UNIVERSITI PUTRA MALAYSIA

IMPROVED PERFORMANCE OF OIL PALM MESOCARP FIBER BIOCOMPOSITE USING SUPERHEATED STEAM TREATMENT

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By

NOOR IDA AMALINA BINTI AHAMAD NORDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

August 2016

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Dedicated to …

MY LATE FATHER AND DEAR MOTHER(Kelthum binti Ismail),
MY LOVING HUSBAND(Ahmad Shukri Sahri),
MY BELOVED SONS,
(Ahmad Yahya, Ahmad Yusuf, Ahmad Yunus)
MY DEAR BROTHERS AND SISTERS
FAMILIES AND FRIENDS…

Who have always be at my side, through thick and thin along my study. Thank you for the never ending love, support and care. I love you…

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Doctor of Philosophy

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August 2016

Chairman : Associate Professor Hidayah Ariffin, PhD
Faculty : Biotechnology and Biomolecular Sciences

Surface modification of lignocellulose material is crucial in order to improve compatibility between polymer matrix and the lignocellulose. Superheated steam (SHS) treatment has potential as pre-treatment method for lignocellulose as it has been shown that this treatment could alter chemical composition of oil palm biomass. In this study, oil palm mesocarp fiber (OPMF) was treated in a SHS oven at temperatures of 190, 210 and 230 °C for 1 - 3 h. SHS-treated OPMF was then evaluated for its chemical composition, thermal stability, morphology and crystallinity via chemical analysis, thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Then, the SHS-treated OPMF was melt-blended with polypropylene (PP) at various fiber loadings (30 to 50 wt%) and the mechanical, thermal and water absorption properties of OPMF/PP biocomposites were determined.

SHS-treated OPMF demonstrated lower composition of hemicellulose compared to untreated-OPMF with treatment at 230 °C exhibited the lowest hemicellulose content (9%). The best treatment condition of OPMF was at 210 °C and 1 h resulted better thermal stability and crystallinity by 7% and 11%, respectively, compared to untreated OPMF. Treatment condition above 210 °C for more than 1 h partially hydrolyzed the cellulose component. SEM/EDX and ICP analyses of SHS-treated OPMF showed that silica bodies were removed from OPMF after the SHS treatment.

Biocomposites prepared from SHS230-OPMF/PP had lower mechanical and crystallinity properties by 6 – 42% and 16%, respectively in comparison to SHS210-OPMF/PP. This can be explained by disruption in cellulose structure at higher SHS treatment temperature. On the other hand, results showed that SHS210-OPMF/PP biocomposites having a tensile strength of 20.5 MPa, which was 25% higher than untreated-OPMF/PP biocomposites. A significant reduction of water absorption by 31% and improved thermal properties by 8% at $T_{5\%degradation}$ were also recorded. SEM

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images of fractured SHS-OPMF/PP biocomposites revealed that there was less fiber pull-out, proving that SHS treatment improved interfacial adhesion between fibers and PP. Results obtained exhibited that SHS-treatment which caused the treated OPMF to have rougher surface, higher thermal stability and increased in crystallinity compared to the untreated OPMF; had contributed to the improved mechanical strength of the biocomposite.

Subsequently, a comparison was made with the biocomposite prepared from chemically-treated OPMF, *i.e.* NaOH, KOH, $NaClO_2$ and two-stage treatment ($NaClO_2$+KOH). For chemical treatment of OPMF, it was demonstrated that NaOH-OPMF/PP and KOH-OPMF/PP biocomposites had the highest mechanical properties (tensile strength 18 – 19 MPa, flexural strength 29 – 32 MPa and impact strength 77 – 78 MPa) followed by ($NaClO_2$+KOH)-OPMF/PP and $NaClO_2$-OPMF/PP biocomposites.

Overall, alkaline-treated OPMF exhibited better compatibility with polymer compared to $NaClO_2$-OPMF due to the reduction of hemicellulose causing it to be more compatible with PP. Removal of lignin in $NaClO_2$-OPMF caused the fiber to lose hydrophobic region and hence led to the poor interaction between fiber and polymer. SHS-treated biocomposite exhibited slightly better properties compared to alkaline-treated biocomposite despite of the same treatment effect, *i.e.* hemicellulose removal. All in all, SHS treatment meets green chemistry principles such as waste prevention, no involvement of hazardous chemicals, safe treatment agent and produces less chemical by-products. Results obtained in this research exhibited that SHS treatment could be an alternative eco-friendly method to treat lignocellulosic materials prior to biocomposite production.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENINGKATAN PRESTASI BIOKOMPOSIT SERAT KELAPA SAWIT MENGGUNAKAN RAWATAN STIM PANAS LAMPAU

Oleh

NOOR IDA AMALINA BINTI AHAMAD NORDIN

Ogos 2016

Pengerusi : Profesor Madya Hidayah Ariffin, PhD
Fakulti : Bioteknologi dan Sains Biomolekul

Pengubahsuaian permukaan bahan lignoselulosa adalah penting dalam usaha untuk meningkatkan keserasian antara matrik polimer dan lignoselulosa itu. Rawatan stim panas lampau (SHS) mempunyai potensi sebagai kaedah pra-rawatan untuk lignoselulosa kerana rawatan ini telah menunjukkan kemampuan untuk mengubah komposisi kimia biojisim kelapa sawit. Dalam kajian ini, serat mesokarp kelapa sawit (OPMF) telah dirawat di dalam ketuhar SHS pada suhu 190, 210 dan 230 ° C selama 1 – 3 jam. Setiap sampel OPMF-terawat SHS telah dinilai dari segi komposisi kimia, kestabilan terma, morfologi dan penghabluran melalui analisis kimia, analisis gravimetri terma (TGA), mikroskopi imbasan elektron (SEM) dan pembelauan sinar-X (XRD). Kemudian, OPMF-terawat SHS telah diadun-lebur dengan polipropilena (PP) pada peratusan kandungan serat (30 hingga 50 % berat) dan sifat mekanik, haba dan penyerapan air bagi OPMF/PP biokomposit telah ditentukan.

OPMF-terawat SHS menunjukkan komposisi hemiselulosa yang lebih rendah berbanding OPMF tidak terawat di mana kandungan hemiselulosa paling rendah (9%) adalah pada rawatan 230 °C. Rawatan terbaik terhadap OPMF adalah pada 210 °C dan 1 jam yang menghasilkan kestabilan terma dan penghabluran yang lebih baik iaitu sebanyak 7% dan 11%, setiapnya berbanding OPMF tidak dirawat. Suhu rawatan melebihi 210 °C dan masa melebihi 1 jam menghidrolisiskan komponen selulosa. SEM/EDX dan ICP analisis bagi OPMF-terawat SHS menunjukkan bahawa silika telah dikeluarkan dari OPMF selepas rawatan SHS.

