# DEVELOPMENT AND CHARACTERIZATION OF HIGH STRENGTH CELLULOSIC NANOFIBER AND POLYVINYL ALCOHOL (PVA) COMPOSITE MATERIALS

MARCH 2017

**Graduate School of Advanced Technology and Science**
**Tokushima University**

NOOR HISYAM BIN NOOR MOHAMED

# TABLE OF CONTENTS

# GENERAL INTRODUCTION

In this study, the mechanical properties of cellulosic nanofibers-reinforced polyvinyl alcohol (PVA) composite were studied. The two types of cellulosic nanofibers used were microfibrillated cellulose (MFC) and bacterial cellulose (BC) and the reinforcement effect of both types of cellulose nanofibers to PVA polymer was extensively studied. Various experiments involving several heat treatment methods and different heat treatment temperatures were conducted and the effects to the properties of the samples were investigated. Several characterization methods were conducted in order to justify and further understand the findings from the mechanical testing results.

Chapter 1 describes the introduction on the topic of green composites and the main materials which comprise this type of composites. The development and various studies which have been conducted previously by various researchers were also listed out in order to grasp the latest technology and findings regarding this topic.

Chapter 2 explains about preliminary works which were done to investigate the mechanical properties of MFC-reinforced PVA composites. The neat PVA films, MFC sheets, and their nanocomposites containing MFC weight ratios of 10, 15, 30, 40, 50 and 80 wt% were fabricated. Heat treatment by hot pressing at 180°C was conducted on the samples to study its effect to the mechanical properties and the results were compared with the non heat-treated samples. Morphology of the composites was studied by scanning electron microscopy (SEM), the thermal degradation properties of PVA films and MFC was studied by thermogravimetric analysis (TGA) and the mechanical properties were evaluated by means of tensile tests. Results from this preliminary work will be referred for further experimentation work in this study.

Chapter 3 is the study based on the preliminary data and results, where we further investigate the properties of MFC/PVA composites using MFC at 40 to 80 wt% content, and two different heat treatment methods were studied, which consisted of the hot press method and the oven heat method. The results were compared and characterization was conducted by X-ray diffraction analysis and FT-IR analysis to understand the effect of different heat treatment methods on the mechanical and physical properties of the composite materials. Morphology of the samples surfaces and fracture surfaces were examined by SEM observations.

Chapter 4 presents further investigation which was made on composites using different heat treatment processes of bacterial cellulose (BC) to yield the highest mechanical properties and the samples were characterized to understand the effect of the different manufacturing methods on the molecular structure, the thermal behavior and the chemical composition of the composites. The mechanical properties and the characterization results were studied and discussed in detail.

Finally, the conclusion from this study was presented considering all results and discussion obtained from the experimentation works.

# CHAPTER 1

# INTRODUCTION

## 1.1 Green composites based on biodegradable polymer materials

Due to rapid progress in technology and the demand from the expanding industry throughout the world, engineers and scientists have managed to create high-end machines and explored science to a level never achieved before. From gigantic scale machines to nano-sized electronic parts, each of the inventions was made to meet the need of the industry and to prepare for the coming future challenges. In terms of materials technology, scientists have been able to manipulate molecular structures of materials to enhance their properties and to further expand their potential for wider application. In recent decades, plenty of inventions for utilizing nature-based and renewable materials are made to ensure no harmful effect from the rapid industrial progress.

One of the most promising materials for renewable purposes is natural fibers. They are known as abundant natural materials which are almost inexhaustible and available throughout the world where the main sources are plants and some from animals. Plant-derived natural fibers have been widely extracted and used in various ways to accommodate the needs of human and their living. To name a few, fibers such as cotton, jute, flax, kenaf, hemp and coir are among the famously utilized natural fibers which are beneficial as they are utilized for paper making, packaging and also brilliantly utilized as textiles and other house appliances.

Natural fibers are known to consist mainly of several elements, namely cellulose, lignin and hemicelluloses. Therefore, natural fibers are also known as cellulosic fibers. Cellulose is basically a natural polymer which is mainly stacked together forming fibrils, and these fibrils form the main structural component of plant cell walls. Since a few decades ago, scientists have been exploring the potential of cellulose. Recently, cellulose-derived nanofibers have been given much attention as a promising reinforcement of polymers. They are mainly derived from plants such as wood, hemp and cotton (Klemm et al., 2011). The reinforcing capability of these nanofibers is exploited in polymers to produce composites with better properties compared to those of polymer alone. These nanofibers refer to cellulose fibrils of 10-40 nm thickness with length of more than 1,000 nm and high aspect ratios L/*d* of about 100-150 (Siró & Plackett, 2010).

Among many types of cellulose nanofibers, microfibrillated cellulose (MFC) and bacterial cellulose (BC) are two of the most interesting types and have been studied by many researchers in the last few decades. The MFC is the cellulose being fibrillated longitudinally to form a 3D network of microfibrils, while bacterial cellulose (BC) is cellulose nanofiber produced by a type of bacteria. The extraction of fibers from wood dates back to 1980s where a high pressure homogenizer was used to produce MFC from wood pulp (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983). The MFC extracted was rather entangled and the networks were not structured. The process of extracting MFC was known to be labor-intensive, and the major methods used were mechanical extraction, chemical treatment and enzymatic pre-treatment. Recent manufacturing methods were developed based on mechanical extraction method using high-pressure homogenizing processes, where fine structures of MFC are produced.

Research has been conducted on the composite properties of MFC and biodegradable polymers to produce green materials which are nontoxic and safe to the environment. Due to the hydrophilic properties of MFC, polymers having similar hydrophilicity characteristics are presumed to produce biodegradable composites with enhanced properties due to good compatibility between both materials. Polyhydroxy polymers such as polyvinyl alcohol (PVA) are commonly used in industry due to its good film formability and hydrophilicity. The PVA is a water soluble polymer, possessing excellent film forming property and outstanding capability to resist oil, grease and solvents. Some known applications of PVA polymers are in the production of adhesives and paper coatings, in medicine and in the manufacturing of biodegradable polymer films. The easy film forming and the environmentally friendly properties of PVA attract researchers to conduct studies on their properties.

The reinforcing effect of MFC has the potential to replace synthetic and non-renewable materials such as plastics and some metals, thus promoting a more environmentally-friendly future. The hydrophilic characteristic of MFC makes them suitable with hydrophilic polymers (Siró & Plackett, 2010). Many studies have been conducted to alter the parameters of the composite production to obtain desired properties. Heat treatment of PVA is a typical method to reduce hydrophilicity and sensitiveness to humidity. Another practical method commonly used is cross-linking using chemical reagents which can react with the hydroxyl groups in the PVA. The cross-linking has been practiced industrially, but its limitation involves the use of chemical substances. Studies about the effect of cross-linking of PVA have shown good results in order to increase the properties of PVA and its composites (Gohil, Bhattacharya, & Ray, 2006; Peresin et al., 2014). Furthermore, the combination of crosslinking and heat treatment was also explored by many researchers (Hasimi, A.Stavropoulou, Papadokostaki, & Sanopoulou, 2008; Krumova, 2000; Kumeta, Nagashima, Matsui, & Mizoguchi, 2003).

Introducing nano-sized MFC into the PVA polymer allows the increase of surface area for contact between MFC and PVA, allowing more chemical bonding to occur. Heat treatment of PVA theoretically enables the water molecules in the crystal lattice to be removed thus reducing the *d* spacing of the lattice space. This produces PVA with better resistance to water and humidity (Kumeta et al., 2003). However, to our knowledge, very little study has been done on the effect of heat treatment alone to the mechanical properties of PVA and their composites. The practical and simple process of heat treatment might enable mass production at an industrial scale with advantages of cost reduction and time consumption without usage of chemical reagents. At the same time the enhanced properties such as higher strength, lower water solubility and resistance to humidity might enable wider application of the MFC/PVA composites.

### 1.1.1 Polyvinyl alcohol polymer

PVA is a water soluble and biodegradable synthetic polymer which consists of a structural repeat unit of $-[-CH_2-CH(OH)-]_n-$. It is one of the most produced water-soluble polymers, commercially produced by hydrolysis of polyvinyl acetate (PVAc) as shown in Figure 1.1. PVA is mainly used in film form in paper industry, plywood manufacturing, in packaging and also as modifier of thermosetting resins. The final properties of PVA are dependent of the properties of PVAc, polymerization degree and the degree of hydrolysis. Despite being very useful, the major drawbacks which limit the application of

PVA are the low mechanical properties, water absorption sensitivity and thermal stability. A study has revealed that diffusion of water into semi-crystalline samples of the polymer gradually destroyed the crystalline regions of the PVA polymer, where water was found to disrupt the intermolecular hydrogen bonds in the interface region between crystalline and amorphous regions (Hodge, Edward, & Simon, 1996).

Modification of PVA was done using formaldehyde or maleic acid for improved solubility and thermal properties (Han, Li, Chen, Xu, & Wickramasinghe, 2003). In order to tailor the properties, one well known method used is the popularly called cross-linking method. Chemical cross-linking is one effective method to increase the mechanical properties of PVA. Cross-linked PVA shows a good application possibility for biomedical field. Among the chemicals used for crosslinking are formaldehyde, glutaraldehyde, maleic anhydride and etc. A study by M. Krumova et al. attempted to crosslink PVA with hexamethylene diisocyanate to observe the effect to mechanical and thermal properties. Their study showed that the glass transition ($T_g$) value increased abruptly until 20% crosslinking degree, then levelled off on the increase of crosslinking degree of about 74% (Krumova, López, Benavente, Mijangos, & Pereña, 2000).

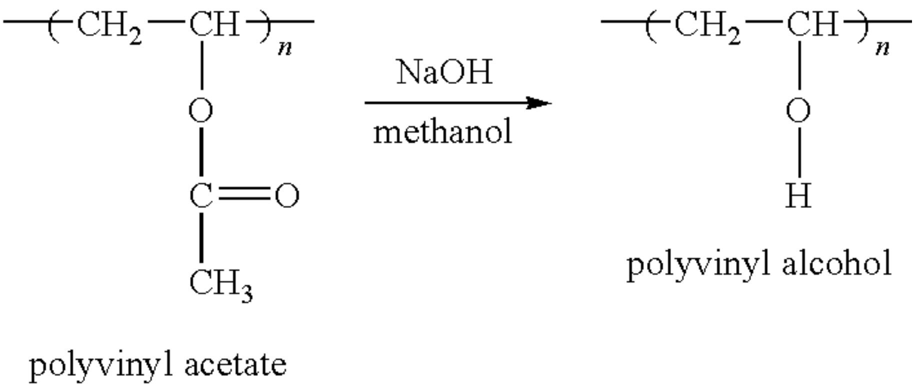


Figure 1.1: The formation of polyvinyl alcohol.

On the other hand, heat treatment of PVA provides another simple method to increase the properties of PVA polymer, specifically to increase crystallinity and significantly reduce swelling and solubility of PVA films in water. An early study by Byron et al. in 1897 confirmed the increase of crystallinity of heat-treated PVA membranes. Heat treatment of PVA films was conducted at temperatures of 100˚C to 200˚C for 1 hour period. The permeability of the PVA films decreased as the heating temperature increased (Byron, PR Dalby, 1987). A study by Kumeta et al. has crosslinked PVA via esterification with poly (acrylic acid) (PAA) followed by heat treatment at 200°C. The study found that heat treatment at low pH condition has managed to enhance the hydroxyl group degradation of PVA (Kumeta et al., 2003).

### 1.1.2 Cellulose nanofibers

Cellulose is considered as an inexhaustible resource while being a basic structural material of plants such as wood, cotton and hemp, particularly in stalks, stems and trunks. Cellulose is also synthesized by other living organisms such as tunicates or bacteria (Henriksson, Henriksson, Berglund, & Lindström, 2007; Yamanaka, Ishihara, & Sugiyama, 2000).

Cellulose is made from a chain of glucose which gives wood and plants their strength that enables them to stand up to few meters high for many years. An example of a natural form of cellulose is cotton. The chemical structure of basic cellulose is shown in Figure 1.2. The hydroxyl groups in the cellulose forms strong hydrogen bonds which directs crystalline packing (John & Thomas, 2008). The length of polymer chain of the cellulose often varies according to different sources and part of the plant.

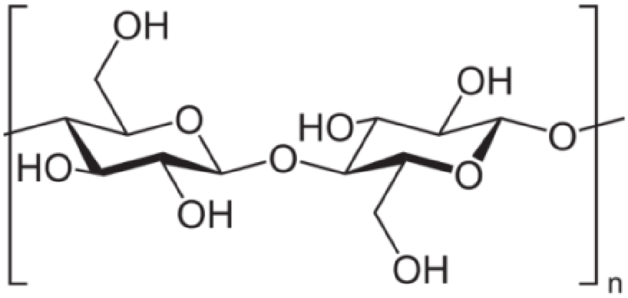


Figure 1.2: Structure of cellulose.

Bacterial cellulose is comprised of natural nano-sized fibers (25-200 nm) produced by a type of bacteria called *Acetobacter* species, and was known to possess superior mechanical properties of high purity without lignin, hemicelluloses or pectin that makes it well used in the food industry (Shi, Zhang, Phillips, & Yang, 2014). These bacteria also produce super fine and pure cellulose fiber network structure in the form of pellicles. They are composed of finer microfibril bundles of 2 to 4 nm in diameter (Yamanaka, Watanabe, & Kitamura, 1989). At the same time, BC also exhibits high tensile strength and Young's modulus which offer wide potential application in the biomedical field such as wound dressings, tissue generation and some electronic devices (Shah, Ul-Islam, Khattak, & Park, 2013). The nano-sized fiber diameter and high aspect ratio lead to larger fiber surface which enables better interaction and bond with the material around it, such as polymer compounds (Klemm et al., 2011), and is also attractive due to its optical and barrier properties. The manufacturing process is direct and produces a natural network structure, high degree of polymerization (DP) and high crystallinity. Nata de coco is a type of BC produced by fermentation using coconut water, and it is a type of famous food commonly served as dessert in Asian countries. Nata de coco contains pure cellulose; therefore several studies have been conducted to investigate the drying process and the effect of the morphology on properties of nata de coco.

BC is known to be one of the reinforcing materials in biocomposites, combined with polymer materials such as polylactic acid, polypropylene and polyvinyl alcohol, where enhanced properties are expected due to the reinforcing effect of the cellulose nanofibers. The reinforcing effect of BC with polylactic acid using compression molding has yielded an increase in tensile strength and Young's modulus by 315% and 100% respectively, compared to neat polylactic acid resin (Quero et al., 2010). BC based phenolic resin composites are found to possess higher Young's modulus up to 28 GPa due to its uniform and continuous nano-scalar network of cellulosic elements as reported by Nakagaito et al. (Nakagaito, Iwamoto, & Yano, 2005). By this notion, further investigation on the processing method of BC and its composite will expand the possibilities of tailoring the properties and widen their application.

## 1.2 Development of biodegradable polymer composites and enhancement of properties

For the past decade, researchers have put their focus and interest on the reinforcing effect of microfibrillated cellulose (MFC) on polymeric materials, including PVA polymer. The study includes observation on the effect of MFC loading, various chemical treatments and MFC orientation to the properties of the composites. Knowing the reinforcing potential of MFC, various efforts have been conducted and are reported in various research papers worldwide.

An effort to study the alignment effect of MFC has started as early as 1992 by Sugiyama and his team, where they managed to control the orientation of highly crystalline, long rods of tunicate cellulose microcrystals by using strong magnetic fields of 7 T. Their study has revealed that the introduction of magnetic field has oriented the long axes of the tunicate cellulose microcrystals perpendicularly to the field direction (Sugiyama, Chanzy, & Maret, 1992). Due to difficulty in obtaining a high magnetic field in lab scale, Nishiyama et al. introduced a shearing method to achieve high degree of cellulose microcrystal orientation (Nishiyama, Kuga, Wada, & Okano, 1997). Their study managed to yield a film with highly oriented microcrystals by drying a gel layer in the inner surface of a glass tube. More recent studies on this magnetic method were further conducted by several researchers. A study by I. Kvien aimed to align cellulose whiskers in PVA polymer using a 7 T magnetic field was conducted. PVA polymer incorporating 2 wt% cellulose nanowhiskers was casted while the magnetic field was applied during the drying process. The study has managed to obtain cellulose nanowhiskers oriented perpendicularly to the direction of the magnetic field, and dynamic modulus of the nanocomposites was 2 GPa higher than the samples with fiber direction along the magnetic field direction (Kvien & Oksman, 2007). The use of magnetic field to align cellulose fibers has initiated the idea to align bacterial cellulose by introducing a new fabrication method where electric field is introduced while the bacteria are producing nanocellulose. Sano et al. have managed to introduce a bottom-up concept to control fiber orientation of *A. xynilum* bacteria at nanoscale level to produce tailored fiber layers (Sano, Rojas, Gatenholm, & Davalos, 2010). Drawing method has also been introduced to increase the orientation of MFC in nanopaper samples. The MFC sheet was stretched at tensile rate of 50 %/min until the strain reached 20, 40 and 60 % and the orientation of the nanofibers were studied. The results showed increase in tensile modulus and tensile strength compared to the non-drawn samples (Sehaqui et al., 2012).

Research on fabrication and characterization of MFC/PVA-based composites has been extensively carried out recently where many promising breakthroughs are revealed. The filler loading effect to the mechanical properties are studied by various researchers to understand the best combination of MFC as reinforcement in PVA polymer. A study by Lee et al. has the tensile properties of nanocellulose-reinforced PVA increased as 1 wt% of nanocellulose content are introduced. However further increases of nanocellulose content to 3 and 5 wt% has decreased the strength by 3.0 % and 55.3 % relative to that of 1 wt% samples, respectively (Lee et al., 2009). Similar trends were obtained by Zhou et al. where an increase in tensile strength was observed for PVA reinforced with 2 wt% of nanocellulose, however the value decreased as the nanocellulose content was further increased to 6 and 10 wt%, although an increase of tensile modulus was obtained as higher nanocellulose content were introduced (Zhou, Fu, Zheng, & Zhan, 2012). At higher contents of cellulose nanofiber, researchers have done some studies to explore the potential and the properties of MFC-reinforced polymer composites. Qiu and Netravali have introduced microfibrillated cellulose (MFC) to PVA solution up to 40 wt% and the results showed a positive increase of fracture stress with an increase of up to 150% as compared to neat PVA samples. The Young's modulus of the samples also showed sharp increase as the MFC content increased (Qiu & Netravali, 2012). However, research with high MFC content in PVA matrix is rarely found, which opens a new possibility to be explored. Comparing MFC to other types of nano-sized elements such as cellulose nanocrystals, there are reports which shows that MFC yields higher strength and modulus in polymer composites due to MFC's larger aspect ratio and fibrils entanglement (Xu et al., 2013).

In terms of manufacturing methods, some studies on the effects of different processing methods on nanofiber composites have been done worldwide. Pa'e et al. has conducted a study on different drying methods such as oven drying and freeze drying and the effects of these drying methods to the morphology, crystallinity, tensile strength and swelling ability of nata de coco pellicles (Pa'e et al., 2014). Other different methods such as grinding and chemical treatment of nanofibers before composite preparation were also done to study the effect of these treatments to the composite sheets (Oishi, Nakaya, Matsui, & Hotta, 2015). The processing condition effect on the flexural properties of cellulose nanofiber/PLA composite was studied by Takagi et al. and the results showed increases in flexural strength and modulus as the hot press pressure changes (Takagi & Asano, 2008).

## 1.3 Research objectives

The reinforcement of cellulose nanofiber in polymer has yet to be explored to its limit; therefore continuous research to further explore the possibilities has to keep on going. In this study, the mechanical properties of MFC, BC and their reinforced PVA composites were studied to understand the effect of the nanofibers as reinforcement material. The effect of heat treatment on the mechanical properties of PVA and the composites fabricated from these two different types of cellulose nanofiber were also studied. Different weight ratios of MFC were incorporated to study the effect on the mechanical properties of the MFC/PVA composites. The MFC content which yields the highest mechanical properties was determined and the effect of heat treatment to the mechanical properties of the MFC/PVA composites were evaluated. Two types of PVAs with different degree of hydrolysis were used to study the mechanical properties of the composites. The morphology of the composites was analyzed by scanning electron microscopy (SEM) to observe the MFC dispersion in PVA at different MFC weight ratios. Thermal analysis was also done by thermogravimetric analysis (TGA); meanwhile other characterizations such as X-ray diffraction (XRD) analysis and FT-IR analysis were conducted to study the crystallinity and molecular structure of the samples due to the heat treatment.

From this study, we aim to understand the reinforcement characteristics of MFC and BC nanofibers with PVA polymer and the effect of heat treatment by investigating the following:

1. The mechanical properties of two types of polyvinyl alcohols (PVAs) with different degrees of hydrolysis.
2. The mechanical properties of sheets made from both MFC and BC nanofibers and their PVA composites by means of tensile test.

3. The effect of the nanofiber content especially at higher content and heat treatment effect on the mechanical properties of the PVA films and MFC/PVA composites;
4. Optimum condition of heat treatment to obtain improved mechanical properties of MFC/PVA and BC/PVA composites.
5. The morphology and the microstructure of all the MFC and BC sheets and their composites with PVA.

Having known results and methods that have been conducted by previous studies, we try to further explore and propose methods to increase the properties of the MFC and BC sheets, and also their PVA composites for wider applications in future. The findings from this study are expected to give more insight on the unknown properties of heat-treated PVA and MFC/PVA composites which information are scarce and yet to be explored by other researchers. This study would also open for possibility to replace chemical-involving processes such as chemical crosslinking which are likely to produce harmful residues of chemical, whereby heat treatment provides a more direct method of altering the mechanical properties of MFC/PVA composites and produces no residue after the treatment process.

# CHAPTER 2

# PRELIMINARY STUDY ON THE PROPERTIES OF HEAT-TREATED MICROFIBRILLATED CELLULOSE/POLYVINYL ALCOHOL COMPOSITES

## 2.1 Introduction

Heat treatment is one of the methods to improve the properties of PVA, made possible by removal of water and formation of new hydrogen bonds between PVA molecules. The water sensitivity of PVA also was found to be significantly reduced by heat treatment due to the decrease in interplanar spacing (Sakurada & Okaya, 2006). The reinforcement effect of MFC in PVA polymer was expected due to the compatibility of both materials and the nano-scale size of MFC which allows greater interaction between both materials.

In this study, we conducted preliminary studies to evaluate the reinforcing effect of MFC in PVA polymer. The MFC was incorporated in PVA polymer with different weight contents of 10, 15, 30, 40, 50 and 80 wt%. The mechanical properties of pure PVA films, pure MFC sheet and MFC/PVA composite films were investigated. The effects of the different weight contents of MFC in the MFC/PVA composites were studied to obtain the optimum weight content of MFC to achieve the highest mechanical properties of the composites. Furthermore, we conducted heat treatment by hot pressing the samples at 180°C for 10 minutes under 10 MPa pressure to study the effect of heat treatment on the mechanical properties of the samples. The mechanical properties of the heat-treated samples were compared with the untreated samples to analyze the effect of heat treatment. These results will be crucial to obtain information on the reinforcing behavior of MFC, the heat treatment effect and the highest mechanical properties of the composites.

## 2.2 Materials and methods

### 2.2.1 Raw materials

The cellulose nanofiber used in this research was microfibrillated cellulose (MFC) with product name Celish KY100G manufactured by Daicel Corporation, Japan. This material comes in a wet slurry condition containing 90 wt% water and the remaining 10 wt% consisting of MFC. The SEM image of the MFC used in this experiment is shown in Figure 2.1.

