaller mesh size were investigated.

Chapter 5 provided the general conclusion of the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Filler materials sources

Wood is the most abundant biomass resource and has attracted considerable attention as a reinforcement filler combined with polymers in the preparation of WPC (Iwamoto *et al*., 2014). WPC technology continues to mature, with improvements being made in the manufacturing processes, profiles and parts, durability, and the development of product standards for building construction. New developments for WPC are being made especially in the area of nano-additives like nanocellulose for new types of products and market application areas (Gardner *et al*., 2015).

The influence of different wood species (8 hardwoods and 2 softwoods) on the appearance and durability performance of WPC was investigated by Kim *et al*. (2008). The color of the WPC was initially quite different, reflective of the various wood species used, but became similar in appearance after outdoor exposure. Evaluation of water sorption and durability of WPC revealed WPC made from eastern redcedar and Osage orange had low water sorption and lower levels of fungal decay than those made from other wood species (Kim *et al*., 2008). Tisserat *et al*. (2013) evaluated the Paulownia wood flour as a reinforcement for thermoplastic composites. The composite made from Paulownia wood flour and maleic anhydride polyethylene (MAPE) pellets showed significantly higher tensile and flexural strengths than neat high-density polyethylene (HDPE). Flexural and impact strengths of WPC with Paulownia wood flour were comparable with or superior to the WPC made from pine filler.

Najafi *et al*. (2011) studied the effect of lignocellulosic fillers, such as flour of rice hull, wood sawdust, sanding flour from medium density fiberboard (MDF), and sawdust

from particleboard, on the mechanical properties of recycled HDPE composite. The composites containing sanding flour from MDF showed higher short-term water absorption and thickness swelling. The composites made from sawdust and rice hull had higher and lowest for water absorption, thickness swelling, and long-term diffusion coefficients, respectively. However, composites made from sanding flour of MDF and particle board sawdust showed higher flexural strength than the other composites studied.

The physical and mechanical properties of WPC made from recycled particleboard and PP were evaluated by Gozdecki *et al*. (2015). Recycled wood particles (RWPs), virgin wood particles (VWPs), and wood flour were used as fillers for the manufacturing of WPC. The properties of WPC made from RWPs did not significantly differ from those of WPC made from VWPs and were comparable with WPC made from wood flour. These results suggested that the particles derived from milled particleboard was proved to be an effective alternative of the wood component of WPC.

Martins *et al*. (2017) reported the optimization of WPC made from industrial residues of pine sawdust, HDPE, and MAPE as a coupling agent. The results showed that the best properties of composites were obtained for the composition of 55 wt% HDPE, 35 wt% fine wood particle, and 10 wt% MAPE. It could be processed by extrusion and possesses enough tensile strength (22 MPa) for application as a shutter unit in a shading system. The high mechanical strength was due to the high amount of filler used and the good interfacial adhesion obtained by the addition of coupling agent. Physical and mechanical properties of WPC made from Sengon and recycled HDPE were evaluated by Arnandha *et al*. (2017). WPC had higher compression and shear strength compared to the common Sengon wood itself. They found that the thus-prepared WPC is suitable for both outdoor and indoor applications, under low moisture content (MC), swelling, and water absorption.

Outdoor usage of WPC requires that its service life and safety must be considered because changes in weather increase the corrosion (Zhang *et al*., 2016) and the risk of damage due to microbial colonization (Sudár *et al*., 2013). Catto *et al*. (2016) investigated the effects of natural weathering on WPC and subsequent material degradation by soil and fungi, and reported that natural weathering by ultraviolet radiation, rain water, and high temperatures produced micro and macro-cracks in the WPC surface, which accelerate the subsequent biodegradation in soil and fungal decay. The raw material (types of wood and the coupling agent) used in the manufacturing of WPC also influences the degradation process. Ogunleye and Aina (2017) found that the density, dimensional properties, and strength of WPC decreased but its elasticity modulus increased with increasing plastic content. Isa *et al*. (2013) evaluated the effect of three factors—plastic content, coupling agent, and micro-fibrillated cellulose (MFC) on the water resistance of bamboo flour/plastic composite. The water resistance increased with increasing plastic content. Rheological and mechanical properties of the composite were improved by using higher contents of the coupling agent and MFC.

Turku *et al*. (2017) investigated the possibility of using recycled plastic waste for manufacturing WPC, in terms of flexural, tensile, un-notched impact strength, hardness properties, and water absorption. They found that the strength of the composites was lower than those of the reference WPC manufactured from virgin low-density polyethylene (LDPE), while the composites' hardness was comparable, and stiffness was higher than those of the LDPE-based WPC. The plastics recycled from electronic waste and recycled particleboard can be used as a raw material for WPC (Sommerhuber *et al*., 2016). The water uptake, density, tensile strength, and modulus of elasticity of WPC increased by increasing the wood content. WPC made from Norway spruce exhibited reinforced strength and stiffness, while WPC made from particleboard showed reduced strength properties.

Rahman *et al*. (2013) investigated the technical evaluation of WPC fabricated from sawdust and recycled polyethylene terephthalate (PET) mixed at different ratios. They found that the physical and mechanical properties of WPC depended on the raw material and these mixing ratios. Increasing PET content reduced the MC, water absorption, and thickness swelling of the composites. With increasing immersion temperature, water absorption and thickness swelling increased. These results indicated that the fabrication of WPC from mixed sawdust and the recycled PET is technically feasible and additives like a coupling agent could be used for further improvement of the properties. However, heavy metal element such as Cadmium, Chromium, Copper, and Lead were found in the recycled resources by elemental analysis; therefore, more sophisticated waste management systems, policies, and treatment technologies are needed (Sommerhuber *et al*., 2016).

2.2 The composition of raw materials

Nowadays, many researchers are studying the effect of the composition of raw materials on the manufacturing of WPC. Nourbakhsh *et al*. (2010) investigated that wood flour could be considered a potential source of low-cost natural fibers for composites. With increasing filler particle size and aspect ratio, the mechanical properties of composites increased due to formation of strong interfacial bonds among the filler, coupling agent, and the matrix. Composites containing 2 wt% MAPP showed higher tensile and impact properties than those without treatment. This observation was supported by Stark and Rowlands (2003), who found that the strength of wood flour/PP composites increased upon using higher aspect ratio of wood fibers and adding the coupling agent.

Stark and Berger (1997) studied the effects of wood flour species and particle size on the mechanical properties of PP filled with wood flour. With increasing wood flour content, tensile and flexural moduli, density, heat deflection temperature, and notched

impact energy of composites increased. However, tensile and flexural strength, tensile elongation, mold shrinkage, melt flow index, and unnotched impact energy decreased.

Leu *et al*. (2012) investigated the effects of changing the material composition on the physical and mechanical properties of extruded WPC made from recycled PP and spruce, using pine and fir wood flour. The optimal composition was found to be 47 wt% wood flour (100-120 mesh size), 47 wt% recycled PP, 3 wt% MAPP, and 0–3 wt% ZnSt as the lubricant. Increasing wood content improves the flexural and tensile moduli, but was less favorable for MC, thickness swelling, and tensile strength. Adding the proper amount of the coupling agent could improve the mechanical properties and significantly reduce the swelling; however, excessive addition of lubricant significantly increased the swelling and reduced the mechanical properties of WPC.

Tazi *et al*. (2015) studied the mechanical properties and structure of WPC made from HDPE with different sawdust contents in the presence of a coupling agent. Wood flour addition increased the degree of crystallinity and improved the tensile strength and the ductility of WPC. However, increasing wood flour content reduced water resistance. Although the addition of sawdust improved the mechanical properties, it accelerated the biodegradation of WPC. The addition of wood fibers increases the tensile, flexural, and compression properties of WPC (Garcia *et al*., 2009).

Poly(methylene(polyphenyl isocyanate)) (PMPPIC) can be used as a coupling agent to improve the compatibility of hydrophilic wood fibers and hydrophobic polymer matrix (Maldas *et al*., 1989). Adding 2 wt% PMPPIC provided the largest increase in mechanical properties like impact strength compared with those of nontreated composites or composites treated with 8 wt% PMPPIC. Fibers can be incorporated without adversely affecting performance up to a maximum content of 20–30%. They found that flexible softwood spruce

pulps provided higher reinforcement to WPC mechanical properties than denser hardwood birch or hardwood aspen pulps.

The effects of material compositions, including different plastic matrices, wood flour, and coupling agents on the mechanical properties of WPC manufactured by injection, have been investigated by Kuo *et al*. (2009). They found that the tensile strength and modulus of rupture of WPC manufactured with LDPE and PP were higher than those of LDPE and PP themselves. However, contrasting results were found when the polymer matrix was acrylonitrile-butadiene-styrene. WPC manufactured with RPP showed higher modulus of rupture but lower tensile strength than RPP itself. Kuo *et al*. (2009) reported that superior properties were found for WPC manufactured using PP mixed with 47 wt% wood flour (< 180 μm) and 3–4.5% MAPP.

WPC with high flexural and admirable physical properties can be produced from LDPE, sawn sawdust, and by using automotive engine oil as a coupling agent (Animpong *et al*., 2017). The optimum properties of WPC, which allowed for outdoor applications, were found for a plastics:sawdust:coupling agent weight ratio of 34:54:10. The optimum amount of fillers used in the manufacturing of WPC was less than 60 wt%.

2.3. Size and shape of fillers

Two kinds of step, wet milling or dry milling by a disk mill can be applied for filler production of WPC. This procedure makes it easy to produce a uniform size of fibrillated wood flour. The mechanical properties of PP-based WPC were improved by the addition of the produced wood flour (Ito *et al*., 2017). Tensile and bending properties of the composites containing the wood filler were 10% higher than those of the unfilled composite. The average diameter of the wood flour decreased and the degree of fibrillation of wood fibers increased with the ball milling time (1 to 16 h) at each rotational speed (150, 200, and 250

rpm) (Isa *et al*., 2014).

The effect of the particle size (Leu *et al*., 2012), coupling agent, and types of filler on tensile and flexural properties of Paulownia WPC was studied by Tisserat at al. (2014). They found that the particle size distribution of Paulownia wood filler affects the tensile and flexural properties of the composites. Addition of dried distiller's grain with solubles (DDGS) combined with Paulownia wood fillers showed superior tensile and flexural moduli, and impact strength of the WPC. However, the flexural and tensile strengths decreased with increasing size of the wood flour (Leu *et al*., 2012). Salemane and Luyt (2006) studied the effect of the wood flour and compatibilizer content on the properties of the composites. They found that the wood flour size and content, as well as the presence of MAPP, played a significant role in the tensile properties, thermal stability, and oxygen permeability. The tensile properties of the composites improved owing to the presence of MAPP. The increase of wood flour generated better tensile properties. Isa *et al*. (2016) evaluated the influence of the wood flour on the physical properties of the wood flour/PP composites. The morphological change of the wood flour in case of the milling process reduced its influence on the physical properties of the composites, such as increased compound fluidity. Addition of the wood flour with nanoscale surface fibrils to the PP composites positively influenced the physical properties of the composites.

Zimmermann *et al*. (2014) investigated the effects of different particle sizes and content of the wood flour on the mechanical properties of cellular polyethylene - co - vinyl acetate (EVA)/wood flour composites. They found that decreasing the particle size of the wood flour increased the viscosity of the composite. The presence of the wood flour in the cellular composite increased the nucleation of cells (the voids created by the blowing agent in the polymer matrix), providing a larger number of smaller cells with increased filler content. The highest cell density and cell size homogenity were observed in the composites

made with wood flour 80–150 mesh. With increasing particle size, melt flow index, flexural and tensile properties, heat deflection temperature, and notched impact energy of the composites increased (Stark and Berger 1997). However, with increasing particle size, the unnotched impact energy decreased and did not affect the specific gravity of the composites.

The effect of oil palm mesocarp flour (OMF) and rubber wood flour of different particle sizes on the physical, mechanical, and thermal properties of recycled PP composites have been evaluated by Ratanawilai *et al*. (2014). Recycled PP composites based on rubber wood flour have better flexural, tensile, and compressive properties (strength and modulus), and higher hardness and thermal stability than composites prepared using OMF of the same particle size as rubber wood flour. However, rubber wood flour was less homogeneuously distributed in the recycled PP matrix than OMF. Decreasing the particle size of filler for the recycled PP/OMF or rubber wood flour, improved the tensile, flexural, and compressive properties as well as hardness. Thermal stability of the composites was considerably affected by the particle size. This finding is in contrast with that of a previous study that reported that thermal stability was affected by the wood type of raw material used for manufacturing WPCs (Ratanawilai *et al*., 2012).

Bledzki and Faruk (2003) investigated the effect of four types of wood fiber (hardwood fiber, softwood fiber, longwood fiber, and wood chips) on wood fiber reinforced–PP composites with the addition coupling agent of 5% MAPP. They found that wood chips–PP composites had better tensile and flexural properties than the other composites. Hardwood fiber–PP composite had better impact characteristics than others. The damping index decreased to about 60%, while Charpy impact strength increased for long wood fiber–PP composites under this addition. Khonsari *et al*. (2015) studied the effects of types and mesh–size of wood flour on the physical and mechanical properties of WPC. The mechanical properties of WPC were significantly lower when only sawdust was

used. The aspect ratio of ground wood shavings was higher than that of sawdust. Using larger particles for manufacturing WPCs increased the water absorption.

Composites made from bark particles exhibited lower water absorption than those made with wood particles due to the different chemical compositions of the particles (Bouafif *et al*., 2009). Increasing the fiber size and content improved the strength and stiffness of the WPC. However, it reduced elongation and the energy to break. Water uptake by the WPC increased substantially with increase in fiber content.

The water sorption and diffusion properties of WPCs were investigated by Kaboorani (2017) as a function of the formulation design. Increasing wood content, increased the susceptibility of WPCs to water. Improving the adhesive forces between the wood and polymer by adding a coupling agent, decreased the water absorption, diffusion coefficients, and thickness swelling. The optimum formula of the coupling agent was dependent on the size and content of wood. Composites with large particles in their formulations absorbed water rapidly, resulting in high MC at the saturation point, high diffusion coefficients, and high thickness swelling (Kaboorani 2017).

2.4. Chemical pretreatments

The MFC was surface treated with silicate hydrate to develop an effective filler material for the production of WPC. This modification resulted in high-heat resistance and prevented irreversible aggregation. The composite materials demonstrated high mechanical strength and elastic modulus when the modified MFC filler was added to PP-based WPC (Ito *et al*., 2013).

Koohestani *et al*. (2017) investigated the influence of silanized micro-sized silicate-based minerals on the mechanical, thermal, and rheological properties of WPC. They found that the wood filler is primarily attributable for the increase in viscosity, modulus of

elasticity, tensile, and flexural strength. Any changes in the other properties of the WPC are more dependent on the wood filler content than on the mineral filler content. Mineral fillers modified with vinyl-silane could improve tensile and flexural strength more effectively but were less effective on rheological behavior. Both the surface-modified minerals could improve the thermal stability of the WPC; amine-modified minerals had no negative effect on the rheological performance. However, it decreased the rigidity of the WPC considerably.

Tascioglu *et al*. (2014) investigated the dimensional stability, mechanical and biological performance, and thermal degradation of the WPC made from HDPE and recycled wood treated with chromated copper arsenate. The influence of MAPE was also investigated. The recycled chromated copper arsenate-treated wood flour and coupling agent could improve the dimensional stability and mechanical performance of the WPC, excluding the Izod impact strength. The biological test showed that resistance to termites and fungus was improved with this treatment. This treatment can be utilized as an alternative recycling method for chemically treated wood. Further, chemically treated bagasse fibers can be used as a raw material for manufacturing WPCs (Naguib *et al*., 2015). Composites prepared with chemically treated (with 5% NaOH and diluted HCL solutions) bagasse fibers exhibited stronger interaction at the fiber-matrix interface than composites prepared with untreated bagasse fibers. Additionally, increasing the content of chemically treated bagasse fibers, increased water adsorption by the composites and enhanced their mechanical properties.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Commercial wood flour of Japanese red pine (*Pinus densiflora*) was used as a filler in this study. At first, wood flour was screened by a rotor mill (FRITSCH, Pulverisette 14, Germany) at 20,000 rpm of speed. PP (J107G, Prime Polymer Co., Ltd., Japan) and (MAPP (Kayabrid 006PP-N, Kayaku Akzo Co., Ltd., Japan) were used as a matrix and compatibilizer, respectively. PP was used in the form of a homopolymer powder, with a melt flow rate of 30 g/10 min (230 °C/2.16 kg) and 0.91 g/cm^3 of density. The MAPP powder had 2 wt.% MA contents with an average molecular weight of 75 kg/mol.

Injection and extrusion molding are two popular plastic molding methods in the industrial and manufacturing sector that are used to make products with varying shapes and sizes. Based on what is the useful of WPC product, they can be classified into: exterior use, interior use, and high-performance use. Exterior use usually made for decking, flooring, etc. In the case of this research, the WPC will be used for a special interior and high-performance product such as the part of bath, kitchen, some part of a machine, interior of the car, etc. Therefore, the kind of injection PP grade was used in this research.

3.2 Methods

3.2.1 Filler fabrication

Wood flour of the Japanese pine 13.5 g was milled with 200 ml of water by a ball mill (Pulverisette 5, Fritsch, Germany). This was the standard method of wet milling condition for “one pot” in this research. The rotating speed of 200 rpm was applied and the different wet milling times were conducted for 0, 10, 20, 30, 40, 60, and 120 minutes. After wet

milling, two kinds of drying conditions were applied. Those are seven days of freezed-drying at temperature -45 °C by a freeze dryer (FDU-1200, Eyela, Japan) and 24 hours of heat drying by an oven dryer (SOFW-450S, Ettas, Japan) at a temperature of 80 °C. After drying, wood flour was fibrillated for 1 minute by a blender (IFM-800DG, Iwatani, Japan). Dried wood flour was screened to classify into six fractions as follows; >425 μm, 180-425 μm, 90-180 μm, 53-90 μm, 32-53 μm, and <32 μm. Vibrational acceleration ± 20 G was applied for 30 minutes of each condition by a compact vibrating shaker (VSS-50D, Tsutsui, Japan).

In order to analyze the weight distribution at wood flour size of 6 classifications and at 7 milling times, total amount of wood flour weight in each fraction of 6 x 7 matrix conditions was weighed and calculated. The number of pots used in wet milling to obtain fibers was listed in Table 1 for heat drying and freezed drying conditions. The number of pots for each condition was determined to obtain a sufficient amount for test piece fabrication and to analyze the particle size distribution. This study focused on the fraction 90 - 180 μm for all the different wet milling times, 180 – 425 μm on 0, 30, and 120 minutes, and 32 – 53 μm of 30 minutes wet milling time. The micro-structure of wood flour was investigated through a scanning electron microscope (SEM) (JSM-6510LV, JEOL, Japan) examination.

The particle size distribution of wood flour after milling, drying, and screening was analyzed by a laser diffraction particle analyzer (LA-950S2, Horiba, Japan). This laser diffraction particle analyzer was used to measure wet and dry samples by the range of 10 nm to 3000 μm. Wet sample method was applied in this research. Small amount of wood flour was put into sample bath to scatter the light at an angle determined by that particle size; larger particles scatter at small angles and smaller particles scatters at large angles. A collection of particles produced a pattern of scattered light defined by intensity and angle that was transformed into a particle size distribution.

3.2.2 Manufacture of WPC

PP and MAPP was used as a matrix and compatibilizer of WPC compound. The ratio of the weight of wood flour, PP, and MAPP in the compound was 25:74:1, respectively. This ratio of the weight was same as previous research, and it was applied to avoid the interaction between wood flour itself (Murayama *et al*., 2019). The WPC compound was kneaded at 190 °C and a screw rotation speed of 30 rpm for 10 minutes by an extruder machine (Laboplast Mill 30 R 150, Toyo Seiki Seisakusho, Japan). After kneading, the WPC compound was crushed by a crusher machine, pulverizer (SA-23, Stolz). Melt kneading was carried out for 5 minutes at a temperature of 190 ° C and a screw rotation speed of 50 rpm by a twin-screw small kneader (Micro 5 cc Twin Screw Compounder, DSM Xplore). After that, the injection molding machine (Micro 5.5 cc Injection Moulding Machine, DSM Xplore) was used to make WPC test pieces.

The condition of wood flour for WPC fabrication was seen in Table 3. We focused on the fraction of 90-180 μm, because this size was knows as an optimum condition by the previous study. The fractions of 180-425 μm by 0, 30, and 120 minutes were chosen for evaluated the effect of the differences drying conditions, and the fraction of 32-53 μm by 30 minutes for freezed-drying was added, because it was thought to be the ideal condition for comparison. The dimensions of a tensile test were 50 mm in length, 2 mm in thickness, 4 mm in width and those of the bending specimen was 50 mm in length, 2 mm in thickness and 6 mm in width. The specimens were conditioned for 5 days or more in a constant temperature and humidity room (20° C, RH 65%) before testing.

Table 3. The condition of WPC fabrication.

Mesh size (μm) \ Time (min)	0'	10'	20'	30'	40	60'	120'
> 425							
180 - 425	□ ○			□ ○			□ ○
90 - 180	□ ○	□ ○	□ ○	□ ○	□ ○	□ ○	□ ○
53 - 90							
32 - 53				○			
< 32							

□ Heat drying ○ Freezed-drying

3.2.3 Mechanical properties test

Bending test

Three points of bending test were conducted using a universal testing machine (BT-805, Yasui Kikai, Japan). The speed of the test was 5 mm/min and by a span of 32 mm based on the JIS A 5741 standard. The number of replications for each test was 5. Then, the values of the bending properties including flexural strength and flexural modulus were calculated equation 1 and equation 2, respectively.

$$\boldsymbol{\sigma_f = \frac{3PL}{2bh^2}} \quad \ldots (1)$$

Where σ_f is flexural strength (MPa), P is the maximum load (N), L is the distance between fulcrum or span (mm), b is the width of the test specimen (mm) and h is the thickness of test specimen (mm).

$$\boldsymbol{E_f = \frac{\Delta F}{\Delta s} \times \frac{L^3}{4bh^3} \times 10^3} \quad \ldots (2)$$

Where E_f is flexural modulus (MPa), ΔF is the difference between upper limit load and lower limit load in the proportional range (N), Δs is the difference between upper limit deflection and lower limit deflection in the proportional range (mm).

Tensile test

The tensile test was carried out by a universal testing machine (AGS-5kNX, Shimadzu Seisakusho, Japan) according to the JIS A 5741 standard. The speed of the test was 20 mm/min and the distance between the gripper was 30 mm. The number of replications for each test was 5. the values of the tensile strength were calculated using the equation 3.

$$\boldsymbol{\sigma_t = \frac{F_t}{A}} \quad \ldots (3)$$

Where σ_t is tensile strength (MPa), F_t is the maximum load (N) and A is the cross sectional are at the beginning of the test specimen (mm^2).

Impact test

An unnotched Izod Impact test was conducted by the U-F Impact Tester machine (Ueshima Seisakusho, Japan) according to the JIS K 7110 standards. The dimension of the test specimen was same the likes as the bending test's specimen and the number of replications was 5 for each test. The values of the impact strength were calculated using the equation 4.

$$\boldsymbol{a_{iN} = \frac{W}{hb_N} \times 10^3} \quad \ldots (4)$$

Where a_{iN} is Izod impact strength (kJ/m^2), h is the thickness of the test specimen (mm), b_N is the width of the test specimen (mm) and W is the impact energy absorbed by the test specimen (J).