Biokomposit disediakan daripada SHS230-OPMF/PP mempunyai ciri mekanik dan penghabluran lebih rendah sebanyak 6 - 42% dan 16%, setiap satunya berbanding dengan SHS210-OPMF/PP. Ini dapat dijelaskan oleh struktur selulosa yang terjejas pada suhu rawatan SHS yang tinggi. Sebaliknya, keputusan menunjukkan bahawa SHS210-OPMF/PP biokomposit mempunyai kekuatan tegangan 20.5 MPa, iaitu 25%

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lebih tinggi daripada biokomposit tidak dirawat-OPMF/PP. Turut dicatatkan pengurangan ketara bagi ujian penyerapan air iaitu sebanyak 31% dan sifat terma yang lebih baik sebanyak 8% pada $T_{5\%}$ degradasi. Imej SEM bagi sampel patah SHS-OPMF/PP biokomposit mendedahkan bahawa terdapat kurang serat tertarik keluar, membuktikan bahawa rawatan SHS menambahbaik keupayaan lekatan antara serat dan PP. Keputusan ini mempamerkan bahawa rawatan SHS menyebabkan OPMF-terawat mempunyai permukaan kasar, kestabilan haba yang tinggi dan peningkatan dalam penghabluran berbanding OPMF tidak dirawat yang telah menyumbang kepada peningkatan kekuatan mekanikal biokomposit itu.

Kemudiannya, perbandingan telah dibuat dengan biokomposit yang disediakan daripada OPMF-terawat kimia iaitu rawatan dengan NaOH, KOH, $NaClO_2$ dan dua-peringkat rawatan ($NaClO_2$+KOH). Bagi OPMF yang dirawat dengan rawatan kimia, ia telah menunjukkan bahawa NaOH-OPMF/PP dan KOH-OPMF/PP biokomposit mempunyai sifat mekanik tertinggi (kekuatan tegangan 18 - 19 MPa, kekuatan lenturan 29 – 32 MPa dan kekuatan hentaman 77 – 78 J/m) diikuti oleh ($NaClO_2$+KOH)-OPMF/PP dan $NaClO_2$-OPMF/PP biokomposit.

Secara keseluruhan, didapati OPMF-terawat alkali mempunyai keserasian yang lebih baik dengan polimer berbanding $NaClO_2$-OPMF, disebabkan oleh pengurangan komponen hemiselulosa dalam OPMF yang meningkatkan keserasian dengan PP. Penyingkiran lignin dalam $NaClO_2$-OPMF menyebabkan serat kehilangan bahagian hidrofobik dan dengan itu membawa kepada interaksi yang lemah antara serat dan polimer. SHS-terawat biokomposit mempamerkan sifat yang sedikit lebih baik berbanding alkali-terawat biokomposit walaupun kesan rawatan adalah sama, iaitu menyingkirkan hemiselulosa. Secara keseluruhan, rawatan SHS memenuhi prinsip kimia secara hijau seperti pencegahan bahan buangan, tiada penglibatan bahan kimia berbahaya, ejen rawatan yang selamat dan menghasilkan produk kimia sampingan yang kurang. Keputusan yang diperolehi dalam kajian ini mempamerkan bahawa rawatan SHS boleh menjadi satu kaedah alternatif yang mesra alam untuk merawat bahan lignoselulosa sebelum penghasilan biokomposit.

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LIST OF ABBREVIATIONS

ASTM	American Standard Testing Method
CrI	Crystallinity index
$T_{5\%, 20\%, 50\%}$	Degradation temperature at 5%, 20% or 50% weight loss
X_c	Crystallinity
DSC	Differential scanning colorimetry
EDX	Energy Dispersive X-ray
h_{fg}	Enthalpy of evaporation
FTIR	Fourier transmitted infra red
FFB	Fresh fruit bunch
GNI	Gross national income
ICP	Inductively coupled plasma
w_o	Initial weight of the sample
LCC	Lignin-carbohydrate complex
h_f	Liquid enthalpy
LDPE	Low density polyethylene
ΔH_m	Melting entalphy
T_m	Melting temperature
MAH	Maleic anhydride
OPMF	Oil palm mesocarp fiber
(OP)EFB	(Oil palm) Empty fruit bunch
OPF	Oil palm frond
OPT	Oil palm trunk
POME	Palm oil mill effluent
PP	Polypropylene
rpm	Rotation per minute
SEM	Scanning electron microscopy
$\Delta H^{*PP}{}_m$	Specific heat of fusion of 100% crystalline PP
SHS	Superheated steam
TGA	Thermal gravimetry analysis
M_t	Water absorbed
wt%	Weight percent
w_t	Weight of the specimens at *t* time
XRD	X-ray radiation diffraction

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CHAPTER 1

INTRODUCTION

1.1 Research overview

In recent years, research on the replacement of man-made fibers with natural fibers as reinforcement in plastic composites has increased dramatically (Sgriccia et al., 2008; Kaewkuk et al., 2013; Etaati et al., 2014). The potential applications for biocomposites are for car interior such as door panel, dashboards, boot liner and sun visor (Pickering et al., 2015); and non-structural applications such as floor panel, furniture and household products (Bledzki and Gassan, 1999). This is due to the advantages of natural fiber, such as lower density (Rozman et al., 2003), lower price (Mohanty et al., 2004), non-toxic (Mir et al., 2013) and environmentally friendly over man-made fiber (Then et al., 2013). Natural fibers have proven to be suitable reinforcement materials for composite. In addition, they are available in large amounts, renewable (Cao et al., 2006), causing less equipment abrasion and simple in processing (Bengtsson et al., 2007). There have been many reports on the use of cellulosic fibers such as sisal (Jacob et al., 2004), jute (Khan et al., 2009), hemp (Kabir et al., 2010), coir (Hill et al., 2000; Mir et al., 2013), bamboo (Lee et al., 2013), wood (Iwamoto et al., 2008), banana (Sumaila et al., 2013), kenaf (Tajeddin et al., 2009), oil palm biomass (Fahma et al., 2010; Then et al., 2013) and others in composites as reinforcements.

Oil palm biomass fiber has big potential in biocomposites production. The porous surface morphology of EFB is advantageous for better mechanical interlocking with matrix resin in composite fabrication (Sreekala et al., 2002). On the other hand, high cellulose content (Shinoj et al., 2010; Sreekala et al., 2004) and high toughness of oil palm biomass making it suitable for biocomposite applications (Rozman et al., 2003; Sgriccia et al., 2008; Norul Izani et al., 2013).