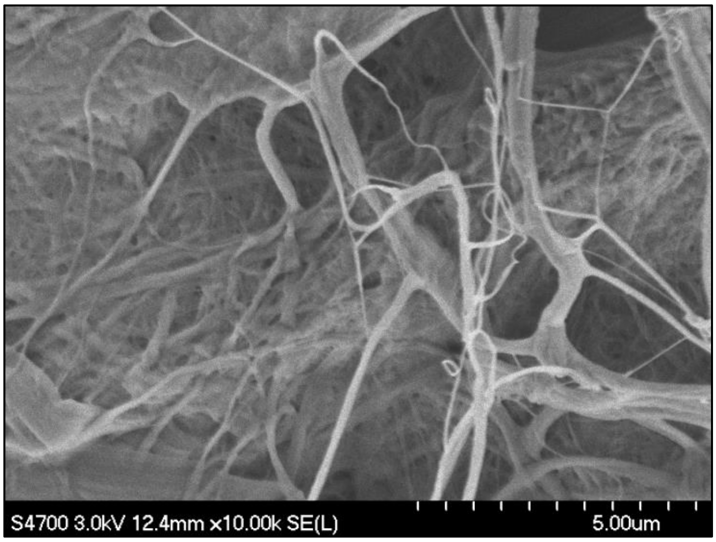


Figure 2.1: SEM image microfibrillated cellulose (MFC).

The matrix polymers used in this research were two types of polyvinyl alcohols (PVAs), completely hydrolyzed and partially hydrolyzed, both purchased from WAKO Pure Chemical Industries, Ltd. Japan. The completely and partially hydrolyzed PVAs will be named PVA-f and PVA-p, respectively, throughout this report. The general properties of the two PVA polymers based on the manufacturer's data sheet are listed in Table 2.1. Fully hydrolyzed PVA has more acetate group being replaced by alcohol groups compared to the partially hydrolyzed PVA.

Table 2.1: Properties of PVA polymers.

| Types of PVA | Degree of hydrolysis | Molecular weight |
|---|---|---|
| Fully hydrolyzed PVA (PVA-f) | >96.0 mol% | 900~1100 |
| Partially hydrolyzed PVA (PVA-p) | 86.0~90.0 mol% | 900~1100 |

### 2.2.2 Fabrication of PVA films, MFC sheets and MFC/PVA composite sheets

*Preparation of PVA films*

A 2 wt% concentration of PVA solution was prepared by adding 10 g of PVA powder in 500 ml of distilled water. The process was done while heating the distilled water in a beaker and the PVA powder was added slowly until the water temperature reached 90°C and was continuously stirred until totally diluted as shown in Figure 2.2. The PVA solution was then cooled to room temperature and kept in an airtight container prior to its use. For the PVA film, 200 g of PVA solution was poured into a polystyrene tray and was oven-dried at 30°C until totally dry to produce thin PVA films.

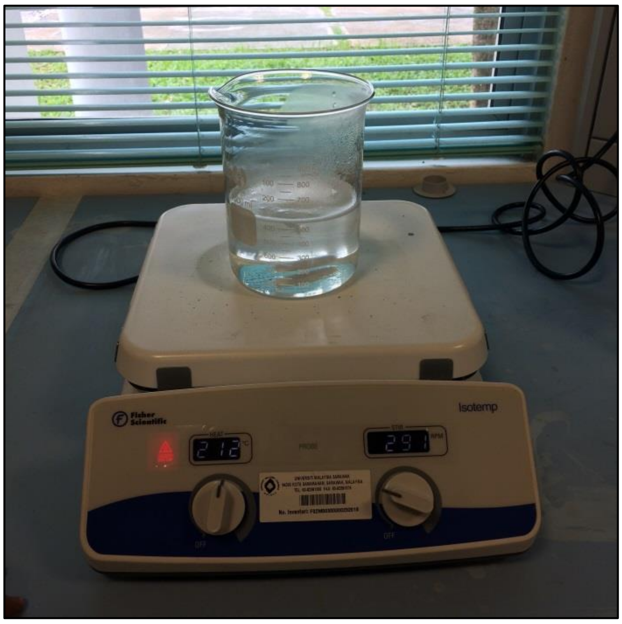


Figure 2.2: Preparation of PVA solution.

### *Preparation of MFC sheet*

The MFC sheet was manufactured by mixing 20 g of slurry MFC with 200 ml distilled water and stirred at 300 rpm for 2 hours to produce a homogeneous MFC aqueous suspension. Then, the aqueous suspension was vacuum filtered for 2 hours to eliminate most of the water content, resulting in a wet sheet, which was then dried in an oven at 30°C for at least 48 hours. The resultant thickness of the MFC sheet was approximately 0.2 mm.

### *Preparation of MFC/PVA sheet*

The MFC/PVA sheet was prepared by mixing the MFC suspension and the PVA solution with the desirable weight ratio to obtain 10, 15, 30, 40, 50 and 80 wt% MFC content. The MFC suspension and PVA solution were mixed in a glass beaker and stirred at 300 rpm for 2 hours to enable thorough mixing and avoid agglomerations. Then, the air bubbles were removed by placing the mixture in a vacuum chamber until no visible bubbles were observed. The MFC/PVA suspensions were poured into polystyrene trays and left to dry at 30°C in an oven. The MFC content was calculated as below:

$$\frac{W_{MFC}}{W_{MFC/PVA}} \times 100 \text{ [wt\%]}$$

Where $W_{MFC}$ is the weight of the MFC after deducting the weight of water content in the MFC slurry (MFC slurry contains 10 % MFC and 90 % water), and $W_{MFC/PVA}$ is the total weight of the dried composite sheet of mixed MFC suspension and PVA solution after being dried in 30˚C oven. The MFC content will be expressed in weight percent [wt%].

### *Heat treatment by hot press*

To study the effect of heat treatment by hot pressing method, all samples underwent hot-pressing at 180°C for 10 minutes under 10 MPa pressure. The samples were loaded into a 10 mm x 100 mm mold and the temperature was raised from room temperature to 180°C. Once the temperature had reached 180°C, the samples were loaded with 10 MPa pressure for 10 minutes, then the load was removed and the sample in the mold was left to cool to room temperature. The hot-press setup in this experiment is shown in Figure 2.3.

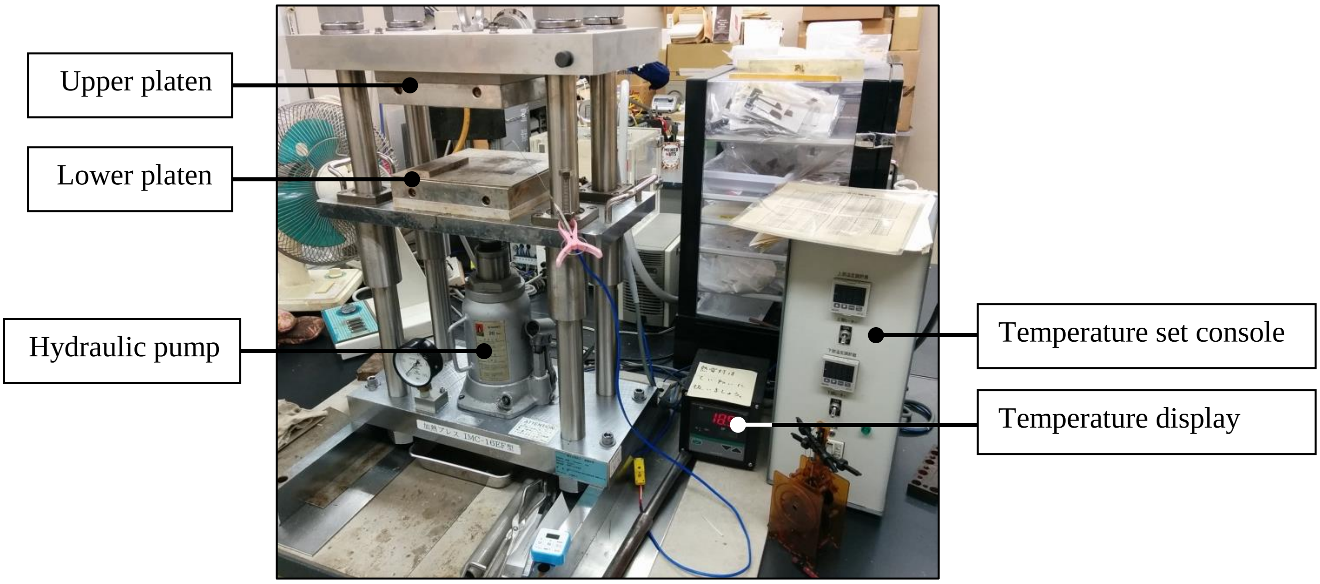


Figure 2.3: Hot-press setup.

### 2.2.3 Characterization

*Tensile test*

Tensile test samples of PVA films, MFC sheets and MFC/PVA composites were prepared in 10 mm x 100 mm size with the thickness ranging from 0.08 to 0.11 mm. The widths and thicknesses were measured at three points along the gauge length of 30 mm to obtain the average thickness and width of the samples and to ensure no irregular sample dimension due to manufacturing defects. Then, the samples were glued at both ends with paper tabs to prevent damage caused by gripping (Figure 2.4). The samples were stored in a desiccator under controlled humidity for 24 hours and tensile tests were conducted immediately after the samples were taken out to avoid the effect of humidity on the samples. Mechanical properties of the samples were evaluated by tensile tests conducted using Instron 5567 (Instron Corporation, USA) universal testing machine at room temperature. Tests were performed with a 500 N load cell with the crosshead speed of 1.0 mm/min. At least three samples were prepared from each sample and average values of the tensile strength were calculated and reported.

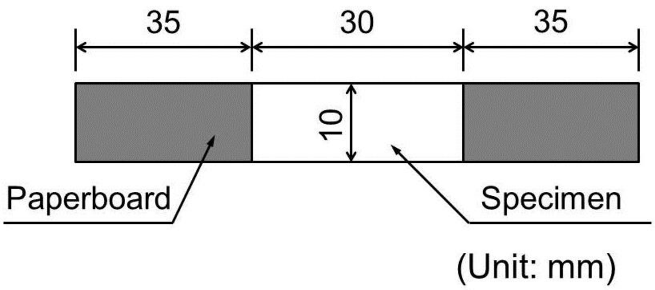


Figure 2.4: The configuration of tensile test sample.

*Thermogravimetric analysis (TGA)*

The thermal degradation behavior of PVA-f, PVA-p, MFC sheets and MFC/PVA composite sheets were conducted using a thermogravimetric/differential thermal analyzer TG/DTA 6200 (Hitachi High-Tech Science Corp., Japan). The TGA scans were recorded from 50 to 500°C at a heating speed of 10°C/min under nitrogen flow.

*Morphological analysis*

A field emission scanning electron microscope (FE-SEM HITACHI S-4700, Japan) was used to observe the samples and nanofibers to identify the morphology, diameter and the fibrils dispersion. The sample was coated with platinum for 60 seconds prior to SEM observation. This coating is to avoid charge up phenomenon which will badly affect the observation of the sample. The surface of the sheets and the fracture surface after tensile tests were observed under scanning electron microscope at an accelerating voltage of 1.5kV.

## 2.3 Results and discussion

### 2.3.1 Tensile properties

*Tensile properties of PVA films*

The dried PVA sheets resulted in transparent thin films having a thickness of 0.07-0.09 mm. The films of fully hydrolyzed PVA (PVA-f) and partially hydrolyzed PVA (PVA-p) were transparent with a smooth surface. The picture of the PVA film is shown in Figure 2.5. The tensile strength and Young's modulus values for both PVA types after tensile tests were listed in Table 2.2.

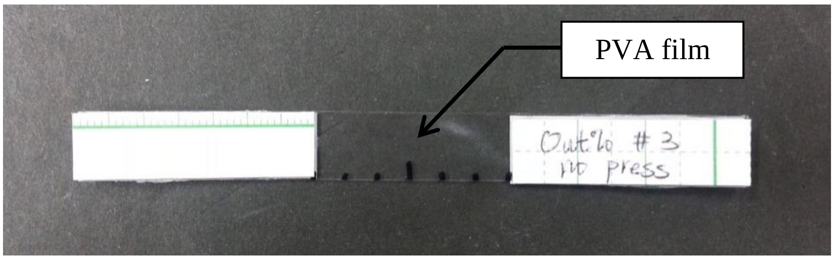


Figure 2.5: A sample of PVA film after oven drying.

Table 2.2: Tensile test results for two types of PVA films.

| PVA type | Untreated | | 180°C hot pressed | |
|---|---|---|---|---|
| | **Tensile strength [MPa]** | **Young's modulus [GPa]** | **Tensile strength [MPa]** | **Young's modulus [GPa]** |
| PVA-f | 88.3 | 5.2 | 128.8 | 7.1 |
| PVA-p | 75.6 | 5.0 | 80.0 | 5.5 |

The tensile strength of PVA-f yielded slightly higher values compared to that of PVA-p. Reports have shown that stress-strain characteristics of PVA films were affected by their crystallinity, molecular weight and the additives content (Miller, 1996). The PVA with higher degree of hydrolysis was known to have higher amount of hydroxyl groups in the PVA molecule, therefore tend to have more hydrogen bonding produced compared to PVA with lower degree of hydrolysis, which results in a higher strength with almost similar Young's modulus value (Dai & Yu, 2003; Limpan, Prodpran, Benjakul, & Prasarpran, 2012). The hot-pressed PVA samples generally yielded higher tensile strength compared to untreated samples. The hot-pressed PVA-f yielded an increase of 50%.

The Young's modulus for both types of PVA shows almost similar values of 5.0 GPa for PVA-f and 5.2 GPa for PVA-f. Comparing these results with other types of PVA, they are rather high compared to PVA types with similar film thickness and degree of hydrolysis which ranges from 1.7 to 1.9 GPa (Chan, Hao, & Heng, 1999). The strength of the PVA films is greatly affected by the chemical properties, namely molecular weight and degree of polymerization. Although the elongation is independent of the degree of hydrolysis, it is proportional to the molecular weight of the PVA (Mark, 2007). The hot-pressed PVA films yielded an increase in Young's modulus value of 36% for PVA-f and 10% for PVA-p samples respectively, showing an increase in the brittleness of the heat-treated PVA samples. The increase in Young's modulus value was most probably attributed to the change from ductile to the brittle condition of the PVA as heat was introduced and water molecules evaporated from the PVA samples. The high temperature yields to more melting and molecule recrystallization involved, therefore the materials become more brittle (Es-saheb & Elzatahry, 2014).

### *Tensile properties of MFC sheets*

The dried MFC sheet resulted in a whitish hard sheet of a thickness of about 0.1 mm as shown in Figure 2.6. The tensile strengths of the MFC sheets are shown in Figure 2.7 for both untreated and 180°C hot-pressed sheets. The results show an increase in both tensile strength and Young's modulus for the hot-pressed samples as compared to untreated samples. The tensile strength increases from 120 MPa to 140 MPa (approximately 16% increase) while Young's modulus increases from 6.5 GPa to 10.0

GPa (approximately 45% increase). The tensile strength value was comparable to those reported by Nobuta et al. where MFC sheets from kenaf/bast fibers with different chemical treatments yielded tensile strength of 123 MPa to 209 MPa (Nobuta et al., 2016).

The water content in the MFC sheet (on the surface of the fibrils and in the fibrils) evaporates as the heat treatment occurs, therefore the distance between the fibrils reduces, enabling molecular contact due to the effect of capillary and diffusion forces. This creates stronger intermolecular hydrogen bonds which form a more solid bulk material (Peng, Gardner, & Han, 2012). Dufresne et al. reported similar tendency of decrease in Young's modulus of sugar beet cellulose microfibril films under higher moisture condition (Dufresne, Cavaille, & Vignon, 1997).

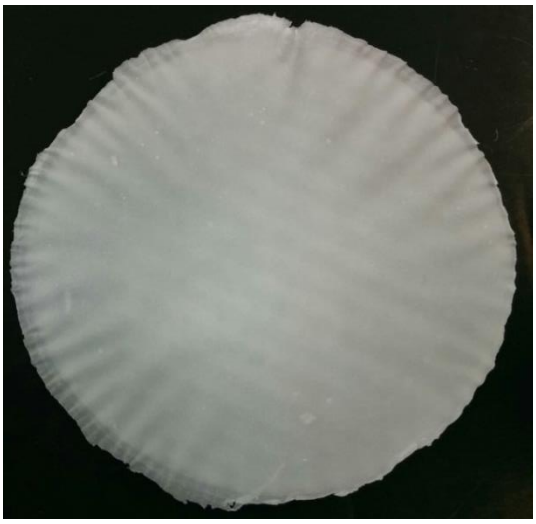


Figure 2.6: MFC sheet after oven dried at 30˚C in convection oven.

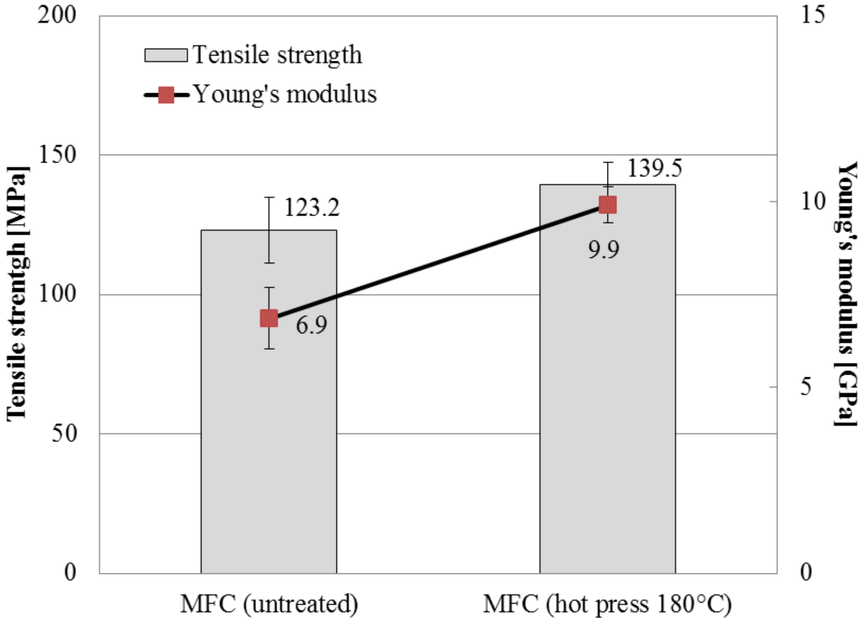


Figure 2.7: Tensile strength and Young’s modulus of MFC sheets.

*Tensile properties of MFC/PVA composite sheets*

The tensile test of MFC/PVA-f samples was conducted with nanofiber contents of 10 to 80 wt%. The results of tensile strength and Young’s modulus of untreated and heat-treated composite sheets are shown in Figures 2.7 and 2.8 respectively. In general, from the tensile test results, it was observed that hot-pressed samples exhibit higher tensile strength as compared to the untreated samples. The tensile strength for untreated samples shows an increasing pattern from 10 to 80 wt%; with the highest value recorded at 170 MPa with MFC content of 80 wt%. The highest tensile strength value recorded for hot-pressed samples was 185 MPa also at 80 wt% MFC content. The reinforcement effect of the MFC was noticed as the nanofiber content is increased especially at above 40 wt% where the tensile strength of the untreated samples was higher than those of pure PVA and pure MFC sheets.

The Young’s modulus values of both untreated and hot-pressed samples of MFC/PVA-f showed an increase from 10 wt% to 50 wt% as shown in Fig. 2.8. However, further increase of MFC content above 50 wt% showed a slight decrease. The Young’s modulus value of heat-treated samples showed relatively higher values compared to those of untreated samples, showing a stiffer characteristic of the heat-treated samples.

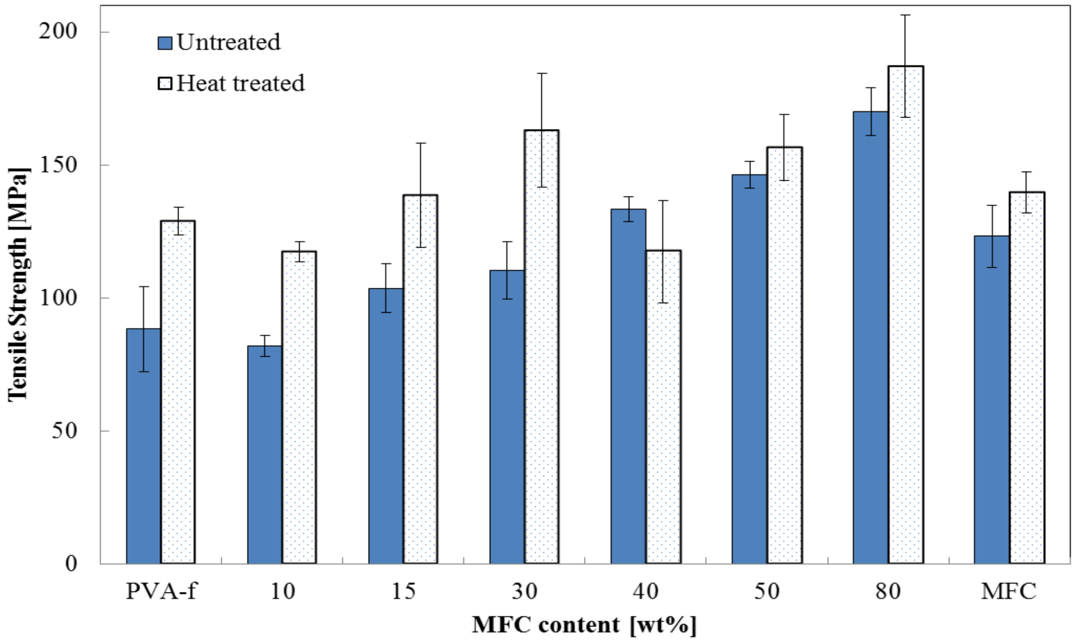


Figure 2.7: Tensile strength of MFC/PVA-f composites.

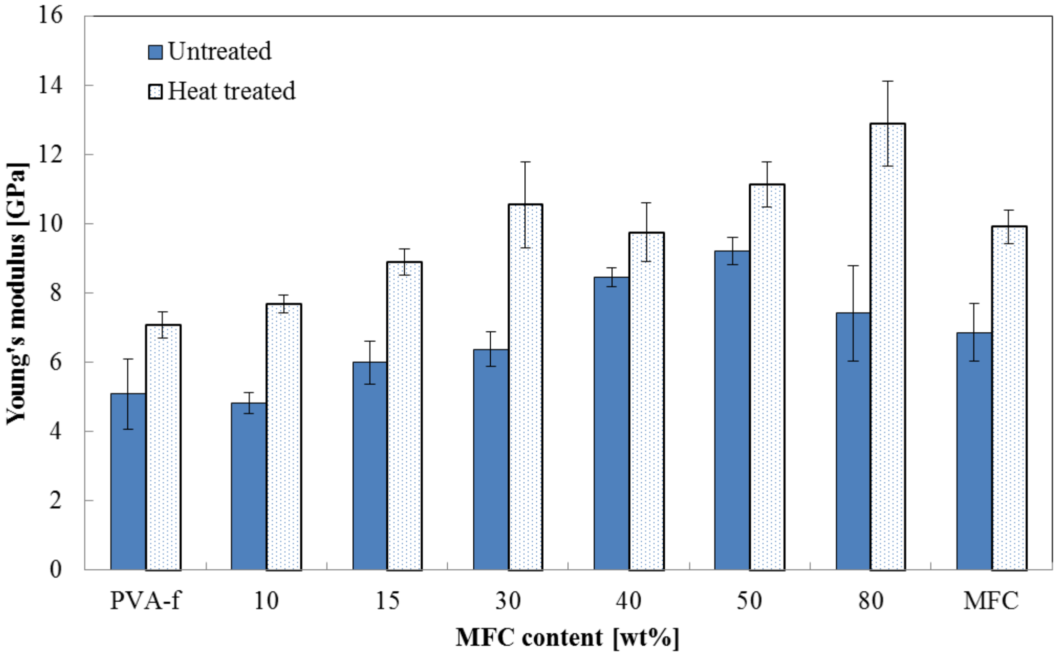


Figure 2.8: Young's modulus of MFC/PVA-f composites.