Water resistance test

Water resistance test was included two kinds of test, ie water absorption and thickness swelling. It was conducted using heat drying by an oven dryer (SOFW-450S, Ettas, Japan). The test specimen was put in the water and heated by oven at the temperature of 70 °C. The test specimen dimension measurements were performed after 0, 1, 3, 4, 6, 12 hours. Then, measurements occurred once a day for the first week, followed by once every three days until saturation. The values of the water absorption in percentage were calculated in equation 5.

$$\boldsymbol{WA(t) = \frac{W(t) - W_0}{W_0} \times 100} \quad \ldots (5)$$

Where $WA(t)$ is the water absorption at time t, W_0 is the oven dried weight and $W(t)$ is the weight of the specimen at a given immersion time *t*. Also the values of the thickness swelling in percentage were calculated using the equation 6.

$$\boldsymbol{TS(t) = \frac{T(t) - T_0}{T_0} \times 100} \quad \ldots (6)$$

Where $TS(t)$ is the thickness swelling at time *t*, T_0 is the initial thickness of the specimens and $TS(t)$ is the thickness at time *t*. The value of thickness swelling and water absorption were predicted using the equation 7.

$$\boldsymbol{f = A(1 - e^{-\frac{t}{B}})} \quad \ldots (7)$$

Figure 1. showed the relationship between the time *t* and predicted of thickness swelling and water absorption of WPC. Where *A* is the saturation point at a maximum thickness swelling or water absorption and *B* is the specific value of thickness swelling or water absorption, when the time *t* is 0.632A

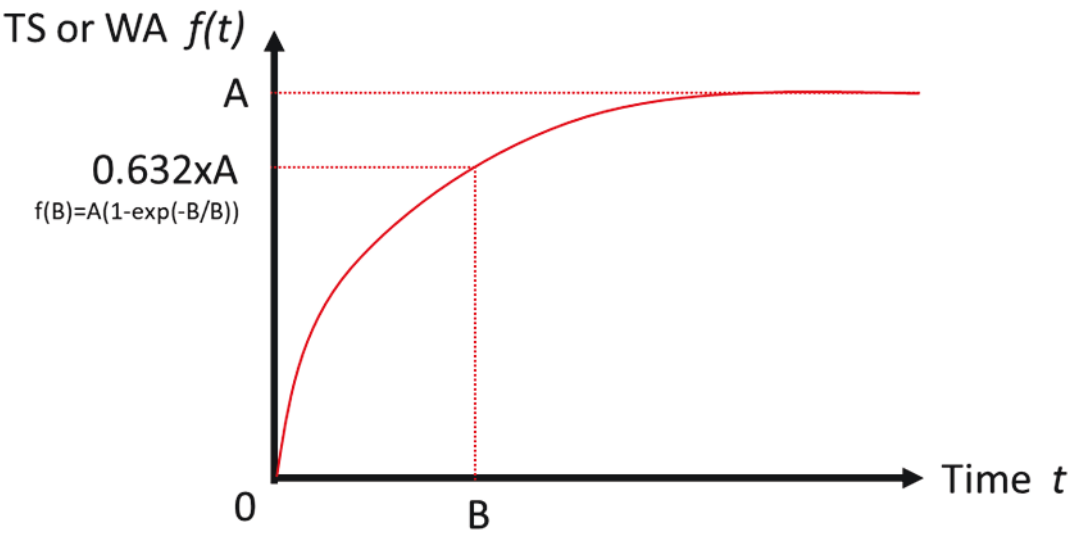

Fig. 1 The relationship between time *t* with predicted maximum water resistance properties.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 The effect of drying conditions on the mechanical properties of WPC

4.1.1 Percentage of wood flour and particle size distribution

The percentage of produced wood flour after drying process obtained with heat drying condition were shown in Table 4. Focused on 0 minutes of wet milling time, the largest percentage in the vertical fractions was 34.5 % at the size 180 - 425 μm and the second largest was 30.9 % at the size of >425 μm. The percentage of the size 90-180 μm was 15.1 % and the other fractions showed less than 10 %. This proportion of 0 minutes was the initial stage, and the distribution of weight fraction changed according to the wet milling time. It was found clearly that the distribution of wood flour size become smaller from 0 minutes to 40 minutes of milling time. The largest percentage was found in the wood flour size of 90 – 180 μm and 53 – 90 μm, at the milling time of 30 minutes and 40 minutes, respectively. However, at the milling time of 120 minutes, the distribution changed again, showing the largest portion in the size of >425 μm. This reason could be aggregation as mentioned later.

Table 4. The percentage of produced wood flour for heat drying conditions.

Mesh size (μm)	Wet milling time (minutes)						
	0	10	20	30	40	60	120
> 425	30.9	15.1	4.1	6.8	9.8	21.8	62.1
180 - 425	34.5	37.2	22.8	14.3	5.3	18.6	18.6
90 - 180	15.1	21.2	29.1	33.6	25.5	22.0	9.2
53 - 90	8.9	12.1	20.6	22.5	32.1	20.7	3.9
32 - 53	9.8	9.9	15.6	14.7	21.0	13.0	3.3
< 32	0.8	4.4	7.8	8.1	6.2	3.9	3.0

The percentage of produced wood flour after drying process obtained with heat drying condition were shown in Table 5. Almost same in the Table 4, the largest percentage

at 0 and 30 minutes of wet milling time by vertical fractions was found at the size 180 - 425 μm and 90 – 180 μm. At that time the percentage was showed 37.8 % and 42.0 %, respectively. However, for 120 minutes of wet milling time the largest percentage was found at the size 90 – 180 μm. At that time the percentage of wood flour was showed about 34.9 %. The reason of these might be due to the aggregation. Both of Table 4 and 5 showed that the difficulty to get wood flour at the lowest size of fractions, < 32 μm. It showed that the percentage nearly zero percent although the number of pots that obtained was high.

Table 5. The percentage of produced wood flour for freezed-drying conditions.

Mesh size (μm)	Wet milling time (minutes)						
	0	10	20	30	40	60	120
> 425	35.8	13.7	4.3	1.4	2.6	4.2	12.3
180 - 425	37.8	35.6	23.6	17.7	40.8	54.3	32.8
90 - 180	16.8	24.7	33.8	42.0	38.9	24.8	34.9
53 - 90	6.3	13.4	21.2	23.3	10.8	12.3	14.1
32 - 53	3.2	11.0	13.5	12.2	5.3	4.1	5.4
< 32	0.2	1.5	3.5	3.4	1.6	0.3	0.5

Figure 2 shows the particle size distribution of wood flour after ball milling process. Particle size distribution of produced wood flour depended on the milling conditions. The highest intensity for the largest particle size (peak) was observed for 0 minutes wet milling time. At that condition, the average of particle size around 800 μm and the intensity around 12 %. As the increasing time of ball milling process, particle size decreased. At 10 and 20 minutes of wet milling time the peak were found same trend and the particle size as 0 minutes of wet milling time. It was showed that the intensity around 6 and 4 %, respectively. However, it was showed the particle size has wide range and lower compared to un-milled wood flour. Two peaks were appeared at 30 and 40 minutes of wet milling time. At that time both of peaks were showed the same intensity around 4 %. However, it showed the different particle size that were around 800 and 80 μm, respectively. At 60 minutes of wet milling

time was found that the first peaks around 800 μm were disappeared. However, there was two peaks with the particle size around 70 and 10 μm, respectively. In the case of 120 minutes of wet milling time was found that the peak around 10 μm increased nearly 5 % of intensity. The peaks around 800 μm of the particle size was increased at 4 % of the intensity. This might be due to the milled wood flour into finer or fibers caused by the high rotating speed of the ball mill.

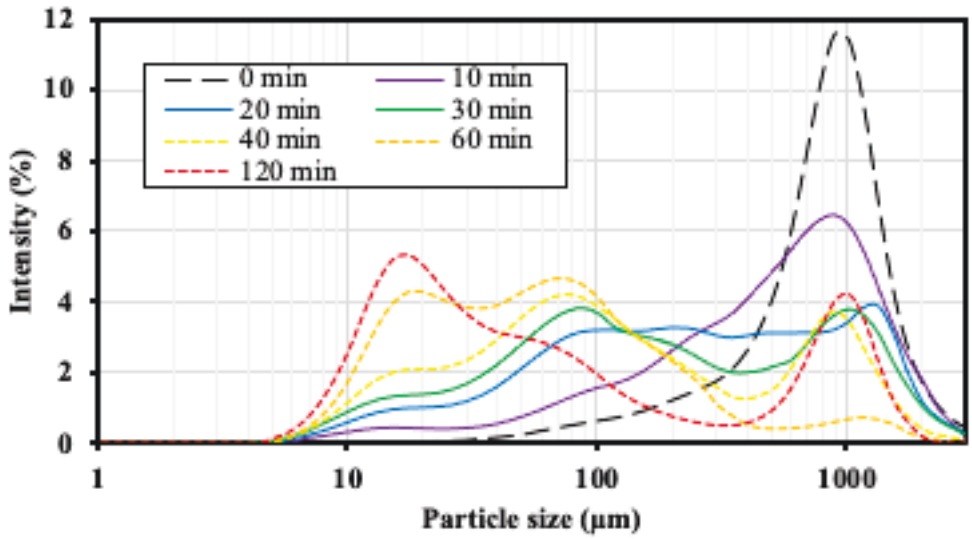

Fig. 2 The particle size distribution after pulverization by a ball mill.

The particle distribution after re-fibrillation process obtained by heat drying condition and the freezed-drying condition were shown in Fig. 3. As can be seen that between heat drying and freezed-drying had same trend of the particle size distribution. The highest intensity of particle size around 6 % was found at 0 minutes of wet milling time. At that time showed the particle size around 800 μm. At 10 minutes of wet milling time was found that the peaks decreased and wider of range then un-milled wood flour. The intensity for heat drying and freezed-drying at this time were 5 and 4 %, respectively. It showed that for heat drying conditions was steeper than that for freezed-drying conditions.

At 20 minutes of wet milling time both of drying condition were found the two peaks appeared. The first peaks nearly one thousand micrometers and the second peaks around 90 μm with 4 % of the intensity both of drying conditions. At this time the freezed-drying showed was wider range than heat drying condition. Two peaks also appeared at 30 and 40 minutes of wet milling time. At that time both of peaks were showed the same trend of particle size around 1000 and 80 μm, respectively. However, the intensity of heat drying condition was higher than freezed-drying condition. It was around 4 to 5 % and 2 to 4 %, respectively. At 60 and 120 minutes of wet milling time, the different trend of particle size distribution were found. At 60 minutes of wet milling time for heat drying condition showed that only one peaks appeared around 100 μm with 5 % of the intensity. However, three of peaks at freezed-drying condition with different particle size and intensity were found. The first peak around one thousand micrometers with 3 percent of the intensity, followed by two peaks around 20 and 80 μm with 3.5 to 4 % of the intensity, respectively. In the case of 120 minutes of wet milling time was found that the peak around 1000 μm decreased nearly 2 % of intensity. The peaks around 80 μm has same percentage of intensity and the particle size with 60 minutes of wet milling time. However, the third peaks nearly 20 μm was increased up to 5 % of the intensity due to the aggregation.

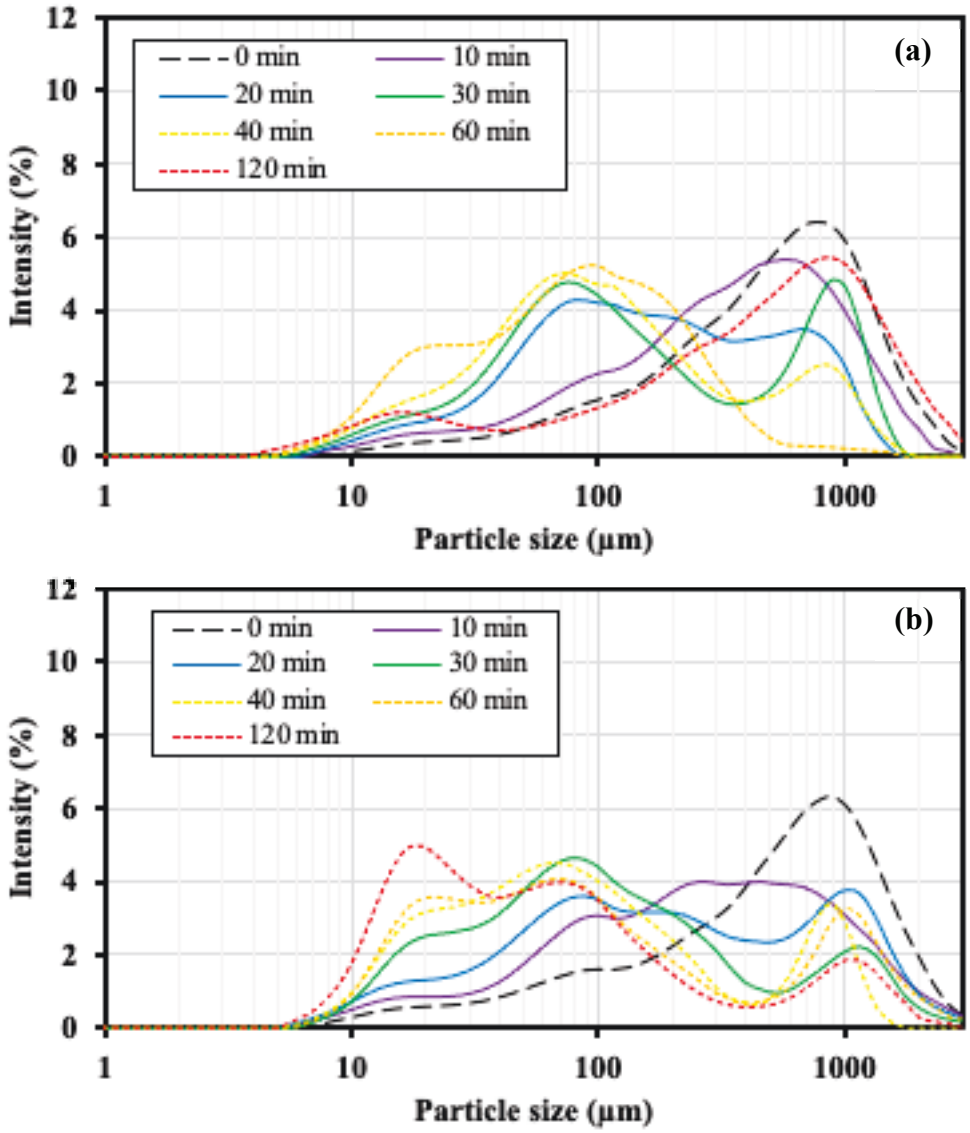

Fig. 3 The particle size distribution after re-fibrillation process obtained by (a) heat drying condition and (b) freezed-drying condition.

The particle distribution of dried-wood flour after the screened process for 180 to 425 µm were shown in Fig. 4. The wood flour that obtained with heat drying condition can be seen in Fig. 4(a) and for the dried wood flour with the freezed-drying condition in Fig. 4(b). Particle size distribution of produced wood flour depended on the milling conditions. Focused on the large particle size around 800 µm for both heat drying and freezed-drying conditions, the highest intensity (peak) was observed for 0 minute of wet milling time. Under that condition, the intensity was approximately near 10%, and it decreased with increase in wet milling time up to 30 minutes. The deviation of the particle size distribution

demonstrated that there are various sizes and shapes in milled wood flour. However, the wood flour that obtained by heat drying showed increased from 30 to 120 minutes of wet milling time. It was meant the aggregation occurred longer 30 minutes of wet milling time. The intensity near 100 μm for heat drying and freezed-drying conditions increased with increasing the wet milling time. Same trend found at the smaller particle size (near 20 μm) for both drying conditions and the peak appeared at 120 min of wet milling time. Under those conditions, the intensity for the freezed-drying condition was higher than that for the heat drying condition. This might be due to the milled wood flour into finer or fibers caused by the high rotating speed of the ball mill.

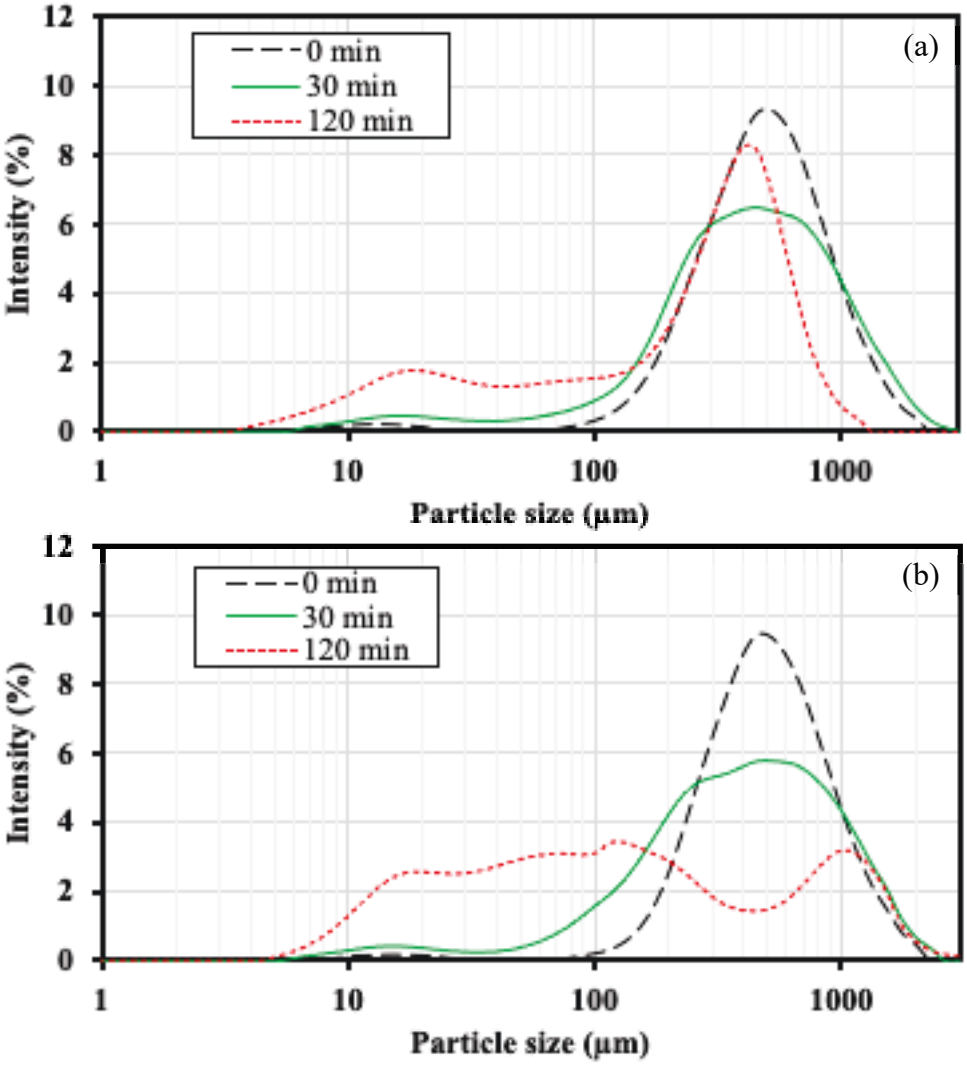

Fig. 4 The particle size distribution after the screened process for 180 to 425 μm obtained by (a) heat drying condition and (b) freezed-drying condition.

SEM images of wood flour for 180 to 425 μm at 0, 30 and 120 minutes of wet milling time was shown in Fig. 5. As can be seen in Fig. 5(a) and (d), there was an intact single particle for un-milled wood flour. At the time of wet milling was 30 minutes there was fibrillated particle on both of heat drying and frezed-drying conditions as shown in Fig. 5(b) and (e). However, in the wet milling time 120 minutes there was a fibrillated and aggregated particle as can be seen in Fig. 5(c) and (f). There was an aggregated particle with the different surface characteristic between heat drying and freezed-drying conditions. The surface of heat drying wood flour was flat due to the aggregation. Figure 5(c) and (f) showed that the heat drying conditions had a bigger average of particle size compared to the freezed-drying conditions. It also as can be seen in Fig. 3 and 4 that for milled wood flour around 800 μm of heat drying particle size was higher intensity and wider range than freezed-drying. It proved that the aggregation occurred in this condition higher than freezed-drying conditions. It was clearly showed the increasing of intensity and the peak occurred at 120 minute of wet milling time.

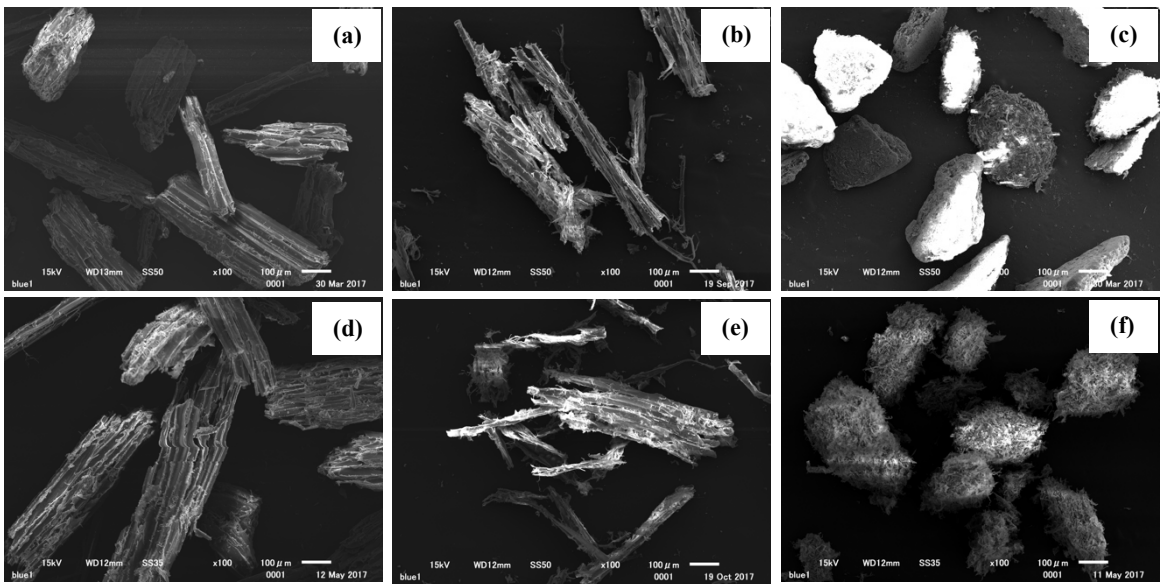

Fig. 5 The SEM image of 180 to 425 μm wood flour. Heat drying condition; (a) 0, (b) 30 and (c) 120 minute of wet milling time. Freezed-drying condition; (d) 0, (e) 30 and (f) 120 minute of wet milling time. 100 times of magnification.

4.1.2 Flexural properties of WPC

Figure 6 showed the relationship between flexural strength of WPC made from 180 – 425 μm wood flour with the wet milling time (a) and the average particle size (b). Figure 6(a) showed that the flexural strength of WPC increased from 0 to 30 minutes of wet milling time. After that, the flexural strength of WPC shows decreased at 120 minutes of wet milling time. The highest and the lowest flexural strength of WPC was found at milling time of 30 minutes and 120 minutes, respectively. Referring to the SEM image on Fig. 5, when focused on un-milled wood flour, we can see the single particle clearly. During the increasing of wet milling time, fibrillation of wood flour occurred. However, we can still see the single particle at 30 minutes of wet milling time. In the case of 120 minute, the aggregated wood flour was found. It was suggested that the aggregation of wood flour occurred when the ball milling time more than 30 minutes applied. The results showed that the flexural strength of WPC for freezed-drying were higher than heat drying conditions for un-milled and milled wood flour. When focused on the un-milled wood flour (0 minutes) and at the maximum flexural of WPC, 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of flexural strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time. These might be due to the difference in aggregation.

Figure 6(b) showed at around 500 μm of average the particle size, during the increasing of wet milling time, the flexural strength of WPC was increased. At this average particle size, it was found the highest flexural strength for freezed-drying condition which is around 90 MPa. After that, the flexural strength decreased at 120 minutes of wet milling time both for heat and freezed-drying. At this condition, the average particle size is lower than 300 μm. In the case of the wet milling time at 120 minutes heat drying was bigger

particle size compared to freezed-drying condition. However, at 120 minutes heat drying showed that flexural strength was smaller and significant difference compared to others condition. The reason of these might be due to the aggregation.