Components of natural fiber which are cellulose and hemicellulose contain large amount of hydroxyl group. The presence of hydroxyl group makes the fibers hydrophilic, causing poor interfacial adhesion with hydrophobic polymer matrices (Shinoj et al., 2011; Kabir et al., 2012; Siyamak et al., 2012; Then et al., 2014a). This may lead to poor physical and mechanical properties of the biocomposite. It has been reported that removal of hemicellulose can reduce hydrophilicity of fiber (Rozman et al, 2001; Bismarck et al., 2001; Cantero et al., 2003; Alix et al., 2009). Surface modification of natural fiber aimed at hemicellulose removal can be used as a method to improve interfacial adhesion between fiber and polymer matrices.

Treatments such as physical (Ohgren et al., 2007; Sinha and Panigrahi, 2009) and chemical treatments (Xiao et al., 2001; Sreekala and Thomas, 2003) have been used to decrease hydrophilic property of the fibers. These method have been extensively studied. Chemical treatment is widely used in the manufacture of biocomposites

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(Sreekala et al., 1997; Pothan et al., 2002; Mwaikambo and Ansell, 2002; Shinoj et al., 2010; Sawpan et al., 2011) due to its effectiveness. Among the chemical treatments, alkalization is one of the most economical treatments for natural fibers (Li et al., 2007; Taha et al., 2007; Shinoj et al., 2011; Kabir et al., 2012). This treatment process removes noncellulosic substance, such as impurities, waxes, pectin and hemicellulose which cover the cellulose fiber and bind these fibrils together. Removal of these substances also gives rise to a rougher fiber surface resulting in an increase in surface contact of the fiber. This causes an improvement of mechanical interlocking between the polymer and the fiber leading to enhanced mechanical properties.

Generally, polypropylene (PP) is widely used as a matrix for biocomposite due to its excellent mechanical properties, low cost and easy processability. Hence, PP was an ideal choice for experimentation in this study.

1.2 Problem statement

The drawbacks of using natural fiber for biocomposite are related to its poor compatibility with polymer, low thermal degradation and high water absorption, making surface modification of fiber becomes necessary. Apart from chemical treatment, physical treatment such as hydrothermal treatment (saturated steam) has been used to modify the fiber surface for improving compatibility between natural fiber and polymer matrix and it was proven that the treatment managed to remove hemicellulose component in lignocellulose samples (Han et al., 2009; Hosseinaei et al., 2011; Eslam et al., 2011). Superheated steam (SHS) is another type of steam which can be potentially used as a candidate for the treatment of lignocellulose fiber. At present, SHS is used in the food industry for drying purpose. Reports have shown that SHS can be used to alter the structure of oil palm biomass meant for biosugar production (Bahrin et al., 2012; Nik Mahmud et al., 2013). It is hence in this study SHS was being used for surface modification of lignocellulose material for biocomposite production.

Palm oil industries produce large amount of lignocellulosic fibers each year, such as oil palm mesocarp fiber (OPMF) and empty fruit bunch (EFB) (Jacob et al., 2004; Ariffin et al., 2008; Khalid et al., 2008; Ariols et al., 2009). Palm oil mills in Malaysia produce about 7.7 million tonnes of OPMF per year (Kheang and May, 2015). It is mainly used as boiler feed together with palm kernel shell to generate steam energy for palm oil mill (Chua et al., 2009; Neoh et al., 2011; Zakaria et al., 2014). However, due to the abundance of OPMF produced daily, most of the OPMF is burnt inefficiently in the boiler as a matter of disposal. It is believed that OPMF has great properties to be used as reinforce material for biocomposite, similarly with EFB (Shinoj et al., 2011). This study aimed at characterizing the chemical and mechanical properties of OPMF and subsequently used the OPMF in biocomposite making.

It is interesting to note that, inefficient burning of OPMF also contributed to the excess production of steam energy at the palm oil mill. Since the backpressure vessel

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at the mill can contain steam with pressure up to 3.5 MPa only, the excess steam produced need to be exhausted (Nasrin et al., 2011). This eventually leads to the waste of energy at the mill.

Realizing the availability of both OPMF and steam at the palm oil mill, hence this research was conducted, mainly to determine the feasibility of the steam to be the treatment agent for surface modification of OPMF intending for biocomposite production, and to determine the properties of biocomposite produced from PP reinforced with OPMF.

1.3 Objectives of study

The main objective of this research was to treat OPMF with SHS aimed for biocomposite with enhanced properties.

The specific objectives of the study were:

1. To characterize OPMF treated with SHS for their chemical and physical properties in comparison with untreated OPMF.
2. To determine the effect of SHS treatment temperature and fiber loading on mechanical, thermal, crystallinity, morphological and water absorption properties of SHS-treated OPMF/PP biocomposite.
3. To compare and evaluate the properties of OPMF/PP biocomposites prepared from SHS and chemical treatments.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, some information on characteristics of natural fibers, treatments applied to natural fibers for biocomposite application and the mechanical properties of biocomposite were discussed. The discussion generally describe overview on varies type of natural fiber which has potential to act as a filler in the biocomposite production. However, due to some drawback of the natural fibers, a fiber treatment is needed. There are vast treatment methods that is established and being applied including chemical treatment and steam treatment. At the end of this chapter, highlight on the potential used of oil palm mesocarp fiber (OPMF) and superheated steam (SHS) treatment in the proses of biocomposite production were also discussed.

2.2 Natural fiber

Natural fibers can be classified according to which part of the plant they are obtained from, as shown in Figure 2.1. These fibers have been used conventionally as ropes, matting and carpet. The economic interest on developing countries has create an urgent need for new application for these natural fibers. The combination of acceptable mechanical and physical properties of natural fibers together with their environmentally friendly character has triggered various studies in the area of green biocomposites.