Tensile test of MFC/PVA-p composites was conducted and the results are shown in Figures 2.9 and 2.10 with similar MFC contents as of the previous MFC/PVA-f composites excluding the 10 wt% samples. The tensile strength of the composites increased as the MFC content increased, similar to those exhibited previously by MFC/PVA-f composites. The tensile strength of these composites peaked at 50 wt% with both untreated and heat-treated composites yielding the highest values of 140 MPa and 175 MPa respectively. Further increase of MFC content to 80 wt% has resulted in a lower tensile strength similar to that of 50 wt% MFC/PVA-p composite.

A study by J. Lu et al. has yielded similar results where increasing MFC content up to 10 wt% has shown an increase to the tensile strength of the composite, however, the values levelled off as the content was further increased to 15 wt% (Lu, Wang, & Drzal, 2008). The increasing tensile strength at MFC content above 40 wt% was rather remarkable; furthermore, heat treatment has significantly increased tensile strength than that of the untreated composites. We believe that higher MFC content allowed more interaction between MFC nanofibers and the PVA molecules by hydrogen bonding (Dubief, Samain, & Dufresne, 1999). We understand that the small nanofiber size creates more contact surface which allows MFC to bond with PVA molecules as the content increases.

The Young’s modulus of all heat-treated samples regardless of MFC content showed higher values compared to untreated samples, similar to those of PVA-f samples previously reported. The highest Young’s modulus value was recorded at 12.0 GPa at 50 wt% MFC content of heat-treated samples. We can notice a similar trend of the tensile strength and Young’s modulus result, where higher MFC content increases the values yielded.

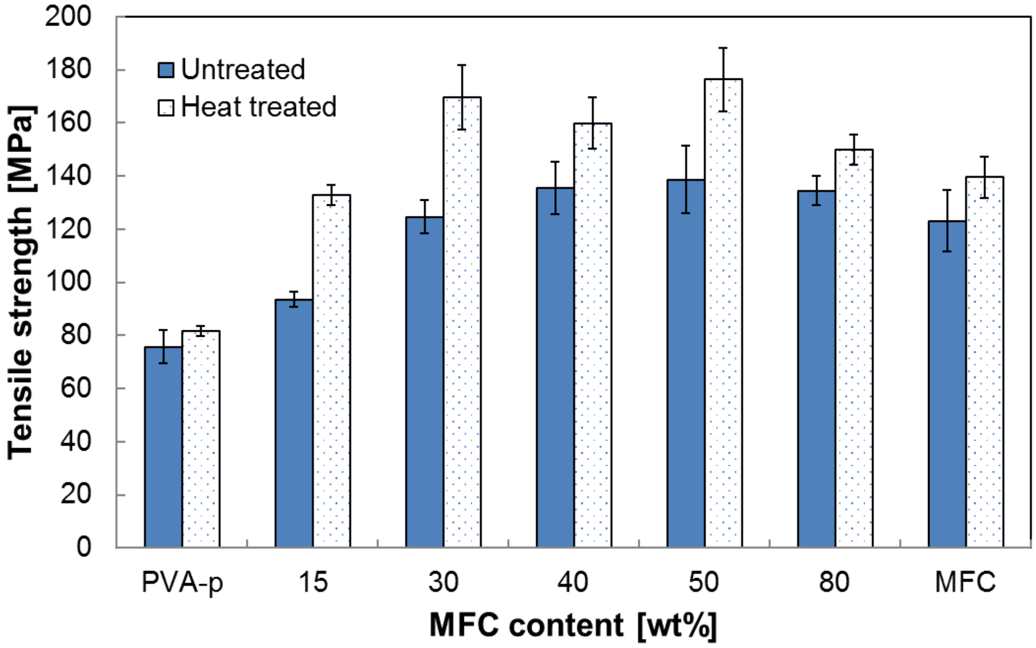


Figure 2.9: Tensile strength of MFC/PVA-p composites.

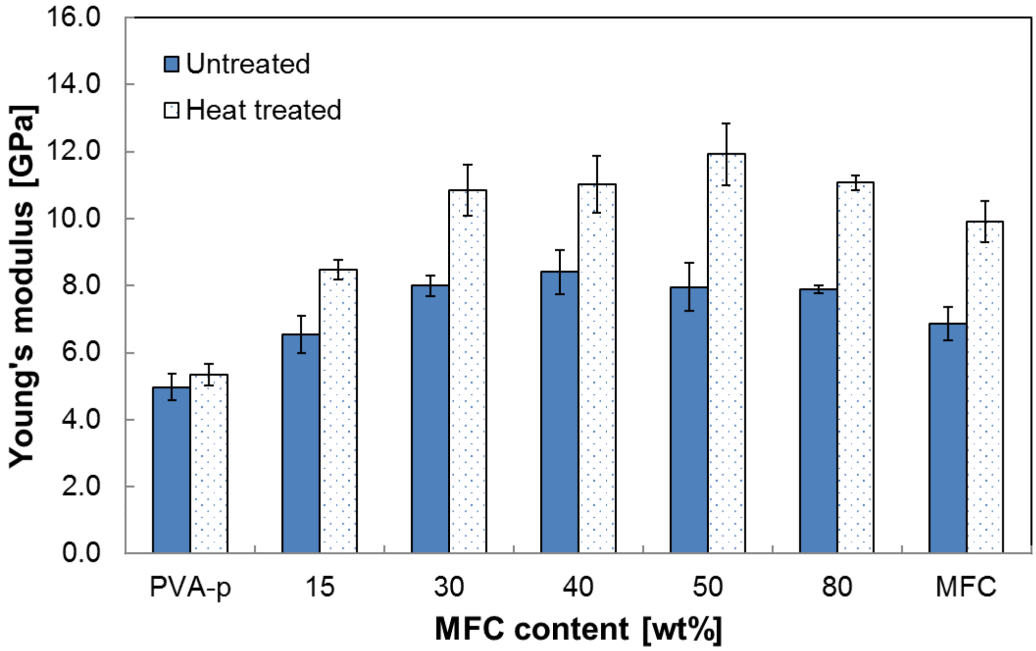


Figure 2.10: Young’s modulus of MFC/PVA-p composites.

The higher tensile properties at high MFC content yielded by both types of PVA showed a good compatibility between both hydrophilic materials. The highest tensile strength of MFC/PVA-f composites was obtained at 80 wt% sample, while MFC/PVA-p samples were at a lower MFC content of 50 wt%. This was due to the higher availability of hydroxyl groups in PVA-f compared to PVA-p samples which contain lower hydroxyl groups and more acetate groups. At lower content of MFC below 10 wt%, Jang et al. has obtained a similar trend of increase of tensile strength and Young's modulus using the same type of MFC used in this study (Celish KY 100G). The highest tensile strength of 110 MPa was obtained at 10% MFC content (Jang, Lee, Endo, & Kim, 2015). Similar trends were obtained by Lu et al. where higher MFC content from 10 to 15 wt% in PVA has yielded higher tensile strength (Lu et al., 2008). Qiu et al. hve incorporated higher MFC content up to 50 wt% and similar results were yielded where higher fracture stress was recorded at the highest MFC content of 50 wt% with 84.9 MPa (Qiu& Netravali, 2012).

Heat treatment conducted in this study has yielded higher tensile strength compared to the samples without heat treatment. The combination of heating at 180°C and pressing at 10 MPa has significantly increased the properties of the composites. It was believed to be due to the heating which allows rearrangement of PVA molecules to a more crystalline structure when slowly cooled, and the pressure had enabled better interaction between fiber and matrix, increasing the bonding between the two materials. Different heat treatment of PVA at various temperatures from 40°C to 200°C has resulted in higher crystallinity of PVA films (Iwamoto, Miya, & Mima, 1979), where higher crystallinity has increased the strength of PVA.

### 2.3.2 Thermal analysis

*Thermogravimetric (TG) analysis of PVA-f, PVA-p and MFC samples*

The thermal degradation behavior of PVA films and MFC sheets was analyzed by thermogravimetric (TG) analysis. The thermogravimetric method gives insight on the mass change of the samples during heating of the samples. The TGA curve is shown in Figure 2.11 and the derivative weight loss curve is shown in Figure 2.12.

For both PVA types, we could observe three weight loss stages at around 100-150°C, 250-350°C and 375-450°C. The first stage until 150˚C was due to the evaporation of physically weak bound water in the samples (Lee et al., 2009), while the second stage at 250˚C to 350˚C was attributed to dehydration in the sample (Lu et al., 2008). The third stage was the final stage which shows degradation of polyene residue which yields carbon and hydrocarbon (Finch, 1973). The peak of DTG curve at temperatures above 400C was reported to be related to the breakdown of PVA backbone (Fernandes, Hechenleitner, & Pineda, 2006). The residue of both PVA-f and PVA-p at 500˚C was around 10% of the total initial weight.

The thermal degradation of MFC sheet showed two major weight loss stages at 100-150˚C and 300-400˚C. The first curve could be attributed to the evaporation of moisture from the MFC sample which reduced the weight by about 5 %. The second stage of weight loss shows that the degradation starts at 300˚C which reduces most of the weight of the sample and the process ends at approximately 400˚C, similar to cellulose nanofiber extracted from bamboo reported by He et al. (He, Jiang, Zhang, & Pan, 2013). The final residue of MFC at 500˚C was 25% of the initial mass.

From the derivative weight loss curves in Figure 2.12, the highest weight loss peak of PVA-p occurred at a higher temperature compared to PVA-f sample. This is due to the fact that as the degree of hydrolysis decreases, the content of residual acetate groups increases (Taghizadeh, Yeganeh, & Rezaei, 2015) which increases the extent of scission reactions with the formation of small and more volatile fragments (Yang, Xu, Jiang, & Dan, 2012). MFC sample showed the highest peak of weight loss at the temperature of 350˚C, which is much higher than both PVA samples.

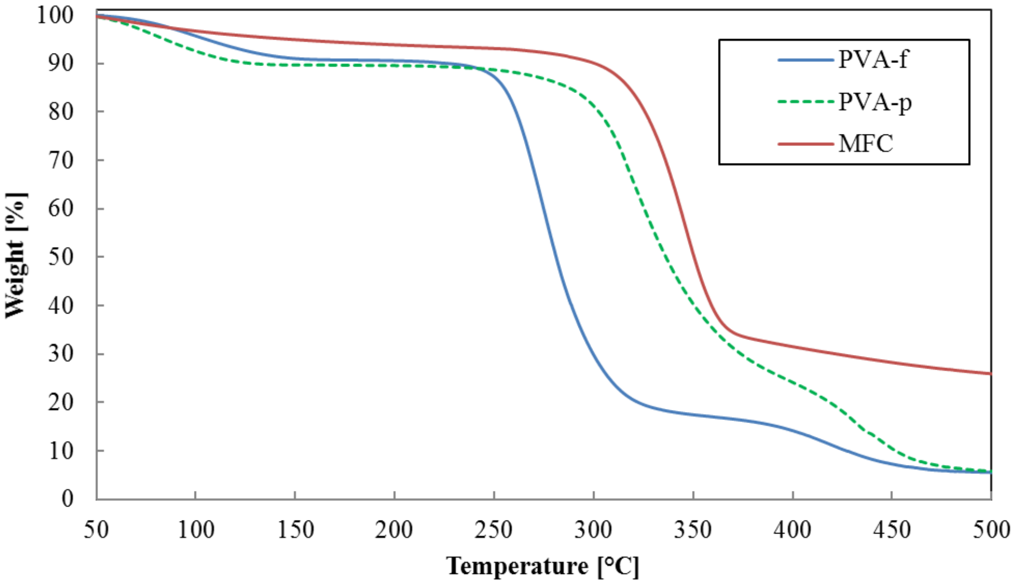


Figure 2.11: TGA curves of PVA-f, PVA-p and MFC samples.

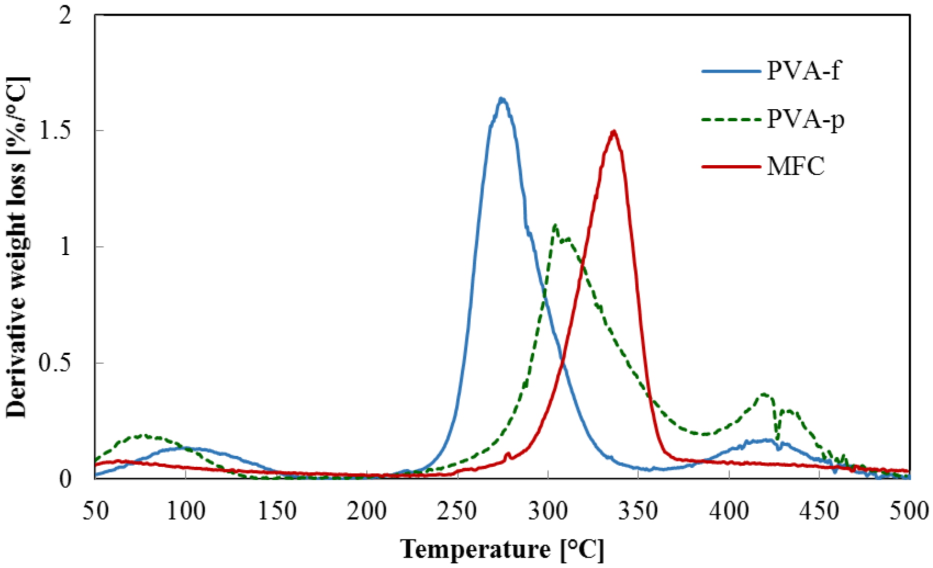


Figure 2.12: Derivative weight loss of PVA-f, PVA-p and MFC samples.

*Thermogravimetric analysis of 45 wt% MFC/PVA sample*

To understand the thermal degradation of MFC/PVA composite, thermogravimetric analysis of 45 wt% MFC/PVA samples were conducted and the results were compared with pure PVA and MFC samples. The results are shown in Figures 2.13 and 2.14 for PVA-f samples and PVA-p samples, respectively.

From the thermogravimetric analysis results, both 45 wt% MFC/PVA composite samples showed better thermal degradation properties which were in between the individual properties of MFC and PVA polymer. The onset degradation temperature of both composites of PVA-f and PVA-p had increased compared to their pure PVA samples. Similarly, the 50% weight loss temperature was also increased for the MFC-reinforced samples of PVA-f and PVA-p, showing a more stable characteristic of the composite samples. We could conclude that reinforcement of MFC has increased the thermal stability of pure PVA material.

Table 2.3: Onset temperature of major degradation step of PVA-f, PVA-p, 45 wt% MFC/PVA-f and 45 wt% MFC/PVA-p samples.

| | 1st Onset temperature $T_{on}$ | 2nd onset temperature $T_{on}$ | 50% weight loss temperature |
|---|---|---|---|
| PVA-f | 250˚C | 380˚C | 275˚C |
| MFC/PVA-f 45 wt% | 275˚C | 420˚C | 340˚C |
| PVA-p | 280˚C | 420˚C | 335˚C |
| MFC/PVA-p 45 wt% | 300˚C | 425˚C | 350˚C |

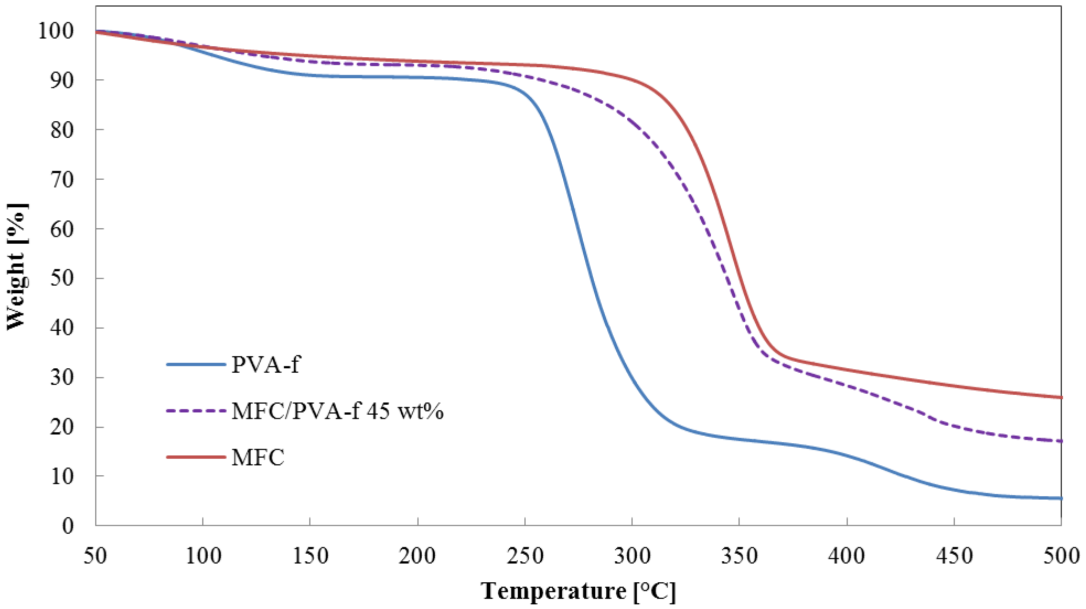


Figure 2.13: TGA curves of PVA-f, MFC/PVA-f 45 wt% and MFC samples.

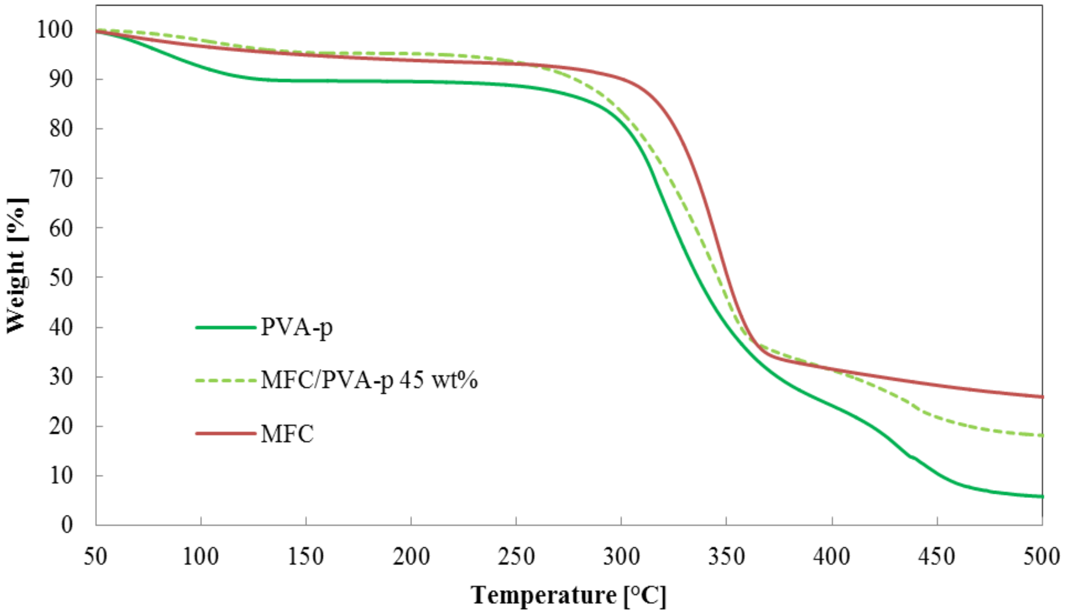


Figure 2.14: TGA curves of PVA-p, MFC/PVA-p 45 wt% and MFC samples.

### 2.3.3 Morphological analysis

*Morphological analysis of MFC sheets*

The MFC fibers were observed under scanning electron microscopes to view the nanofibers size and distribution. The nanofibers distribution in an MFC sheet is shown in Figure 2.7. The nanofibers were well dispersed throughout the sample and we could notice bundles of nanofiber at certain parts of the sample. Nanofibers with diameters smaller than 10 nm were observed abundantly throughout the sample.

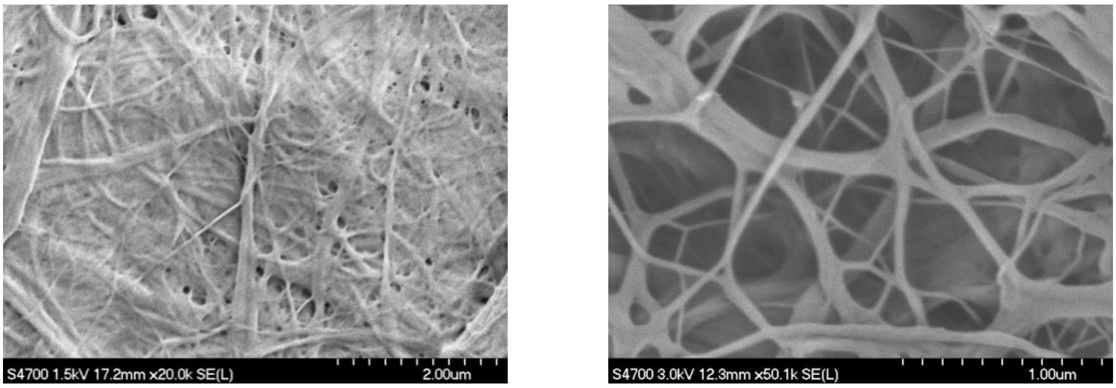
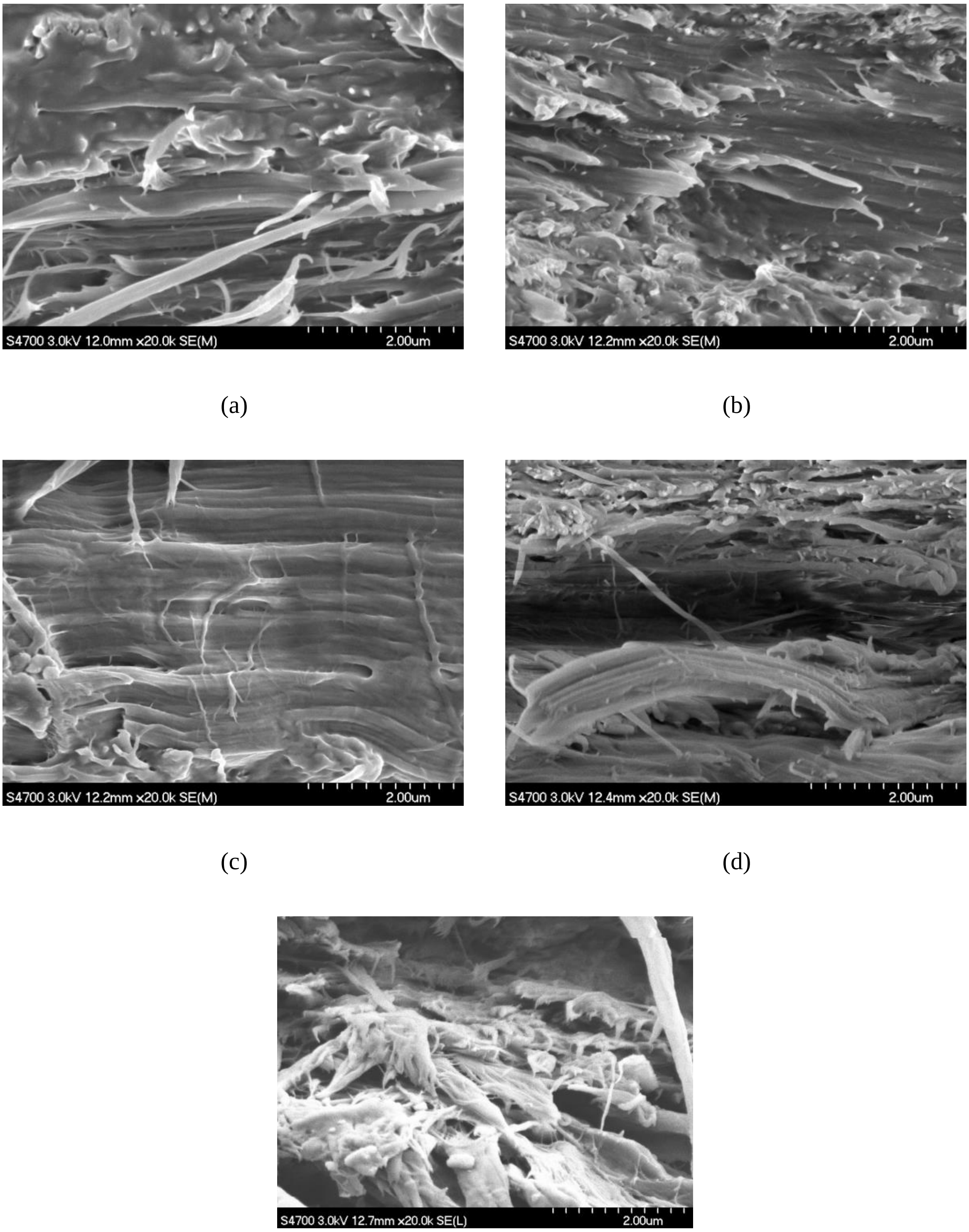


Figure 2.7: SEM image of pure MFC sheet at 20.0k magnification (left) and 50.0k magnification (right).