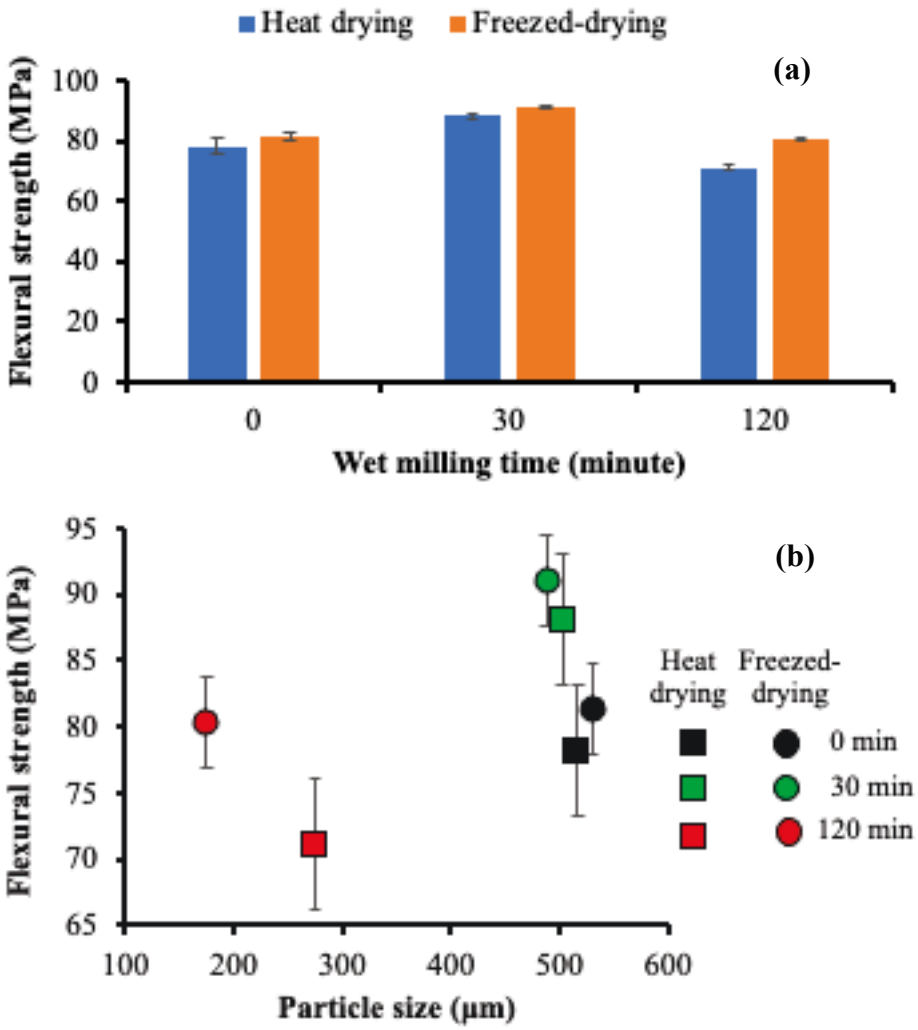

Fig. 6 The relationship between the flexural strength of WPC made from 180 – 425 µm wood flour with (a) the wet milling time and (b) the average particle size.

The relationship between the flexural modulus of WPC made from 180 – 425 µm wood flour with the wet milling time and the average particle size were shown in Fig. 7(a) and (b), respectively. As same trend with flexural strength, Fig. 7(a) showed that the flexural modulus of WPC increased from 0 to 30 minutes of wet milling time. The highest flexural modulus of WPC was found at milling time of 30 minutes. After that, at the wet milling time is 120 minutes, the flexural modulus of WPC decreased. Referring to the SEM image on Fig.

5, when focused on un-milled wood flour, we can see the single particle clearly. During the increasing of wet milling time, fibrillation of wood flour occurred. However, we can still see the single particle at 30 minutes of wet milling time. In the case of 120 minute, the aggregated wood flour was found. It was suggested that the aggregation of wood flour occurred when the ball milling time more than 30 minutes applied. The results showed that the flexural strength of WPC for freezed-drying were higher than heat drying conditions for un-milled and milled wood flour. When focused on the un-milled wood flour (0 minutes) and at the maximum flexural of WPC, 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of flexural strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time. These might be due to the difference in aggregation.

Figure 7(b) showed the same trend with Fig. 6(b) that showed at around 500 μm of average the particle size, during the increasing of wet milling time, the flexural strength of WPC was increased. At this average particle size, it was found the highest flexural strength for freezed-drying condition which is around 3,5 x 10^3 MPa. After that, the flexural strength decreased at 120 minutes of wet milling time both for heat and freezed-drying. At this condition, the average particle size is lower than 300 μm. In the case of the wet milling time at 120 minutes heat drying was bigger particle size compared to freezed-drying condition. However, at 120 minutes heat drying showed that flexural strength was smaller and significant difference compared to others condition. The reason of these might be due to the aggregation.

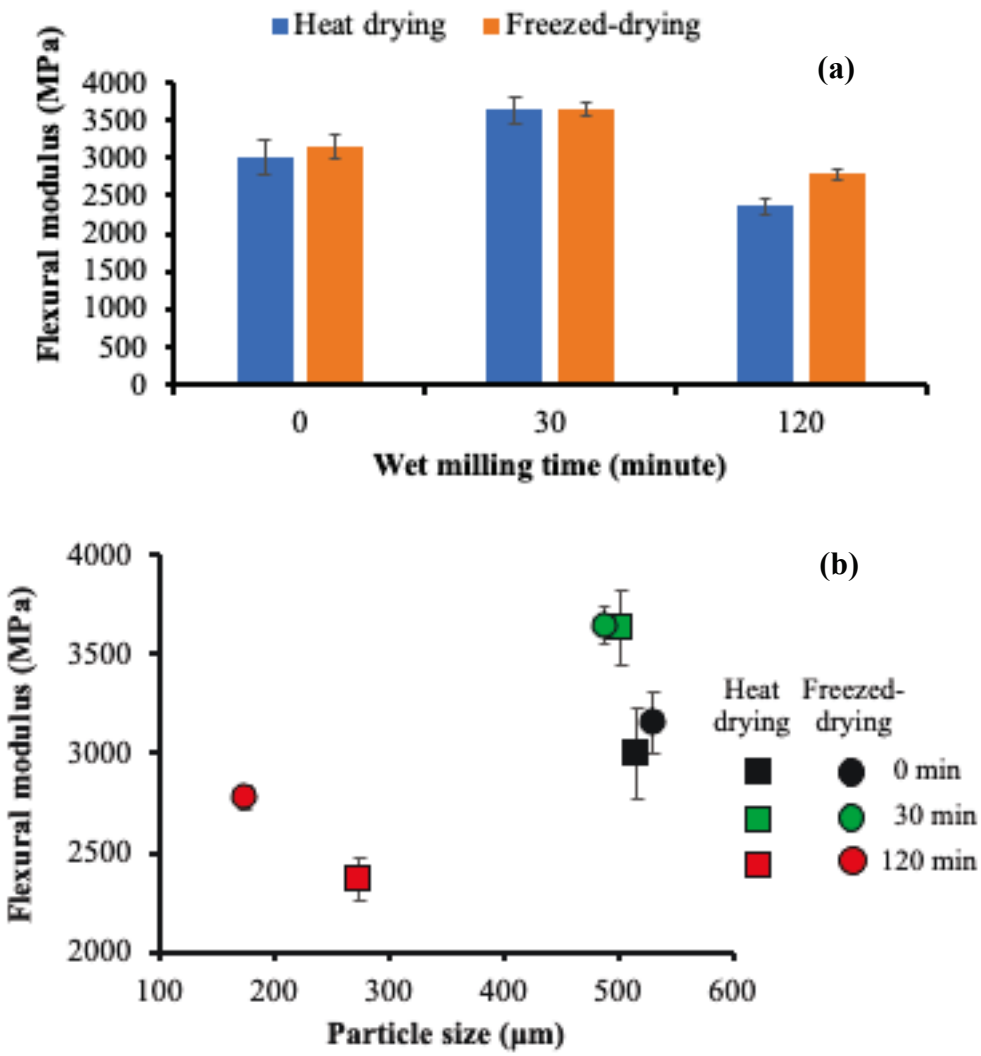

Fig. 7 The relationship between the flexural modulus of WPC made from 180 – 425 µm wood flour with (a) the wet milling time and (b) the average particle size.

4.1.3 Tensile strength of WPC

Figure 8 showed the relationship between tensile strength of WPC made from 180 – 425 µm wood flour with the wet milling time (a) and the average of particle size (b). The result as can be seen in Fig. 8(a) showed that the tensile strength of WPC was increased from 0 to 30 minutes of wet milling time. The highest tensile strength of WPC was found at milling time of 30 minutes. At that time the tensile strength was around 50 MPa for both heat and freezed-drying. After that, at the wet milling time is 120 minutes, the flexural modulus of WPC decreased. Referring to the SEM image on Fig. 5, when focused on un-milled wood flour,

we can see the single particle clearly. During the increasing of wet milling time, fibrillation of wood flour occurred. However, we can still see the single particle at 30 minutes of wet milling time. In the case of 120 minute, the aggregated wood flour was found. It was suggested that the aggregation of wood flour occurred when the ball milling time more than 30 minutes applied. The results showed that the flexural strength of WPC for freezed-drying were higher than heat drying conditions for un-milled and milled wood flour. When focused on the un-milled wood flour (0 minutes) and at the maximum flexural of WPC, 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of flexural strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time. These might be due to the difference in aggregation.

Figure 8(b) showed the same trend with Fig. 8(b) that showed at around 500 μm of average the particle size, during the increasing of wet milling time, the flexural strength of WPC was increased. At this average particle size, it was found the highest flexural strength for freezed-drying condition which is around 3,5 x 10^3 MPa. After that, the flexural strength decreased at 120 minutes of wet milling time both for heat and freezed-drying. At this condition, the average particle size is lower than 300 μm. In the case of the wet milling time at 120 minutes heat drying was bigger particle size compared to freezed-drying condition. However, at 120 minutes heat drying showed that flexural strength was smaller and significant difference compared to others condition. The reason of these might be due to the aggregation.

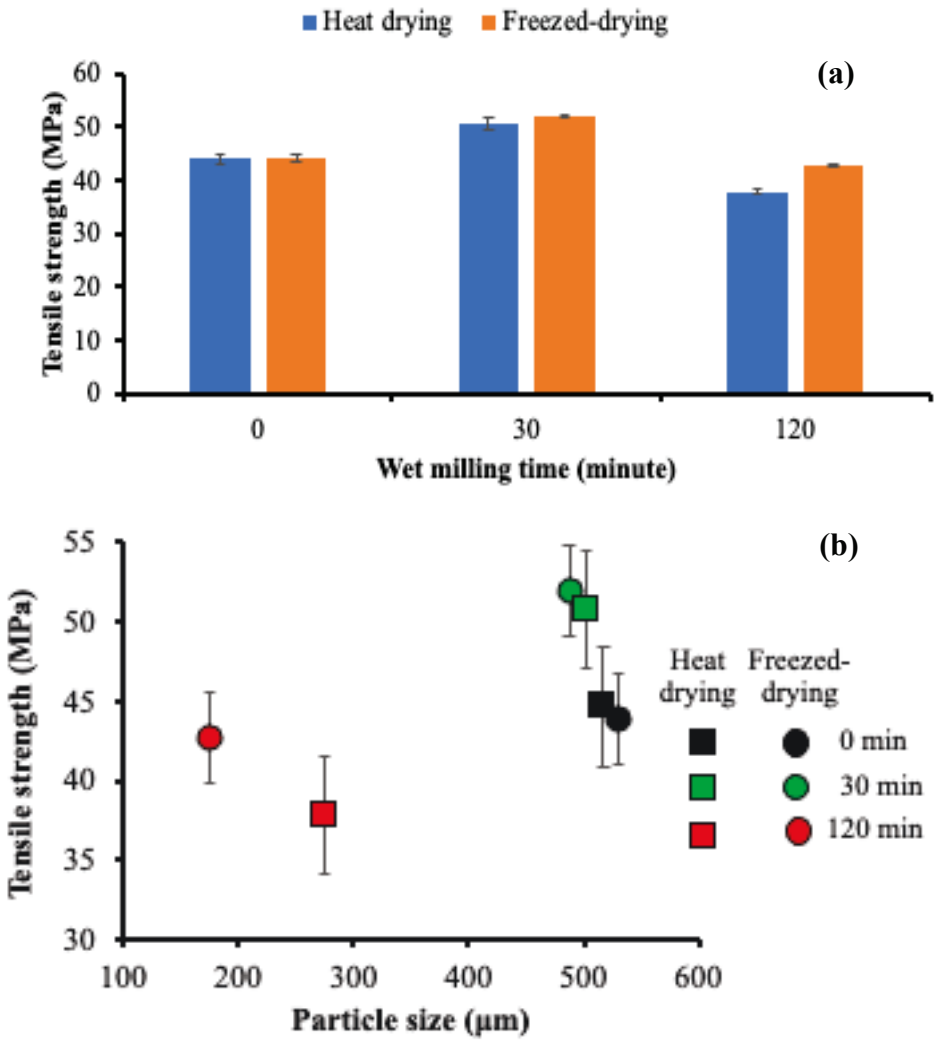

Fig. 8 The relationship between the tensile strength of WPC made from 180 − 425 µm wood flour with (a) the wet milling time and (b) the average particle size.

4.1.4 Izod impact strength of WPC

Figure 9 showed the relationship between Izod impact strength of the WPC made from 180 – 425 μm wood flour with the wet milling time (a) and the particle size (b) of WPC obtained by heat drying and freezed-drying condition. The result showed that the impact strength of WPC for heat drying conditions increased with increasing wet milling time up to 30 minutes. In the case of the wet milling at 120 minutes it shows decreased as shown in Fig. 9(a). When focused on freezed-drying conditions, the trend is similar with heat drying conditions at wet milling time up to 30 minutes. However, in the case of 120 minutes of wet milling time, the impact strength for freezed-drying conditions was higher than heat drying and the has different trend with others condition. The highest impact strength was found for freezed-drying at 120 minutes of wet milling time. These might be due to the difference in aggregation. The result showed that there was no significant difference between impact strength of WPC for heat drying and freezed-drying condition at 0 and 30 minutes of wet milling time. However, there were significant difference of impact strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time.

Figure 9(b) shows the different trend of impact strength compared to the flexural and tensile properties. At the average particle size around 500 μm, during the decreasing of particle size, the impact strength of WPC increased. It was found that there was no significant difference impact strength of WPC for heat drying and freezed-drying condition at 0 and 30 minutes of wet milling time. However, there were significant difference of impact strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time. And the highest impact strength was found for freezed-drying condition at 120 minutes of wet milling time, which is 16 MPa. At this condition, the average particle

size is lower than 300 µm and the freezed-drying has bigger particle size compared to heat drying condition. The reason of these might be due the difference in aggregation.

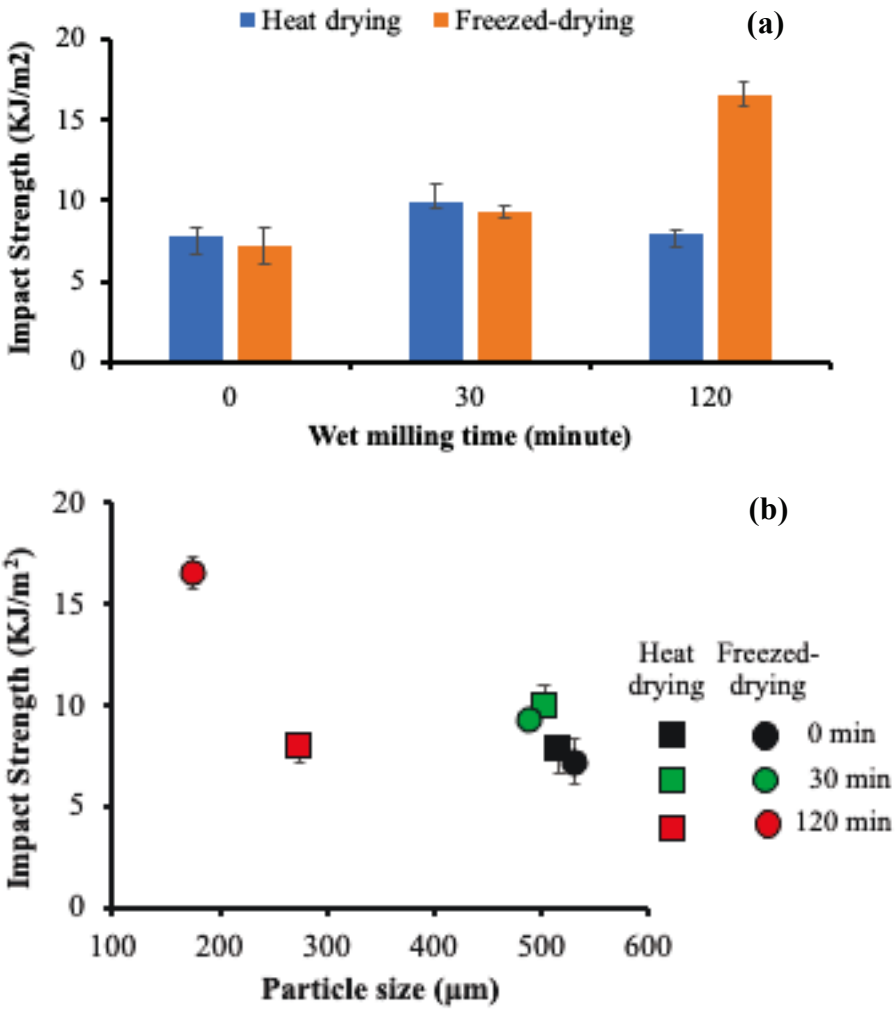

Fig. 9 The relationship between the impact strength of WPC made from 180 – 425 µm wood flour with (a) the wet milling time and (b) the average particle size.

4.1.5 Water resistance properties of WPC

Figure 10 showed the relationship between water absorption of WPC made from 180 – 425 μm wood flour with the time of water resistance test (a) and the average particle size (b) obtained by heat drying and freezed-drying condition. As can be seen in Fig, 10(a), the water absorption of WPC increased during the increasing time of water resistance test, especially from 0 to 360 hours. After that, there was fluctuation value of water absorption around 400 hours and it was saturated at around 5 to 6 % start from 648 to 1032 hour of water resistance test time. When focused on the saturated condition, water resistance properties showed the same trend, even for the large and small particle of wood flour. As observed in Figs. 10(b), there is no significant difference on water absorption at the large and small particle for both of heat drying and freezed-drying condition. However, the lowest water absorption was observed at 120 minutes of wet milling time heat drying condition. The reason of these might be due to the differences of aggregation.

The different structures of the particle may also contribute to different degrees of water uptake. The possibility water to absorb is same because the amount of water itself is same. In the case of aggregated wood flour, even the water amount is same, the size of dimension will expand higher compared to the singular particle of wood flour. During the absorption, first, the water uptake occurred on the surface of the particles; then, the water transferred from one cell lumen to another over time (Mu *et al.*, 2018). The primary and secondary kneading also might influence the speed of water absorption. Under a temperature of 190 ºC, the thermoplastic polymer PP was able to cover the surface of wood flour and would provide greater strength to the WPC. In the case of this kneading process, the particles of thermoplastic polymer PP might be unable to cover such a large number of surfaces of

wood particles. This would affect the water absorption of WPC as a result of the water absorption by the wood.

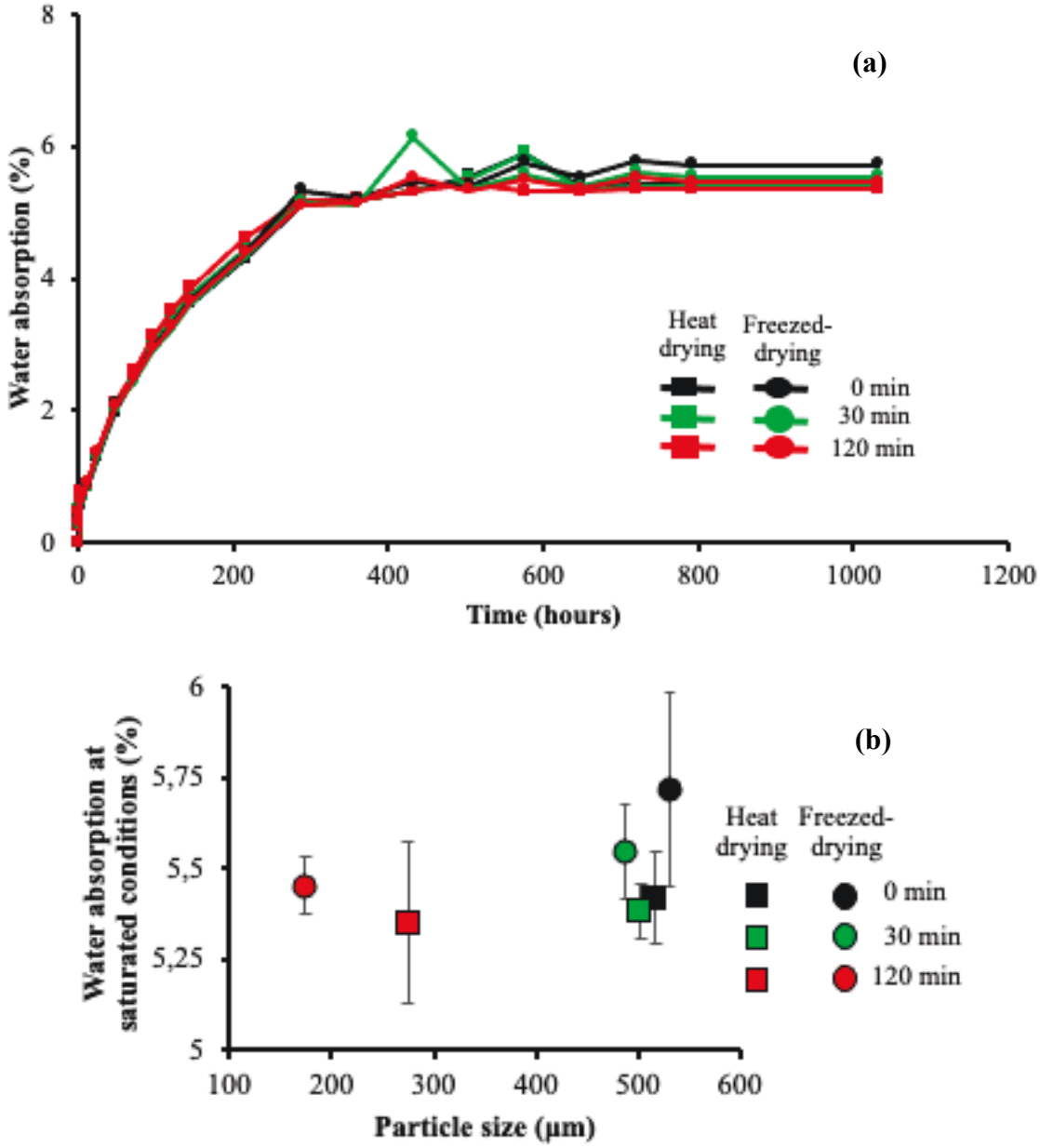

Fig. 10 The relationship between water absorption of WPC made from 180 – 425 µm wood flour at saturated conditions with (a) the time of water resistance test and (b) the average particle size.

Figure 11 showed the relationship between thickness swelling of WPC made from 180 – 425 µm wood flour with the time of water resistance test (a) and the average particle size (b) obtained by heat drying and freezed-drying condition. As similar with water

absorption trends, an increasing the time of water resistance test, the thickness swelling of WPC increased. As can be seen in Fig 11(a) it was occurred at 0 to 360 hours of water resistance test time. After that, there was fluctuation value of thickness swelling up to 600 hours and it was saturated from 648 to 1032 hour of water resistance test time. When focused on the saturated condition, water resistance properties showed the same trend, even for the large and small particle of wood flour. As observed in Figs. 11(b), the highest thickness swelling of WPC was observed at un-milled (0 minutes) of wet milling time. In the case of milled wood flour, there is fluctuation of thickness swelling among different wet milling times. During decreasing of particle size, the thickness swelling of WPC decreased. It was meant the milling process has positive effect for thickness swelling properties of WPC. The reason of these might be due to the difference of aggregation and contributed to difference degrees of water uptake, especially dimensional swelling of the composites. The result showed that there was no significant difference on thickness swelling at the large and small particle. However, there were significant difference of thickness swelling between the heat drying and freezed-drying condition at 0, 30, and 120 minutes of wet milling time, respectively.