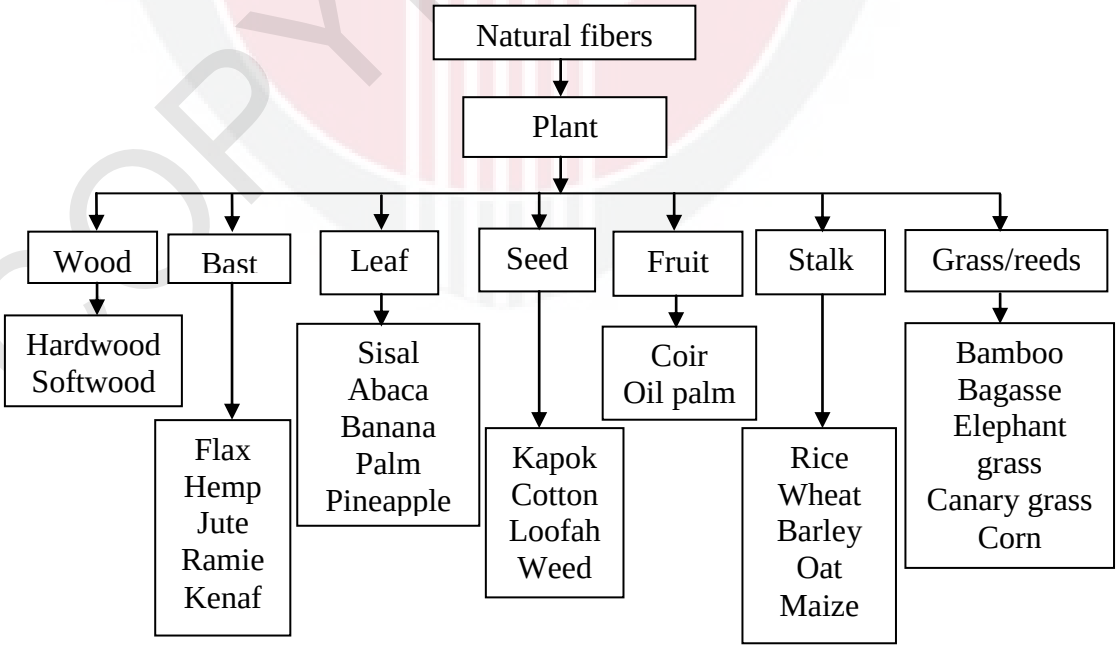

Figure 2.1: Categories of natural fibers (Kabir et al., 2012).

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Due to environmental awareness, the utilization of natural fibers as an alternative for man-made fibers in biocomposite materials has attracted interest among researchers. Studies on natural fibers have shown that natural fibers have the potential to be an effective reinforcement in thermoplastic materials (Li et al., 2007; Kabir et al., 2012; Faruk et al., 2014; Then et al., 2015). These fibers are abundantly available, especially in developing countries such as Malaysia, Indonesia, Thailand, India and Bangladesh. Table 2.1 shows the amount of fibers generated and the largest producers.

Table 2.1: Plant fiber generated and their producers.

Fiber	World production (10^3 tonnes)	Largest producers
Kenaf	970	India, Bangladesh, USA
Flax	830	Canada, France, Belgium
Jute	2,300	India, China, Bangladesh
Hemp	214	China, France, Philippines
Abaca	70	Philippines, Costa Rica
Pineapple	74	Philippines, Thailand, Indonesia
Sisal	378	Tanzania, Brazil
Coir	100	India, Sri Lanka
Oil palm	40	Malaysia, Indonesia
Baggase	75,000	Brazil, India, China
Bamboo	30,000	India, China, Indonesia

References: Faruk et al., 2012; Ramamoorthy et. al, 2015.

2.2.1 Advantages of natural fiber

Economic and environmental concerns have encouraged research to find environmentally alternatives to replace glass fibers. Much of this research has focused on the development of biocomposites couple with natural renewable materials. The growing interest in using natural fibers is mainly due to their abundant and renewable sources (Saheb and Jog, 1999; John and Thomas, 2008; Then et al., 2015). The key differences between natural fibers and glass fibers were shown in Table 2.2.

Table 2.2: Comparison between natural and glass fibers.

Properties	Natural fibers (NF)	Glass fibers
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Density	Low	Twice that of natural fibers
Recyclability	Yes	No
Energy consumption	Low	High
CO_2 neutral	Yes	No
Abrasion to machines	No	Yes
Disposal	Biodegradable, energy harvesting	Non-biodegradable, landfill

Reference: Wambua et al., 2003.

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Natural fibers also have low specific density, which is typically 1.25–1.50 g/cm^3 as compared to glass fibers at about 2.6 g/cm^3, allowing natural fibers to provide higher specific strength and stiffness in plastic materials (Jawaid and Abdul Khalil, 2011). The other key driver to substituting natural fibers for glass is the lower price of natural fibers (200-1000 USD/tonnes) compared to glass (1200-1800 USD/tonnes) (Jawaid and Abdul Khalil, 2011). Natural fibers also offer several advantages as they are exhibit good mechanical properties, provide better working conditions and are less abrasive to equipment compared to common synthetic fibers, which can contribute to significant cost reductions (Satyanarayana et al., 2009; Shinoj et al., 2011; Faruk et al., 2014). All these characteristic make their use very attractive for the manufacture of polymer matrix biocomposites.

2.2.2 Disadvantages of natural fiber

The first and most important problem in producing biocomposite is fiber-matrix adhesion (Mohanty et al., 2004; Cao et al., 2006; Bengstsson et al., 2007; Lee et al., 2013). Poor adhesion between hydrophobic polymers and hydrophilic fibers such as oil palm fibers resulted in poor mechanical properties of the biocomposites (Sreekala et al., 1997; Rozman et al., 2003; Shinoj et al., 2011; Norul Izani et al., 2013). The role of the matrix in a fiber reinforced biocomposite is to transfer the load to the stiff fibers through shear stresses at the interface. This process requires a good bond between the matrix and fibers. Poor adhesion at the interface means that the full capabilities of the fibers in the biocomposite cannot be exploited. Natural fibers also have low degradation temperature (~200 °C), which make them unsuitable for processing with thermoplastic above 200 °C (Quajai and Shanks, 2005; Sinha and Rout, 2009; Eslam et al., 2011). The advantages and disadvantages of natural fibers are shown in Table 2.3.

Table 2.3: Advantages and disadvantages of natural fiber.

Advantages	Disadvantages
Lower specific weight results in a higher specific strength and stiffness than glass	Lower mechanical properties especially impact resistance
Renewable resource	Heterogeneous quality
Production with low investment at low cost	Moisture sensitivity (hydrophilic character)
Low abrasion, therefore tool wear	Low thermal stability
Non toxic	Low durability
Abundantly available	Poor fire resistance
Biodegradable	Poor fiber-matrix adhesion
Thermal recycling is possible	Price fluctuation by harvest results or agricultural politics

References: Sreekumar, 2008; Jawaid and Abdul Khalil, 2011.

Their high moisture uptake (Bismarck et al., 2001; Alvarez et al., 2006; Hosseinaei et al., 2011), incompatibility (Jacob et al., 2004; Then et al., 2014a), heterogeneous

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quality and their tendency to form aggregates during processing due to strong hydrogen forces between the fibers (Li et al., 2007; Kabir et al., 2012), represent some of the drawbacks to produce biocomposites. Their hydrophilic nature causes the fibers to take on water causing degradation leading to fiber-matrix interface problems. These drawbacks may be improved by physical and chemical treatments.