*Morphological analysis of MFC/PVA sheets*

The fractured surfaces of pure PVA sheet, MFC sheet and MFC/PVA sheet were observed using scanning electron microscope (SEM). The images are shown from Figure 2.8 (a) to (e) below. The SEM observation indicates a good penetration of MFC sheets with PVA where the surfaces of the MFC nanofibers are seen to be covered with PVA. Higher MFC content reveals a much rougher fracture surface as the MFC content is higher.



(a) (b)

(c) (d)

(e)

Figure 2.8: Fracture surfaces of MFC/PVA composites (a) 20 wt%, (b) 30 wt%, (c) 40 wt%, (d) 50 wt% and (e) 80 wt% of MFC content.

## 2.4 Summary

From this study, we observed a good compatibility of MFC in PVA polymer as the fibers were well distributed throughout the composite samples. This was achieved by ample mixing of the MFC suspension and PVA solution at 300 rpm using magnetic stirrer for 2 hours. Furthermore, voids and air bubbles were eliminated by vacuuming the sample solution before oven drying. PVA was observed to be well distributed between MFC entanglements from the cross-section SEM image of the samples.

The reinforcement effect of MFC was confirmed from this study, based on the increase in tensile strength of the composite samples. Tensile test results showed that reinforcement of MFC in PVA polymers has increased proportionally with the MFC content, especially at higher fiber contents of 40 to 80 wt%, where it was proved by the higher tensile strength and Young’s modulus yielded. The strength was due to the nature of MFC having a rigid network linked by hydrogen bonds as reported by Favier et a. (Favier, Cavaille, Canova, & Shrivastava, 1997). They also reported that the behavior of the composite was driven mainly by the mechanical properties of the cellulose network. Heat treatment by hot pressing at 180°C had drastically improved both tensile strength and Young’s modulus of the composites of both types of PVA polymer. The temperature of 180°C was a stable temperature for both PVA and MFC based on thermogravimetric analysis, where it is the stage after water evaporation, and no degradation of the materials occurs at this temperature.

Thermogravimetric analysis proved an increase in thermal stability of 45 wt% MFC/PVA composite samples where onset degradation temperatures were observed to shift to higher value compared to those of pure PVA samples. This improvement will allow a wider range of application environment.

# CHAPTER 3

# FABRICATION AND CHARACTERIZATION OF HEAT-TREATED MICROFIBRILLATED CELLULOSE/POLYVINYL ALCOHOL COMPOSITES

## 3.1 Introduction

The reinforcing capability of microfibrillated cellulose has sparked research since two decades ago. The demand for green composites had led researchers to extensively conduct various experiments involving cellulose nanofibers and biodegradable polymer to meet the demand. The term “microfibrillated cellulose” was known to be first introduced in 1983 by Herrick et al. referring to nano-sized fibers obtained by disintegration of lignocellulose biomass such as wood fibers using high-pressure homogenizer (Herrick et al., 1983; Turbak et al., 1983). Since then, research publications on this material has increased significantly, however still considered modest compared to research publications related to organic and inorganic nanofillers (Siró & Plackett, 2010). Microfibrillated cellulose has a hydrophilic nature, which makes them suitable for combination with hydrophilic polymers. Research on microfibrillated cellulose reinforced PVA composite were done due to this hydrophilic nature of both materials.

The strength of polymer composites was reported to depend on the properties of the matrix, the properties of the reinforcement, the reinforcement-matrix compatibility and interaction and the dispersion of the reinforcement in the matrix (for short fiber- and particle-reinforced system) (Miao & Hamad, 2013). Thermal and mechanical properties of MFC/PVA composites were studied by Lu et al. where they concluded that MFC is an excellent reinforcement material. The web-like structure of MFC could possibly render much better toughness when incorporated into polymer matrices, compared to discrete microfibrils (Lu et al., 2008). Lee et al. conducted fabrication and characterization of nanocellulose reinforced PVA with different filler loadings of 1 to 5 wt% and reported significant increase of tensile and thermal properties of the composites as the nanocellulose loading increased (Lee et al., 2009). A study by Tang observed an increase of up to 50% and 600% of mechanical strength and

Young’s modulus of cellulose nanofiber mat (CMT) reinforced PVA composite films (Tang & Liu, 2008). The study also incorporated cellulose nanofiber up to 70 wt% and concluded that the optimal cellulose nanofiber content in the composite was 40 wt%. This value was rather in agreement with our preliminary study reported in Chapter 2. The impressive reinforcing effect by cellulosic fibers was explained by the strong interaction between the fibrils that form a rigid network linked by hydrogen bonds, which are governed by a percolation mechanism (Favier et al., 1997).

Based on the preliminary study on MFC/PVA composites in Chapter 2, it was found that the strength and Young’s modulus of the MFC/PVA samples increased as fiber content increased up to 50 wt%. It was due to the improved interfacial interaction between PVA and MFC owing to the increase of surface area as the fine MFC content increases. The hot-press treatment significantly further increased these properties of MFC/PVA composites for both PVA-f and PVA-p samples.

Heat treatment had been applied to PVA polymers, mainly to reduce the sensitivity to water to meet the demand on the application where insolubility in water is required. However, in the case of cellulose nanofiber-reinforced PVA polymer, the combined effect of heat treatment and the reinforcing characteristics of the cellulose nanofiber have yet to be extensively studied and discussed. Furthermore, besides the reduction of water solubility, the effect of the heat treatment to the strength of the composites is also of interest. It was reported that among the effect of heat treatment at moderate temperatures of below 160˚C, the crystalline portion of PVA increases; however further increase above this temperature will induce chemical changes such as chain scission, unsaturation and crosslinking (Katz & Wydeven, 1982). We are interested in investigating on the effect of different heat treatment method, namely oven heating and hot pressing on the properties of the MFC/PVA composites. Due to the higher mechanical properties obtained by high MFC content in our preliminary study, we will focus on MFC content higher than 40 wt%. Different heat treatment temperatures of 150˚C, 180˚C and 200˚C were also applied in order to investigate the effect of heat temperature on the mechanical properties of the samples. The mechanical and thermal properties of untreated and hot-pressed MFC reinforced PVA composites are studied and discussed. The combined effect of heat treatment and MFC reinforcement was assessed by evaluation of mechanical properties through tensile test. Different heat treatment methods and different hot-press temperatures were applied and the suitable condition in obtaining enhanced properties of MFC/PVA composites are discussed. It was observed that the increase in MFC content has significantly increased the tensile strength and Young's modulus of the composites. Hot-pressed samples yielded better results to those of oven-heated samples. A hot-pressing temperature of 180°C was proved to yield better composite properties compared to 150°C and 200°C.

## 3.2 Materials and methods

### 3.2.1 Microfibrillated cellulose (MFC) and polyvinyl alcohol (PVA)

The microfibrillated cellulose (MFC) and PVA polymers used in this study were the same materials used in the preliminary study reported in previous chapter.

### 3.2.2 Fabrication of PVA films, MFC sheets and MFC/PVA composites sheets

*Preparation of PVA films*

The preparation procedure for PVA films, MFC sheets and MFC/PVA composite sheets in this study was similar to the procedure explained in Chapter 2.

*Preparation of MFC sheets*

The preparation of MFC sheets was similar to the method described in Chapter 2.

*Preparation of MFC/PVA sheet*

The preparation of MFC/PVA composite sheets was similar to the procedure described in Chapter 2.

*Heat treatment process*

In order to study the effect of different heat treatment methods to the properties of the samples, two methods of heat treatment process were conducted; the hot-press method and the oven-heat method. The hot-press method is where samples were hot-pressed at 180°C for 30 minutes under 10 MPa pressure. The samples were loaded into a 10 mm x 100 mm mold and the temperature was raised from room temperature to 180°C. Once the temperature has reached 180°C, the samples were loaded with 10 MPa pressing load for 30 minutes, then it was left to cool to room temperature. As for the oven-heated samples, samples were heated at 180°C in a convection oven for 30 minutes and then left to cool in the oven before they underwent the tensile test. To study the effect of different heat treatment temperature, the samples were hot-pressed at different temperatures of 150˚C, 180˚C and 200˚C.

*Mechanical test of MFC/PVA composite sheets*

The mechanical testing conducted in this study was similar to the procedure elaborated in Chapter 2.

*Swelling properties*

The swelling properties of PVA films, MFC sheets and MFC/PVA composite sheets were measured by a water absorption test. The samples were heat-treated at 100˚C and 180˚C and the samples were weighed before and after heat treatment to measure their water content. The heat-treated samples were then immersed in water at room temperature and the weight change was measured at a constant time frame until no change of sample weight was recorded. The swelling properties were calculated based on the final weight of the sample after water immersion compared to the weight after heat treatment.

### 3.2.3 Characterization

*XRD analysis*

X-ray diffraction measurement of PVA-f, PVA-p and MFC samples were conducted by RIGAKU Multiflex X-ray diffractometer (Rigaku Corporation, Japan) using CuKα1 radiation under a voltage of 40 kV and 20 mA at room temperature. Diffraction intensities were counted at $2\theta$ from 5° to 40° with a scan step of 0.05°/s.

*FT-IR analysis*

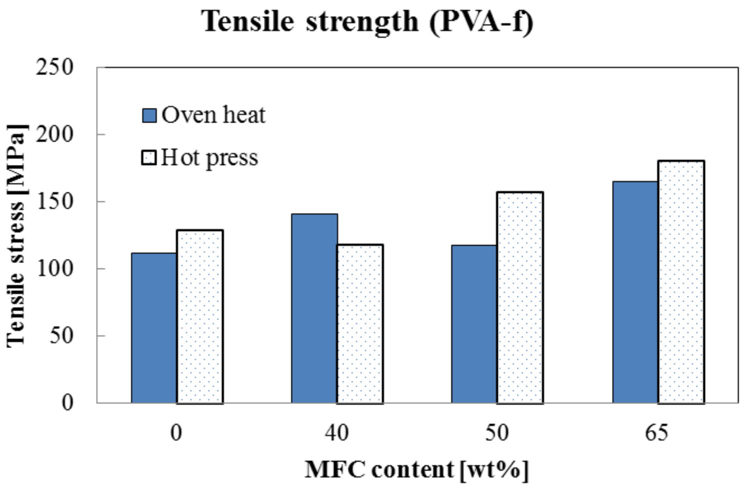
FT-IR measurements were performed at room temperature using a Bio-Rad VARIAN FTS 3000MXT spectrometer (Varian, Inc. USA). The infra-red spectra were recorded by averaging 64 scans in the range of 4000-400 $cm^{-1}$. The powdered samples were mixed with KBr powder and pelletized using a hand-operated pressing mold.

## 3.3 Results and discussion

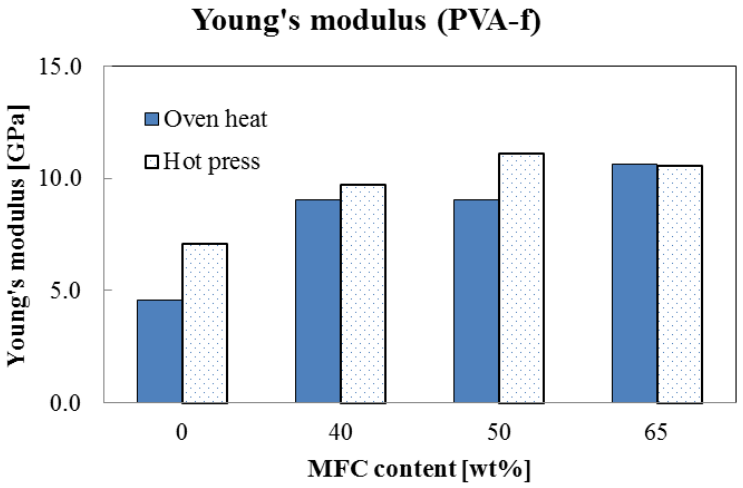
### 3.3.1 Tensile properties

The tensile test results for composites of MFC/PVA-f treated by oven-heating and hot-pressing methods are plotted in Figure 3.1. The MFC contents were varied at 40, 50 and 65 wt% and the heat treatment temperature was set to 180°C for both oven-heat and hot-press methods. Oven-heated samples showed an increase in tensile strength from 0 wt% to 65 wt% except for 50 wt% which yielded a slight decrease. Hot-pressed samples exhibited similar trend except for 40 wt% sample. This increasing trend was similar to the results obtained in Chapter 2, thus repeatability of this study was confirmed. The highest tensile strength obtained was at 65 wt% MFC content for both oven-heated and hot-pressed samples with the tensile strength of 160 MPa and 175 MPa. The increasing strength as MFC content increases was again due to the increase in fine web-like networked nanofibers which increases surface area for better interaction between the reinforcing elements and the PVA matrix material.

The Young’s modulus value increased as the MFC content increased and the value was highest at 11 GPa for hot-pressed 50 wt% MFC/PVA-f sample. Generally, it was observed that the Young’s modulus values of hot-pressed samples were higher than those of oven-heated samples. Samples of 65 wt% showed almost similar Young’s modulus values of oven-heat and hot-pressed samples of about 10.5 GPa. The reinforcing effect of MFC was due to fiber interaction of the fiber and matrix, as well as the rigidity of the web-like MFC fibrils structure. The higher concentration of MFC was required to increase interaction between fibrils and forming a web-like network structure (Nakagaito & Yano, 2005).



(a)



(b)

Figure 3.1: The results of (a) tensile strength and (b) Young’s modulus of MFC/PVA-f composites treated by oven heating and hot pressing method.

### *Mechanical properties of MFC/PVA composites at different hot-press temperatures*

The effect of different hot-press temperature (150˚C, 180˚C and 200˚C) on the mechanical properties of MFC/PVA composites was studied. We chose MFC content of 50 wt% and the composites were prepared using both PVA-f and PVA-p. The tensile strength and Young's modulus of these composites are shown in Figures 3.2 and 3.3. From the results, we could observe that the tensile strength of the 50 wt% MFC/PVA composites hot-pressed at 180˚C was the highest with a value of approximately 175 MPa for both PVA type samples. The difference of the three different temperatures was not as obvious, however, the tensile strength increased slightly from 150˚C to 180˚C hot-press temperature, and then decreased slightly as the hot-press temperature became 200˚C. The Young's modulus values showed a similar trend with 180˚C samples showing almost similar values with 200˚C heat-treated samples of about 12.0 GPa while Young's modulus of 150˚C heat-treated samples were the lowest at about 10.5 GPa for both PVA-f and PVA-p samples. From the TGA results of PVA and MFC samples conducted in the preliminary study, we could understand that the temperature of 180˚C is the region where the samples are thermally stable. The reason was due to they have just experienced water evaporation process under 150˚C while at near 200˚C and above, they start to experience material degradation. Therefore, 180˚C is considered a suitable heat treatment temperature due to the stable condition of the samples.

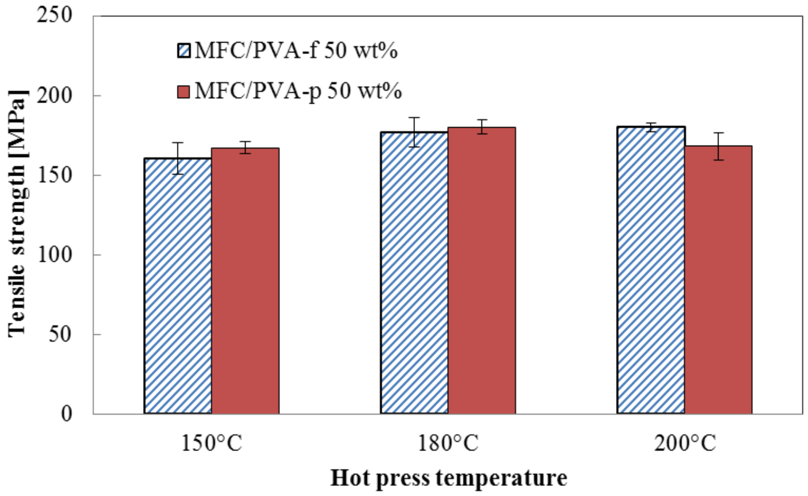


Figure 3.2: Tensile strength of 50 wt% MFC/PVA composite at different hot press temperatures.

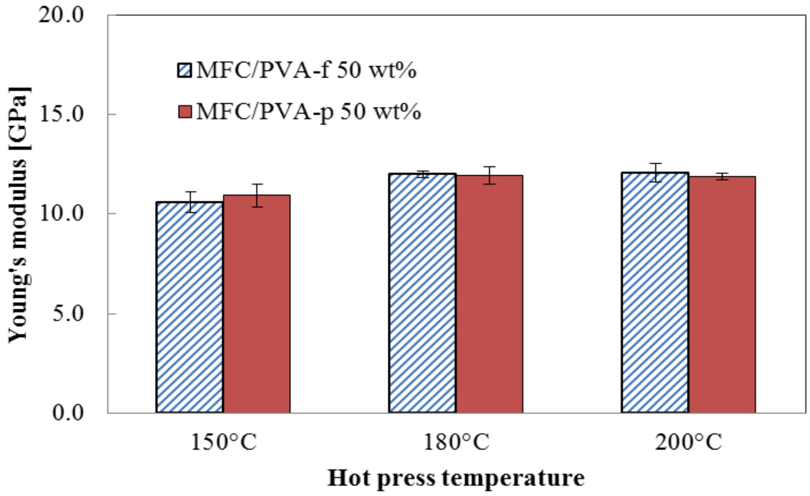


Figure 3.3: Young’s modulus of 50 wt% MFC/PVA composite at different hot press temperatures.

*Mechanical properties of untreated and hot-pressed MFC/PVA composites*

Based on the preliminary experiment result, we could see an increasing trend of the tensile strength of MFC/PVA composites as the MFC content was increased. We conducted a similar experiment with the selected MFC content of 20 wt%, 40 wt%, 50 wt% and 60 wt% and the results were studied and analyzed in terms of tensile strength, Young’s modulus and strain at break. The results are shown in Figure 3.4 for MFC/PVA-f samples and Figure 3.5 for MFC/PVA-p samples. The tensile strengths of MFC/PVA-f composites showed an increasing pattern for both untreated and hot-pressed samples as the MFC content increased from 20 wt% to 60 wt%, though the relation was not linear. We could notice a slight decrease of tensile strength at MFC content of 50 wt% for both untreated and hot-pressed samples, however, the strength increases again at MFC content of 60 wt%. The untreated samples of 50 wt% and 60 wt% MFC/PVA-f recorded almost similar tensile strength values of 145 MPa and were the highest compared to other MFC content results. The hot-pressed samples yielded the highest strength at MFC content of 60 wt%.

The Young's modulus increased from 7 GPa to 8.5 GPa as the MFC content increased from 20 wt% sample to 40 wt%, then decreased to 7GPa at 50 wt%. A slight increase was noticed when the MFC content increased to 60 wt%. The untreated 40 wt% MFC/PVA-f yielded the highest Young's modulus value of 8.0 GPa, while the hot-pressed sample of 60 wt% recorded the highest Young's modulus value of 12.0 GPa. Strain at break for untreated and hot-pressed samples showed an increasing pattern as the MFC content was increased. This is probably due to the increase of MFC which are initially entangled nanofibers are straightened as the tensile loading was exerted to the samples. Hot pressed samples recorded almost 50% lower strain at break compared to untreated samples. The hot-press has created an in-plane orientation of the fibril network and increased density due to the pressure exerted; resulting in a more rigid composite structure as expressed by the increasing value of Young's modulus; whereby the increased temperature increased the crystallinity of the PVA matrix.

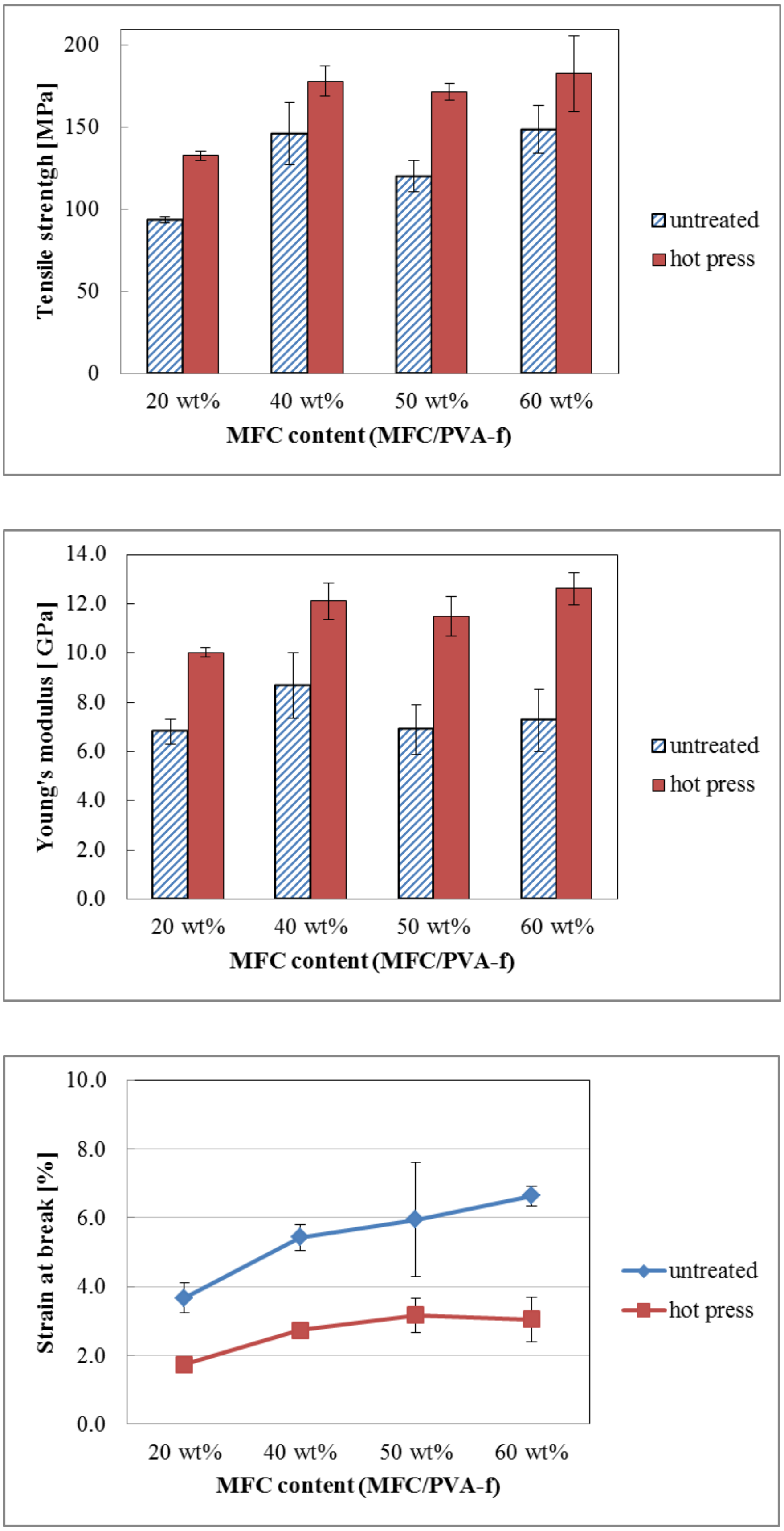


Figure 3.4: Tensile strength, Young’s modulus and strain at break of MFC/PVA-f samples.