According to Mu *et al.*, (2018) that said different particle structure may also contributed to different degrees of water uptake on the dimensional swelling of the composites. The possibility water to absorb is same because the amount of water itself is same. However, in the case of thickness swelling, specifically on the aggregated wood flour, even the water amount is same, the size of dimension will expand higher compared to the singular particle of wood flour. The primary and secondary kneading also might be affected the speed of water absorb. Under a temperature of 190 ºC conditions, the thermoplastic polymer PP was able to cover a more specific area of wood particles and will provide the greater strength of WPC. In the case of this kneading process, allegedly that the particles of

thermoplastic polymer PP were unable to cover such a large number of surfaces of wood particles. This would be affected the thickness swelling of WPC as a result of wood absorbs the water and plastic instead of it, does not absorb the water.

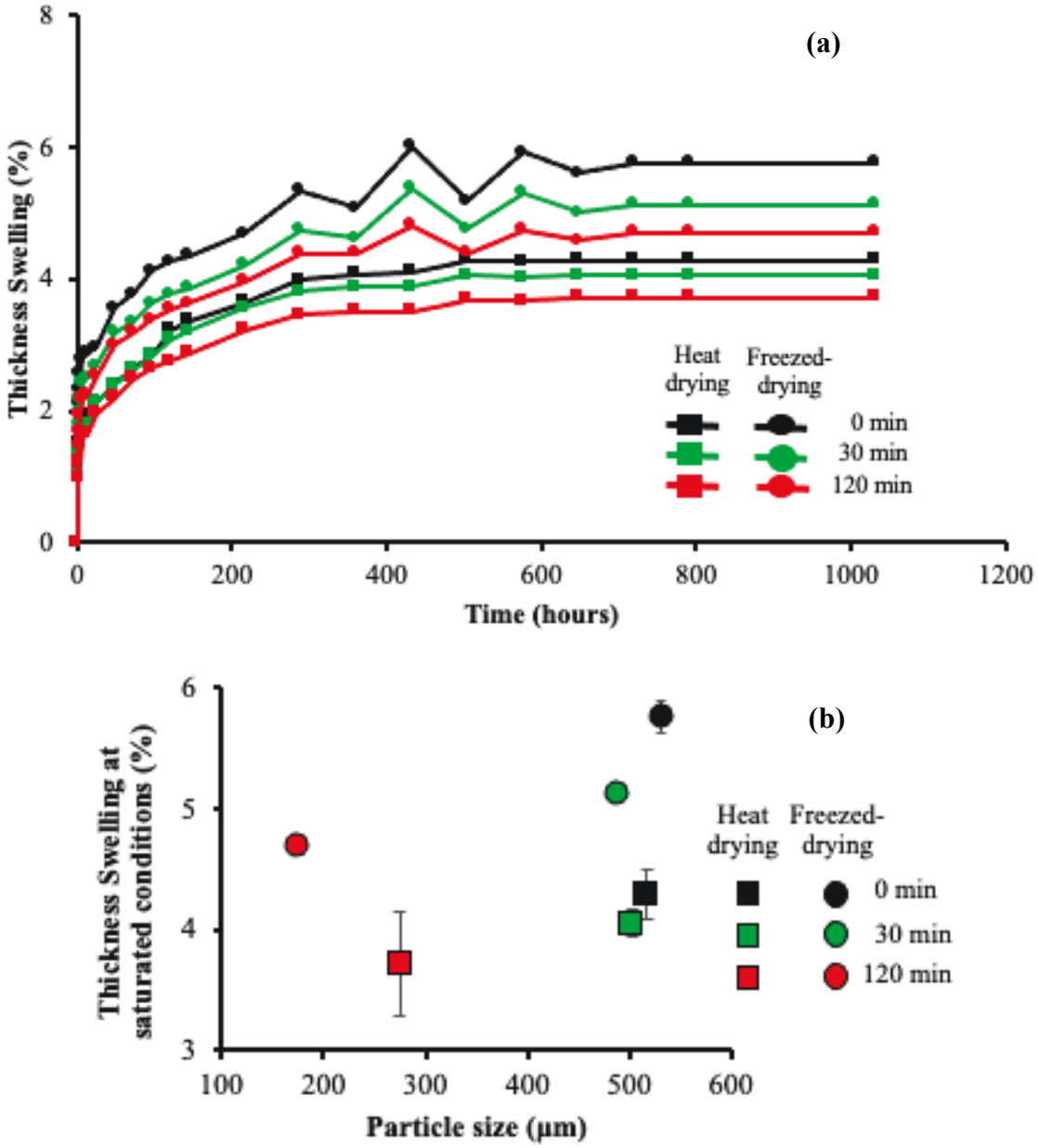

Fig. 11 The relationship between the thickness swelling of WPC made from 180 – 425 µm wood flour at saturated conditions with (a) the time of water resistance test and (b) the average particle size.

The relationship between predicted maximum water absorption or thickness swelling of WPC with the adsorption speed of water was shown in Fig. 12. As mentioned in chapter

3, the saturation point at a maximum of water resistance properties was A, and the speed of water uptake was B. The lower A would have a positive effect on the mechanical properties of WPC and the higher value of B signify that it was lower speed of absorb and drain the water. The result showed that during the increasing of wet milling time, the maximum water absorption for heat drying and freezed-drying was decreased as can be seen in Fig. 12(a). However, in the case of the speed of water uptake showed he opposite trend. As increasing of the wet milling time, the speed of water uptake was increased both for heat and freezed-drying. Figure 12(b) showed the maximum thickness swelling of heat drying and freezed-drying was decreased during the increasing of wet milling time. It was followed by same trend of the water uptake speed heat drying condition, that was also decreased during the increasing of wet milling time. In the case of freezed-drying condition, the speed of water uptake was increased from 0 to 30 minutes of wet milling time. After that, it was decreased during the increasing of wet milling time to 120 minutes. Based on the fact, the optimum condition would occur when the WPC has low water absorption and thickness swelling with the low speed of water uptake was observed.

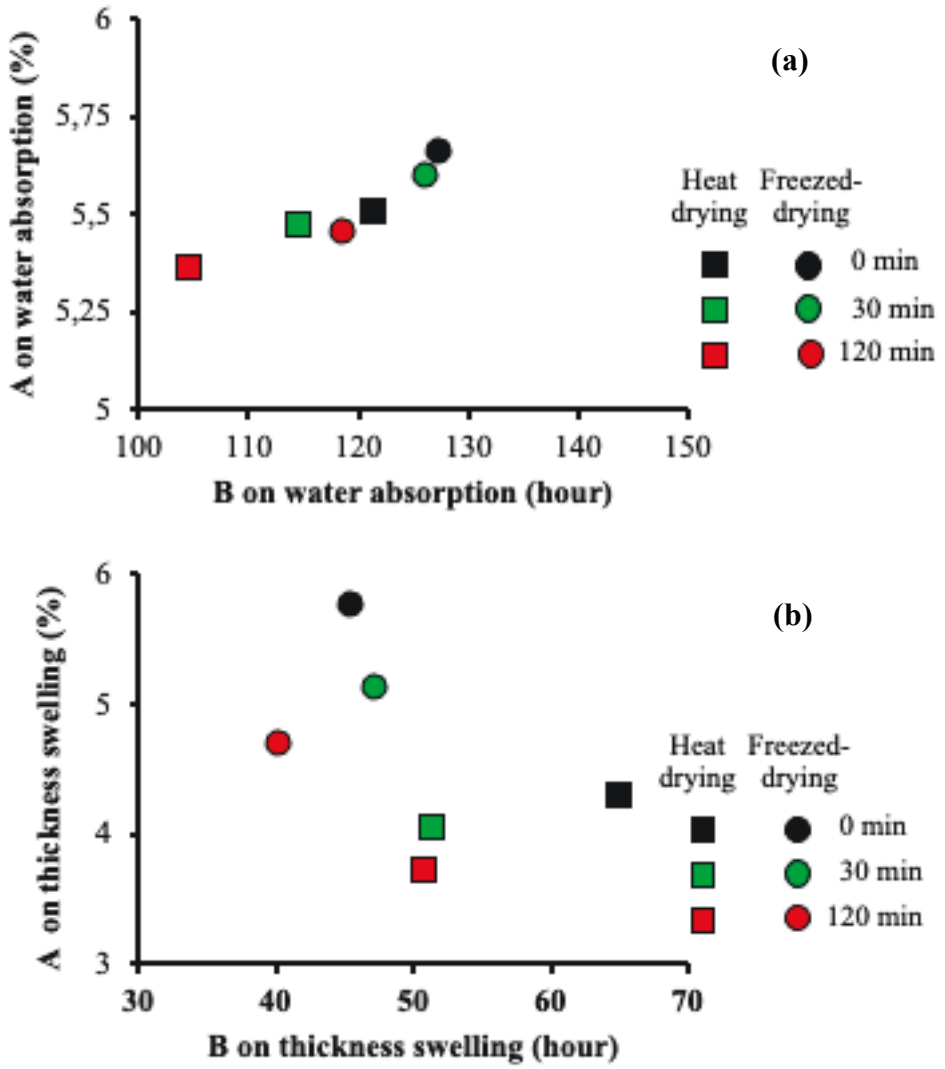

Fig. 12 The relationship between predicted maximum value A versus B on (a) water absorption and (b) thickness swelling of WPC made from 180 – 425 µm wood flour.

4.2 The effect of wet milling time on the mechanical properties of WPC

4.2.1 Percentage of wood flour and particle size distribution

According to Table 5 and 6, the percentage of dried wood flour for 90 - 180 μm of mesh pass obtained by heat drying and freezed-drying were investigated. Upon increasing the time of ball milling, the percentage of dried wood flour increased up to 30 min of wet milling time. Thereafter, the percentage of dried wood flour slightly decreased up to 60 min of wet milling time. However, a significant decline from 22 to 9% was found for heat drying at a milling time of 60 to 120 min. The reason for this could be aggregation, which is discussed later. Conversely, at the same wet milling time, the percentage of dried wood flour showed a significant increase for the freezed-drying condition. Under this condition, the percentage increased from 25 to 35%. It is suggested that freezed-drying prevented the aggregation of wood flour.

The particle distribution of dried-wood flour after the screening process for 90 to 180 μm is shown in Fig. 13. Even after the screening process, there were particles with sizes of less than 90 μm and more than 180 μm. This caused the particles to exhibit complex and irregular shapes, such that their particle size cannot be directly defined by this measurement. Therefore, there may be some particle sizes outside of the range of the relevant category. The wood flour obtained with heat drying condition can be seen in Fig. 14(a) and the dried wood flour under the freezed-drying condition can be seen in Fig. 14(b). Deviation of particle size distribution of the produced wood flour depends on the milling conditions. The standard deviation of freezed-drying condition showed higher than the standard deviation for heat drying, especially at the longer wet milling time. It was meant the particle size distribution of the freezed-drying condition was wider than that for the heat drying condition.

Therefore, the highest intensity of particle size for the freezed-drying condition was lower than that for the heat drying. From 0 to 30 min of wet milling time, there was no peak for the larger particle size near 1000 μm. However, for milling times of 40 up to 120 min, the peak was shown to decrease with increase in the wet milling time. Under those conditions, the intensity for the freezed-drying condition was higher than that for the heat drying condition. For the particle size near 100 μm, the intensity decreased as the wet milling time increased up to 30 min. However, the intensity for a particle size near 100 μm from 40 - 120 min increased with increase in the wet milling time. The highest intensity of milled wood flour for the heat drying condition was observed at a wet milling time of 120 min, which might be due to aggregation. In the case of the smaller particle size near 20 μm, heat drying and freezed-drying conditions showed the same trend. As the wet milling time increased, the intensity near 20 μm increased. Under this condition, the intensity for freezed-drying was higher than that for the heat drying condition.

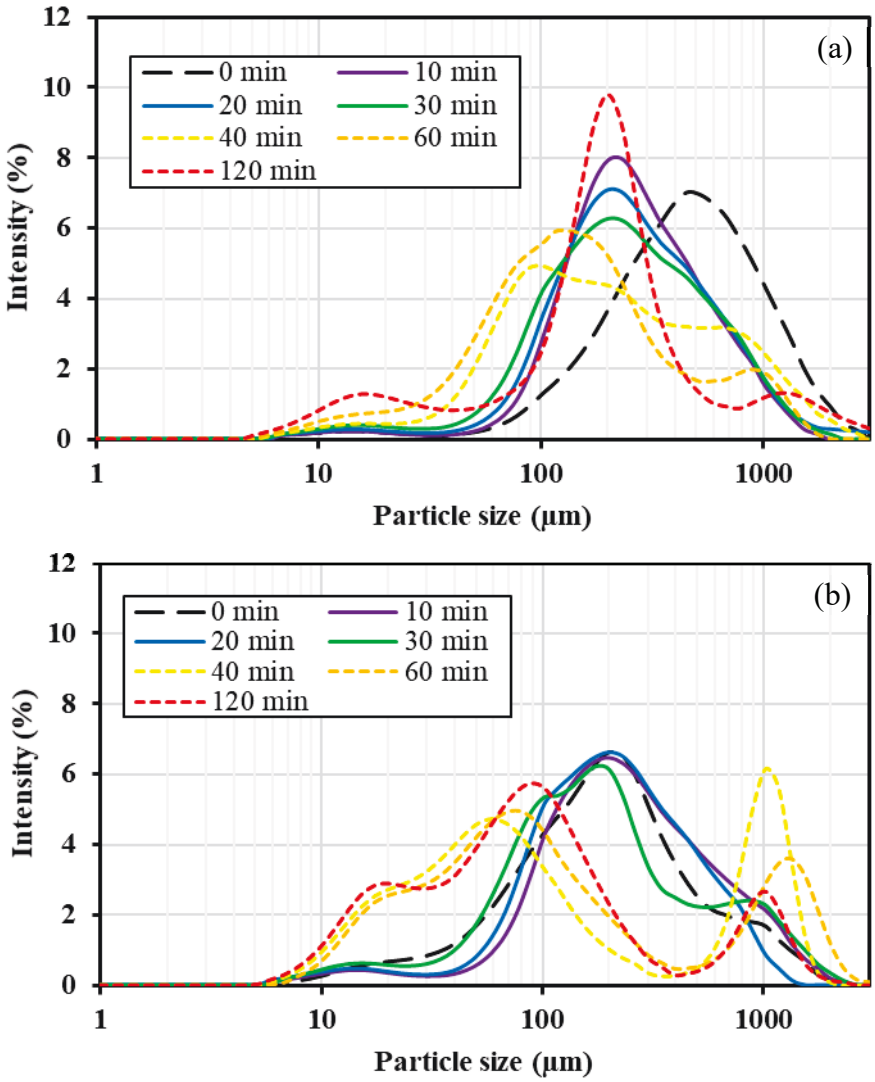

Fig. 13 The particle size distribution after the screened process for 90 to180 μm obtained by (a) heat drying condition and (b) freezed-drying condition.

SEM images for wood flour at wet milling times 0, 30, and 120 min are shown in Fig. 14. As can be seen in Figs. 14(a) and (d), there was an intact single particle for 0 min wood flour. At the wet milling time of 30 min, there was a fibrillated particle under both heat drying and freezed-drying conditions, as shown in Figs. 14(b) and (e). However, at 120 min of wet milling time, it was found that the different surface characteristic of particle size between heat drying and freezed-drying. As can be seen in Fig. 14(c), the surface of the heat drying wood flour was flat and low aspect ratio compared to 30 min (see Fig. 14(b)). This is due to the strong aggregation of milled small wood flour. This observation reinforces the

drastic increase of the intensity around 200 μm at wet milling time of 120 min in the particle size distribution on Fig. 14(a). As can be seen in Fig. 14(f), in the case of freezed-drying at ball milling time of 120 min, each particle size was smaller than heat drying and its surface was fibrillated. It is suggested that the 120 min of wet milling time produced the fibrillated particle and freezed-drying suppressed the aggregation of smaller particles compared to heat drying. The average particle size at a wet milling time of 120 min for the heat drying condition was higher than that for freezed-drying (see Fig. 15), demonstrating that aggregation occurred in this condition. However, wood flour became finer in the case of freezed-drying conditions.

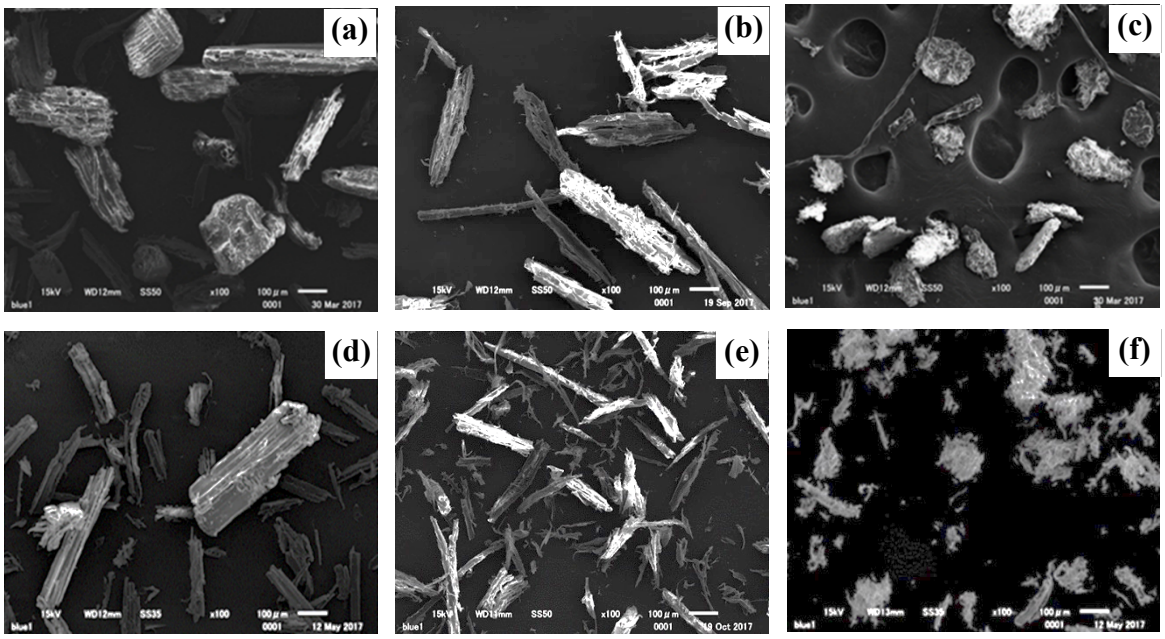

Fig. 14 The SEM image of 90 to180 μm wood flour. Heat drying condition; (a) 0, (b) 30 and (c) 120 minute of wet milling time. Freezed-drying condition; (d) 0, (e) 30 and (f) 120 minute of wet milling time. 100 times of magnification.

The average particle size is calculated from the particle size distribution data by a laser diffraction particle analyzer machine. As shown in Fig. 15, the average particle size of wood flour for heat drying decreased at a wet milling time of 10 min. At that time, the average particle size significantly decreased from 527 to 311 μm and then increased to 333 μm at 20 min. However, the average particle size was decreased to 305 μm at a wet milling time of

30 min and increased again to 329 μm at a wet milling time of 40 min. Finally, it increased drastically from 227 to 293 μm, from 60 to 120 min of wet milling time. There was an increase in the average particle size under freezed-drying conditions from 266 to 320 μm at a wet milling time of 0 to 10 min, then decreased to 250 μm at 20 min. However, the average particle size increased again from 287 to 322 μm from a wet milling time of 30 to 40 min. Finally, it decreased rapidly from 331 to 194 μm when the wet milling time was 60 up to 120 min. There was no clear relationship between the average particle size and wet milling time. Therefore, another parameter, which could be used to explain the relationship between wet milling time and mechanical properties of the WPC was needed.

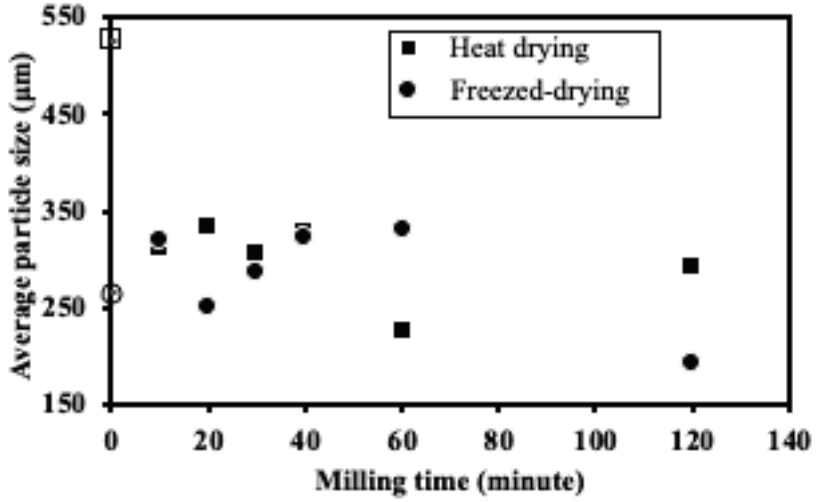

Fig. 15 The relationship between average particle size and milling time. □ heat drying at 0 min and ○ freezed-drying at 0 min.

The correlation coefficient (*R*) between the intensity at any particle size (*Ip*) and mechanical properties are calculated as the following equation (8).

$$R_{M,Ip} = \frac{\sum(M_t - \bar{M})\,(Ip_t - \overline{Ip})}{\sqrt{\sum(M_t - \bar{M})^2 \sum(Ip_t - \overline{Ip})^2}} \qquad \text{... (8)}$$

where $M_t, \bar{M}, Ip_t,$ and $\overline{Ip}$ are any mechanical property at wet milling time *t*, mean mechanical property, intensity at *p* μm on the particle size distribution of wet milling time *t* and its mean intensity, respectively. *R* is calculated for the intensity at any particle size versus flexural

modulus, tensile strength, and Izod impact strength. Because the particle size distribution pattern on freeze-dried and heat dried wood flour were different, *R* for freezed-drying and heat drying were separately calculated. Note that *R* is the parameter to evaluate only the 'linear' relationship between intensity and mechanical properties. The relationship between intensity and mechanical properties is not necessarily linear; therefore, *R* is not a perfect parameter to determine the effective particle size that relates to the mechanical properties.

The correlation vector of the mechanical properties for each wood flour size was observed. The results showed that the mechanical properties at a particle size smaller than 100 μm had negative correlation. Inversely, particle size from 100 – 900 μm had positive correlation for each mechanical properties of WPC. For heat dried wood flour, correlation vector for mechanical properties at smaller particle less than 30 μm had a negative correlation. However, particle size around 40 – 100 μm and around 200 μm showed positive and negative correlation, respectively. The highest correlation between mechanical properties was observed at a particle size 77.3 μm. Therefore, the intensity at 77.3 μm was used as the parameter of smaller particle. On the other hand, the intensity at 678.5 μm, which also indicated a higher correlation between each mechanical property, was defined as the parameter of larger particle. Figure 16 shows the relationship between wet milling time and the intensity at the (a)small and (b)large particles. As milling time increased, the intensity increased until 60 min. In the case of heat drying, the intensity at wet milling time of 120 min drastically decreased. This results in the decrease of smaller particles due to aggregation during heat drying. In the case of freezed-drying, the intensity at 678.5 μm linearly decreased until 60 min and then reached saturation. This suggests that the large particle was successfully pulverized at 60 min of wet milling time. In the case of heat drying, the intensity did not decrease at less than 40 min. The wet milling condition for both freeze and heat

drying were identical; therefore, this might be due to the aggregation of small wood flour particles.