2.3 Characteristics of natural fiber

There are many types of natural fiber exists. However, the characteristics of the fibers are almost similar that will attribute to its properties such as chemical composition and thermal degradation.

2.3.1 Components of natural fiber

The main components of natural fiber are cellulose, hemicellulose and lignin (Mohanty et al., 2001; Shinoj et al., 2011; Bahrin et al., 2012). Natural fibers are hydrophilic and absorb moisture. This means that the mechanical and physical properties of the fibers are mainly influenced by their composition. Figure 2.2 shows a schematic structure of natural fiber. Cellulose microfibrils have their own cell geometry which is a factor responsible for the properties of the fiber (Rozman et al., 2003; Sgriccia et al., 2008; Kabir et al., 2012).

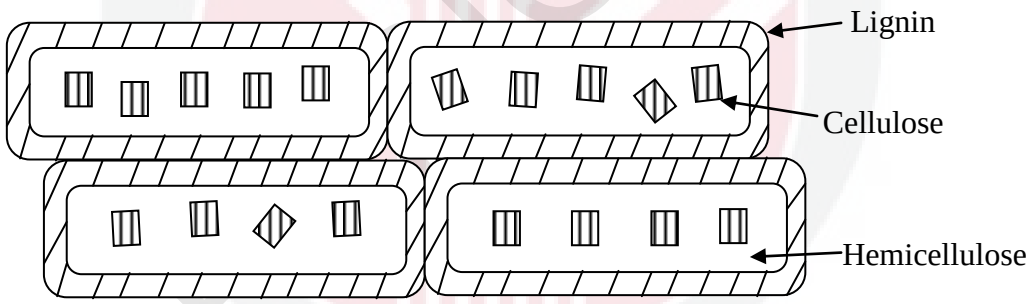

Figure 2.2: Structural organization of the three major components in the fiber cell (adopted from Kabir et al., 2012).

Fibers contains more crystalline cellulose may have higher tensile strength and thermally stable (John and Thomas, 2008; Norul Izani et al., 2013). While, high hemicellulose content will promote fiber degradation at low temperature and absorb more moisture (Gomes et al., 2007; Islam et al., 2012). Fibers contain hydroxyl and other oxygen-containing groups that attract moisture absorption through hydrogen bonding. Table 2.4 shows the variations of chemical contents of common natural fibers.

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Table 2.4: Chemical compositions of natural fiber.

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Ash (wt%)
Kenaf	36	21	0.8-2	2-5
Flax	71	19-21	2	1-2
Ramie	67-76	13-17	0.6	-
Jute	61-72	14-20	12-13	8
Hemp	70-74	18-22	4-6	1-2
Sisal	67-78	10-14	8-11	7
Abaca	70	22	6	1
EFB	48	26	14	2
OPMF	30-60	22-32	11-24	3
Coir	32-43	0.15-0.25	40-45	-
Cotton	93	3	-	1
Wheat straw	51	26	16	7

References: Sreekala et al., 1997; Biagiotti et al., 2004; Fowler et al., 2006, Mazaheri et al., 2010; Then et al., 2015; Ramamoorthy et al., 2015.

2.3.1.1 Cellulose

Cellulose is the primary component of natural fibers. Cellulose is made of long unbranched chain that are composed exclusively of glucose that held together by hydrogen bonding as illustrated in Figure 2.3. The chemical formula of cellulose is $(C_6H_{10}O_5)_n$; n, represents the number of glucose groups. The overall structure of cellulose consists of crystalline and amorphous regions (Cantero et al., 2003; Demir et al., 2006; Etaati et al., 2014). It mainly contains carbon (44.44%), hydrogen (6.17%) and oxygen (49.39%) (Bledzki et al., 2002). There are roughly 4,000 to 8,000 glucose molecules chains together. The polymer chain in cellulose was joined by glycosidic linkages at C_1 and C_4 position. Each repeating unit contains three hydroxyl groups. The presence of hydroxyl group makes the cellulose hydrophilic in nature (Bledzki et al., 2002; Li et al., 2007).

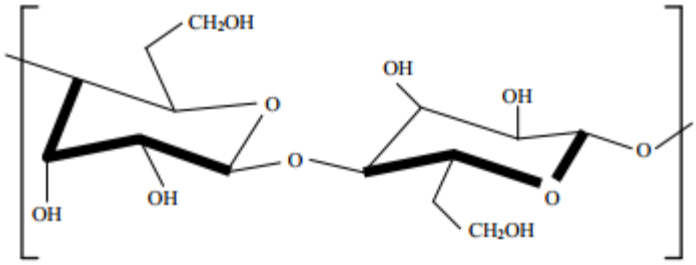

Figure 2.3: Cellulose chain with hydrogen bonds.

It is noted these hydroxyl groups and their ability to form hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. The hydrogen bonding of many cellulose molecules to each other

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results in the formation of microfiber that can interact to form fiber. Cellulose fiber usually has more than 500,000 cellulose molecule. Therefore, a cellulose fiber with 5,000 glucose resides/cellulose molecules may contain about 2.5 billion hydrogen bonding. It is the hydrogen bonding that forms the basis for the high tensile strength of cellulose (Biagiotti et al., 2008). Hydrogen bonding may not have the same strength as covalent bond, however, the cumulative bonding energy of 2.5 billion of hydrogen bonding is incredible.

2.3.1.2 Hemicellulose

Hemicelluloses are polysaccharides and differ from cellulose in that they consist of several sugar moieties. These sugars include glucose and monomer such as hexoses (galactose, mannose) and pentoses (xylose and arabinose) as illustrated in Figure 2.4.

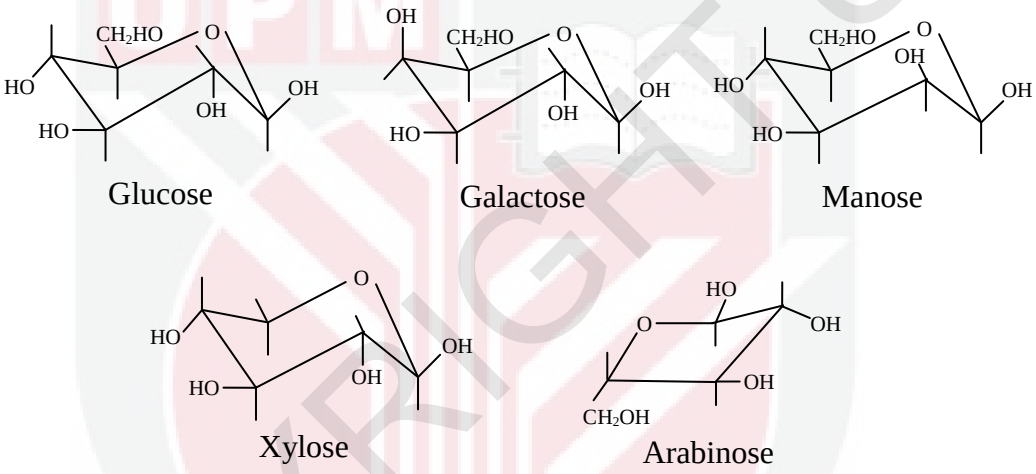

Figure 2.4: Structure of hemicellulose.