As for MFC/PVA-p samples, we noticed similar increasing trend of tensile strength as the MFC content was increased from 20 wt% to 60 wt%. The highest tensile strength recorded was 150 MPa of untreated 60 wt% sample and 175 MPa of hot-pressed 50 wt% sample. The Young's modulus peaked up at 50 wt% samples where both untreated and hot-pressed samples recorded the highest value of 8.0 GPa and 12.0 GPa respectively.

The strain at break for both untreated and hot pressed samples showed an increase as the MFC content increased. The values yielded by the hot-pressed samples were about 50% lower than that of the untreated samples, similar to the trend exhibited by those of MFC/PVA-f samples. We relate this to similar reason with MFC/PVA-f samples where hot-pressing has created a planar orientation of the fibril network due to a slightly flattened cross-sectional shape of the samples, increasing the crystallinity of the PVA matrix, density of the composite and more rigid fiber-matrix structure as expressed by Young's modulus.

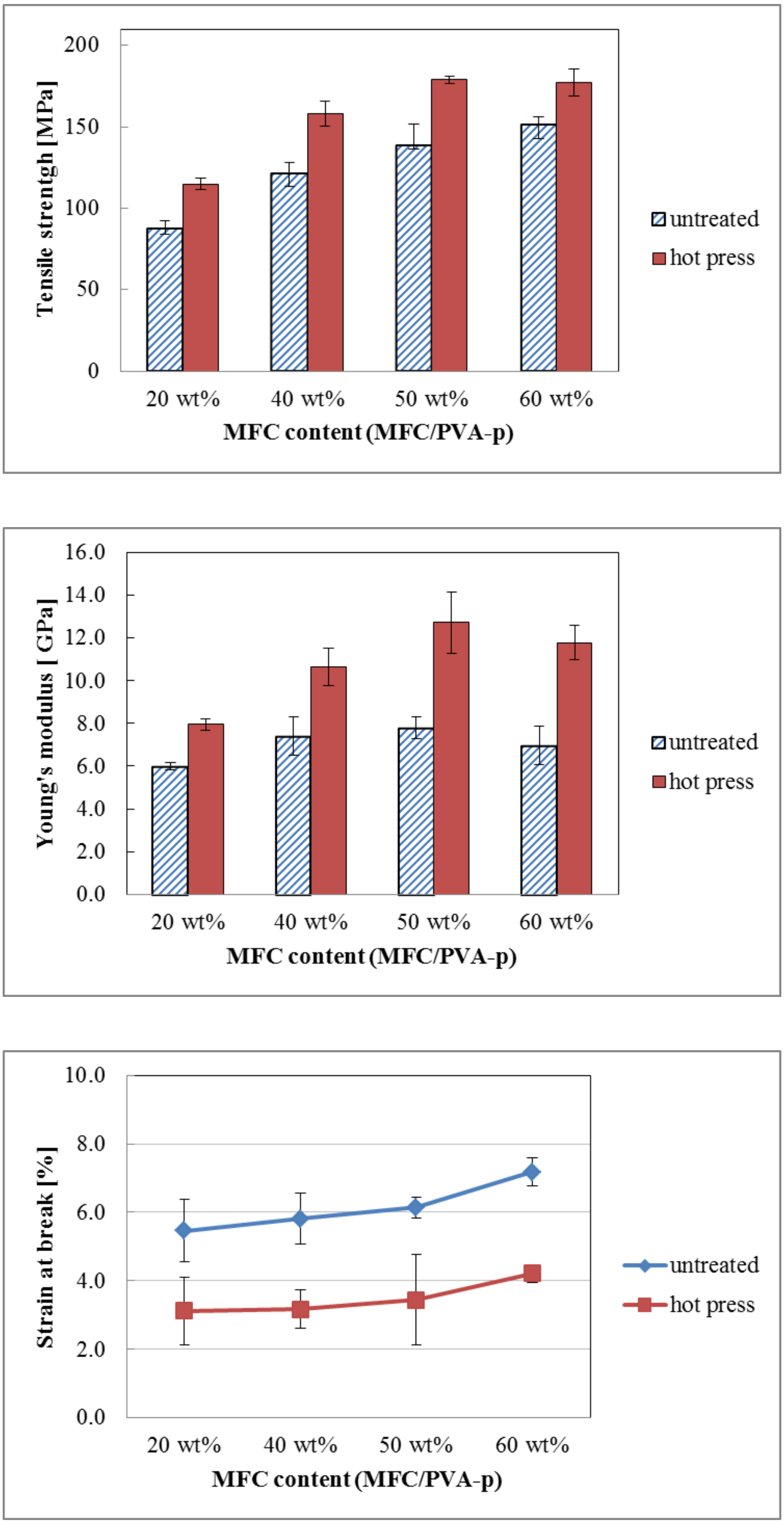


Figure 3.5: Tensile strength, Young's modulus and strain at break of MFC/PVA-p samples.

### 3.3.2 XRD analysis

The XRD patterns of untreated and hot-pressed PVA films, MFC sheets and MFC/PVA 45wt% composite sheets were studied. X-ray diffraction intensities give information on crystal morphology of a material. A well-defined sharp peak represents a highly crystalline material, whereas a non-crystalline or also called amorphous material shows broad peaks instead of a sharp peak. From the data analysis software, we managed to obtain the crystallinity values of the samples based on the ratio of crystalline area to the total of the crystalline and amorphous area.

Firstly, we compared the XRD patterns of the two types of PVAs used in this study, the untreated and hot-pressed (180˚C) PVA-f and PVA-p samples. The XRD patterns are shown in Figure 3.6. For the untreated PVA-f and PVA-p samples, we could observe a broad peak at $2\theta = 19.5°$ corresponding to its crystalline structure. The intensity of this peak for PVA-f sample was observed to be higher than that of PVA-p. This is due to the higher content of hydroxyl groups in the PVA-f compared to PVA-p (Shao et al., 2003). The hot-pressed samples of the PVA-f and PVA-p showed more peaks at $2\theta$ of 11°, 17°, 22°, 27°, 32° and 35° which indicates crystallization being induced by the heat treatment (Kang et al., 2010). New sharp peaks are observed in the XRD pattern due to the diffraction of the X-ray beam by the aligned chains in the polymer forming crystalline regions. The peak of PVA-p samples was broader compared to PVA-f samples which also shows an indication of lower crystallinity compared to PVA-f samples. The higher crystallinity of the hot-pressed samples leads to the increase of mechanical properties of the samples. In order to confirm these findings, crystallinity measurements of the PVA samples were conducted using FT-IR measurements which are explained later in this chapter.

In Figure 3.7, the XRD pattern of MFC samples showed a typical Cellulose 1 structure as three peaks of $2\theta$ at 15˚, 16.5˚ and 22.5˚ was observed (Liu & Hu, 2008). The crystallinity value of the untreated MFC sample was measured as 81.6% meanwhile the value slightly increased 5.7% to become 86.3% after hot-pressing at 180˚C. This crystallinity value of hot-pressed MFC sheet was in agreement with the value obtained by Lu et al. which recorded a value of 86.7% (Lu et al., 2008) which is higher than the value of a general kraft pulp (Liitia, Maunu, & Hortling, 2000). The increase in diffraction peak at 19° corresponds to the crystalline peak of the MFC samples. The increase in the crystallinity after hot-pressing was due to crystallization in quasi-crystalline of the amorphous region due to rearrangement of cellulose molecules in this region (Bhuiyan, Hirai, & Sobue, 2000).

The XRD patterns of 45 wt% MFC/PVA composite sheets are shown in Figure 3.8. The XRD pattern shows the combined curves of PVA and MFC samples. Distinct peaks are observed at $2\theta$ of 15°, 19.5° and 22.5° corresponding to one amorphous peak from PVA and two crystalline peaks from MFC. When two polymers are mixed, a different pattern is expected to appear due to new atomic or cell arrangement. The increase in the intensity at $2\theta = 19.5^\circ$ was obvious due to the increase in the crystallinity of the PVA portion of the composite due to the hot-press.

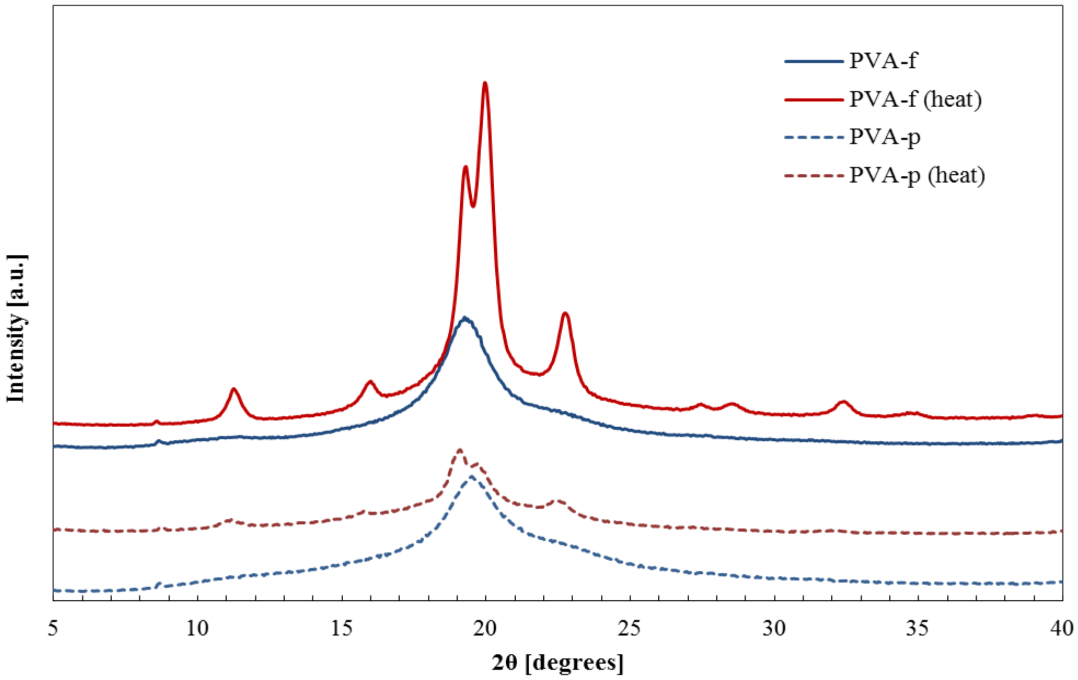


Figure 3.6: X-ray diffraction curves for untreated and hot-pressed PVA-f and PVA-p samples.

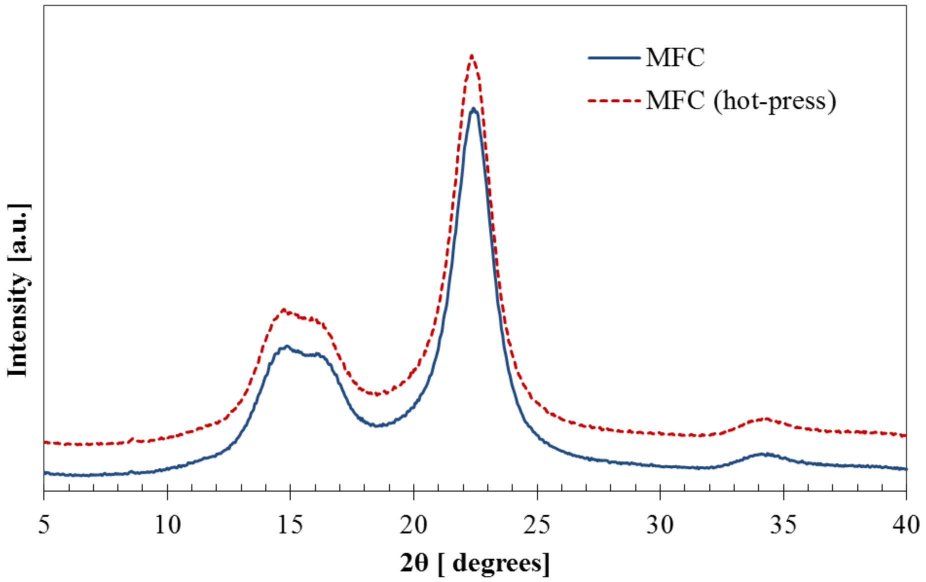


Figure 3.7: X-ray diffraction curves for untreated and hot-pressed MFC samples.

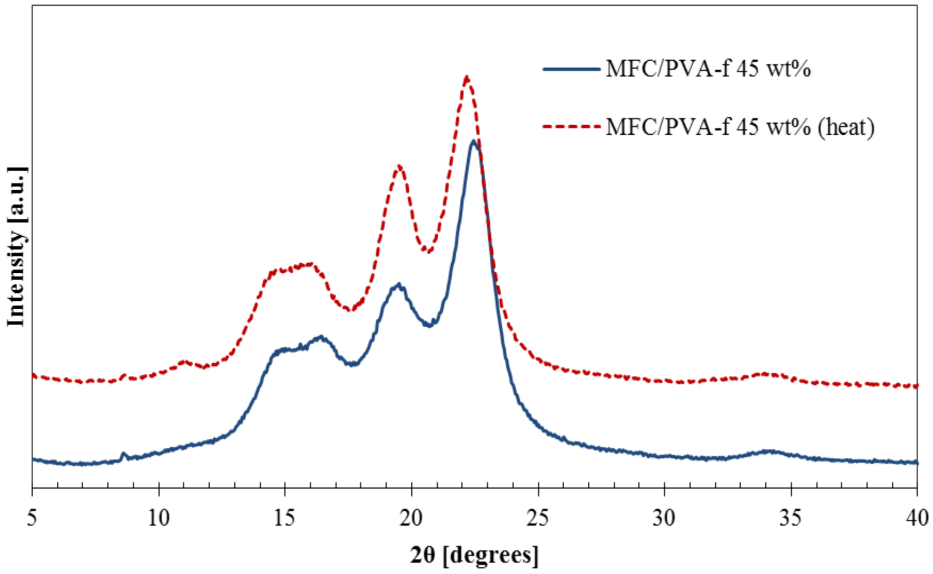


Figure 3.8: X-ray diffraction curves of MFC/PVA-f 45 wt%.

The data from XRD measurements of MFC/PVA samples of 40 wt%, 50 wt% and 65 wt% are listed in Table 4.1. From the results, it was observed that PVA-f samples showed relatively higher crystallinity values compared to those of PVA-p samples. The difference of crystallinity value of both 150˚C and 180˚C was not very clear; this might be due to the small difference in the temperature value.

A more significant trend could be observed if compared with a larger temperature difference. As the MFC content in the composites increases from 40 to 65 wt%, the intensity of the peaks at 15° and 22° from MFC increases, and in contrast, the peak intensities at 19° from PVA decreases due to the decreasing PVA content. However, the increase of MFC contents does not show any significant trend to the crystallinity value.

Table 4.1: The crystallinity extracted from XRD analysis of 40 wt%, 50 wt% and 65 wt% of MFC/PVA samples.

| **Temperature** | **PVA type** | **MFC content [wt%]** | **Crystallinity [%]** |
|---|---|---|---|
| 150˚C | PVA-f | 40 | 88.6 |
| | | 50 | 92.4 |
| | | 65 | 82.5 |
| | PVA-p | 40 | 85.5 |
| | | 50 | 85.2 |
| | | 65 | 86.0 |
| 180˚C | PVA-f | 40 | 87.3 |
| | | 50 | 82.1 |
| | | 65 | 83.0 |
| | PVA-p | 40 | 79.6 |
| | | 50 | 83.3 |
| | | 65 | 92.5 |

### 3.3.3 FT-IR analysis

The IR absorbance spectrum of the PVA was measured in order to understand the effect of heat treatment on the chemical groups of the PVA samples. From Figures 3.7 and 3.8, all major peaks associated with hydroxyl and acetate groups were observed at 3300 cm$^{-1}$, 2940 cm$^{-1}$, 1730 cm$^{-1}$, 1141 cm$^{-1}$ and 1070 cm$^{-1}$. The broad band between 3200 and 3500 cm$^{-1}$ are associated to O-H stretching from the intermolecular and intramolecular hydrogen bonds (Kumeta et al., 2003; Mansur, Sadahira, Souza, & Mansur, 2008) meanwhile peaks at 1730 cm$^{-1}$ band are associated to the stretching C=O and C-O from the acetate group remaining from polyvinyl acetate (PVAc). The intensity of 1730 cm$^{-1}$ of PVA-f was weaker than that of PVA-p. This indicates that fewer acetate groups were present in the polymer chain as PVA-f has a higher degree of hydrolysis (Mansur et al., 2008).

On the other hand, the intensity at 1141 $cm^{-1}$ band was referred to as crystallinity sensitive band as mentioned by Tadokoro et al (Tadokoro, 1959). A similar report was done by Mallapragada and Peppas which concludes that the intensity of the 1141 $cm^{-1}$ band occurred due to symmetric C-C stretching mode resulting from increases in the crystallinity of the polymer due to heat treatment (Mallapragada & Peppas, 1996). The peak at this band was proved to be more intense due to heat treatment (Nagai, Mima, Kuribayashi, & Sagane, 1955).

From the FT-IR measurements, we observed that the intensity of the 1141 $cm^{-1}$ peak increased as the PVA was hot-pressed at 180˚C, however, it decreased when 200˚C heat treatment was applied. This was attributed to the thermal decomposition of the samples when heating above 190˚C was applied (Tadokoro, Seki, & Nitta, 1955). Associating these results with the tensile strength of 50 wt% MFC/PVA samples at different heat temperature as described earlier in this chapter, we could see that the increase of tensile strength at 180˚C and decrease at 200˚C heat treatment was due to this reason. Therefore, this peak was of importance to understand the heat treatment effect to the crystallinity of the samples.

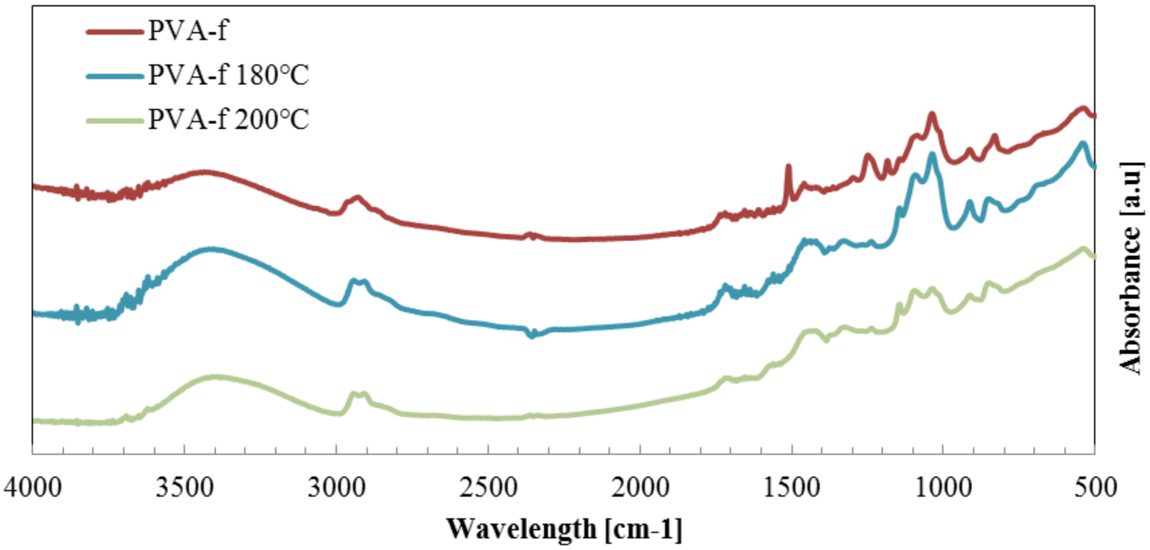


Figure 3.7: FT-IR spectra of PVA-f samples.

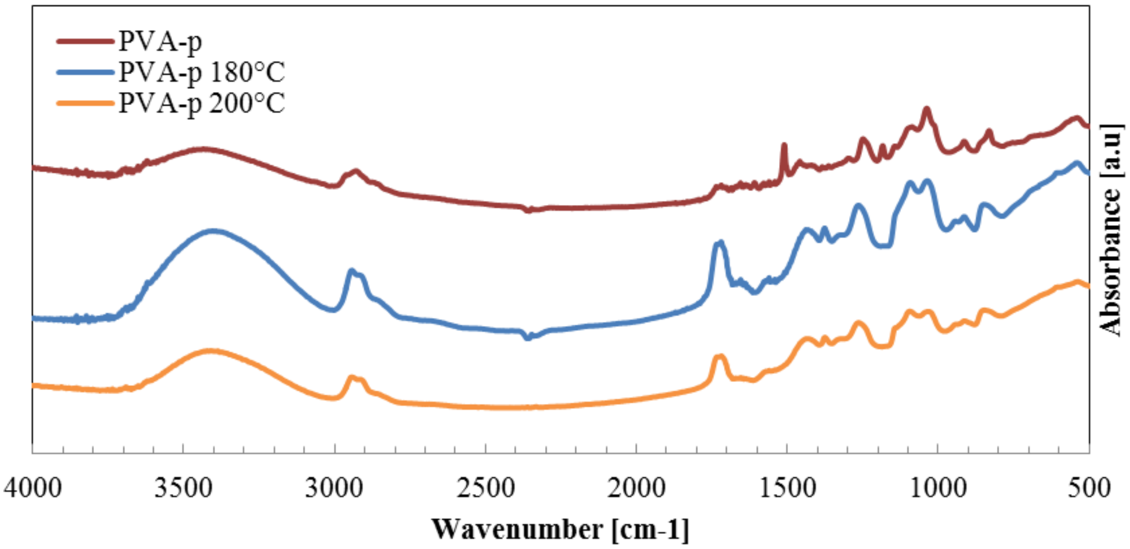


Figure 3.8: FT-IR spectra of PVA-f samples.

A report by Tretinnikov has described a simple and direct method to determine degree of crystallinity of PVA by FT-IR spectrum (Tretinnikov & Zagorskaya, 2012). The method was by measuring the ratio of the intensity of 1144 $cm^{-1}$ and 1094 $cm^{-1}$ in the IR spectrum. It is worth mentioning that the 1144 $cm^{-1}$ band here was referring to similar peaks of 1141 $cm^{-1}$ mentioned earlier taking into consideration of slight variation in the wavenumber reading.