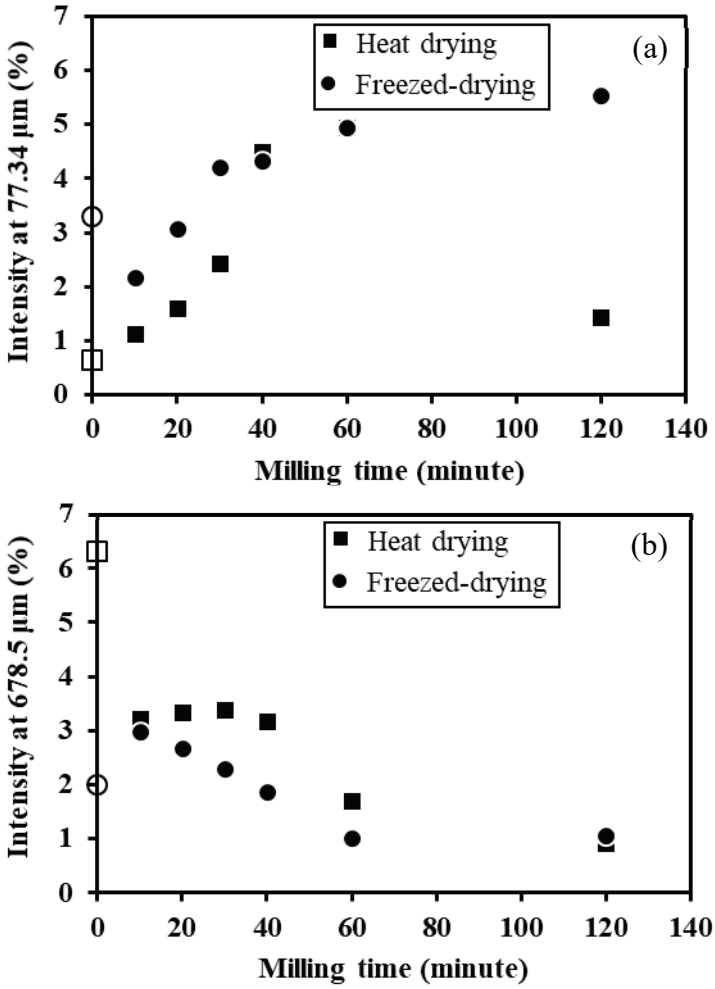

Fig. 16 The relationship between wet milling time and intensity of the particle size distribution analysis at (a) 77.3 µm and (b) 678.5 µm. □ heat drying at 0 min and ○ freezed-drying at 0 min.

4.2.2 Flexural properties of WPC

Figure 17 showed the relationship between flexural strength with the wet milling time (a) and the average particle size (b). Figure 17(a) showed that the flexural strength of WPC increased from 0 to 30 minutes of wet milling time. The highest flexural strength of WPC was found at milling time of 30 minutes. After that, from 40 to 120 minutes of wet milling time the flexural strength of WPC decreased. Referring to the SEM image on Fig. 14, it was

suggested that the aggregation of wood flour occurred start from 40 minutes of wet milling time. In the case of 120 minutes wet milling time, the flexural strength of WPC decreased under the same wet milling time. At that time the flexural strength of WPC for freezed-drying were higher than heat drying conditions. When focused on the maximum flexural of WPC, 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of flexural strength between both of heat drying and freezed-drying condition at 120 minutes of wet milling time. These might be due to the difference in aggregation.

Figure 17(b) showed at 300 to 500 μm of average the particle size, during the increasing of wet milling time, the flexural strength was increased. Around 300 μm of the average particle size were found the optimum flexural strength. At this condition, the average particle size, the flexural strength was around 90 MPa. When focused on the average particle size lower than 300 μm, during the decreasing of wet milling time, the flexural strength of WPC decreased. In the case of the wet milling time at 120 minutes heat drying was bigger particle size and be around the optimum average particle size. However, it showed that flexural strength was smaller compared to others condition. The reason of these might be due to the aggregation.

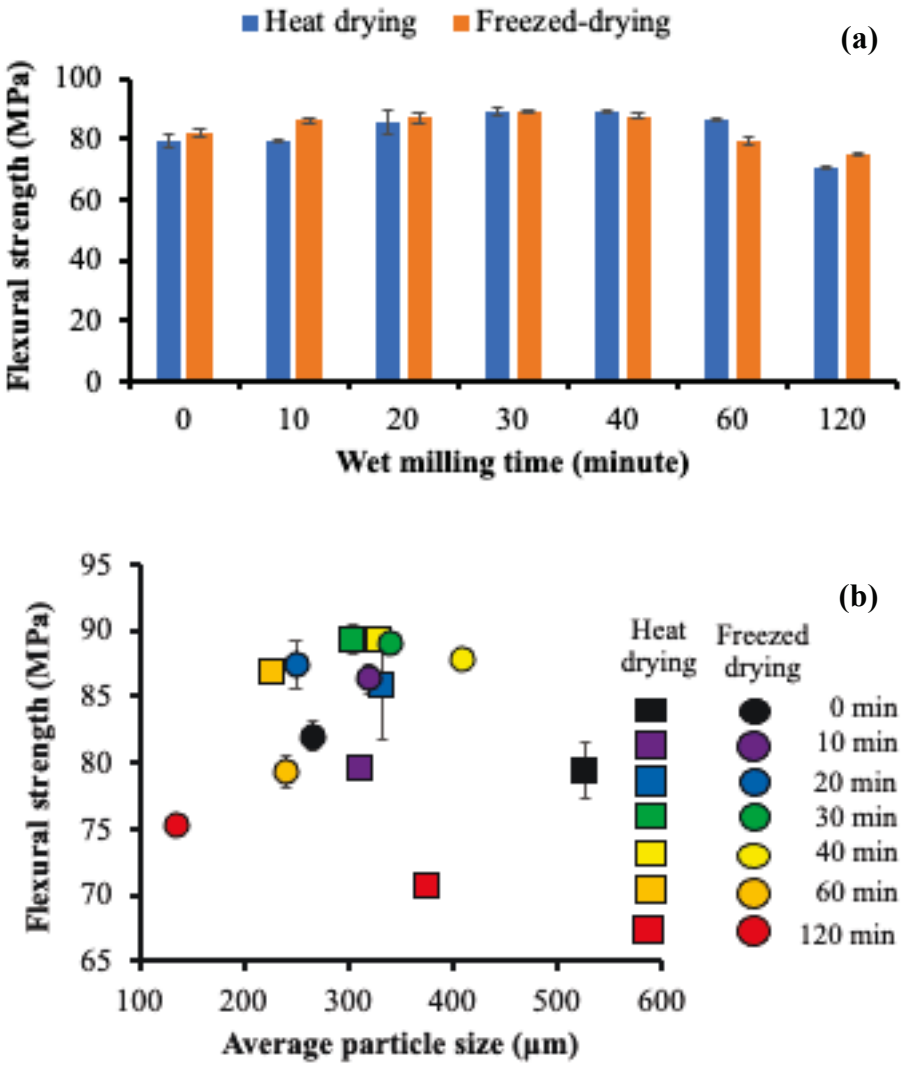

Fig. 17 The relationship between the flexural strength of WPC with (a) the wet milling time and (b) the average particle size.

The relationship between the mechanical properties of WPC and the intensity of small or large particles were investigated. Figure 18 shows the relationship between the flexural strength and the intensity of small and large particles. As shown in Fig. 18(a), an excessive percentage of small particles resulted in the decrease of flexural strength. In the case of large particle, as shown in Fig. 18(b) the flexural modulus decreased during decreasing the intensity. The lowest flexural modulus was observed under the condition of heat drying with a wet milling time of 120 min. As described above, the wet milling condition is the same for both freezed and heat drying. Therefore, the actual amounts of

smaller particles for the same milling time must be identical. It is suggested that the aggregation of smaller particles during heat drying reduces the apparent intensity for the small particles. The fact that the flexural strength for small and large particle at 120 min of wet milling time showed a similar trend, that for freezed-drying is higher than that for heat drying. When the number of particles existing in WPC is considered, number of freeze-dried particles should be larger than that of heat dried particles. By contrast, when we focused on the size of the particle, flexural modulus for heat drying condition should be higher than freezed-drying one since heat drying wood flour is larger than freezed-drying wood flour. However, heat drying sample showed slightly lower flexural strength than freezed-drying sample. It is suggested that in the case of increasing this aggregated wood flour, the flexural strength decreased. These results suggest that the aggregated particle may reduce the reinforcement efficiency between the entanglement of PP side.

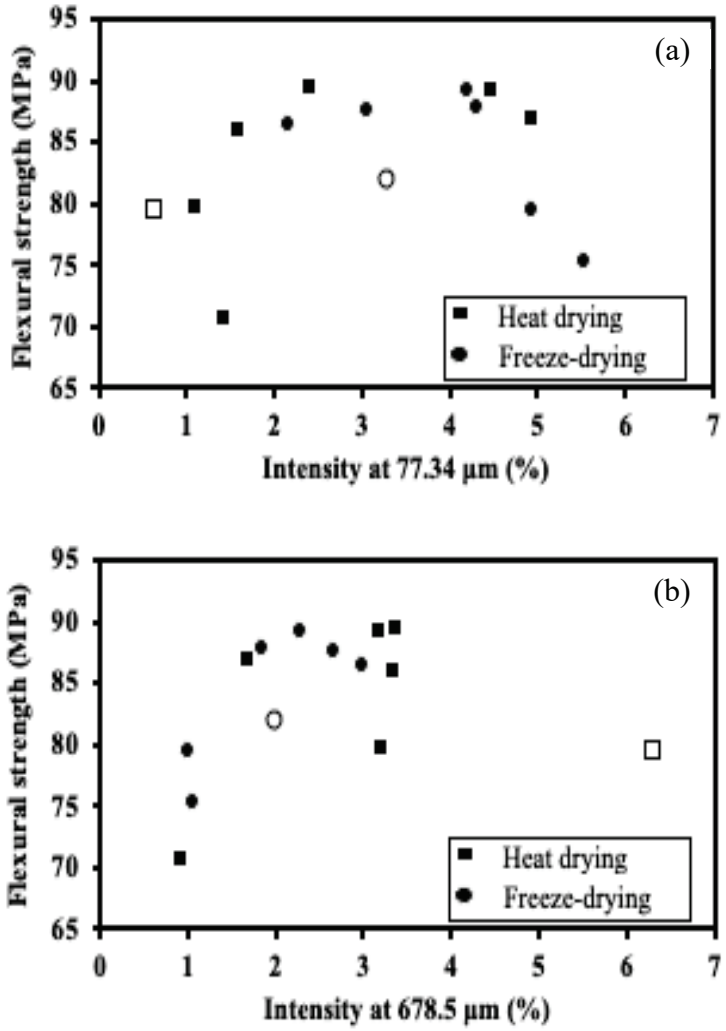

Fig. 18 The relationship between flexural modulus of WPC and intensity of the particle size distribution analysis at (a) 77.3 µm and (b) 678.5 µm. □ heat drying at 0 min and ○ freezed-drying at 0 min.

Figure 19 showed the relationship between the flexural properties with the average particle size in unit of micrometers. The relationship between the flexural modulus with the wet milling time and the average particle size were shown in Fig. 19(a) and (b), respectively. As same trend with flexural strength, Fig. 19(a) showed that the flexural modulus of WPC increased from 0 to 30 minutes of wet milling time. The highest flexural modulus of WPC was found at milling time of 30 minutes. After that, from 40 to 120 minutes of wet milling time the flexural modulus of WPC decreased. Referring to the SEM image on Fig. 14, it was suggested that the aggregation of wood flour occurred start from 40 minutes of wet

milling time. In the case of 120 minutes wet milling time, the flexural modulus of WPC decreased under the same wet milling time. At that time the flexural modulus of WPC for freezed-drying were higher than heat drying conditions. When focused on the maximum flexural of WPC, 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of flexural modulus between both condition of heat drying and freezed-drying at 120 minutes of wet milling time. These might be due to the difference in aggregation.

Figure 19(b) showed the same trend with Fig. 18(b) that at 300 to 500 μm of average the particle size, during the increasing of wet milling time, the flexural modulus was increased. Around 300 μm of the average particle size were found the optimum flexural modulus. At that average particle size, the flexural modulus was around 3.5 x 10^3 MPa. When focused on the average particle size lower than 300 μm, during the decreasing of wet milling time, the flexural modulus of WPC decreased. In the case of the wet milling time at 120 minutes heat drying was bigger particle size and be around the optimum average particle size. However, it showed that flexural modulus was smaller compared to others condition. The reason of these might be due to the aggregation.

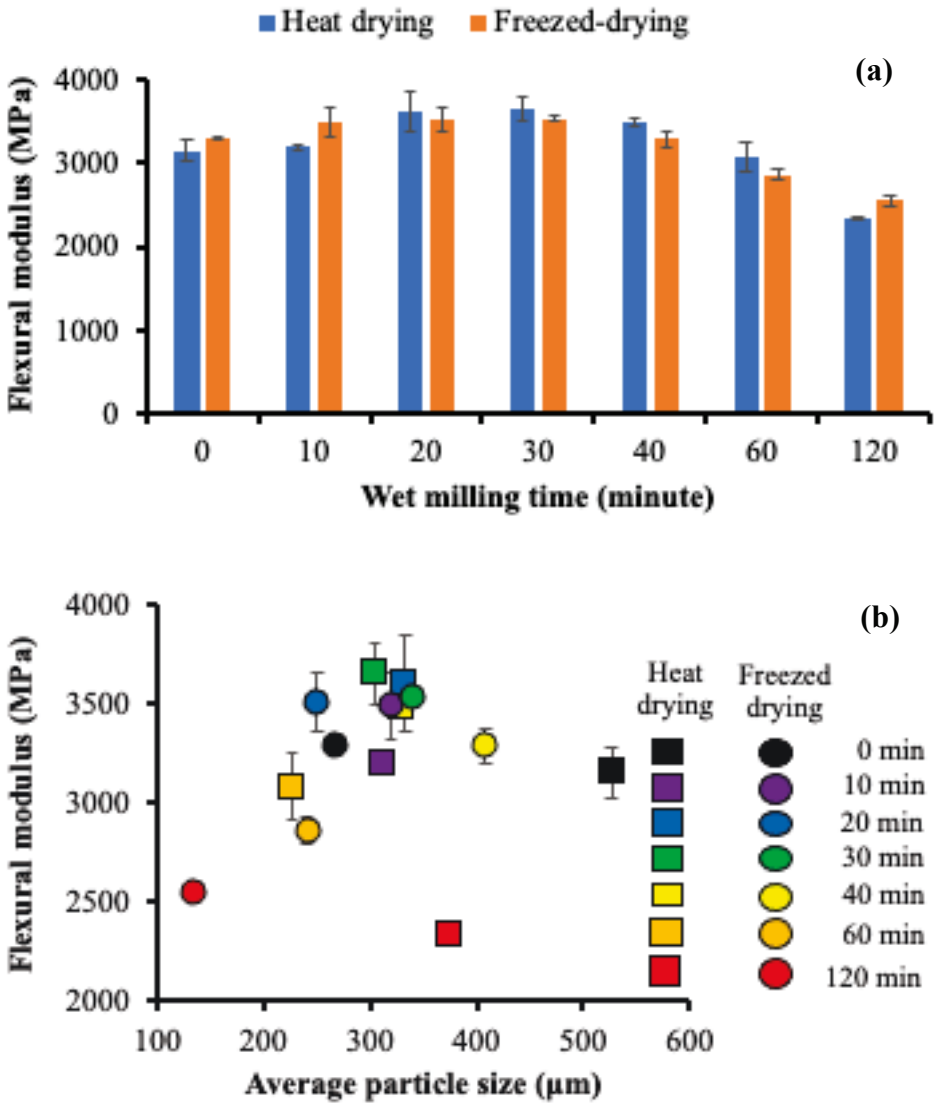

Fig. 19 The relationship between the flexural modulus of WPC with (a) the wet milling time and (b) the average particle size.

The relationship between the mechanical properties of WPC and the intensity of small or large particles were investigated. Figure 20 shows the relationship between the flexural modulus and the intensity of small and large particles. As shown in Fig. 20(a), an excessive percentage of small particles resulted in the decrease of flexural modulus. In the case of large particle, as shown in Fig. 20(b) the flexural modulus decreased during decreasing the intensity. The lowest flexural modulus was observed under the condition of heat drying with a wet milling time of 120 min. As described above, the wet milling condition is the same for both freeze and heat drying. Therefore, the actual amounts of

smaller particles for the same milling time must be identical. It is suggested that the aggregation of smaller particles during heat drying reduces the apparent intensity for the small particles. The fact that the flexural modulus for small and large particle at 120 min of wet milling time showed a similar trend, that for freezed-drying is higher than that for heat drying. When the number of particles existing in WPC is considered, number of freeze-dried particles should be larger than that of heat dried particles. By contrast, when we focused on the size of the particle, flexural modulus for heat drying condition should be higher than freezed-drying one since heat drying wood flour is larger than freezed-drying wood flour. However, heat drying sample showed slightly lower flexural modulus than freezed-drying sample. It is suggested that in the case of increasing this aggregated wood flour, the flexural modulus decreased. These results suggest that the aggregated particle may reduce the reinforcement efficiency between the entanglement of PP side.

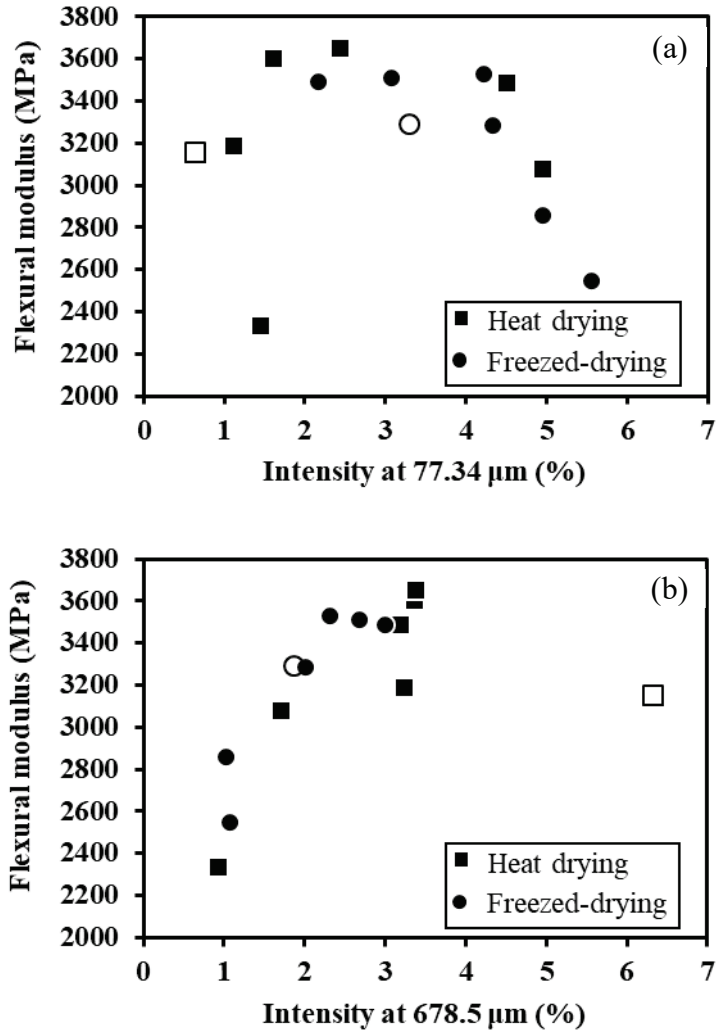

Fig. 20 The relationship between flexural modulus of WPC and intensity of the particle size distribution analysis at (a) 77.3 µm and (b) 678.5 µm. □ heat drying at 0 min and ○ freezed-drying at 0 min.

4.2.3 Tensile strength of WPC

Figure 21 showed the relationship between tensile strength with the wet milling time (a) and the average of particle size (b), respectively. The result as can be seen in Fig. 21(a) showed that the tensile strength of WPC was increased from 0 to 30 minutes of wet milling time. The highest tensile strength of WPC was found at milling time of 30 minutes. At that time the tensile strength was around 50 MPa for both heat and freezed-drying. After that, from 40 to 120 minutes of wet milling time the tensile strength of WPC was decreased. Referring

to the SEM image on Fig. 14, it was suggested that the aggregation of wood flour occur start from 40 minutes of wet milling time.

Figure 21(b) showed that the as decreasing of average particle size, the tensile strength was increased. Around 300 μm of the average particle size was found the optimum tensile strength. In the case of 120 minutes wet milling time, the tensile strength of WPC decreased under the same wet milling time. At that time the tensile strength of WPC for freezed-drying was higher than heat drying. When focused on the maximum flexural property of WPC, that was at 30 minutes of wet milling time, there was no significant difference between heat drying and freezed-drying condition. However, there were significant difference of tensile strength between heat drying and freezed-drying condition at 120 minutes of wet milling time. These might be due to the differences in the aggregation.

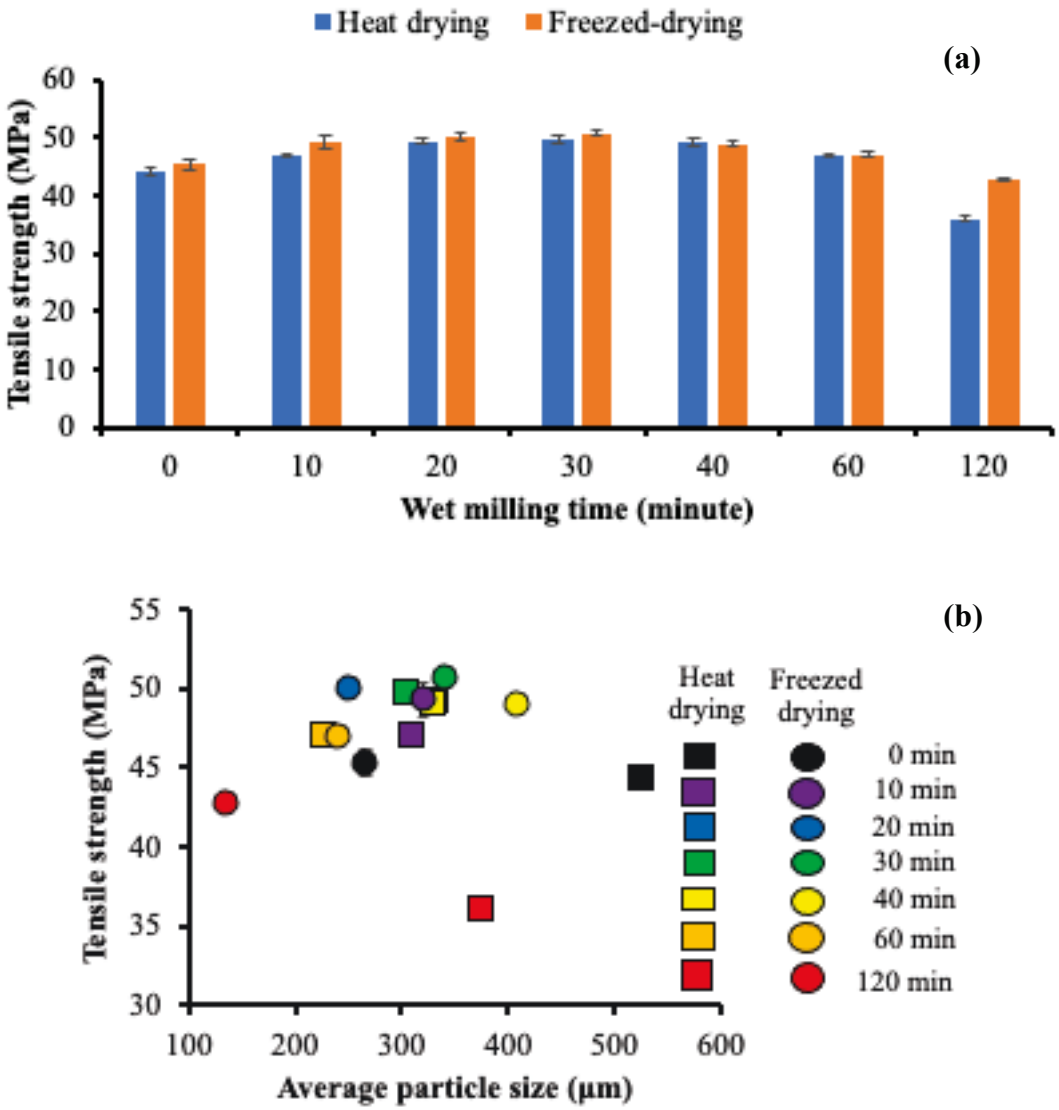

Fig. 21 The relationship between tensile strength of WPC with (a) the wet milling time and (b) the average particle size.