Structure of hemicellulose mostly a branched carbohydrate (hexoses and pentoses) and have low molecular weight. Table 2.5 showed the comparison between cellulose and hemicellulose.

Table 2.5: Differences between cellulose and hemicellulose.

	Cellulose	**Hemicellulose**
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5μm)	Short
Molecular weight	High (10 000 units)	Low (hundred units)
Polymer topology	Linear	Branched
Side groups substitution	No subsitution	On C_2, C_3 and C_6
Polymer morphology	Crystalline+amorphous	Amorphous
Solubility	Low	High
Reactivity	Less reactive	More reactive
Hydrolysis	Partial	Readily (susceptible)

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It is strongly bound to cellulose fibrils by hydrogen bonding. It is partly soluble in water and hydroscopic because of its open structure which contains hydroxyl and acetyl groups (Mohanty et al., 2000; Bismarck et al., 2001; Hosseinaei et al., 2012). This characteristic also allows the natural fibers to absorb significant amounts of water and making it a weaker polymer compared to cellulose (Khalid et al., 2008; Kabir et al., 2012). Hemicellulose is amorphous and has low degradation temperature.

2.3.1.3 Lignin

Lignin is a phenolic compound. Lignin is the second large source of organic material (Brebu and Vasile, 2009). It is a complicated amorphous polymer, hydrophobic in nature, highly complex copolymers of aliphatic and aromatic constituents (Mohanty et al., 2000; John and Thomas, 2008) as illustrated in Figure 2.5. Lignin contains hydroxyl, methoxyl and carbonyl groups. The high carbon and low hydrogen content of lignin suggest that it is highly unsaturated or aromatic in character (Mohanty et al., 2000; Yang et al., 2007; Brebu and Vasile, 2010).

The presence of hydroxyls and many polar groups in the lignin structure, resulting in strong intramolecular and intermolecular hydrogen bonds, making lignin insoluble in any solvent. Phenolic hydroxyl and carboxyl makes the lignin able to be dissolved in alkaline solution. Lignin binds the elementary fibers together with hemicellulose as cementing elements. Means lignin imparts the rigidity to the cell walls and fills the space between hemicellulose and cellulose (Mohanty et al., 2000; Bismark et al., 2001; John and Thomas, 2008; Rowell, 2008).

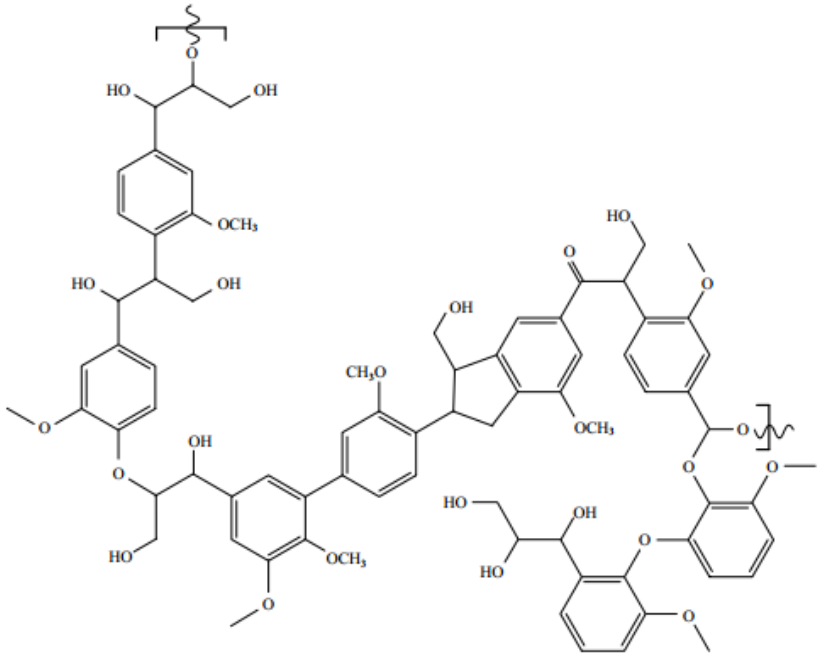

Figure 2.5: Structure of lignin.

Due to its hydrophobic character, lignin acts as a sealant to water, a protection against biological attack and a stiffener to the fibers (Joseph et al., 2002; Brebu and Vasile, 2010; Ramamoorthy et al., 2015). Lignin may also act as a compatibilizer between hydrophilic natural fibers and hydrophobic matrix resulting in stronger fiber-matrix interface (Rozman et al., 2001; Hosseinaei et al., 2012; Then et al., 2014).

2.3.2 Thermal properties

The degradation of natural fibers is a crucial aspect in the development of natural fibers biocomposites and can limit the use of some thermoplastics. The thermal degradation of natural fibers is a three-stage process. The first stage, from 250 to 300 °C, is attributed to the low molecular weight components such as hemicellulose (Han et al., 2009; Deepa et al., 2011, Bahrin et al., 2012). The second decomposition process is in the temperature range of 300 to 400 ^{o}C which is associated with degradation of cellulose (Sinha and Rout 2009; Kabir et al., 2010; Eslam et al., 2011). The third which have a broader degradation range until high-temperature is observed around 450 to 900 ^{o}C is due to lignin (Lee and Wang, 2006; Yang et al., 2007; Brebu and Vasile, 2010). Due to its complex composition and structure, lignin decomposes slower over a broader temperature range.

Typical melt processing temperature is around 200 °C, almost in the range of degradation temperature of fibers. This will results in production of volatiles at processing temperatures above 200 ^{o}C. This can lead to porous polymer products with lower densities and inferior mechanical properties (Saheb and Jog, 1999; Li et al., 2007; Kabir et al., 2010; Kaewkuk et al., 2013). For improvement of thermal stability, treatment have been done to modify the surface or to reduce the low degradation components of the fibers (Mohanty et al., 2004; Quajai and Shanks, 2005; John and Anandjiwala, 2008; Kabir et al., 2012).