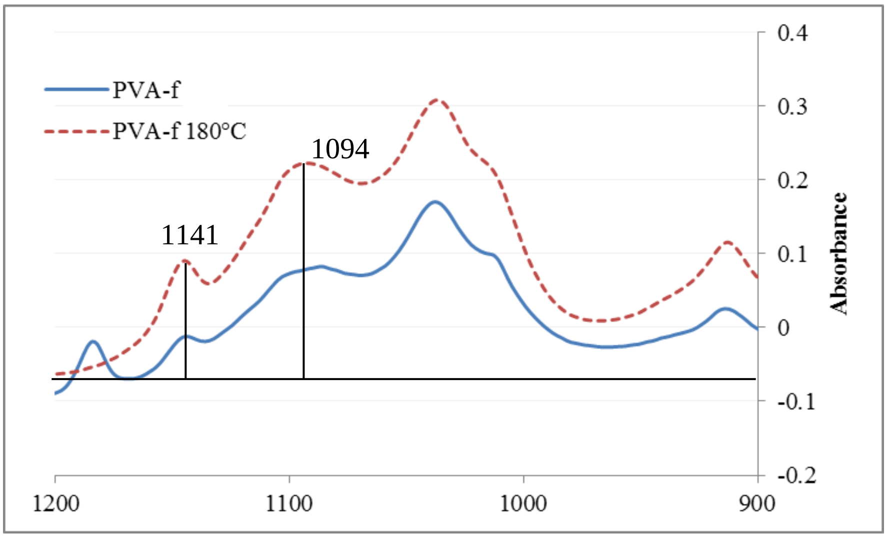
The degree of crystallinity proposed by Tretinnikov was measured as below:

$$\alpha(\%) = -13.1 + 89.5(A_{1144}/A_{1094})$$

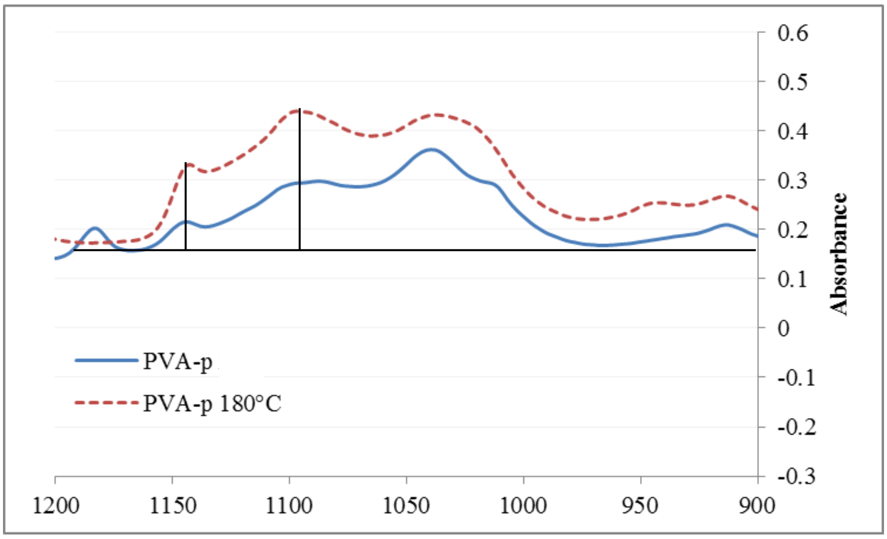
where $\alpha$ is the degree of crystallinity and $A_{1144}$ and $A_{1094}$ are the peak intensities of the bands of 1144 $cm^{-1}$ and 1094 $cm^{-1}$. We followed this method to derive the crystallinity of PVA samples to associate with the mechanical properties of PVA samples reported earlier. The calculation was made by referring to the peak intensity of the bands of 1144 $cm^{-1}$ and 1094 $cm^{-1}$ as shown in Figure 3.9. The crystallinity calculation results are listed in Table 4.2. The calculated value showed an increase in crystallinity of the heat-treated PVA samples which explains the higher strength of the samples as reported earlier. In the previous chapter, we noticed that hot pressing had significantly increased the crystalline structure portion of the PVA sample, associated with the new peaks that appeared in the XRD data.

Table 4.2: Crystallinity of untreated and hot-pressed PVA-f and PVA-p based on peak intensity ratio of 1144 $cm^{-1}$ and 1094 $cm^{-1}$.

| Sample name | Crystallinity value [%] |
|---|---|
| PVA-f | 25 |
| PVA-f 180˚C | 36 |
| PVA-p | 21 |
| PVA-p 180˚C | 28 |



(a)



(b)

Figure 3.9: Measurement of intensity ratio of 1144 cm$^{-1}$ and 1096 cm$^{-1}$ peaks of (a) PVA-f samples and (b) PVA-p samples.

### *Swelling properties*

One of the major drawbacks of PVA which limits its application is the affinity to water, resulting in high degree of swelling and sometimes occurrence of complete solubility (Sriupayo, Supaphol, Blackwell, & Rujiravanit, 2005). Heat treatment of PVA is one of the most direct and efficient methods to overcome the solubility issue. The degree of swelling of PVA films, MFC sheets and 40 wt% MFC/PVA composite sheets were measured by soaking in water at room temperature to compare the swelling rate of untreated and heat-treated samples. Heat treatment was conducted to the samples by oven heating at 100˚C and 180˚C and the properties were compared. From the results, we could conclude that the water absorption by PVA-p was much higher than those of PVA-f samples. At room temperature, PVA-f samples do not dissolve, however PVA-p samples diluted in water very quickly. Samples of PVA-p and 40 wt% MFC/PVA-p heat-treated at 100℃ became diluted in water at room temperature; therefore they do not appear in Table 4.2. The PVA-f and 40 wt% MFC/PVA-f samples experienced more than 100% swelling but did not dissolve. The swelling of 180˚C heat-treated PVA-f samples was reduced drastically compared to the swelling of 100˚C heat-treated PVA-f samples. We could identify the effect of heat treatment at 180˚C to significantly reduce the solubility of the samples in this test.

Table 4.2: Degree of swelling of samples heat-treated at 100˚C and 180˚C [in %].

| Sample type | Heat treatment temperature | | |
|---|---|---|---|
| | Room temperature [25°C] | 100°C | 180°C |
| PVA-f | 154 | 244.4 | 31.0 |
| PVA-f 40wt | 150 | 118.2 | 43.5 |
| PVA-p | Dissolved | Dissolved | 128.9 |
| PVA-p 40wt | Dissolved | Dissolved | 128.6 |

## 3.4 Summary

From this study, we concluded that the hot press method has yielded higher mechanical properties compared to oven-heating of MFC/PVA composites based on the tensile test results. Both MFC/PVA-f and MFC/PVA-p composites have shown an increase in tensile strength and Young's modulus when hot pressed compared to oven-heated samples.

Different heat treatment temperatures of 150˚C, 180˚C and 200˚C have yielded the highest mechanical properties obtained at 180˚C. From the TG analysis result which shows the stability of the sample at heat treatment of 180˚C, whereby increasing the heat treatment temperature to 200˚C might lead to material degradation of the MFC/PVA samples. It was also noticed that PVA-f and PVA-p samples showed very little difference in both tensile strength and Young's modulus value in this experiment.

XRD measurements showed higher crystallinity of PVA-f samples compared to those of PVA-p samples, which reflects the higher mechanical properties yielded by PVA-f samples. This result was proved by FT-IR analysis which showed an increase in crystallinity for PVA samples heated at 180˚C by comparing the peak intensity of the bands of 1144 and 1094 cm$^{-1}$. Further increase of the heating temperature to 200˚C resulted in a decrease in the crystallinity, probably due to thermal degradation of the PVA samples.

Further investigation on mechanical properties of untreated and heat-treated (180˚C) samples of 20wt% to 60 wt% samples showed an increase in tensile strength as the MFC content increased. However, Young's modulus showed decrease at higher than 40 wt% samples. Strain at break of the samples showed an increase as the MFC content increased. Heat-treated samples showed a decrease of more than 50% of strain at break compared to the untreated samples.

# CHAPTER 4

# FABRICATION AND CHARACTERIZATION OF HEAT-TREATED BACTERIAL CELLULOSE/POLYVINYL ALCOHOL COMPOSITES

## 4.1 Introduction

Bacterial cellulose (BC) is a very unique type of pure cellulose produced by bacteria called *Acetobacter*. They commonly come in the form of hydrogels, popularly known as nata de coco, which contains a lot of water in between the three-dimensional network of ultrafine fibers. The well-arranged nanofibers and pure nature of the fibers enables the application of BC to range widely from medical field to electric and electronic fields, where BC composites are used in biosensors, e-papers, speaker diaphragm, display devices and electrical instruments (Shah et al., 2013). Bacterial cellulose is produced by synthesizing cellulose and from building up straight, continuous and dimensionally uniform bundles of microfibrils (Nakagaito et al., 2005). One of the major drawbacks of BC is the amount of water contained in the BC gel, which tends to be expelled even under slight pressure. However, elimination of this water content will produce a BC in sheet form which will enable further application of BC in more mechanically demanding applications such as high-strength paper and diaphragms for electroacoustic transducers.

Among the early studies conducted on BC sheets was by Yamanaka et al. on the mechanical properties of sheets prepared from bacterial cellulose. It was found that the air-dried BC sheets has shown remarkably strong mechanical properties with Young’s modulus as high as 15 GPa (Yamanaka et al., 1989). Further research was conducted by Nishi et al. on treatment of gel-like pellicles or dried sheets of BC with alkaline and/or oxidative solutions which resulted in a higher Young’s modulus of the resulting BC sheets to reach 30 GPa (Nishi et al., 1990). Bacterial cellulose has the potential to act as both matrix and reinforcement in the process of producing various composite materials. Bacterial cellulose and native starch nanocomposites were manufactured by Grande et al. which proved to be a practical approach to produce BC nanocomposites (Grande et al., 2009). Kim et al. prepared BC/chitosan composites by immersing wet BC pellicle in chitosan solution followed by freeze-drying process (Kim et al., 2011), while Nakagaito et al. produced BC and phenol-formaldehyde (PF) composites by immersing BC sheets in PF resin (Nakagaito et al., 2005). From these findings, we are interested to study the properties of BC/PVA composites and the heat-treated BC sheets. A considerable improvement on the mechanical properties of BC/PVA composites was expected due to the excellent reinforcement-matrix interactions.

In this study, we conducted fabrication and evaluation of BC sheet and BC reinforced PVA composite to understand the reinforcing effect of BC in PVA polymer and to make comparison with MFC reinforced PVA composites. While MFC fibers are obtained through fibrillation of fibers, BC is produced in the reverse way, where the bacteria synthesize cellulose to form bundles of microfibrils with uniform sizes. This difference in fiber production was considered interesting to be discussed in terms of the yielded mechanical properties. The mechanical properties of disintegrated BC sheet were compared with those of MFC sheet. The BC sheets produced from pressed BC pellicles manufactured and two types of heat treatment, namely oven-heating and hot-pressing of the BC pellicles were conducted to study their effect on the mechanical properties of the BC sheets. We conducted different heat treatment methods and the characteristics of the samples under the different treatments were compared. The disintegrated BC sheets showed an increase in both tensile strength and Young’s modulus compared to those of MFC sheets. Hot-pressed BC sheet has exhibited higher mechanical properties compared to the oven heated BC sheet.

## 4.2 Materials and methods

### 4.2.1 Bacterial cellulose (BC) and polyvinyl alcohol (PVA)

Bacterial cellulose (BC) used in this study was derived from nata de coco pellicles which were supplied by Fujicco Co. Ltd., Japan in the form of wet pellicles with 10 mm in thickness as shown in Figure 4.1. The acidity of the pellicles was neutralized by soaking in tap water for one week. We did the drying test of the BC samples to know the fiber content and it was measured to be approximately 0.6 wt% from the original weight of the nata de coco pellicle.

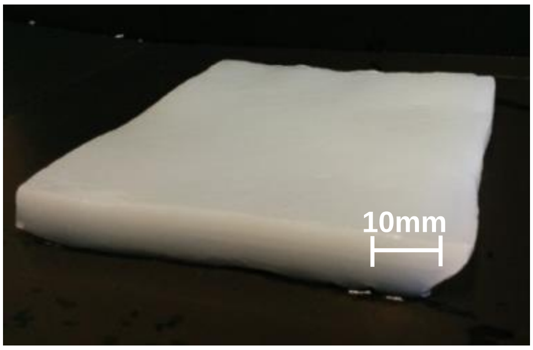


Figure 4.1: The representative photograph of BC pellicle used in this study.

### 4.2.2 Fabrication of PVA films, BC sheets and BC/PVA composite sheets

*BC sheet fabrication*

The BC sheets are grouped into disintegrated and non-disintegrated samples. For the disintegrated BC samples, a certain amount of BC pellicles are disintegrated with distilled water using a heavy duty food blender for 5 minutes. The resultant BC slurry was then filtered using vacuum filtration and the formed sheet separated by filter paper was sandwiched between two metal plates and dried in oven at 30°C until totally dry. Heat treatment of the disintegrated BC sheet was done by hot-pressing the sheet at 180°C for 10 minutes under 10 MPa pressure. As for the non-disintegrated samples, the BC sheet was used in the original form of pellicle. We divide this non-disintegrated BC sheets into two different drying methods, one is the oven-drying method and the other is by hot-pressing method. For the oven-dried samples, the BC pellicle was cut into 100 mm x 100 mm size and then pressed into around 1 mm thick plate at room temperature. The pressed sheet was then cut into 10 mm x 100 mm size, sandwiched between two metal plates and dried in 105°C oven until totally dry and ready for tensile test, and the samples were named BC-OV. On the other hand, the second set of BC sheets was cold-pressed until 1 mm thick and then subsequently hot-pressed at 105°C and 10 MPa pressure until dry. Then, the sheets were dried in an oven at 105°C for 12 hours to ensure totally dry and cut into 10 mm x

100 mm size and ready for test, and named BC-HP. The process diagram for BC-HP is shown in Figure 4.2.

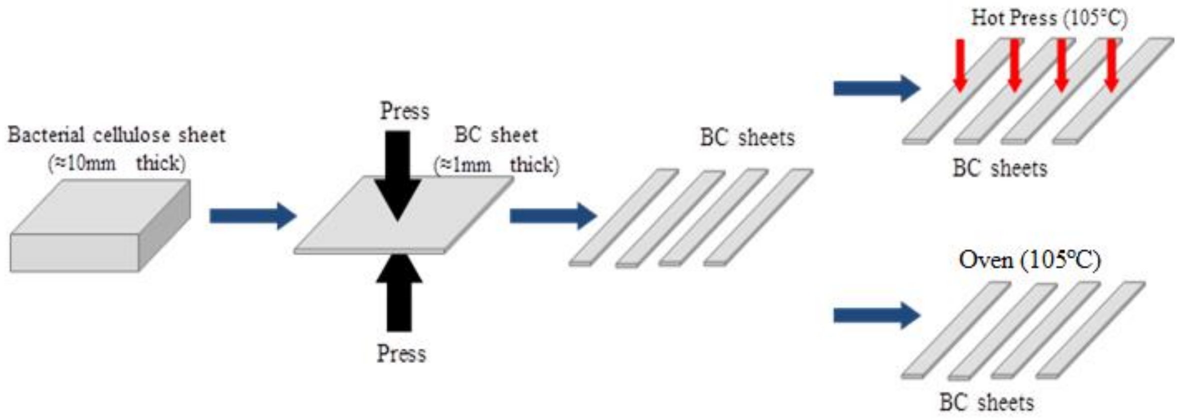


Figure 4.2: Fabrication process of BC-HP.

*BC/PVA composite fabrication*

As for BC/PVA composite sheet, the BC pellicle was pressed until about 1 mm thick. Then, the 1 mm thick BC sheets were inserted into a vacuum chamber, and when the vacuum condition in the chamber reached approximately 1 MPa, the BC sheets were soaked in PVA solution and left for 24 hours for PVA to be absorbed in the BC sheets. Then, the sheets were hot pressed to dry on a hot plate at 105°C for 30 minutes, then dried in an oven at 105°C for 10 minutes to ensure it was fully dried.

*Hot pressing method*

The BC sheets and BC/PVA composite sheets underwent hot pressing treatment and their properties were compared with the untreated samples. The samples of 10 mm x 100 mm size were put in a mold and hot-pressed at a temperature of 180°C for 10 minutes under constant pressure of 10 MPa. After hot pressing, the sample in the mold was left to cool to room temperature.

### 4.2.3 Evaluation and characterization of BC/PVA composites

*SEM observation*

A field emission scanning electron microscope (FE-SEM HITACHI S-4700, Japan) was used to observe the samples and the fracture surfaces. The samples were coated with platinum for 60 seconds prior to SEM observation. The surface of the sheets and the fracture surface after tensile test were observed under the electron microscope at an accelerating voltage of 1.5 kV. The SEM observations were intended to study the morphology of the sample surface, the fiber dispersion in PVA matrix and the fracture surfaces of the samples after tensile test.

*Tensile test*

Test samples of 100 mm x 10 mm size with thickness ranging from 0.08 to 0.11 mm were prepared. The widths and thicknesses were measured at three points along the gauge length of 30 mm to get the average thickness and width and to ensure homogeneity of the sample dimensions. Then, the samples were glued at both ends with paper tabs to prevent damage caused by gripping. The samples were stored in a desiccator under controlled humidity for 24 hours and tensile tests were conducted immediately after the samples were taken out to avoid the effect of humidity on the samples. Mechanical properties of the samples were evaluated by tensile tests conducted using Instron 5567 (Instron Corporation, USA) universal testing machine at room temperature. Tests were performed with a 500 N load cell with crosshead speed of 1.0 mm/min. At least three samples were prepared from each sample and average values of the tensile strength and Young's modulus were calculated and reported.

*XRD analysis*

X-ray diffraction measurement of PVA-f, PVA-p and MFC samples were conducted by RIGAKU Multiflex X-ray diffractometer (Rigaku Corporation, Japan) using CuK$\alpha$1 radiation under voltage of 40 kV and 20 mA at room temperature. Diffraction intensities were counted at $2\theta$ from 5° to 40° with scan step of 0.05°/s.

## 4.3 Results and discussion

The fabrication of the disintegrated BC sheet resulted in a whitish colored sheet with some degree of transparency. The round-shaped sheet was 12 cm in diameter with thickness of approximately 0.9 mm. The sample of dried disintegrated BC sheet is shown in Figure 4.3.

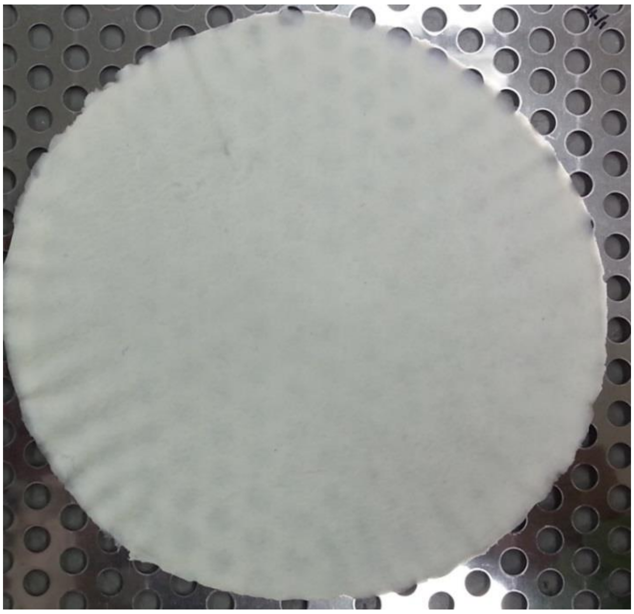


Figure 4.3: BC (disintegrated) sheet after oven dried at 30˚C in convection oven for several days.

### 4.3.1 Tensile test results

The tensile test results of disintegrated BC sheets are shown in Figure 4.4 showing the tensile strength and Young’s modulus of the untreated and hot-pressed BC sheets. Tensile test results showed that the tensile strength of the BC sheets increased after hot-pressing, where an increase of approximately 25% was recorded compared to untreated BC sheets. The tensile strength value of hot-pressed BC sheet was over 200 MPa compared to untreated sheets with tensile strength of 162 MPa. The Young’s modulus of heat-treated BC sheets also showed 34% increase compared to untreated sheets. A study by Nishi et al. reported that Young’s modulus of BC sheet from gel-like pellicle dried under 120˚C and 1 kg/cm$^2$ pressure was 15 GPa which was similar with the value in our study for hot-pressed BC sheet (Nishi et al., 1990). Yamanaka et al. reported almost similar modulus value of 17GPa, and concluded that the high Young's modulus of BC sheets was due to the unique super-molecular structure of BC, where the molecular chain axis lay randomly perpendicular to the thickness and the (110) plane was oriented parallel to the surface (S. Yamanaka et al., 1989). In another report by Yamanaka et al., this high Young's modulus of hot-pressed BC sheets was due to high planar orientation of the elements when pressed and ultrafine structure of the elements which allows more hydrogen bonding (Yamanaka et al., 2000).

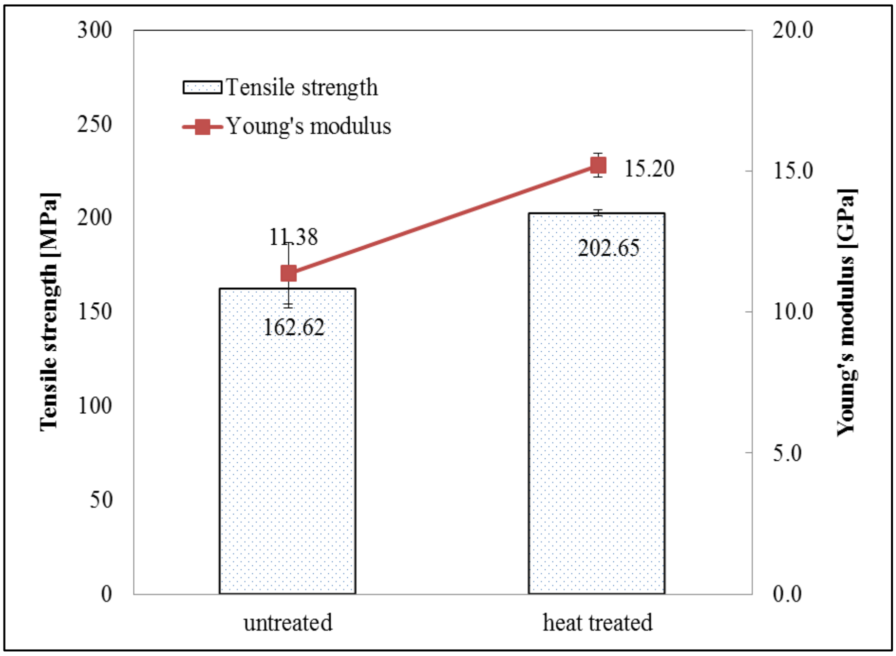


Figure 4.4: Tensile strength and Young's modulus of pure BC (disintegrated) sheet.

The stress-strain curves of untreated and hot-pressed disintegrated BC sheets and MFC sheets were compared and shown in Figure 4.5 and their tensile strength, Young's modulus and strain at break were tabulated in Table 4.1. From the stress-strain curves, we could observe that the Young's modulus of BC sheets was significantly higher than those of MFC sheets. The untreated disintegrated BC sheet showed almost similar modulus value with hot-pressed MFC sheet. Tensile strength of BC sheets was significantly higher than those yielded by MFC sheets. The strain at break of hot-pressed disintegrated BC sheet and MFC sheet showed a large decrease of about 43% and 60% respectively. Nakagaito et al. reported that the deformation of BC sheets differs with MFC sheets due to the fact that BC fiber network are rigid, uniform and continuous straightened fibrils due to the nature of the fiber generation by the bacteria (Nakagaito et al., 2005). The MFC, on the other hand, consists of entangled fibril bundles with broad size distribution; therefore deformations are rather caused by sliding or straightening of individual fibers. Therefore, we could see a large difference on the deformation of BC and MFC sheets. The Young's modulus value of untreated BC sheets was similar to hot-pressed MFC sheet at about 10 GPa. However, untreated BC sheet experienced plastic deformation at earlier stage and showed larger deformation compared to hot-pressed MFC sheet which exhibits more rigidity.