The relationship between tensile strength and intensity on small and large particle is shown in Fig. 22. In the case of 77.3 μm, higher tensile strength was exhibited when the intensity was around 2 - 4% (see Fig. 22(a)). Neither an over- nor an under-percentage of intensity decreased the tensile strength. It is suggested that there is an appropriate amount of small particle that would yield the desired tensile strength of WPC. The flexural modulus for 120 min of wet milling with heat drying showed notably lower values than that for freezed-drying, indicating the aggregation of smaller particle influencing the tensile strength

of WPC. Contrarily, no relation between the intensity at 678.5 μm and tensile strength was observed (see Fig. 22(b)).

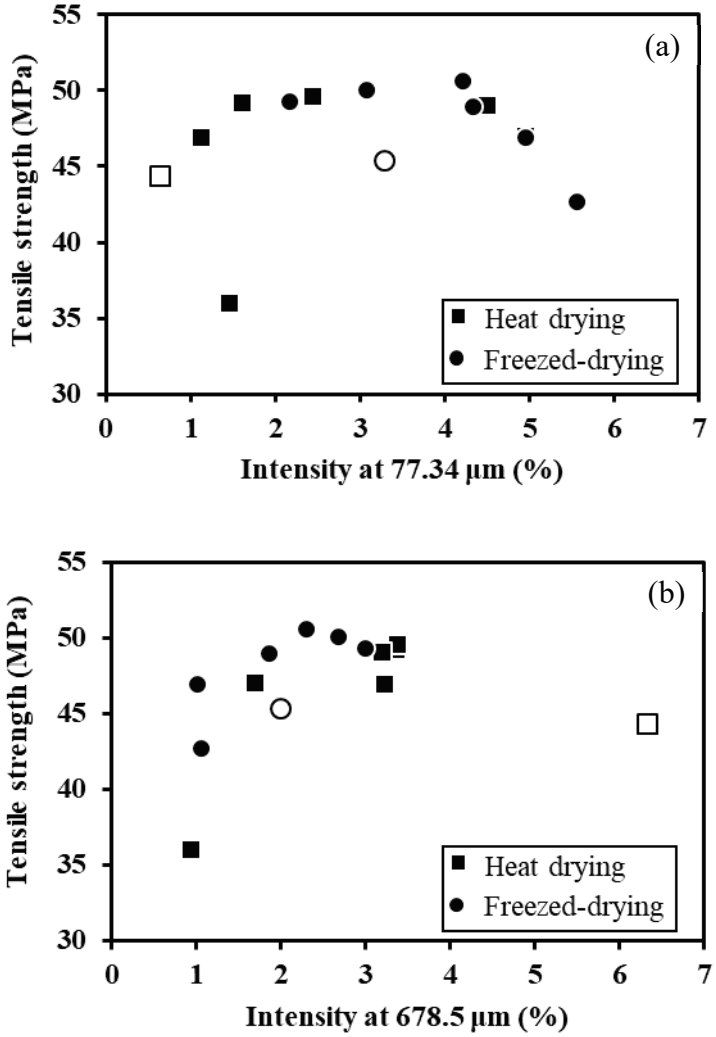

Fig. 22 The relationship between tensile strength of WPC and intensity of the particle size distribution analysis at (a) 77.3 μm and (b) 678.5 μm. □ heat drying at 0 min and ○ freezed-drying at 0 min.

4.2.4 Izod impact strength of WPC

Figure 23 showed the relationship between Izod impact strength and wet milling time (a), also impact strength and particle size (b) of WPC obtained by heat drying condition and freezed-drying. The result showed that the impact strength increased with increasing wet milling time and at the time more than 40 minutes it slightly decreased as shown in Fig.

23(a). In case of the wet milling time at 120 minutes impact strength was higher and has a different trend compare to the others. However, freezed-drying was higher than heat drying due the aggregation. Figure 23(b) showed that there was no big difference of impact strength of WPC per each condition during the decreasing of particle size. In the case of freezed-drying condition at 120 minutes of wet milling time, impact strength higher than other due the aggregation.

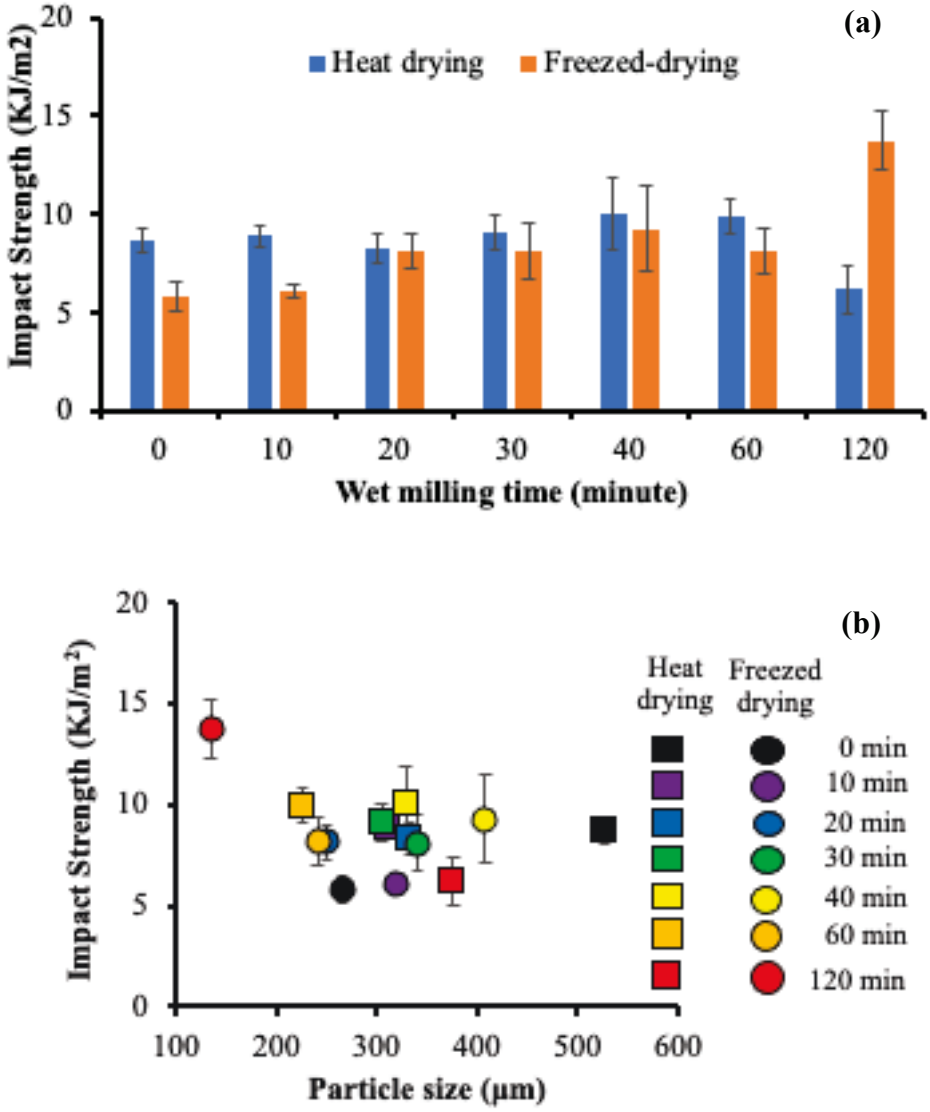

Fig. 23 The relationship between impact strength of WPC with (a) the wet milling time and (b) the average particle size.

Figure 24 shows the relationship between the impact strength and intensity at 77.3 µm and 678.5 µm. In the case of heat drying, except at 120 min, the impact strength

gradually increased with increasing intensity at 77.3 μm. In the case of freezed-drying, increasing intensity increased the impact strength. However, there was no clear relationship between intensity at 678.5 μm and impact strength. The amount of large particle might not affect the impact strength. When focused on Izod impact strength, there is no clear relationship between the Izod impact strength and wet milling time. In the case of the wet milling time at 120 min, the impact strength was higher and has a different trend compared to the others. It is found that the freezed-drying condition was higher than the heat drying condition, which might be due to the difference in aggregation.

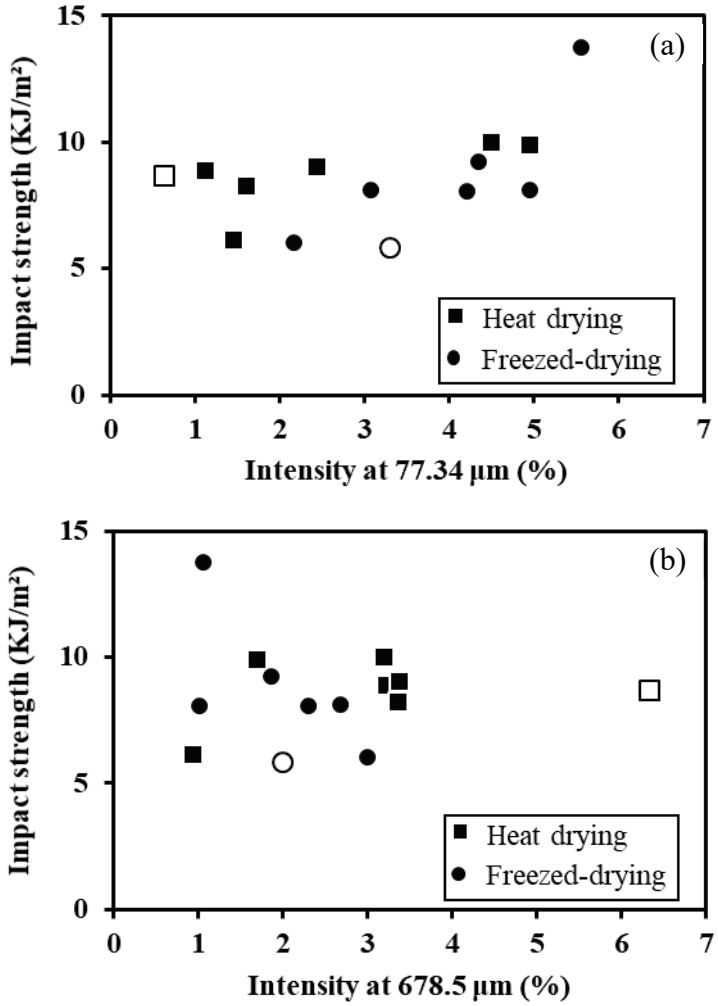

Fig. 24 The relationship between impact strength of WPC and intensity of the particle size distribution analysis at (a) 77.3 μm and (b) 678.5 μm. ☐ heat drying at 0 min and ○ freezed-drying at 0 min.

4.2.4 Water resistance properties of WPC

Figure 25 showed the relationship between water absorption of WPC with the time of water resistance test (a) and the average particle size (b) obtained by heat drying and freezed-drying condition. As can be seen in Fig. 25(a), the water absorption of WPC increased during the increasing time of water resistance test, especially from 0 to 360 hours. After that, there was fluctuation value of water absorption around 400 hours and it was saturated from 648 to 1032 hour of water resistance test time. The highest water absorption was observed at 60 and 120 minutes of wet milling time heat drying condition. The reason of these might be due to the aggregation. The aggregation was thought to be due to the influence of applying milling time and drying condition. Figure 25(b) showed the relationship between the saturated water absorption of WPC (around the 5 %) with the average particle size. The highest water absorption for heat drying condition were observed at 40 to 120 minutes of wet milling time. In the case of freezed-drying condition, the lowest water absorption was observed at 120 minutes of wet milling time. The reason of these might be due to the difference of aggregation.

The different structures of the particle may also contribute to different degrees of water uptake, especially in dimensional swelling, such as thickness of the composites. The possibility water to absorb is same because the amount of water itself is same. In the case of thickness swelling, specifically on the aggregated wood flour, even the water amount is same. However, the size of dimension will expand higher compared to the singular particle of wood flour. During the absorption, first, the water uptake occurred on the surface of the particles; then, the water transferred from one cell lumen to another over time (Mu *et al.*, 2018). The primary and secondary kneading also might influence the speed of water absorption. Under a temperature of 190 ºC, the thermoplastic polymer PP was able to cover

the surface of wood flour and would provide greater strength to the WPC. In the case of this kneading process, the particles of thermoplastic polymer PP might be unable to cover such a large number of surfaces of wood particles. This would affect the water absorption of WPC as a result of the water absorption by the wood.

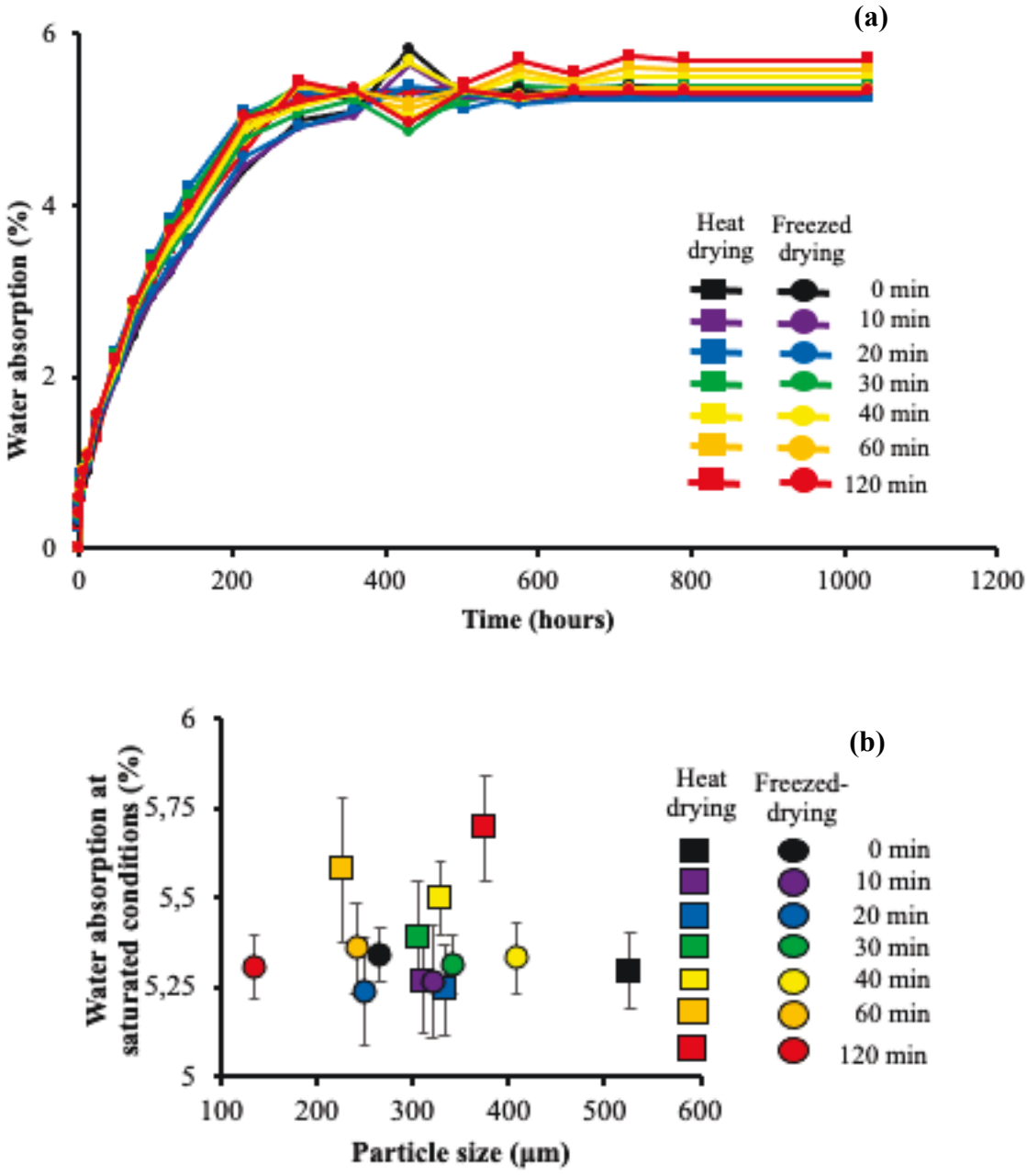

Fig. 25 The relationship between water absorption of WPC with (a) the time of water resistance test and (b) the average particle size.

Figure 26 showed the relationship between thickness swelling of WPC with the time of water resistance test (a) and the average particle size (b) obtained by heat drying and

freezed-drying condition. As an increasing the time of water resistance test, the thickness swelling of WPC increased. As can be seen in Fig. 26(a) it was occurred at 0 to 360 hours of water resistance test time. After that, there was fluctuation value of thickness swelling up to 600 hours and it was saturated from 648 to 1032 hour of water resistance test time. As same water absorption trends, the highest thickness swelling was observed at 60 and 120 minutes of wet milling time heat drying condition. The reason of these might be due to the aggregation. The aggregation was thought to be due to the influence of applying milling time and drying condition.

Figure 26(b) showed the relationship between the saturated thickness swelling of WPC (around the 5 %) with the average particle size. As same as water absorption trend, the highest thickness swelling for heat drying condition were observed at 40 to 120 minutes of wet milling time. In the case of freezed-drying condition, the lowest thickness swelling was observed at 120 minutes of wet milling time. The reason of these might be due to the difference of aggregation and contributed to difference degrees of water uptake, especially dimensional swelling of the composites. During absorption, water uptake occurred on the surface of the particles at first and then the water transferred from one cell to another over time (Mu *et al.*, 2018).

The primary and secondary kneading also might be affected the speed of water absorb. Under a temperature of 190 ºC conditions, the thermoplastic polymer PP was able to cover a more specific area of wood particles and will provide the greater strength of WPC. In the case of this kneading process, allegedly that the particles of thermoplastic polymer PP were unable to cover such a large number of surfaces of wood particles. This would be affected the thickness swelling of WPC as a result of wood absorbs the water and plastic instead of it, does not absorb the water.

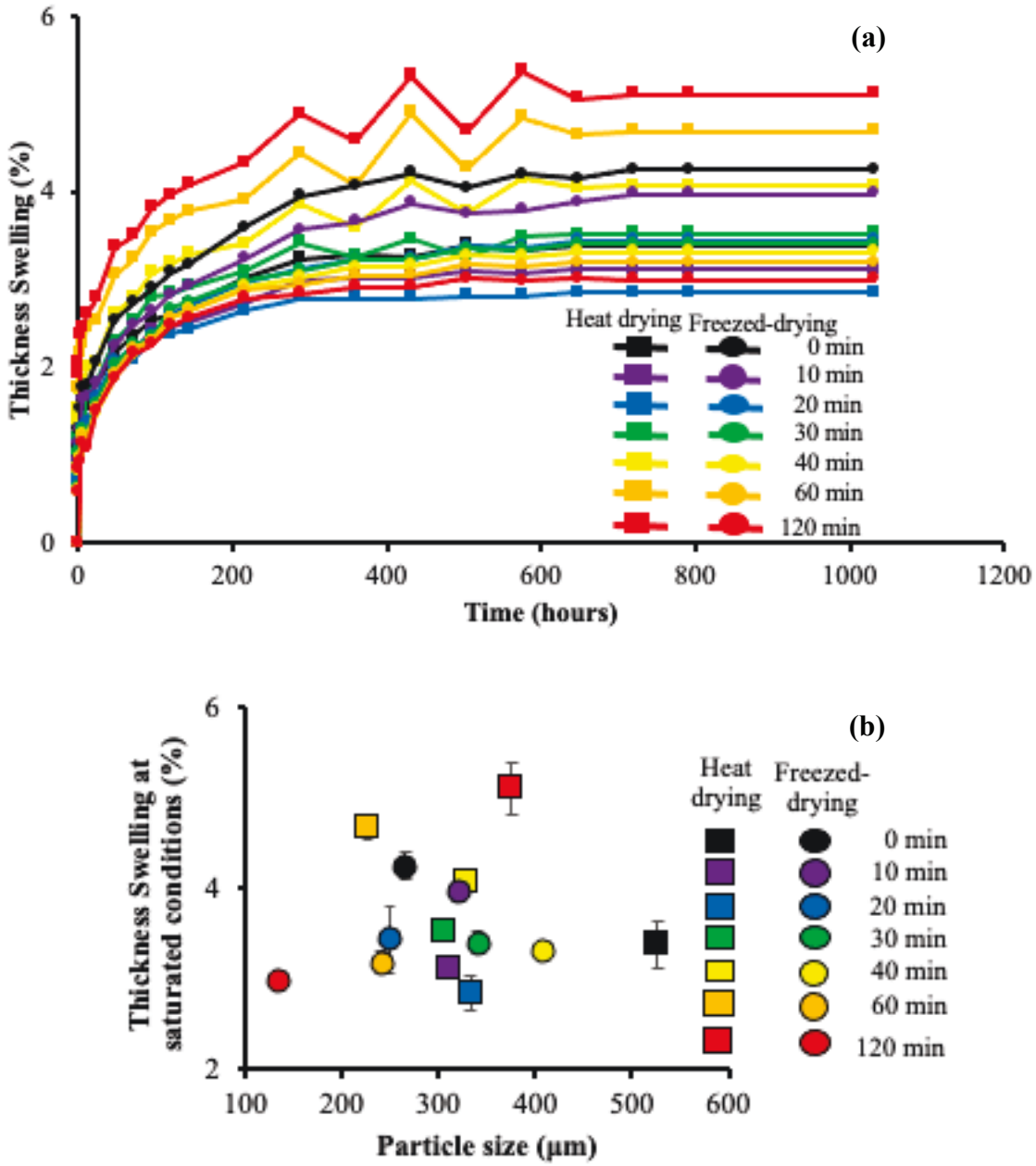

Fig. 26 The relationship between thickness swelling of WPC with (a) the time of water resistance test and (b) the average particle size.

Figure 27 shows the relationship between the intensity at 77.3 μm and 678.5 on the particle size distribution and the water absorption and thickness swelling of the WPC. When focused on the saturated condition, water resistance properties showed the same trend, even for the large and small particle of wood flour. As observed in Figs. 27(a) and (c), there is no significant difference on water absorption at the large and small particle for the heat drying and freezed-drying condition. In the case of thickness swelling showed that there is

fluctuation among different wet milling times (see Figs. 27(b) and (d)). The reason might be to the differences of aggregation. Increase in the aggregation particle corresponds to a decrease in the dimensional stability against water.

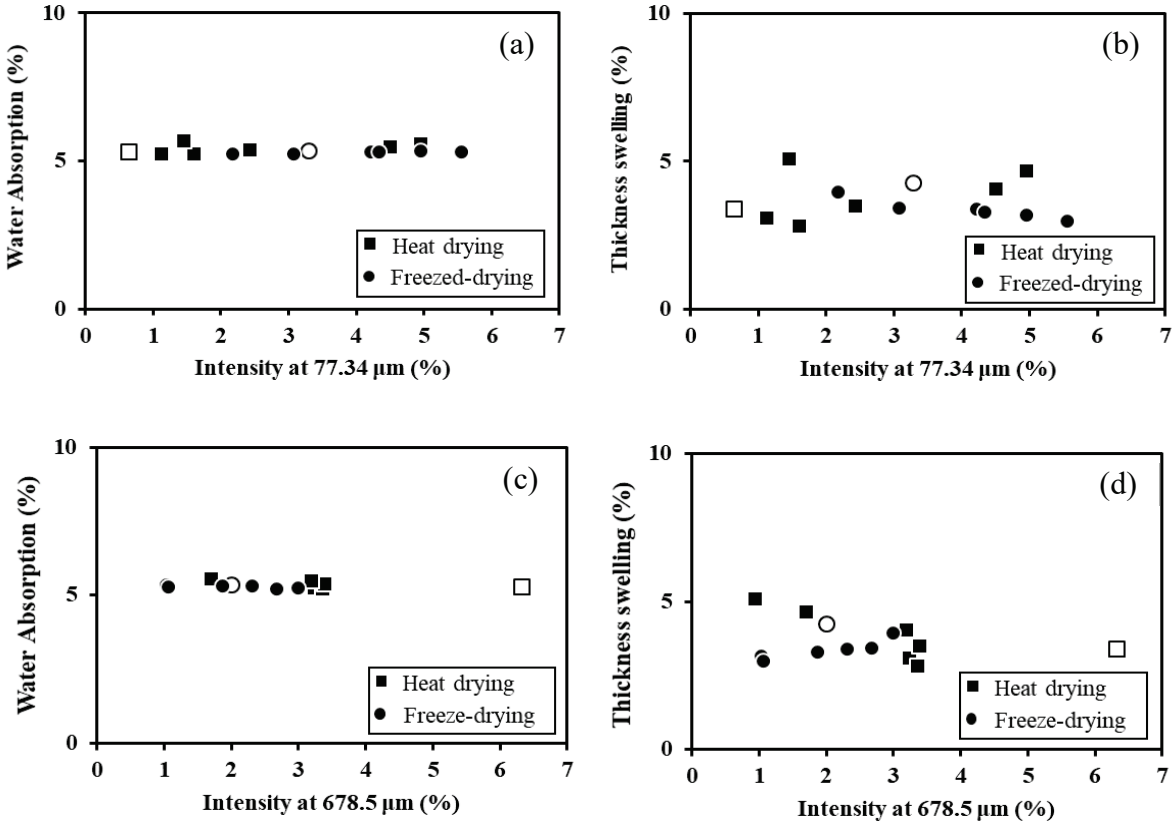

Fig. 27 The relationship between water resistance properties of WPC and intensity of the particle size distribution analysis at (a) 77.3 µm and (b) 678.5 µm. □ heat drying 0 at min and ○ freezed-drying at 0 min.