2.3.3 Mechanical properties of natural fiber

Among all the components in fibers, cellulose is the strongest and degree of polymerization of cellulose will influences the mechanical properties of the fiber (Shinoj et al., 2011; Mir et al., 2013; Lee et al., 2013; Ramamoorthy et al., 2015). It is found that bast fibers have the highest degree of polymerization. Table 2.6 shows the physical and mechanical properties of different natural fibers and glass fibers. The variation in natural fiber properties can be due to several reasons such as geographical location, plant maturity, size of fiber, chemical composition and part of the plant which fiber are taken (John and Thomas, 2008; Mohanty et al., 2000). The variation can also be attributed to different stages of growth, harvesting and storage (Li et al., 2007; John and Thomas, 2008; Ramamoorthy et al., 2015). Small fiber diameter and high aspect ratio will resulted to biocomposite with high mechanical properties (Xinwen et al., 2010; Kabir et al., 2012; Then et al., 2013). High aspect ratio promotes to large surface area for polymer coating and creates better stress transferred from matrix to fiber and vice versa. Ramamoorthy et al. (2015) mentioned that cellulose is the strongest and stiff component of the fiber. It is

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supposed coir shows low tensile strength among all the natural fibers, may attribute to low cellulose content. While high strength of ramie and flax may attribute to its high cellulose content. However, it is not possible to correlate the fiber strength exactly with cellulose content because of the very complex structure of natural fibers. On the other hand, natural fiber are relatively have good strength and potentially to be used as reinforcement and filler in biocomposites industries. In terms of specific strength, natural fibers can be compared with glass fiber (Mohanty et al., 2001; Satyanarayana et al., 2009; Abdul Khalil et al., 2012).

Table 2.6: Physical and mechanical properties of natural fibers and glass fibers.

Fiber	Type	Diameter of fiber (µm)	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Ramie	Bast	18-80	1.5	400-938	62-128	2-3.8
Flax	Bast	5-38	1.4-1.5	800-1500	60-80	1.2-1.6
Hemp	Bast	10-51	1.5	550-900	30-70	1.6
Jute	Bast	25-200	1.3-1.5	393-700	10-55	1.5-1.8
Kenaf	Bast	12-36	1.2	295	21-60	2.7-6.9
Sisal	Leaf	50-200	1.3-1.5	600-700	22-38	2-3
Banana	Leaf	80-250	1.4	529-914	27-33.8	5.3
Pineapple	Leaf	20-80	1.5	170-1627	60-83	1-3
Cotton	Seed	12-35	1.5	287-597	6-12.6	3-10
EFB	Fruit	19.1-25	0.7-1.6	248	3.2	2.5
OPMF	Fruit	20	0.6-1.2	80	0.5	17
Coir	Fruit	100-450	1.1	131-175	4-6	15-40
Bamboo	Grass	14	0.8-1.1	391-1000	48-89	1.9-3.2
Bagasse	Grass	10-34	1.2	20-290	19-27	3-4.7
E-glass	Mineral	13	2.5	2000-3500	70	2.5

References: Rowell, 2008; Mohanty et al., 2000; Jawaid and Abdul Khalil, 2011; Abdul Khalil et al., 2012; Ramamoorthy et al., 2015.

2.3.4 Moisture content of natural fiber

Natural fibers are hydrophilic and absorb moisture. Their moisture content can vary between 5 and 10%. This can lead to dimensional variations and also affects the mechanical and physical properties of the biocomposites. Table 2.7 shows the moisture content of some natural fibers. The high moisture content in fibers generally related to high fiber volume, high relative humidity and low crystallinity.

Table 2.7: Moisture content of some natural fibers.

Fibers	Type	Dry moisture content (%)
Flax	Bast	10.0
Hemp	Bast	10.8
Jute	Bast	12.6
Ramie	Bast	8.0

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Table 2.7 (Cont.)

Fibers	Type	Dry moisture content (%)
Abaca	Leaf	15.0
Pineapple	Leaf	11.8
Sisal	Leaf	11.0
Coir	Fruit	8.0
EFB	Fruit	10
OPMF	Fruit	4.8
Baggase	Grass	8.8
Bamboo	Grass	8.9

References: Mazaheri et al, 2010; Ramamoorthy et al., 2015.

2.3.5 Degradation properties of natural fiber

The natural fibers are degraded biologically because of organism that can recognise the carbohydrate polymers mainly hemicellulose in the cell wall. They have specific enzyme systems capable of hydrolysing these polymers into digestible units. The degradation process depends on how the components interact in different degradation conditions as shown in Table 2.8. Biodegradation of the high molecular weight cellulose weakens the cell wall because crystalline cellulose is primary responsible for the strength of the natural fibers (Mohanty et al., 2000). Natural fibers also degraded when exposed to outside due to photochemical degradation. Firstly, lignin will affected followed by hemicellulose due to poorly bonded carbohydrate. Hemicellulose will degrade first due to heat followed by cellulose and lignin. For moisture sorption, hemicellulose mainly responsible component compared to cellulose and lignin.

Table 2.8: Degradation properties of natural fiber.

Biological degradation	Thermal degradation
↓ Hemicellulose	↓ Hemicellulose
Non-crystalline cellulose	Cellulose
Crystalline cellulose	Lignin
Lignin	
Ultraviolet degradation	**Moisture absorption**
↓ Lignin	↓ Hemicellulose
Hemicellulose	Non-crystalline cellulose
Non-crystalline cellulose	Lignin
Crystalline cellulose	Crystalline cellulose

↓ Ordered of firstly affected.

Reference: Mohanty et al., 2000.

2.4 Palm oil industries in Malaysia

Palm oil is one of the 17 major oils and fats produced globally, it was the highest consumed oil in 2012, with 52.1 million tonnes consumed to almost three billion

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people in 150 countries (Agensi Inovasi Malaysia, 2013). Globally, Malaysia is the second largest producer and the largest exporter of crude palm oil.

2.4.1 Background of palm oil industries

Oil palm is the most important agricultural crop of Malaysia. The palm oil industry is the 4th largest contributor to the Malaysia's gross national income (GNI) which was accounting for about 8% or almost RM80 billion of GNI (Agensi Inovasi Malaysia, 2013).

There was 445 palm oil mills are operating in Malaysia (MPOB, 2014) with total land area of 5.39 million hectares (MPOB, 2014) in 2014. This industry annually generates 6.93 million tonnes of oil palm biomass (dry basis) (Nazir et al., 2013). Biomass from the mills consists of empty fruit bunches (EFB), mesocarp fiber (OPMF), palm kernel shell and palm oil mill effluent (POME) (Abdullah et al., 2015). These biomass are produced daily and more consistent in term of supply compared to oil palm trunks (Zakaria et al., 2014).