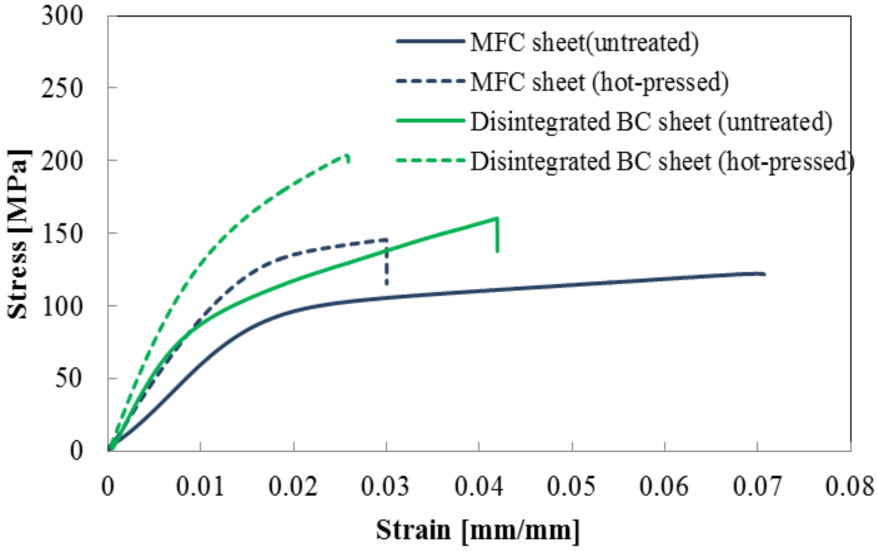


Figure 4.5: Stress-strain curves of untreated and hot-pressed disintegrated BC and MFC sheets.

Table 4.1: Mechanical properties of untreated and hot-pressed MFC and disintegrated BC sheets.

| **Sample type** | **Tensile strength [MPa]** | **Young's modulus [GPa]** | **Strain at break [%]** |
|---|---|---|---|
| MFC | 122.3 | 5.9 | 6.9 |
| MFC hot-pressed | 145.6 | 9.9 | 3.0 |
| BC | 160.3 | 10.5 | 4.2 |
| BC hot-pressed | 203.8 | 15.6 | 2.5 |

The mechanical properties of oven-heated PVA film, oven-heated BC sheet, hot-pressed BC sheet and hot-pressed BC/PVA sheets are described in Table 4.2, where the values of tensile strength, Young's modulus and strain at break are recorded.

The tensile strength of hot-pressed BC sheet was higher as compared to the oven-dried samples. The hot-pressed BC sheet (BC-HP) yielded tensile strength of about 290 MPa compared to oven-dried BC sheet (BC-OV) with 130 MPa, a difference of nearly 120%. Meanwhile, the Young's modulus also increased from 6.0 GPa for oven-dried sample to 15.0 GPa for hot-pressed sample, approximately 144% increase compared to oven-dried sample. The  high planar orientation of the ribbon like fibers when compressed are the main reason which leads to remarkable mechanical properties (Grande et al., 2009). We can imagine this phenomenon by taking cotton for example. Without any external pressure, the cotton will remain fluffy with its three dimensional network, however when pressure is applied so that it becomes a thin layer, the randomly distributed fibers are forced to lay flat, thus the fibers are oriented parallel to the flat surface. Therefore, the hot press has significantly increased the tensile strength and Young's modulus due to this reason.

Table 4.2: Tensile test results of PVA film, BC sheets and BC/PVA composite sheet.

| **Sample** | **Tensile strength [MPa]** | **Young's modulus [GPa]** | **Strain at break [%]** |
|---|---|---|---|
| PVA | 68.5 | 4.7 | 2.7 |
| BC-OV | 130.9 | 6.1 | 3.9 |
| BC-HP | 287.3 | 15.1 | 3.5 |
| BC/PVA | 216.3 | 16.6 | 1.7 |

The BC/PVA composite sheet recorded tensile strength of 216 MPa, a rather high value compared to neat PVA film result of 68.5 MPa. Although lower than BC-HP result, we could indicate that the impregnation of PVA solution in BC/PVA composite sheet has shown significant reinforcing effect which has increased the tensile strength as well as Young's modulus of pure PVA sample by more than 200% increase. The reinforcing effect of bacterial cellulose fibers in the PVA are due to the fact that both the bacterial cellulose fibers and PVA polymer contains hydroxyl functional groups and the hydrogen bond becomes the main source of strength (Yuwawech, Wootthikanokkhan, & Tanpichai, 2015).

The strain at break for BC-OV, BC-HP and BC/PVA composite sheets were rather low at 4%, 3.6% and 1.7% respectively. Comparing BC-OV and BC-HP sheets, we can notice that the difference in drying method (oven-dried vs. hot-pressed) had not significantly affected the strain at break of both samples. The BC/PVA composite sheet shows a remarkably low strain at break, though having a good value of tensile strength. This trend has been reported by previous studies where higher content of bacterial cellulose fibers will result in lower strain at break (Yuwawech et al., 2015). The pure bacterial cellulose fibers network without disintegration retains its rigid fiber network, thus leading to very low value of strain at break.

The stress-strain curves of all samples are plotted in Figure 4.6. The PVA-impregnated BC (BC/PVA) sheet showed a more rigid property compared to the very ductile PVA film. The BC-HP sheet yields much higher Young's modulus compared to BC-OV sheet. This was presumed to be due to the hot-pressing which allows more extensive hydrogen bonding of ultrafine structure of the BC ribbons (Yamanaka et al., 2000).

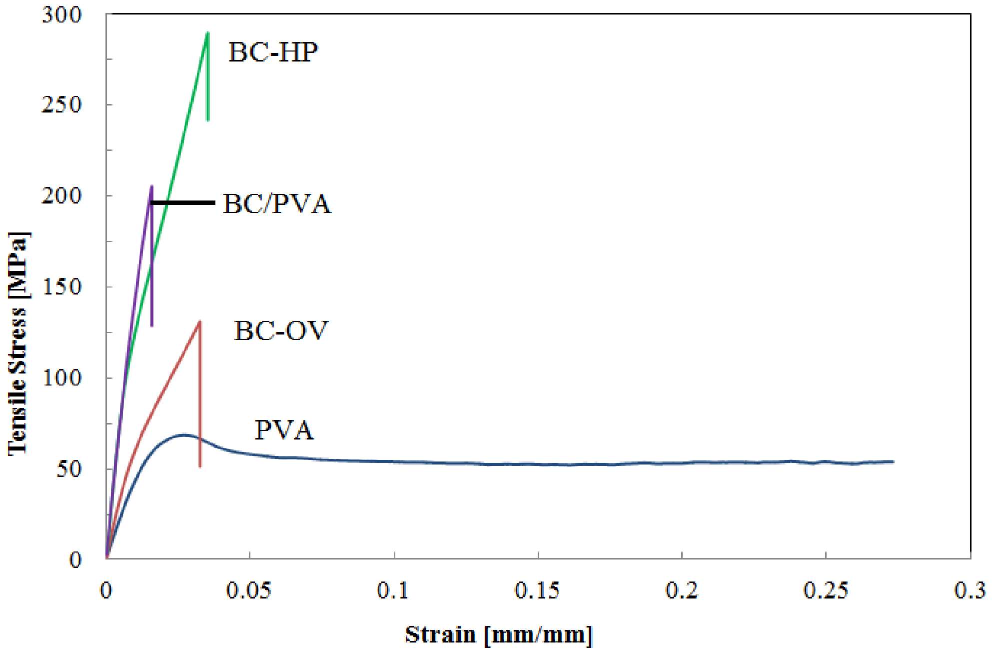


Figure 4.6: Stress-strain curves of PVA film, BC sheets (oven-dried and hot-pressed) and BC/PVA composite sheet.

The diffraction curves of BC and BC/PVA composite sheet was obtained via X-ray diffraction analysis as shown in Figure 4.7. For comparison purpose, the diffraction pattern of pure PVA sample was also inserted in the figure. Three peaks were observed for pure BC sample located at $2\theta = 14.5°$, 16.8° and 22.8° which are the well-established characteristics of bacterial cellulose. The crystallinity value of pure BC sheet was 97.57%. The high crystallinity value of pure BC sheet explains the remarkable mechanical properties yielded in the tensile test. The high Young's modulus value of BC/PVA of 16 GPa was also recorded by Yamanaka et al. where they concluded that the remarkably high Young's modulus was due to its super-molecular structure where molecular chain axis lay randomly perpendicular to the thickness and the (110) plane was oriented parallel to the surface (Takai, Tsuta, Hayashi, & Watanabe, 1975).

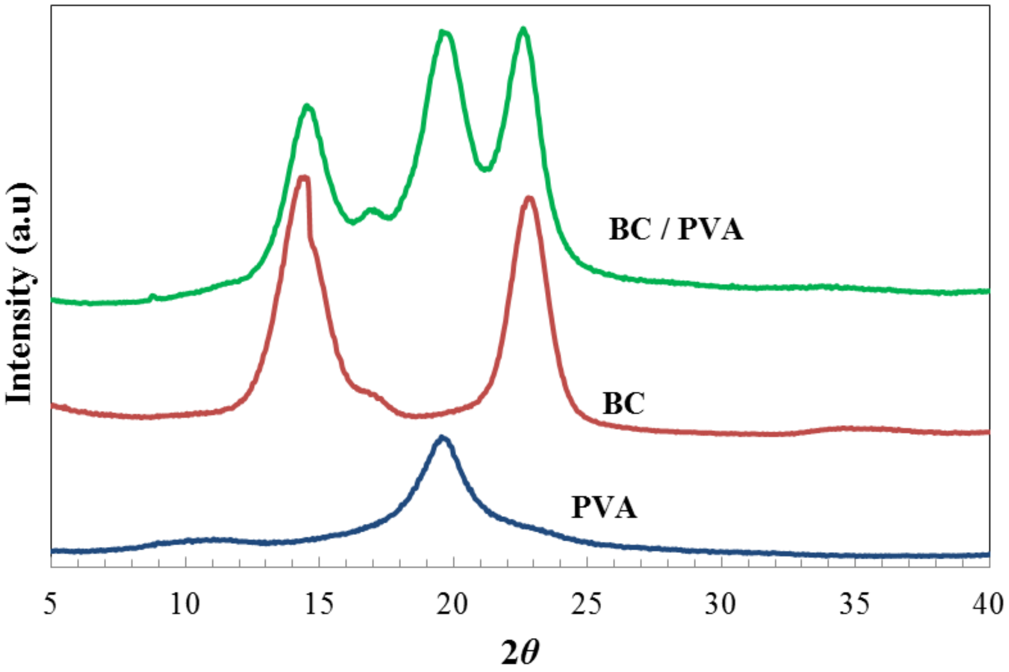


Figure 4.7: X-ray diffraction curves of PVA film, pure BC sheet and BC sheet impregnated with PVA.

### 4.3.2 SEM observation

The SEM image of freeze-dried BC sheet was examined to measure the diameters of the BC fibrils and the fiber diameter distribution based on the SEM image was plotted in Figure 4.8. From the analysis, we found out that most of the fibrils were 20-25 nm in size and some fibrils were much bigger (40 to 55 nm). BC pellicles are known to be made of random assembly of fibrils, which are composed of much finer microfibrils (Brown, Willison, & Richardson, 1976). Keshk reported that BC fibril structure were made of fine fibrils which aggregates to form microfibrils with larger width, and then further aggregate to form typical ribbon assembly with a lateral width of 40 to 60 nm (Keshk, 2014).

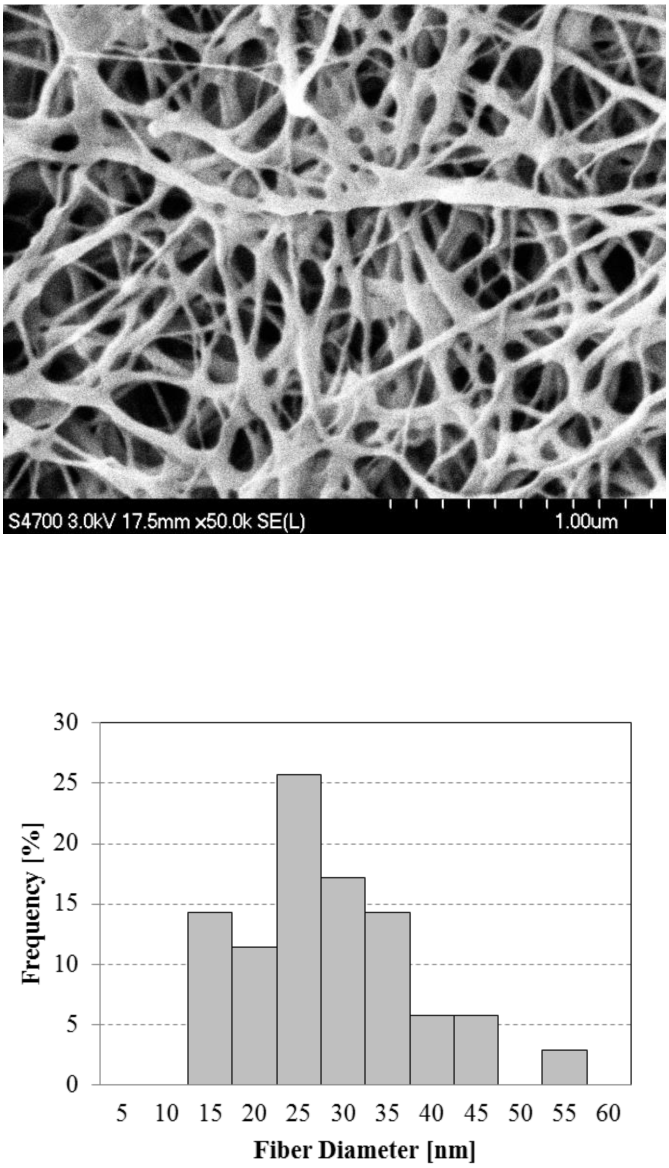
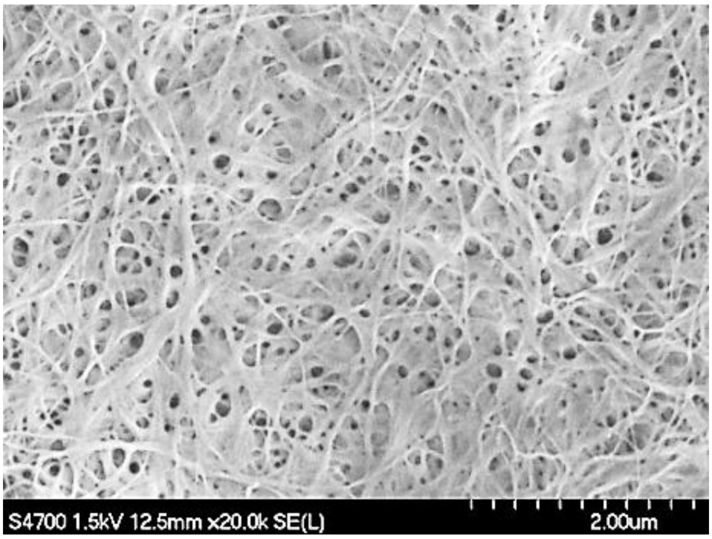
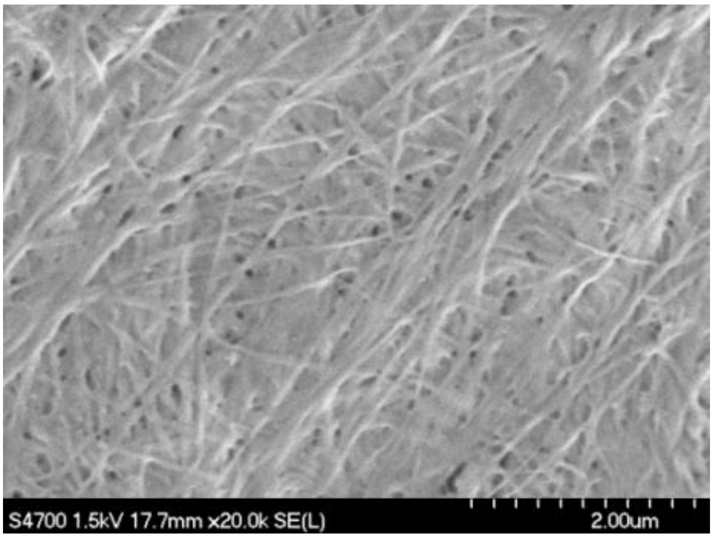


Figure 4.8: The SEM image of BC fibrils (top) and fiber diameter distribution graph (bottom).

The morphology images of BC sheet and BC/PVA sheet are shown in Figure 4.9 showing the images of hot-pressed BC sheet and BC/PVA sheet respectively. As seen in the pictures, the hot-pressed BC sheet has fibers with web-like structure with clear indication of the individual fibers. It has a dense network due to pressure as the bacterial cellulose sheet was hot-pressed and left to dry. The BC/PVA SEM image shows PVA polymer covering the sheet surface and in between the fiber network. We assume a good penetration of PVA solution in between the BC fibers and it has formed a much more homogeneous surface while the nanofibers are still noticeable on the surface. Bacterial cellulose are known to be in average of 20-100 nm in diameter and the nanofibers in our samples are considered very thin types of bacterial cellulose nanofibers. Some bigger size fibers are also noticeable at about 40-50 nm in size, however the fractions are relatively lower than 10% from the overall fiber sizes.



(a)



(b)

Figure 4.9: The FE-SEM images of (a) hot-pressed BC sheet, (c) hot-pressed BC/PVA sheet.

The fracture surface of the BC sheet and BC/PVA sheet are indicated in Figure 4.10. The incorporation of PVA in the BC sheet was visible where rougher fracture surface was observed in the BC/PVA composite sheet. The sheets have a distinct laminated structure as shown in figure, with bacterial cellulose visible in between the layers. The laminated structure was assumed to develop due to the pressing effect during drying process of the sheets. Just as pulp papers, these fibrils are considered bonded with strong hydrogen bonds with much higher density due to finer fibrils (Yamanaka et al., 1989). Though difficult to differentiate, we notice a much rougher fracture surface of the BC/PVA sample as compared to pure BC sheet.

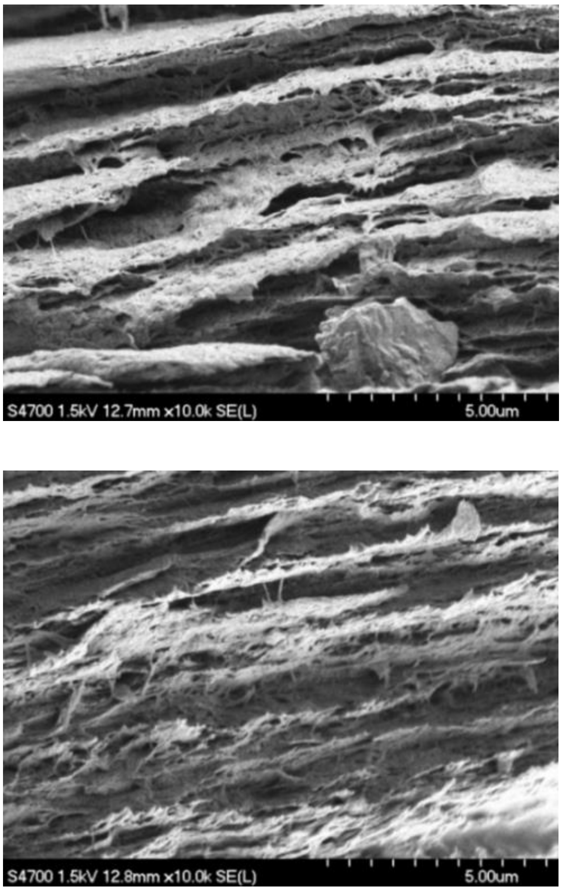


Figure 4.10: Fracture surface of hot-pressed BC sheet (left) and hot-pressed BC/PVA sheet (right).

The penetration of PVA in between the bacterial cellulose fibers is assumed to be good due to the observation of the sheets in Figure 4.11 where the transparency level of the BC/PVA sheet (right) was higher and almost transparent compared to pure BC sheet on the left. The pure BC sheet was rather milky-white in appearance, meanwhile the BC/PVA composite sheet was much clearer and higher in transparency. The high transparency level was assumed to indicate the absorption of PVA in between the fibrils. The nano-sized BC fibers are able to retain the transparency of PVA, and the empty space in between the BC film was filled by PVA with good wetting and interfacial bonding with BC (Iwamoto, Nakagaito, Yano, & Nogi, 2005; Yano et al., 2005).

Figure 4.11: Transparency level of hot-pressed BC sheet (left) and BC/PVA sheet (right).

## 4.4 Summary

In this study, we have managed to increase the tensile strength of BC sheet using hot pressing method where the strength had significantly increased more than 200% compared to oven dried BC sheets. BC had been known to have superior mechanical properties compared to MFC due to the nature of BC fibrils by the building up of straight, continuous and dimensionally uniform microfibril bundles. The high strength and high modulus of hot-pressed BC sheet was due to the high density of interfibrillar hydrogen bonds due to the fine structure of the fibrils which allows larger surface area. Impregnation of PVA into BC pellicles was successfully conducted by conducting impregnation process in vacuum condition. This was clearly proved by the increase in transparency of the BC/PVA sheets which proves proper PVA impregnation. BC/PVA samples showed significant increase of tensile strength and Young’s modulus compared to pure PVA samples which shows good compatibility of both materials. Hydrogen bonds could form between BC fibers, between PVA molecules and in between BC fibers and PVA fibers.

# CONCLUSIONS

In this study, we have conducted a study on the preparation and characterization of high strength nanofiber reinforced PVA composites using two types of cellulose nanofibers, namely microfibrillated cellulose (MFC) and bacterial cellulose (BC). These two materials are expected to show good compatibility with each other as they are all hydrophilic materials and should be suitable for manufacturing composite materials with high mechanical properties due to the unusually high strength of cellulose nanofibers. Heat treatments were done in order to improve the mechanical properties and the effect of different temperature and heat treatment process were studied. In general, we observed good compatibility and reinforcing effect of both types of cellulose nanofibers to the PVA polymer and improvement in the mechanical properties were clearly observed.

In Chapter 2, a preliminary study was conducted to study the properties of PVA films with a different degrees of hydrolysis and MFC reinforced PVA composites with varying MFC content. Fully hydrolyzed PVA (PVA-f) showed better mechanical properties compared to partially hydrolyzed (PVA-p) ones. The reinforcement effects of microfibrillated cellulose (MFC) are visible as the fiber content is increased in the MFC/PVA composite sheets. The increase in tensile strength and Young's modulus were observed as the MFC content was increased from 20 wt% to 80 wt%. The excellent reinforcing effect of MFC is explained by a strong interaction between the fibrils forming a rigid network which was governed by a percolation mechanism. Heat treatment by hot-pressing at 180˚C has significantly increased the mechanical properties of all the samples. Higher tensile properties of heat-treated samples above 40 wt% MFC content was observed, which confirms effective reinforcing capability of the MFC at high nanofiber content. Proper selection of heat treatment temperatures based on thermogravimetric analysis showed that 180˚C was suitable for this purpose due to the thermal stability of the samples at this temperature.