The relationship between predicted maximum water absorption or thickness swelling of WPC with the adsorption speed of water was shown in Fig. 28. As mentioned in chapter 3, the saturation point at a maximum of water resistance properties was A, and the speed of water uptake was B. The lower A would have a positive effect on the mechanical properties of WPC and the higher value of B signify that it was lower speed of absorb and drain the water. The result showed that during the increasing of wet milling time, the maximum water absorption for freezed-drying was decreased 0 to 20 minutes of the wet milling time as can

be seen in Fig. 28(a). At that time, the speed of water absorption was high compared to others condition. After that, the maximum water absorption showed a slightly increased with lower of water absorbs speed. However, in the case of heat drying showed that the opposite trend. As increasing of the wet milling time, the maximum water absorption was decreased from 0 to 20 minutes of the wet milling time. At that time the speed of water adsorption was lower than others condition. After that, the maximum water absorption showed was increased significantly and increasing speed of water absorb.

Figure 28(b) showed that the maximum thickness swelling of freezed-drying was decreased during the increasing of wet milling time. It was followed by same trend of the water uptake speed, that was also decreased during the increasing of wet milling time. In the case of heat drying condition showed that the maximum thickness swelling, and the speed of water uptake were decreased from 0 to 20 minutes of wet milling time. After that, it showed both that the maximum thickness swelling, and the speed of water uptake were increased during the increasing of wet milling time. Based on the fact that the optimum condition would occur when the low speed and low water absorption and thickness swelling was observed. The optimum condition was found at 30 minutes of wet milling. The reason of these might be due to at that time were observed a low of water resistance and also lower time needed to adsorb and drain the water.

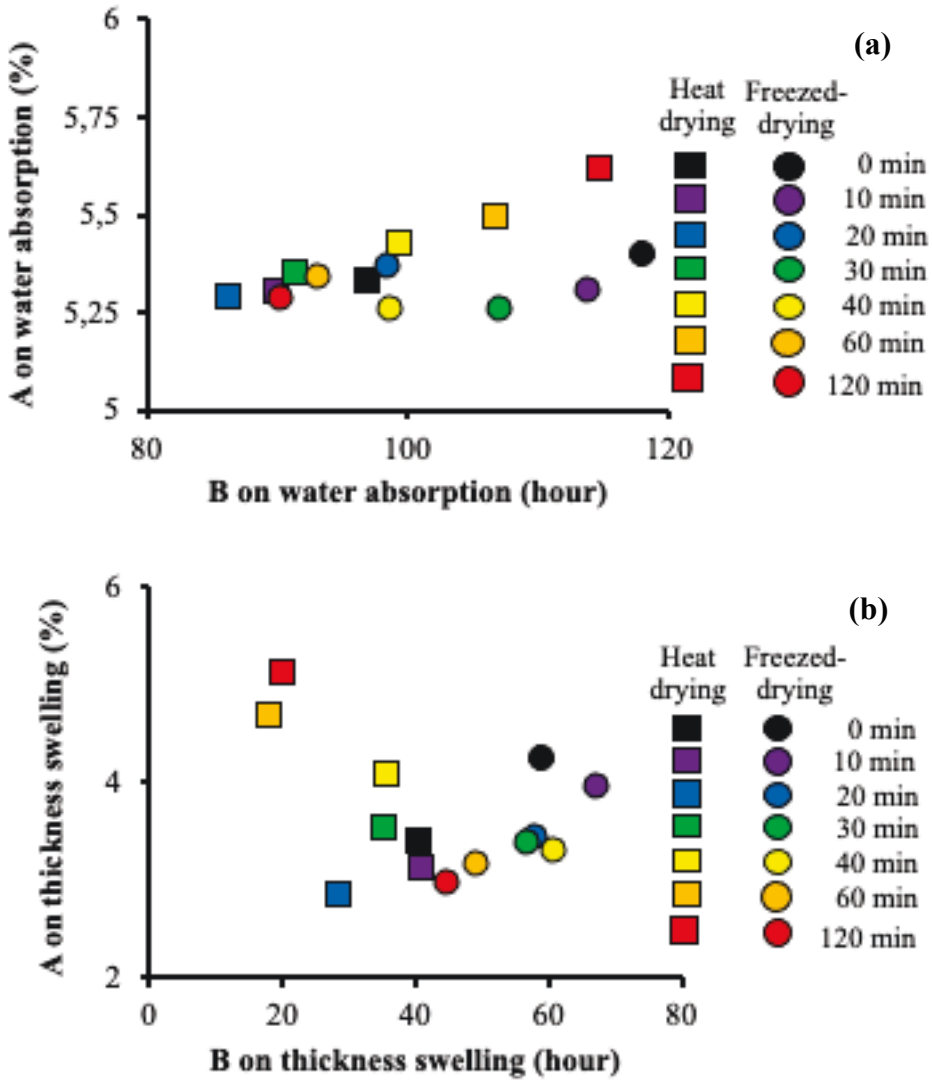

Fig. 28 The relationship between predicted maximum value A versus B on (a) water absorption and (b) thickness swelling of WPC.

4.3 The investigation of mechanical properties of WPC made from smaller mesh size

4.3.1 Bending, tensile, and impact strength of WPC made from smaller mesh size

Table 6 shows the mechanical properties of WPC for targeted condition. As mentioned in the chapter 3, the fraction of 32-53 μm by 30 minutes of wet milling time for freezed-drying was added, because it was thought to be the ideal condition for comparison. Considering at the previous results indicates that the particle size distribution influences the mechanical properties of WPC. Decreasing the particle size corresponded to an increase in the mechanical properties of WPC. And it was also found that the optimum mechanical property of WPC was obtained at 30 min of the wet milling time for freezed-drying conditions. So, it is necessary to compare these optimum mechanical properties with the same wet milling time and drying conditions but different in wood flour size. In this topic, the results showed that the mechanical properties of WPC including the flexural and tensile properties decreased during the decreasing of wood flour size in micrometers. In fact, the lowest mechanical properties except for impact strength were found at the targeted conditions, which is made from 32-53 μm of wood flour. In the case of impact strength, it decreased during decreasing of particle size. However, the highest impact strength was found for WPC made from 32-53 μm of wood flour. It was meant an excessive percentage of small particle decreased the mechanical properties of WPC.

Table 6 The mechanical properties of WPC made from smaller mesh size.

Mesh size (μm)	Freezed-drying 30' WMT			
	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (Mpa)	Impact strength (KJ/m2)
180 - 425	91,03 (0,59)^	3641,74 (92,97)^	51,97 (0,36)^	9,30 (1,17)^
90 - 180	89,03 (0,37)^	3530,41 (30,15)^	50,64 (0,48)^	8,08 (1,42)^
32 - 53	82,58 (0,56)^	2941,14 (22,34)^	43,70 (0,30)^	10,15 (0,75)^

^ Standard deviation

4.3.1 Water resistance properties of WPC made from smaller mesh size

Figure 29 showed the relationship between the water resistance properties of WPC obtained by freezed-drying condition with the time of water resistance test in hours. The result showed that the water resistance and thickness swelling have similar trend as can be seen in Fig. 29(a) and 29(b), respectively. An increasing the time of water resistance test from 0 to 360 hours, both of water absorption and thickness swelling of WPC increased. After that, there was fluctuation value of water absorption and thickness swelling up to 600 hours and they were saturated from 648 to 1032 hour of water resistance test time. When focused on the saturated condition as observed in Figs. 29(a), it showed there was no significant difference on water absorption, even for the large and small particle of wood flour. However, as shown in Figs. 29(b), during decreasing of particle size, the thickness swelling of WPC decreased and the lowest thickness swelling was observed at WPC made from smallest wood flour. It was meant the milling process has positive effect for thickness swelling properties of WPC. The reason of these might be due to the difference of aggregation and contributed to difference degrees of water uptake, especially dimensional swelling of the composites. The result showed that there were significant difference of thickness swelling of WPC during the decreasing of particle size.

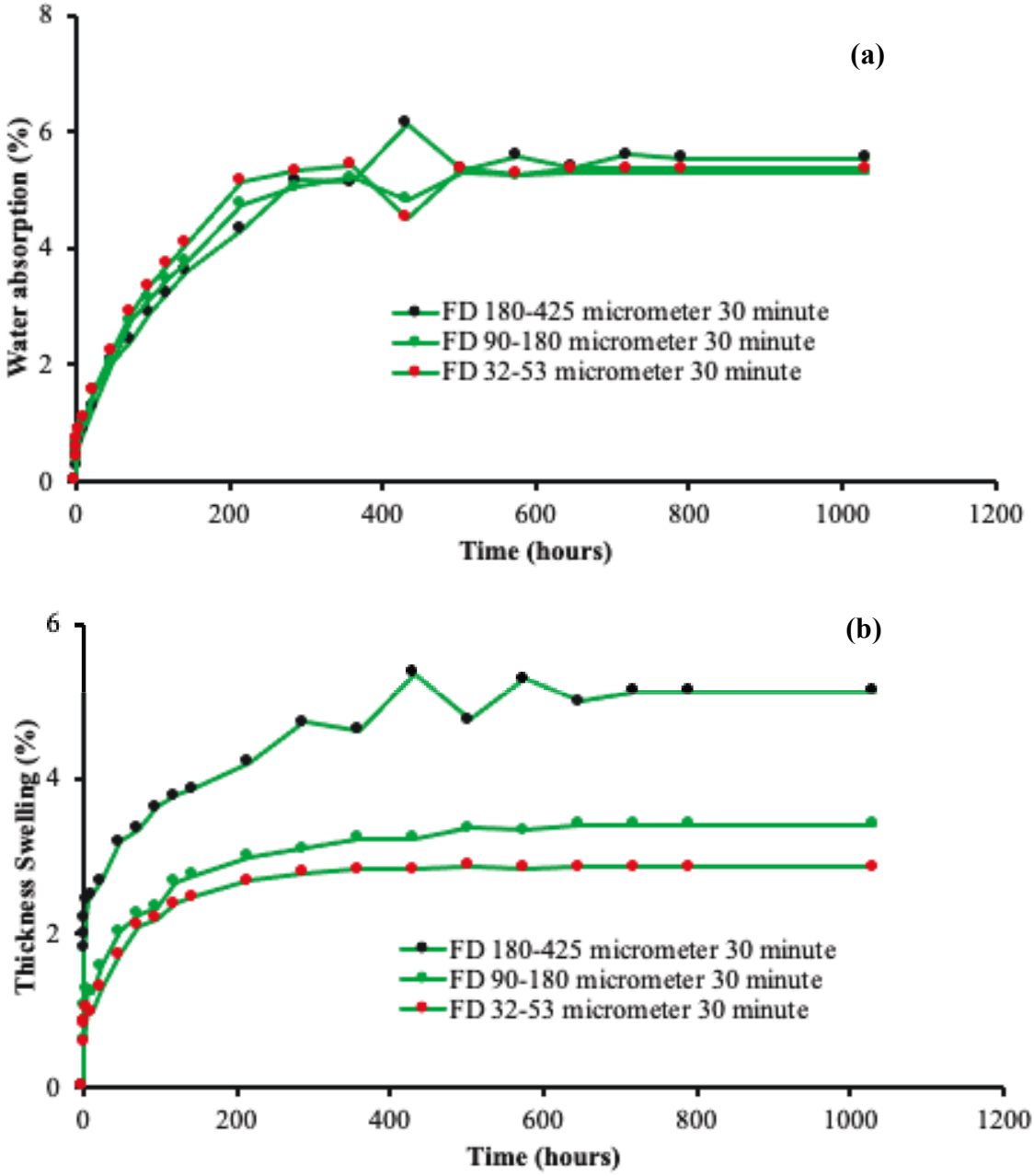

Fig. 29 The relationship between the water resistance properties and the time till saturation. Water absorption (a); thickness swelling (b).

Figure 30(a) showed the relationship between the saturated water resistance properties of WPC with the average particle size. The results showed that there is no clear relationship between the saturated water resistance properties of WPC with the average particle size. When focused on the water absorption, there was no big difference of water absorption of WPC made from different arrangement of mesh size. However, in the case of thickness swelling, during the decreasing of particle size the thickness swelling decreased. And it was found that there was big difference of thickness swelling of WPC made from different arrangement of mesh size. The lowest thickness swelling was observed for WPC that made from mesh size 32-53 μm. It was meant the smaller mesh size has a positive effect for the thickness swelling of WPC.

The relationship between predicted maximum on water absorption or thickness swelling of WPC with the adsorption speed of water was shown in Fig. 30(b). As mentioned in chapter 3, the saturation point at a maximum of water resistance properties was A, and the speed of water uptake was B. The lower A would have a positive effect on the mechanical properties of WPC and the higher value of B signify that it was lower speed of absorb and drain the water. The result showed that during the decreasing of mesh size, the maximum water absorption decreased, and the speed of water absorption was higher. In the case of thickness swelling, as decreasing of the mesh size, the maximum thickness swelling decreased. However, at that time the speed of thickness swelling became slower. Based on the fact that the optimum condition would occur when the slow speed and low water absorption and thickness swelling were observed. It was found that the lowest thickness swelling was observed for WPC that made from mesh size 32-53 μm.

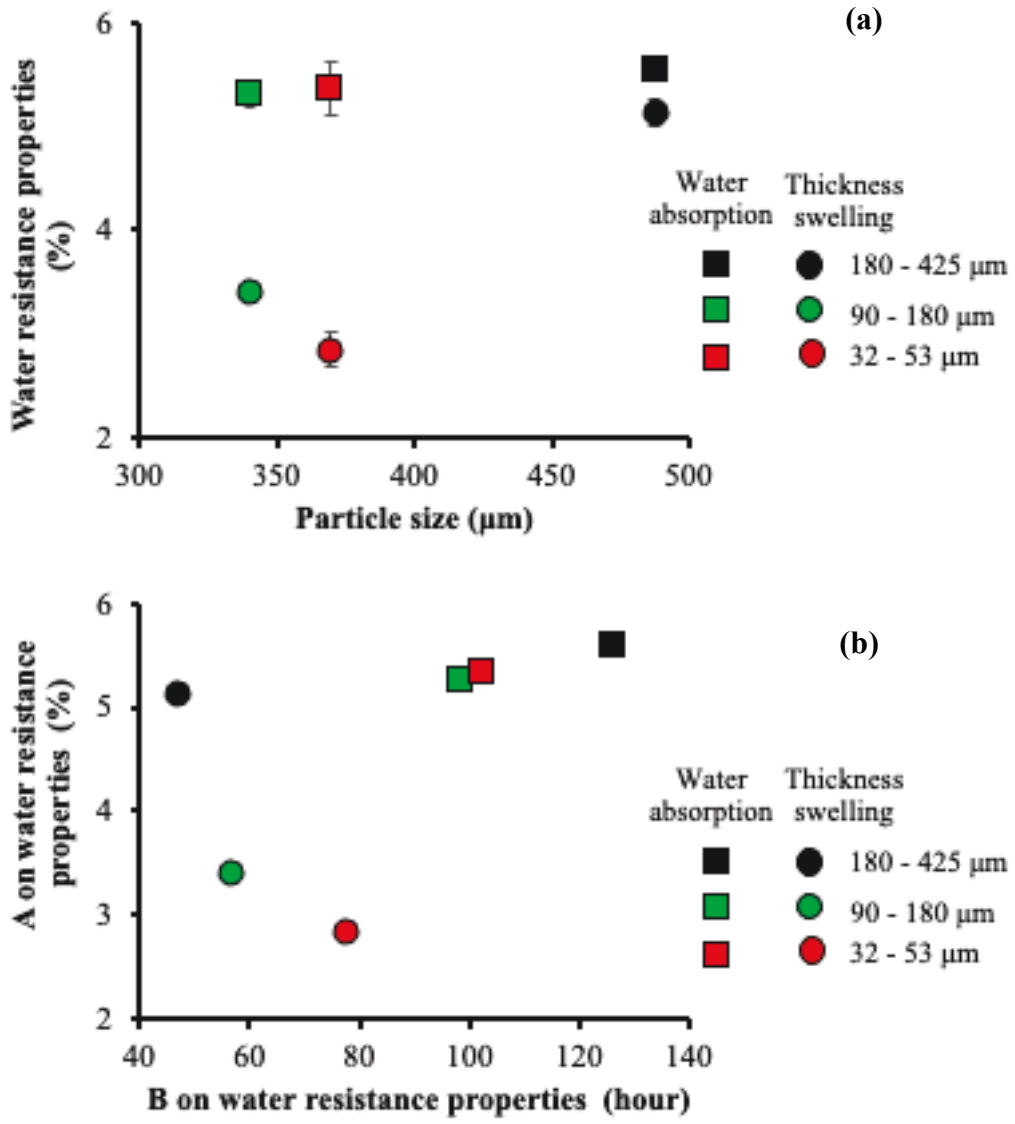

Fig. 30 The relationship between predicted maximum value A versus B on (a) water absorption and (b) thickness swelling of WPC.

CHAPTER 5

CONCLUSIONS

In this study the effect of wood flour characteristics by different filler fabrication treatment on the mechanical properties of WPC were investigated. Two kinds of parameter were evaluated in this research to know the influence on the mechanical properties of WPC. The first experimental item is wet milling time, which ranges for 0, 10, 20, 30, 40, 60, and 120 minutes of pulverization process. The second item is drying condition including heat drying and freezed-drying process. The tests were conducted to determine the mechanical properties such as bending, tensile, impact and water resistance which would be affected by those parameters of milling time and drying conditions.

The milling process changed the characteristic of wood flour, particularly the particle size distribution. Increasing the time of ball milling decreased the wood flour size. However, an excessing milling period of time longer than 40 minutes, the amount of aggregation increased. Particle size distribution of produced wood flour depended on the milling conditions. From the observation of particle size distribution, it was clearly found that the average particle size after ball milling increased as a function of milling time, particularly from 60 to 120 minute. After the re-fibrillation and screening process has similar trends. When focused on the large particle size for both heat drying and freezed-drying conditions, the highest intensity (peak) was observed for 0 minute of wet milling time, and it decreased with increase in wet milling time up to 30 minutes. The deviation of the particle size distribution demonstrated that there are various sizes and shapes in milled wood flour. However, the aggregation occurred longer 30 minutes of wet milling time. In the case of the smaller particle size, for both drying conditions, the peak appeared at 120 min of wet milling time. Under those conditions, the intensity for the freezed-drying condition was higher than

that for the heat drying condition. This might be due to the milled wood flour into finer or fibers caused by high rotating speed of the ball mill. The investigation of SEM images is proved that the aggregation occurred at 120 minute of wet milling time and that for heat drying conditions was higher than freezed-drying conditions. This was meant to avoid the aggregation less than 40 minute of wet milling time is suitable.

This result indicates that mechanical properties such as tensile strength, flexural strength and a flexural modulus of WPC increased up to 30 minutes of wet milling time. At 120 minute of wet milling time the mechanical properties decreased and that for freezed-drying was higher than that for heat drying. It was suggested that the different surface characteristics of aggregated wood flour influence the mechanical properties of WPC. Decreasing of the particle size, the mechanical properties of WPC were increased. The Izod impact strength increased with increasing wet milling time from 0 to 30 minutes and after that it showed a slight decrease. In the case of 120 minutes of wet milling time, the composite had a higher impact strength compared to others condition. The reason for these might be due to the aggregation.

During the increasing time, water resistance properties were increased up to 648 hours and after that showed saturation. The highest water absorption and thickness swelling found at heat drying condition at 60 and 120 minutes of wet milling time. The reason for these might be due to the aggregation. The result showed that there was no significant difference on both of water resistance properties, water absorption and thickness swelling at the large and small particle. However, there were significant difference of thickness swelling between the heat drying and freezed-drying condition at each different wet milling time that applied.

The result showed that the particle size distribution influences the mechanical properties of WPC. An excessive percentage of small particle decreased the mechanical properties of WPC. It was clearly found and occurred at the targeted WPC, which is made

from smallest particle size and for freezed-drying conditions. In the case of large particle, the mechanical properties of WPC decreased during decrease in intensity. The optimum mechanical property of WPC was obtained at 30 min of the wet milling time for freeze-drying conditions. Further research that focuses on these fractions with different particle size is needed to find out what exact size of wood flour is the most optimal in the WPC manufacturing.

REFERENCES

Arnandha Y, Satyarno I, Awaludin A, Irawati IS, Prasetya Y, Prayitno DA, Winata DC, Satrio MH and Amalia A (2017) Physical and mechanical properties of WPC board from Sengon sawdust and recycled HDPE plastic. Procedia Eng., 171: 695-704.

Animpong MAB, Oduro WO, Koranteng J, Benefo KA, Mensah GB, Kumi KA, Tottimeh GO and Amoah JY (2017) Coupling effect of waste automotive engine oil in the preparation of wood reinforced LDPE plastic composites for panels. SAJCE, 24: 55-61.

Bledzki AK and Faruk O (2003) Wood fibre reinforced polypropylene composites: Effect of fibre geometry and coupling agent on physico-mechanical properties. Appl. Compos. Mater., 10: 365-379.

Bouafif H, Koubaa A, Perré P and Cloutier A (2009) Effects of fiber characteristics on the physical and mechanical properties of wood plastic composites. Composites Part A, 40: 1975-1981.

Catto AL, Montagna LS, Almeida SH, Silveira RMB and Santana RMC (2016) Wood plastic composites weathering: Effects of compatibilization on biodegradation in soil and fungal decay. Int. Biodeterior. Biodegrad., 109: 11-22.

English BW and Falk RH (1996) Factors that affect the application of woodfiber-plastic composites. Proc. For. Prod. Soc., 7293: 189-194.

Friedrich D and Luible A (2016) Investigations on ageing of wood-plastic composites for outdoor applications: A meta-analysis using empiric data derived from diverse weathering trials. Constr. Build. Mater. , 124: 1142-1152.

García M, Hidalgo J, Garmendia I and Jaca JG (2009) Wood–plastics composites with better fire retardancy and durability performance. Composites Part A, 40: 1772-1776.

Gardner DJ, Han Y and Wang L (2015) Wood–Plastic Composite Technology. Springer Int. Pub., 1(3): 139-150.

Gozdecki C, Kociszewski M, Wilczynski A and Zajchowski S (2015) Properties of wood–plastic composites made of milled particleboard and polypropylene. Eur. J. Wood Wood Prod., 73: 87-95.

Isa A, Minamino J, Kojima Y, Suzuki S, Ito H, Makise R, Okamoto M and Endo T (2016) The influence of dry-milled wood flour on the physical properties of wood flour/polypropylene composites. J. Wood Chem. Technol., 36: 105-113.

Isa A, Minamino J, Mizuno H, Suzuki S, Kojima Y, Ito H, Makise R, Okamoto M and Hasegawa T (2013) Increased water resistance of bamboo flour/polyethylene composites. J. Wood Chem. Technol., 33: 208-216.

Isa A, Toyoda T, Suzuki S, Kojima Y, Ito H, Makise R and Okamoto M (2014) The effects of wet-milled wood flour on the mechanical properties of wood flour/polypropylene composites. J. Wood Chem. Technol., 34: 20-30.

Ito H, Ogoe S, Okamoto M, Suzuki S, Kojima Y, Kobori H, Isa A and Endo T (2017) Properties of fibrillated wood flour, and of wood-plastic composites made with fibrillated wood flour. J. Wood Soc., 63(3): 131-136 (in Japanese with English abstract).

Ito H, Okamoto M, Makise R, Isa A, Fujinaka E, Kojima Y, Suzuki S, Endo T and Teramoto Y (2013) Surface treatment of microfibrillated cellulose using calcium silicate hydrate. J. Stage, 59(6): 375-382 (in Japanese with English abstract).

Iwamoto S, Yamamoto S, Lee SH, Ito H and Endo T (2014) Mechanical and thermal properties of polypropylene composites reinforced with lignocellulose nanofibers dried in melted ethylene-butene copolymer. Materials., 7: 6919-6929.

JIS A 5741: 2016 (2017) Wood-plastic recycled composite (in Japanese). Japanese Standards Association, Tokyo, pp 1-21

JIS K 7110: 1999 (2012) Plastics determination of Izod impact strength (in Japanese). Japanese Standards Association, Tokyo, pp 1-30

Kaboorani A (2017) Characterizing water sorption and diffusion properties of wood/plastic composites as a function of formulation design. Constr. Build. Mater., 136: 164-172.

Khonsari A, Taghiyari HR, Karimi A and Tajvidi M (2015) Study on the effects of wood flour geometry on physical and mechanical properties of wood-plastic composites. Maderas. Cienc. Tecnol., 17(3): 545-558.

Kim JW, Harper DP and Taylor AM (2008) Effect of wood species on water sorption and durability of wood–plastic composites. Wood Fiber Sci., 40(4): 519-531.

Koohestani B, Ganetri I and Yilmaz E (2017) Effects of silane modified minerals on mechanical, microstructural, thermal, and rheological properties of wood plastic composites. Composites Part B, 111: 103-111.

Kuo PY, Wang SY, Chen JH, Hsueh HC and Tsai MJ (2009) Effects of material compositions on the mechanical properties of wood–plastic composites manufactured by injection molding. Materials and Design, 30: 3489-3496.

Leu SY, Yang TH, Lo SF and Yang TH (2012) Optimized material composition to improve the physical and mechanical properties of extruded wood–plastic composites (WPCs). Constr. Build. Mater., 29: 120-127.

Maldas D, Kokta BV and Daneault C (1989) Thermoplastic composites of polystyrene: effect of different wood species on mechanical properties. J. Appl. Polym. Sci., 38: 413-439.

Martins G, Antunes F, Mateus A, Malça C (2017) Optimization of a wood plastic composite for architectural applications. Procedia Manufacturing, 12: 203-220.

Mu B, Wang H, Hao X and Wang Q (2018) Morphology, mechanical properties and dimensional stability of biomass particles/high density polyethylene composites: effect of species and composition. Polym., 10: 308.

Murayama K, Ueno T, Kobori H, Kojima Y, Suzuki S, Aoki K, Ito H, Ogoe S and Okamoto M (2019) Mechanical properties of wood /plastic composites formed using wood flour produced by wet ball-milling under various milling time and drying methods. J Wood Sci 69:5.

Naguib HM, Kandi UF, Hashem AI and Baghdady Y (2015) Effect of fiber loading on the mechanical and physical properties of "green" bagasse-polyester composite. J. Radiat. Res. Appl. Sci., 8(4): 544-548.

Najafi A and Eslam HK (2011) Lignocellulosic filler/recycled HDPE composites: Effect of filler type on physical and flexural properties. Bioresources, 6(3): 2411-2424.

Nourbakhsh A, Karegarfard A, Ashori A and Nourbakhsh A (2010) Effects of particle size and coupling agent concentration on mechanical properties of particulate-filled. J. Thermoplast. Compos. Mater., 23: 169-174.

Ogunleye MB and Aina KS (2017) Effect of agro-waste (Arundo donax) l particles on physical and mechanical properties of polymer composites. Int. J. Sci. Techn., 5(4): 133-137.

Rahman KS, Islam MN, Rahman MM, Hannan MO, Dungani R, and Khalil HPSA (2013) Flat-pressed wood plastic composites from sawdust and recycled polyethylene terephthalate (PET): physical and mechanical properties. SpringerPlus, 2(629): 1-7.

Ratanawilai T, Thanawattanasirikul N, and Homkhiew C (2012) Mechanical and thermal properties of oil palm wood sawdust reinforced post-consumer polyethylene composites. Sci. Asia, 38: 289-294.

Ratanawilai T, Nakawirot K, Deachsrijan A and Homkhiew C (2014) Influence of wood species and particle size on mechanical and thermal properties of wood polypropylene composites. Fibers Polym., 15(10): 2160-2168.

Salemane MG and Luyt AS (2006) Thermal and mechanical properties of polypropylene–wood powder composites. J. Appl. Polym. Sci., 100: 4173-4180.

Schwarzkopf MJ and Burnard MD (2016) Wood-Plastic Composites—Performance and 419 Environmental Impacts. In: Environmental Impacts of Traditional and Innovative Forest-420 based Bioproducts (Kutnar A and Muthu SS, ed.). pp.19-43. Springer. Singapore.

Sommerhuber PF, Wang T and Krause A (2016) Wood plastic composites as potential applications of recycled plastics of electronic waste and recycled particleboard. J. Cleaner Prod., 121: 176-185.

Stark NM and Berger MJ (1997) Effect of species and particle size on properties of wood-flour-filled polypropylene composites. Proceedings of Functional Fillers for Thermoplastic and Thermosets, 1-22.

Stark NM and Rowlands RE (2003) Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. Wood Fiber Sci., 35(2): 167-174.

Sudár A, López MJ, Keledi G, García MdCV, Estrella FS, Moreno J, Burgstaller C and Pukánszky B (2013) Biodeterioration and ecotoxicity of pp/wood composites: Effect of wood content and coupling. Chemosphere, 93(2): 408-414.

Tascioglu C, Tufan M, Yalcin M and Sen S (2014) Determination of biological performance, dimensional stability, mechanical and thermal properties of wood–plastic composites produced from recycled chromated copper arsenate-treated wood. J. Thermoplast. Compos. Mater., 29(11): 1461–1479.

Tazi M, Erchiqui F, Kaddami H, Bouazara M and Poaty B (2015) Evaluation of mechanical properties and durability performance of hdpe-wood composites. Am. Inst. Phys. Conf. Proc., 1664(150001): 1-5.

Tisserat B, Reifschneider L, Grewell D and Srinivasan G (2014) Effect of particle size, coupling agent and DDGS additions on Paulownia wood polypropylene composites. J. Reinf. Plast. Compos., 33(14): 1279-1293.

Tisserat B, Reifschneider L, Joshee N and Findkenstadt VL (2013) Properties of high density polyethylene - Paulownia wood flour composites via injection molding. Bioresources, 8(3): 4440-4458.

Turku I, Keskisaari A, Kärki T, Puurtinen A and Marttila P (2017) Characterization of wood plastic composites manufactured from recycled plastic blends. Compos. Struct., 161: 469-476.

Wills BA, Napier-Munn TJ (eds) (2006) Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. 7th ed. Butterworth-Heinemann, Oxford, UK

Zhang Y, Xue P, Ding Y, Jia M, Cai J and Jin X (2016) Improvement of mechanical properties of wood-plastic composite floors based on the optimum structural design. Acta Mech. Solida Sin., 29(4): 444-454.

Zimmermann MVG, Turella TC, Santana RMC and Zattera AJ (2014) The influence of wood flour particle size and content on the rheological, physical, mechanical and morphological properties of EVA/wood cellular composites. Materials and Design, 57: 660–666.

ACKNOWLEDGEMENTS

First and foremost, all praises and thanks to Allah Subhanahu wa Ta'ala, Lord of the worlds. The God Entirely Merciful, the Especially Merciful, to Him we worship and ask for help, may Allah always guide us to the straight path.

I would like to express the deep and sincere gratitude of mine to my supervisor, Professor Dr. Yoichi Kojima, for his invaluable guidance, patience, and help throughout my study as well. His kindness not only for my academic, also a great support to my life in Japan. Grateful thanks addressed to my first co-supervisor, Assistant Professor Dr. Hikaru Kobori for all guidance on my research work, helpful suggestion, great discussion and patiently corrected my dissertation writing. I would like to thank my second co-supervisor, Professor Dr. Tohru Mitsunaga, for the great discussion and kind encouragement. Special thanks also addressed to Professor Dr. Shingo Kawai, who was willing to participate in my final defense committee.

I give unlimited thanks of mine to TOCLAS Co. Ltd. Members Mr. Shinji Ogoe, Mr. Masaki Okamoto, Mr. Tomoyuki Ema, Ms. Keiko Kagawa, and Dr. Hirokazu Ito from National Institute of Advanced Industrial Science and Technology for the cooperation, the opportunities to collaborate, and all of support so I can finish research of mine well.

I am extending my heartfelt thanks to Ms. Sanami Nishida for taking care of administrative issues, for a family atmosphere and as like as my second mom in Japan. Grateful thanks to Professor Dr. Kenji Aoki for great guidance and discussion, all of the members of the Laboratory of Wood Biomass Utilization, Shizuoka University, for

kindness and togetherness. Special thanks go to members of WPC group, Mr. Kazushige Murayama and Ms. Ueno Takako for all of guidance to me especially of research field. Also, I said to thank all of the Indonesian friends in Shizuoka, all of member PPI Shizuoka, Formashi, and Shizuoka Muslim Association community for sharing beautiful story and togetherness.

I acknowledge the Ministry of Education, Culture, Sports, Science, and Technology of Japan support through MEXT Scholarship. I would not have been possible to pursue my doctoral course without this great support.

Finally, I dedicated this dissertation to my beloved wife, Bunda Nurlia Damayanti, my lovely son, Abrisyam Naoki Malik, who always kept sending their love, prayers, and support to me. My deepest gratitude to both of them, especially for the patience and tolerance over the last three years which will surely be a beautiful story in our little family. Also, it is fully dedicated to my dear father Muhidin, my mother Darmi Wati, my mother-in-law, Hajah Amsanih, my sister Ayuna Septita Dahlia and Andhina Yulianti. I am deeply indebted and give unlimited thanks for their loves, prayers, tolerance, and sacrifices of me.

SUMMARY

Summary in English

Wood plastic composite (WPC) is a relatively new generation of composite material made from a combination of wood flour and thermoplastic resins on specific heat and pressure. WPC has advantages such as easy to maintain, high durability and longtime service life. WPC can be produced using recycled materials, and several additives can be applied to improve the properties. The characteristics of wood flour as a raw material are important in the manufacturing of WPC. The quality and functionality of WPC should be improved to meet the increasing public demand. Although various studies have been conducted, there are still unsolved factors such as the particle size distribution as a function of wet milling times and drying conditions. It is also necessary to consider the relationship between this factor and the mechanical properties of WPC. The objective of this study is to investigate the effect of wood flour characteristics by different filler fabrication treatment on the mechanical properties of WPC.

Wood flour of the Japanese pine 13.5 g was milled with 200 ml of water by a ball mill. This was the standard method of wet milling condition for “one pot” in this research. Two kinds of parameter were evaluated in this research to know the influence on the mechanical properties of WPC. The first experimental item is wet milling time, which ranges for 0, 10, 20, 30, 40, 60, and 120 minutes of pulverization process by rotating speed of 200 rpm. The second item is drying condition including heat drying and freezed-drying process. Two kinds of drying conditions, seven days of freezed-drying at temperature -45 °C and 24 hours of heat drying (80 °C) was applied. After drying, wood flour was fibrillated for 1 minute by a blender. Dried wood flour was screened to classify into six fractions as follows; >425 μm, 180-425 μm, 90-180 μm, 53-90 μm, 32-53 μm, and <32 μm. Vibrational

acceleration ± 20 G was applied for 30 minutes of each condition by a compact vibrating shaker.

In order to analyze the weight distribution at wood flour size of 6 classifications and at 7 milling times, total amount of wood flour weight in each fraction of 6 x 7 matrix conditions was weighed and calculated. The number of pots for each condition was determined to obtain a sufficient amount for test piece fabrication and to analyze the particle size distribution. This study focused on the fraction 90 - 180 μm for all the different wet milling times, 180 – 425 μm on 0, 30, and 120 minutes, and 32 – 53 μm of 30 minutes wet milling time. The micro-structure of wood flour was investigated through a scanning electron microscope (SEM) examination. Polypropylene (PP) and maleic anhydride-grafted PP (MAPP) was used as a matrix and compatibilizer of WPC compound. The ratio of the weight of wood flour, PP, and MAPP in the compound was 25:74:1, respectively. The WPC compound was kneaded at 190 ℃ and a screw rotation speed of 30 rpm for 10 minutes.

After kneading, the WPC compound was crushed by a crusher machine. Injection molding machine was used to make WPC test pieces. The dimensions of a tensile and bending test pieces were 50 mm in length, 2 mm in thickness, 4 mm and 6 mm in width, respectively. The test pieces were placed for 5 days or more in a saturated temperature and humidity room (20° C, RH 65%) before testing. The tensile test was carried out by a universal testing machine at a speed of 20 mm/min and the distance between the gripper was 30 mm. Bending test was conducted by the speed of 5 mm/min and a span of 32 mm. The number of replications for each test was 5. Izod Impact test was conducted by Impact Tester machine. The dimension of the specimen test was the same likes as the bending test′s specimen and the number of replications was 5 time for each test. Water resistance test was included two kinds of test, i.e. water absorption and thickness swelling. The test specimen

was put in the water and heated by oven at the temperature of 70 °C. The test specimen dimension measurements were performed after 0, 1, 3, 4, 6, 12 hours. Then, measurements occurred once a day for the first week, followed by once every three days until saturation.

The milling process changed the characteristic of wood flour, particularly the particle size distribution. Increasing the time of ball milling decreased the wood flour size. However, an excessing milling period of time longer than 40 minutes, the amount of aggregation increased. Particle size distribution of produced wood flour depended on the milling conditions. From the observation of particle size distribution, it was clearly found that the average particle size after ball milling increased as a function of milling time, particularly from 60 to 120 minute. After the re-fibrillation and screening process has similar trends. When focused on the large particle size for both heat drying and freezed-drying conditions, the highest intensity (peak) was observed for 0 minute of wet milling time, and it decreased with increase in wet milling time up to 30 minutes. The deviation of the particle size distribution demonstrated that there are various sizes and shapes in milled wood flour. However, the aggregation occurred longer 30 minutes of wet milling time. In the case of the smaller particle size, for both drying conditions, the peak appeared at 120 min of wet milling time. Under those conditions, the intensity for the freezed-drying condition was higher than that for the heat drying condition. This might be due to the milled wood flour into finer or fibers caused by high rotating speed of the ball mill. The investigation of SEM images is proved that the aggregation occurred at 120 minute of wet milling time and that for heat drying conditions was higher than freezed-drying conditions. This was meant to avoid the aggregation less than 40 minute of wet milling time is suitable.

This result indicates that mechanical properties such as tensile strength, flexural strength and a flexural modulus of WPC increased up to 30 minutes of wet milling time. At 120 minute of wet milling time the mechanical properties decreased and that for freezed-

drying was higher than that for heat drying. It was suggested that the different surface characteristics of aggregated wood flour influence the mechanical properties of WPC. Decreasing of the particle size, the mechanical properties of WPC were increased. The Izod impact strength increased with increasing wet milling time from 0 to 30 minutes and after that it showed a slight decrease. In the case of 120 minutes of wet milling time, the composite had a higher impact strength compared to others condition. The reason for these might be due to the aggregation.

During the increasing time, water resistance properties were increased up to 648 hours and after that showed saturation. The highest water absorption and thickness swelling found at heat drying condition at 60 and 120 minutes of wet milling time. The reason for these might be due to the aggregation. The result showed that there was no significant difference on both of water resistance properties, water absorption and thickness swelling at the large and small particle. However, there were significant difference of thickness swelling between the heat drying and freezed-drying condition at each different wet milling time that applied.

The result showed that the particle size distribution influences the mechanical properties of WPC. An excessive percentage of small particle decreased the mechanical properties of WPC. It was clearly found and occurred at the targeted WPC, which is made from smallest particle size and for freezed-drying conditions. In the case of large particle, the mechanical properties of WPC decreased during decrease in intensity. The optimum mechanical property of WPC was obtained at 30 min of the wet milling time for freeze-drying conditions. Further research that focuses on these fractions with different particle size is needed to find out what exact size of wood flour is the most optimal in the WPC manufacturing.

Summary in Japanese

混練型木材プラスチック複合材料（WPC）は、木粉と熱可塑性樹脂を溶融混練して作られる複合材料である。 WPC には、メンテナンスが容易で、耐久性が高く、耐用年数が長いなどの利点があり、 またリサイクル材料を使用して製造でき、いくつかの添加剤により特性を向上させることが可能である。 WPC の製造において、原料としての木粉の特性が重要である。 WPC の需要の増大に伴い、その品質と性能を担保することが必要である。木粉の特性がWPCの性能に及ぼす影響についてはさまざまな研究が行われきたが、湿式粉砕時間や乾燥条件ごとの粒度分布など、明らかにされていない事柄も多い。本研究の目的は、フィラーの製造条件が、木粉の性状に及ぼす影響及び、これらがWPCの機械的特性に及ぼす影響を明らかにすることである。

アカマツの木粉13.5gをボールミルで200mlの水とともに200 rpmで湿式粉砕した。粉砕条件が WPC の機械的特性に与える影響を評価するために、0、10、20、30、40、60、および120分の各条件で粉砕を行った。また、乾燥条件による影響を評価するために、粉砕後の木粉は -45° C で 7 日間の凍結乾燥もしくは 80° C で 24 時間の加熱乾燥を行った。乾燥後、ブレンダーで木粉を1分間再解繊し、小型ふるい振とう器により > 425 µm、180 – 425 µm、90 – 180 µm、53 – 90 µm、32 – 53 µm、および <32 µm の6画分に分級した。

本研究では、すべての湿式粉砕時間で90 – 180 µm、0、30、120分で180 – 425 µm、30分の湿式粉砕時間で32 – 53 µmの画分を使用してWPCの製造を行った。各条件の木粉、ポリプロピレン（PP）と無水マレイン酸変性 PP（MAPP）を、重量比は 25：74：1 で190° C、スクリュー回転速度30 rpmで10分間混練しコンパウンドを得た。

得られたWPCコンパウンドは破砕機で粉砕し、射出成形機を使用してWPC試験片を作成した。引張試験片と曲げ試験片の寸法は、それぞれ長さ50 mm、厚さ2 mm、幅4 mmと6 mm とした。試験片は、恒温湿度室（20℃、RH65％）に 5 日以上養生してから各種試験に

供した。引張試験は、つかみ具間距離 30 mm とし、試験速度 20 mm /分で行った。曲げ試験は、スパン 32 mm とし、試験速度 5 mm /分として行った。アイゾット衝撃試験は曲げ試験と同様の試験片寸法で行い、衝撃試験機を使用した。試験片数は 1 条件に付き各 5 体とした。吸水試験では、試験片を 70 ℃の温水に浸漬し、試験片の重量および寸法を 0、10、30、40、60、120 時間後に測定して吸水率および厚さ膨張率を算出した。その後、最初の 1 週間は 1 日 1 回、その後 3 日に 1 回、飽和状態になるまで同様の測定を繰り返した。

ボールミルによる湿式粉砕の時間が増加するに伴って、木粉の粒径が小さくなった。しかしながら、粉砕時間が 40 分を超えると、凝集が増加し、特に 60 分から 120 分に粒径が再度増加することが明らかとなった。レーザー散乱式粒度分布測定の結果から、加熱乾燥条件と凍結乾燥条件の両方で大きな粒子サイズのピークに着目すると、30 分までは湿式粉砕時間の増加とともにピークは減少した。また、粒度分布のばらつきから、分級後の木粉にも様々な粒径・形状の木粉が存在することが示された。また、30 分以上の湿式粉砕では過粉砕に伴う微粉により凝集が発生することが示唆された。SEM 画像から、湿式粉砕 120 分で凝集が発生し、熱乾燥条件の場合は凍結乾燥条件よりもより大きく強固な凝集が生じていることが明らかになった。このことから、凝集を回避するためには 40 分未満の湿式粉砕時間が適切であることが結論付けられた。

湿式粉砕の時間ごとに WPC の引張強度、曲げ強度、曲げ弾性率などの機械的特性を比較すると、粉砕時間 30 分までは各種機械的性能が上昇した。湿式粉砕時間の 120 分では、機械的特性は減少したが、凍結乾燥条件では熱乾燥条件よりも高い値を維持した。このことから、凝集した木粉が WPC の機械的特性に負の影響を与えることが示唆された。また、粒子サイズが小さくなると、WPC の機械的特性が向上する傾向にあった。アイゾット衝撃強度は、湿式粉砕時間 0 分から 30 分では微増し、その後わずかに減少したが、 120

分では他の条件と比較してより高い衝撃強度を有していた。これは木粉の凝集が原因であると考えられた。

吸水試験では、浸漬開始後648時間で吸水量は飽和した。湿式粉砕60分および120分、熱乾燥条件では吸水率および厚さ膨張率が高くなったが、これらは過粉砕により生じた微粉の熱乾燥に伴う凝集が原因であると考えられた。しかしながら、メッシュサイズの異なる木粉を使用したWPCでは、吸水性、および厚さ膨潤の両方に有意差がないことを示した。一方で、同一湿式粉砕時間で比較した場合、熱乾燥条件と凍結乾燥条件との間で厚さ膨張率には有意差があることが確認された。

一連の結果は、粒度分布がWPCの機械的特性に影響を与えることを示すものであった。微小な粒径の木粉の割合が多すぎると、WPC の機械的特性が低下した。また、大粒径の木粉の割合が低下すると、WPC の機械的特性も低下した。WPC の最適な機械的特性は、凍結乾燥条件での湿式粉砕時間の 30 分で得られた。

LIST OF THE PUBLICATIONS AND CONFERENCES CONCERNING THE DISSERTATION

List of Publications Concerning the Dissertation

1. Arif Delviawan, Shigehiko Suzuki, Yoichi Kojima, and Hikaru Kobori (2019). The influence of filler characteristics on the physical and mechanical properties of wood plastic composite(s). **Reviews in Agricultural Science, 7:1-9.** https://doi.org/10.7831/ras.7.1.

2. Arif Delviawan, Yoichi Kojima, Hikaru Kobori, Shigehiko Suzuki, Kenji Aoki, and Shinji Ogoe (2019). The effect of wood particle size distribution on the mechanical properties of wood-plastic composite. **Journal of Wood Science, 65(67):1-11.** https://doi.org/10.1186/s10086-019-1846-9.

List of Conferences Concerning the Dissertation

1. Arif Delviawan, Hikaru Kobori, Yoichi Kojima, Kenji Aoki, Shigehiko Suzuki, Shinji Ogoe, and Hirokazu Ito (2018). The effect of wet milling time on the particle size of wood flour and mechanical properties of wood plastic composite. **JWRS Chubu branch meeting 2018, Pp. 12-13**, 25th October 2018, Shizuoka University, Shizuoka-Japan (Poster session)
2. Arif Delviawan, Yoichi Kojima, Hikaru Kobori, Shigehiko Suzuki, Kenji Aoki, Shinji Ogoe, Tomoyuki Ema, Masaki Okamoto, and Keiko Kagawa (2019). The Relationship Between Particle Size Distribution of Fibrillated Wood Flour and Mechanical Properties of Wood Plastic Composites. **ACMC Session 2019, Pp. 59-60**, 2nd March 2019, Doshisha University, Kyoto-Japan (oral presentation)
3. Arif Delviawan, Yoichi Kojima, Hikaru Kobori, Shigehiko Suzuki, and Kenji Aoki (2019). The influence of particle size distribution on the mechanical properties of wood plastic composite. **UGSAS-GU & BWEL Joint Poster Session on Agricultural and Basin Water Environmental Sciences 2019, Pp. 116-117**, 10th October 2019, Gifu University, Gifu – Japan (Poster session)
4. Arif Delviawan, Yochi Kojima, and Hikaru Kobori (2020). The influence of wet milling time of wood flour on the water resistance of wood plastic composite. **UGSAS-GU & BWEL Joint Poster Session on Agricultural and Basin Water Environmental Sciences 2020**, 10th November 2020, Gifu University, Gifu – Japan (Poster session)