In Chapter 3, the effect of different heat treatment types and heating temperatures on the MFC/PVA composites properties was studied and described. Two types of heat treatment, namely oven-heating and hot-pressing were conducted and it was observed that hot pressing method yields higher mechanical properties to the samples. X-ray diffraction analysis showed an increase in crystallinity of PVAs, MFC sheets and PVA/MFC composite sheets when heat treatment was introduced. The pure PVA-f samples showed higher crystallinity compared to PVA-p samples. Crystallinity calculation based on FT-IR measurements was done and the findings by XRD analysis were confirmed.

Chapter 4 describes the effect of different heat treatment methods on BC samples. The heat treatment was done by oven heating and hot pressing to obtain better properties of the BC sheets. It was observed that sheets made from BC yielded remarkably higher tensile strength and Young's modulus compared to those from MFC, mainly due to its almost defect-free fine fiber network structure naturally produced by bacteria. The BC sheets had lower yield strain compared to MFC sheets, exhibiting its brittle fracture behavior. The reason was due to the continually connected fibrils which are stiff, therefore they do not deform under stress. The BC/PVA composite sample has yielded higher mechanical properties compared to pure PVA samples which show good reinforcement of BC in PVA polymer. Furthermore, the soaking of BC sheet into PVA solution under vacuum condition has produced a very transparent BC/PVA sheet and showed good impregnation of PVA into the samples. We believe that the vacuum condition had assisted the penetration process. Hot-pressed BC sheet exhibited a large increase in tensile strength and remarkably high Young's modulus of about 15 GPa compared to oven heated BC sheet which enables its use in high demanding application.

From this study, we could conclude that:

1. The mechanical properties, mainly tensile strength and Young's modulus of two types of PVA have different results due to the dependency on the degree of hydrolysis. It was observed that PVA with higher value of hydrolysis yields higher strength while hot-pressing at 180°C has significantly increased the strength and Young's modulus of the PVA films.
2. The MFC fiber content in MFC/PVA composites shows that fiber contents at 40 to 65 wt% has the better reinforcing effect compared to lower content of 10 to 30 w% and higher content of above 80 wt%. This is due to the reinforcing effect of the hydrogen bonds in the MFC fibers that increase as the MFC content increases to enable better fiber-matrix interaction, thus improving the mechanical properties of the composites. A suitable amount of reinforcing

material will enable good interaction between both materials, however too low or too much reinforcement materials will result in lower interaction due to insufficient reinforcing capability or on the other end, insufficient room for proper bonding.

3. The morphology and the microstructure of MFC and BC sheets and their composites show uniformly distributed fibers across the sample since ample mixing time are considered during the mixing process, and the PVA managed to be properly absorbed into the sheets as we conducted the sheet soaking in vacuum condition with ample time to penetrate. BC fibers are much stiffer due to the straight, uniform and continuous fiber network structure compared to MFC fibers which are loose and entangled networked fibers that deforms when subjected to stress.
4. The mechanical properties of both MFC and BC nanofibers and their PVA composite show better results by the hot-pressing method, where it has significantly increased the Young's modulus and yielded a higher tensile strength on almost all samples. We believe that this is due to the heat and pressure which eliminates the moisture content, thus allowing better fiber-matrix interaction and increased density to the composites.

# REFERENCES

Bhuiyan, M. T. R., Hirai, N., & Sobue, N. (2000). Changes of crystallinity in wood cellulose by heat treatment under dried and moist conditions. *Journal of Wood Science*, *46*, 431–436. http://doi.org/10.1007/BF00765800

Brown, R. M., Willison, J. H., & Richardson, C. L. (1976). Cellulose biosynthesis in Acetobacter xylinum: visualization of the site of synthesis and direct measurement of the in vivo process. *Proceedings of the National Academy of Sciences of the United States of America*, *73*(12), 4565–4569. http://doi.org/10.1073/pnas.73.12.4565

Byron, PR Dalby, R. (1987). Effects of heat treatment on the permeability of polyvinyl alcohol films to a hydrophilic solute. *J Pharm Sci.*, *76*(1), 65–67.

Chan, L. W., Hao, J. S., & Heng, P. W. S. (1999). Evaluation of Permeability and Mechanical Properties of Composite Polyvinyl Alcohol Films. *Chemical & Pharmaceutical Bulletin*, *47*(10), 1412–1416. http://doi.org/10.1248/cpb.47.1412

Dai, L., & Yu, S. (2003). Effect of degree of saponification on structural and property change of poly (Vinyl alcohol) fibers. *Polymers for Advanced Technologies*, *14*(7), 449–457. http://doi.org/10.1002/pat.351

Dubief, D., Samain, E., & Dufresne, A. (1999). Polysaccharide Microcrystals Reinforced Amorphous Poly ( -hydroxyoctanoate ) Nanocomposite Materials. *Macromolecules*, *32*(Atcc 29347), 5765–5771. http://doi.org/10.1021/ma990274a

Dufresne, A., Cavaille, J.-Y., & Vignon, M. R. (1997). Mechanical Behavior of Sheets Prepared from Sugar Beet Cellulose Microfibrils Mechanical Behavior of Sheets Prepared from Sugar Beet. *Journal of Applied Polymer Science*, *64*(6), 1185–1194. http://doi.org/10.1002/(SICI)1097-4628(19970509)64

Es-saheb, M., & Elzatahry, A. (2014). Post-Heat Treatment and Mechanical Assessment of Polyvinyl Alcohol Nanofiber Sheet Fabricated by Electrospinning Technique. *International Journal of Polymer Science*, *2014*(iv), 1–6. http://doi.org/10.1155/2014/605938

Favier, V., Cavaille, J. Y., Canova, G. R., & Shrivastava, S. C. (1997). Mechanical percolation in cellulose whisker nanocomposites. *Polymer Engineering Science*, *37*(10), 1732–1739. http://doi.org/10.1002/pen.11821

Fernandes, D. M., Hechenleitner, A. A. W., & Pineda, E. A. G. (2006). Kinetic study of the thermal decomposition of poly(vinyl alcohol)/kraft lignin derivative blends. *Thermochimica Acta*, *441*(1), 101–109.

Finch, C. A. (1973). *Polyvinyl alcohol, properties and applications*. New York: Wiley.

Gohil, J. M., Bhattacharya, A., & Ray, P. (2006). Studies On The Crosslinking Of Poly (Vinyl Alcohol). *Journal of Polymer Research*, *13*(2), 161–169. http://doi.org/10.1007/s10965-005-9023-9

Grande, C. J., Torres, F. G., Gomez, C. M., Troncoso, O. P., Canet-Ferrer, J., & Martínez-Pastor, J. (2009). Development of self-assembled bacterial cellulose–starch nanocomposites. *Materials Science and Engineering: C*, *29*(4), 1098–1104. http://doi.org/10.1016/j.msec.2008.09.024

Han, B., Li, J., Chen, C., Xu, C., & Wickramasinghe, S. R. (2003). Effects of Degree of Formaldehyde Acetal Solubility and Diffusivity of Water in, *81*(November). http://doi.org/10.1205/026387603771339609

Hasimi, A.Stavropoulou, A., Papadokostaki, K. G., & Sanopoulou, M. (2008). Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking. *European Polymer Journal*, *44*(12), 4098–4107. http://doi.org/10.1016/j.eurpolymj.2008.09.011

He, W., Jiang, S., Zhang, Q., & Pan, M. (2013). Isolation and characterization of cellulose nanofibers from Bambusa rigida. *BioResources*, *8*(4), 5678–5689.

Henriksson, M., Henriksson, G., Berglund, L. a., & Lindström, T. (2007). An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *European Polymer Journal*, *43*(8), 3434–3441. http://doi.org/10.1016/j.eurpolymj.2007.05.038

Herrick, F., Casebier, R., Hamilton, J., & Sandberg, K. (1983). Microfibrillated cellulose: morphology and accessibility. *Journal of Applied Polymer Science*, *37*, 797–813.

Hodge, R. M., Edward, G. H., & Simon, G. P. (1996). Water absorption and states of water in semicrystalline poly(vinyl alcohol) films. *Polymer*, *37*(8), 1371–1376. http://doi.org/10.1016/0032-3861(96)81134-7

Iwamoto, R., Miya, M., & Mima, S. (1979). Determination of crystallinity of swollen poly(vinyl alcohol) by laser Raman spectroscopy. *Journal of Polymer Science Part B: Polymer Physics*, *17*(9), 1507–1515.

Iwamoto, S., Nakagaito, A. N., Yano, H., & Nogi, M. (2005). Optically transparent composites reinforced with plant fiber-based nanofibers. *Applied Physics A: Materials Science and Processing*, *81*(6), 1109–1112.

Jang, J.-H., Lee, S.-H., Endo, T., & Kim, N.-H. (2015). Dimension change in microfibrillated cellulose from different cellulose sources by wet disk milling and its effect on the properties of PVA nanocomposite. *Wood Science and Technology*, *49*(3), 495–506. http://doi.org/10.1007/s00226-015-0703-2

John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, *71*(3), 343–364. http://doi.org/10.1016/j.carbpol.2007.05.040

Kang, Y. O., Yoon, I. S., Lee, S. Y., Kim, D. D., Lee, S. J., Park, W. H., & Hudson, S. M. (2010). Chitosan-coated poly(vinyl alcohol) nanofibers for wound dressings. *Journal of Biomedical Materials Research - Part B Applied Biomaterials*, *92*(2), 568–576. http://doi.org/10.1002/jbm.b.31554

Katz, M. G., & Wydeven, T. (1982). Selective permeability of PVA membranes. II. Heat-treated membranes. *Journal of Applied Polymer Science*, *27*(1), 79–87.

Keshk, S. M. (2014). Bacterial Cellulose Production and its Industrial Applications. *Journal of Bioprocessing & Biotechniques*, *4*(2). http://doi.org/10.4172/2155-9821.1000150

Kim, J., Cai, Z., Lee, H. S., Choi, G. S., Lee, D. H., & Jo, C. (2011). Preparation and characterization of a Bacterial cellulose/Chitosan composite for potential biomedical application. *Journal of Polymer Research*, *18*(4), 739–744. http://doi.org/10.1007/s10965-010-9470-9

Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., & Dorris, A. (2011). Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie - International Edition*, *50*(24), 5438–5466. http://doi.org/10.1002/anie.201001273

Krumova, M. (2000). Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol). *Polymer*, *41*(26), 9265–9272. http://doi.org/10.1016/S0032-3861(00)00287-1

Krumova, M., López, D., Benavente, R., Mijangos, C., & Pereña, J. . (2000). Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol). *Polymer*, *41*(26), 9265–9272. http://doi.org/10.1016/S0032-3861(00)00287-1

Kumeta, K., Nagashima, I., Matsui, S., & Mizoguchi, K. (2003). Crosslinking reaction of poly(vinyl alcohol) with poly(acrylic acid) (PAA) by heat treatment: Effect of neutralization of PAA. *Journal of Applied Polymer Science*, *90*(9), 2420–2427. http://doi.org/10.1002/app.12910

Kvien, I., & Oksman, K. (2007). Orientation of cellulose nanowhiskers in polyvinyl alcohol. *Applied Physics A*, *87*(4), 641–643. http://doi.org/10.1007/s00339-007-3882-3

Lee, S.-Y., Mohan, D. J., Kang, I.-A., Doh, G.-H., Lee, S., & Han, S. O. (2009). Nanocellulose reinforced PVA composite films: Effects of acid treatment and filler loading. *Fibers and Polymers*, *10*(1), 77–82. http://doi.org/10.1007/s12221-009-0077-x

Liitia, T., Maunu, S., & Hortling, B. (2000). Solid state NMR studies on cellulose crystallinity in fines and bulk fibres from refined kraft pulp. *Holzforschung*, *7*(2), 147–159.

Limpan, N., Prodpran, T., Benjakul, S., & Prasarpran, S. (2012). Influences of degree of hydrolysis and molecular weight of poly(vinyl alcohol) (PVA) on properties of fish myofibrillar protein/PVA blend films. *Food Hydrocolloids*, *29*(1), 226–233. http://doi.org/10.1016/j.foodhyd.2012.03.007

Liu, Y., & Hu, H. (2008). X-ray diffraction study of bamboo fibers treated with NaOH. *Fibers and Polymers*, *9*(6), 735–739. http://doi.org/10.1007/s12221-008-0115-0

Lu, J., Wang, T., & Drzal, L. T. (2008). Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials. *Composites Part A: Applied Science and Manufacturing*, *39*(5), 738–746. http://doi.org/10.1016/j.compositesa.2008.02.003

Mallapragada, S. K., & Peppas, N. a. (1996). Dissolution Mechanism of Semicrystalline Poly ( vinyl alcohol) in Water. *Journal of Polymer Science*, *34*(7), 1339–1346. http://doi.org/10.1002/(SICI)1099-0488(199605)34:7<1339::AID-POLB15>3.0.CO;2-B

Mansur, H. S., Sadahira, C. M., Souza, A. N., & Mansur, A. A. P. (2008). FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Materials Science and Engineering C*, *28*(4), 539–548. http://doi.org/10.1016/j.msec.2007.10.088

Mark, H. F. (2007). *Encyclopedia of Polymer Science and Technology, Concise, 3rd Edition*. John Wiley & Sons, Inc.

Miao, C., & Hamad, W. Y. (2013). Cellulose reinforced polymer composites and nanocomposites: A critical review. *Cellulose*, *20*(5), 2221–2262. http://doi.org/10.1007/s10570-013-0007-3

Miller, E. (Ed.). (1996). *Introduction to Plastics and Composites*. New York: Db Marcel Dekker.

Nagai, E., Mima, S., Kuribayashi, S., & Sagane, N. (1955). No Title. *Kobunshi Kagaku*, *12*, 199.

Nakagaito, A. N., Iwamoto, S., & Yano, H. (2005). Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites. *Applied Physics A*, *80*, 93–97. http://doi.org/10.1007/s00339-004-2932-3

Nakagaito, A. N., & Yano, H. (2005). Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. *Applied Physics A: Materials Science and Processing*, *80*(1), 155–159. http://doi.org/10.1007/s00339-003-2225-2

Nishi, Y., Uryu, M., Yamanaka, Y., Watanabe, K., Kitamura, N., Iguchi, M., & Mitshuhashi, S. (1990). The structure and mechanical properties of sheets prepared from bacterial cellulose Improvement of the mechanical properties of sheets and. *Journal of Materials Science, 25*, 2997–3001.

Nishiyama, Y., Kuga, S., Wada, M., & Okano, T. (1997). Cellulose microcrystal film of high uniaxial orientation. *Macromolecules*, *30*, 6395–6397. http://doi.org/10.1021/ma970503y

Nobuta, K., Teramura, H., Ito, H., Hongo, C., Kawaguchi, H., Ogino, C., … Nishino, T. (2016). Characterization of cellulose nanofiber sheets from different refining processes. *Cellulose*, *23*(1), 403–414. http://doi.org/10.1007/s10570-015-0792-y

Oishi, Y., Nakaya, M., Matsui, E., & Hotta, A. (2015). Structural and mechanical properties of cellulose composites made of isolated cellulose nanofibers and poly(vinyl alcohol). *Composites Part A: Applied Science and Manufacturing*, *73*, 72–79. http://doi.org/10.1016/j.compositesa.2015.02.026

Pa’e, N., Hamid, N. I. A., Khairuddin, N., Zahan, K. A., Seng, K. F., Siddique, B. M., & Muhamad, I. I. (2014). Effect of Different Drying Methods on the Morphology, Crystallinity, Swelling Ability and Tensile Properties of Nata De Coco. *Sains Malaysiana*, *43*(5), 767–773. Retrieved from http://202.185.40.50/jsm/pdf_files/SM-PDF-43-5-2014/16 Norhayati Pa%25D4%25C7%25D6e.pdf

Peng, Y., Gardner, D. J., & Han, Y. (2012). Drying cellulose nanofibrils: In search of a suitable method. *Cellulose*, *19*(1), 91–102. http://doi.org/10.1007/s10570-011-9630-z

Peresin, M. S., Vesterinen, A.-H., Habibi, Y., Johansson, L.-S., Pawlak, J. J., Nevzorov, A. a., & Rojas, O. J. (2014). Crosslinked PVA nanofibers reinforced with cellulose nanocrystals: Water interactions and thermomechanical properties. *Journal of Applied Polymer Science*, *131*(11), n/a-n/a. http://doi.org/10.1002/app.40334

Qiu, K., & Netravali, A. N. (2012). Fabrication and characterization of biodegradable composites based on microfibrillated cellulose and polyvinyl alcohol. *Composites Science and Technology*, *72*(13), 1588–1594. http://doi.org/10.1016/j.compscitech.2012.06.010

Quero, F., Nogi, M., Yano, H., Abdulsalami, K., Holmes, S. M., Sakakini, B. H., & Eichhorn, S. J. (2010). Optimization of the mechanical performance of bacterial cellulose/poly(L-lactic) acid composites. *ACS Applied Materials and Interfaces*, *2*(1), 321–330. http://doi.org/10.1021/am900817f

Sakurada, I., & Okaya, T. (2006). Vinyl Fibers. In M. Lewin (Ed.), *Handbook of Fiber Chemistry* (Third Edit, p. 1056). CRC Press.

Sano, M. B., Rojas, A. D., Gatenholm, P., & Davalos, R. V. (2010). Electromagnetically controlled biological assembly of aligned bacterial cellulose nanofibers. *Annals of Biomedical Engineering*, *38*(8), 2475–84. http://doi.org/10.1007/s10439-010-9999-0

Sehaqui, H., Ezekiel Mushi, N., Morimune, S., Salajkova, M., Nishino, T., & Berglund, L. a. (2012). Cellulose nanofiber orientation in nanopaper and nanocomposites by cold drawing. *ACS Applied Materials and Interfaces*, *4*(2), 1043–1049. http://doi.org/10.1021/am2016766

Shah, N., Ul-Islam, M., Khattak, W. A., & Park, J. K. (2013). Overview of bacterial cellulose composites: A multipurpose advanced material. *Carbohydrate Polymers*, *98*(2), 1585–1598. http://doi.org/10.1016/j.carbpol.2013.08.018

Shao, C., Kim, H. Y., Gong, J., Ding, B., Lee, D. R., & Park, S. J. (2003). Fiber mats of poly(vinyl alcohol)/silica composite via electrospinning. *Materials Letters*, *57*(9–10), 1579–1584. http://doi.org/10.1016/S0167-577X(02)01036-4

Shi, Z., Zhang, Y., Phillips, G. O., & Yang, G. (2014). Utilization of bacterial cellulose in food. *Food Hydrocolloids*, *35*, 539–545. http://doi.org/10.1016/j.foodhyd.2013.07.012

Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, *17*(3), 459–494. http://doi.org/10.1007/s10570-010-9405-y

Sriupayo, J., Supaphol, P., Blackwell, J., & Rujiravanit, R. (2005). Preparation and characterization of ??-chitin whisker-reinforced poly(vinyl alcohol) nanocomposite films with or without heat treatment. *Polymer*, *46*(15), 5637–5644. http://doi.org/10.1016/j.polymer.2005.04.069

Sugiyama, J., Chanzy, H., & Maret, G. (1992). Orientation of Cellulose Microcrystals by Strong Magnetic Fields. *Macromolecular Materials and Engineering*, *25*, 4232–4234.

Tadokoro, H. (1959). Crystallization-sensitive Band of Polyvinyl Alcohol, *32*, 1334–1339.

Tadokoro, H., Seki, S., & Nitta, I. (1955). The crystallinity of solid high polymers. I. The crystallinity of polyvinyl alcohol film. *Bulletin of the Chemical Society of Japan*, *28*(8), 559–564. http://doi.org/10.1246/bcsj.28.559

Taghizadeh, M. T., Yeganeh, N., & Rezaei, M. (2015). The investigation of thermal decomposition pathway and products of poly(vinyl alcohol) by TG-FTIR. *Journal of Applied Polymer Science*, *132*(25). http://doi.org/10.1002/app.42117

Takagi, H., & Asano, A. (2008). Effects of processing conditions on flexural properties of cellulose nanofiber reinforced "' green '" composites, *39*, 685–689. http://doi.org/10.1016/j.compositesa.2007.08.019

Takai, M., Tsuta, Y., Hayashi, J., & Watanabe, S. (1975). Biosynthesis of Cellulose by Acetobacter Xylinum. III. X-Ray Studies of Preferential Orientation of the Crystallites in a Bacterial Cellulose Membrane. *Polymer Journal*, *7*(2), 157–164. http://doi.org/10.1295/polymj.7.157

Tang, C., & Liu, H. (2008). Cellulose nanofiber reinforced poly(vinyl alcohol) composite film with high visible light transmittance. *Composites Part A: Applied Science and Manufacturing*, *39*, 1638–1643. http://doi.org/10.1016/j.compositesa.2008.07.005

Tretinnikov, O. N., & Zagorskaya, S. A. (2012). Determination of the degree of crystallinity of poly(vinyl alcohol) by FTIR spectroscopy. *Journal of Applied Spectroscopy*, (August), 1–6. http://doi.org/10.1007/s10812-012-9634-y

Turbak, A., Snyder, F. W., & Sandberg, K. R. (1983). Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. *Journal of Applied Polymer Science*, *37*, 815–827.

Xu, X., Liu, F., Jiang, L., Zhu, J. Y., Haagenson, D., & Wiesenborn, D. P. (2013). Cellulose nanocrystals vs. Cellulose nanofibrils: A comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Applied Materials and Interfaces*, *5*(8), 2999–3009. http://doi.org/10.1021/am302624t

Yamanaka, S., Ishihara, M., & Sugiyama, J. (2000). Structural modification of bacterial cellulose. *Cellulose*, *7*, 213–225. http://doi.org/10.1023/A:1009208022957

Yamanaka, S., Watanabe, K., & Kitamura, N. (1989). The structure and mechanical properties of sheets prepared from bacterial cellulose. *Journal of Materials*, *24*, 3141–3145.

Yang, H., Xu, S., Jiang, L., & Dan, Y. (2012). Thermal Decomposition Behavior of Poly (Vinyl Alcohol) with Different Hydroxyl Content. *Journal of Macromolecular Science, Part B*, *51*(3), 464–480. http://doi.org/10.1080/00222348.2011.597687

Yano, H., Sugiyama, J., Nakagaito, A. N., Nogi, M., Matsuura, T., Hikita, M., & Handa, K. (2005). Optically Transparent Composites Reinforced with Networks of Bacterial Nanofibers. *Advanced Materials*, *17*(2), 153–155.

Yuwawech, K., Wootthikanokkhan, J., & Tanpichai, S. (2015). Effects of Two Different Cellulose Nanofiber Types on Properties of Poly ( vinyl alcohol ) Composite Films. *Journal of Nanomaterials*, *2015*.

Zhou, Y. M., Fu, S. Y., Zheng, L. M., & Zhan, H. Y. (2012). Effect of nanocellulose isolation techniques on the formation of reinforced poly(vinyl alcohol) nanocomposite films. *Express Polymer Letters*, *6*(10), 794–804. http://doi.org/10.3144/expresspolymlett.2012.85

# ACKNOWLEDGEMENT

The author would like convey special thanks and appreciation to Professor Takagi Hitoshi for his continuous guidance and full support upon completion of this research. Special thanks to Associate Professor Dr. Antonio Norio Nakagaito for his endless guidance and spirit to encourage continuous learning throughout this process.

The author would also like to thank Mr. Ueki from Tokushima University for his assistance with XRD analysis, Mr. Sugano for his kind assistance for SEM analysis, Ms. Nakamura for TGA measurement and all personnel who had been helping directly or indirectly throughout this research work. Not to forget lab members this has been a major support and strength throughout conducting this study. My special appreciation is addressed to the government of Malaysia for their funding for my study and for their continuous support on my career.

Last but not least, special love and thanks to my family members which has been my strength and courage through thick and thin and difficult situations. May Allah bless you all.