2.4.2 Oil palm biomass fibers

As discussed below, there are two types of biomass fiber produced in the palm oil mill which are EFB and OPMF. OPMF also being referred as palm pressed fiber. The EFB will normally be returned to the plantations (Ariffin et al., 2008; Shinoj et al., 2011; Shamsudin et al., 2012), while OPMF are burnt to generate steam to provide energy to the mills (Mazaheri et al., 2010; Nik Mahmud et al., 2013). Due to the huge amount of biomass fiber generated yearly, the palm oil industries have the potential to utilize the biomass fiber efficiently and effectively to other value added products.

2.4.2.1 Empty fruit bunch

EFB is the fibrous left behind after separating the fruits from sterilized fresh fruit bunch (FFB). EFB can yield up to 73% (dry weight) fiber ((Wirjosentono et al., 2004) as shown in Figure 2.6.

Figure 2.6: Empty fruit bunch.

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Realizing the potential of EFB, researchers have done studies on its characterization and its utilization. EFB has a very good potential to be converted into renewable energy sources (Shuit et al., 2009; Idris et al., 2010; Shinoj et al., 2011), production of bioethanol (Shamsudin et al., 2012; Bahrin et al., 2013) and biocomposite production (Sreekala et al., 2003; Khalid et al., 2008; Fahma et al., 2010; Then et al., 2013). Some studies done on EFB are shown in Table 2.9. EFB is rich in cellulose and hemicellose which can be converted to biosugar (Shinoj et al., 2009). In study done by Shamsudin et al. (2012) showed that EFB-treated with saturated steam produced higher conversion of sugar which is useful for bioethanol production. High biosugar conversion from EFB also was demonstrated by Bahrin et al. (2012) using SHS treatment.

Table 2.9: Studies done on utilization of EFB.

Research	References
Steam treatment of EFB to enhance biosugar production	Shamsudin et al., 2012; Bahrin et al., 2012
Physical, chemical and thermal treatment for cellulase production	Ariffin et al., 2008a; Ariffin et al., 2008b
Surface modification of EFB for biocomposite production	Sreekala et al., 2003; Khalid et al., 2008; Siyamak et al., 2012; Norul Izani et al., 2013
SHS treatment as drying method for EFB	Hasibuan and Daud, 2009

Apart from biosugar production, there is a growing interest on EFB for biocomposite production due to its hard and tough properties. Norul Izani et al. (2013) successfully demonstrated improved thermal stability and tensile strength of alkaline-treated EFB. Improved characteristics of EFB will enhanced the compatibility of fiber with polymer. The production of nanofiber done by Fahma et al. (2010) was beneficial to produce biocomposite with high mechanical properties.

2.4.2.2 Oil palm mesocarp fiber

For oil extraction FFB is cook under hot steam and pressed. Figure 2.7 shows the components in palm oil fruit.

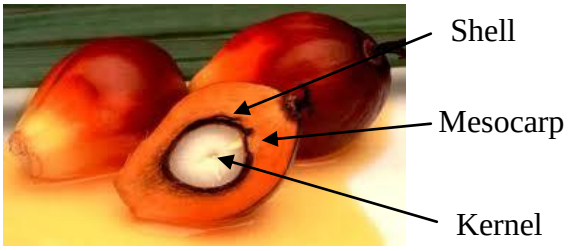

Figure 2.7: Components in palm oil fruit.

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OPMF and palm kernel nut are left as biomass. The OPMF is then separated from palm kernel nut by cyclone separator. OPMF is elongated cellulose with 30-50 mm length. Mesocarp layer is the outer part and quite thick.

Figure 2.8 shows the abundant of OPMF generated in the palm oil mill. Due to its porous nature, OPMF is used as biomass feed for boiler to produce steam (Sreekala et al., 1997; Lik Nang Lau et al., 2008; Neoh et al., 2011).

Figure 2.8: Mesocarp fiber after oil extraction.

Studies have been done on OPMF focussing on extraction of residual oil and producing chemical. In the other hand, OPMF shows the potential to be used as reinforcement in biocomposites (Sreekala et al., 1997; Thawien et al., 2009; Then et al., 2013). Table 2.10 shows the summaries of OPMF study.

Table 2.10: Studies done on utilization of OPMF.

Nature of Research	References
Extraction of oil containing vitamin E and carotene	Lik Nang Lau et al., 2008
Extraction of phospoholipids using ultrasonic device	Chua et al., 2009
Production of furfural from hemicellulose using acid hydrolysis and dehydration (freeze dried)	Riansa-ngawong and Prasertsan, 2011
Extraction of high quality oil using hexane	Neoh et al., 2011
Superheated steam treatment for biosugar production	Nik Mahmud et al., 2013

2.5 Biocomposites

Biocomposites are defined as the materials made by combining natural fiber and petroleum derived non-biodegradable polymer or biodegradable polymer. These biocomposites are termed as green composites (John and Thomas, 2008). The most

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important factor to produce biocomposites with good mechanical strength is strong fiber-polymer adhesion and well fiber distribution in matrix.

Mechanical properties are the major concern in biocomposite production consists of tensile, flexural and impact strength. Tensile strength is the maximum stress that a material can withstand without tearing apart, measured in unit of force per unit area. Tensile properties can be determined according to American Society for Testing and Materials (ASTM) D638. Flexural strength is defined as a material's ability to resist deformation under load which represents the maximum stress experienced within the material at the moment of rupture. Flexural is determined according to ASTM D790 which is three-point loading. Impact strength is the ability of a material to resist suddenly applied loads. Two different types of testing method which are charpy test and izod test, conducted according to ASTM D6110 and ASTM D256, respectively.

2.5.1 Natural fiber/polymer biocomposites

Natural fibers such as kenaf, jute, banana, flax, oil palm fiber among the considerable reinforced materials in the biocomposite production. The advantage of natural fiber is a driving force to use them and replaced man-made fibers. There is a large number of literature detailing the mechanical, thermal and crystallinity properties of natural fiber biocomposites. Tensile properties are among the most widely tested properties of natural fiber biocomposites. Table 2.11 shows the mechanical properties of oil palm fiber/polymer biocomposite.

Table 2.11: Studies on varies type of chemically-treated natural fiber with polymer biocomposites.

Matrix	Reinforcement	Characteristic	References
PP	Alkaline treated sisal (10 – 30 wt%)	Increase of 9% in tensile strength and modulus. Significant improvement in tensile modulus for 30 wt% fiber loading	Kaewkuk et al., 2013
PP	NaOH-clay treated sisal fiber (20 wt%)	Increased by 14%, 18% and 14% in tensile, modulus and strain. Improved thermal stability and 2.6 times reduction of water uptake	Mohan and Kanny, 2012
PP	Coir fiber (20 – 30 wt%) with addition of MAPP (4%) and lignin (5 and 10%)	Addition of MAPP increased the tensile strength and when lignin content was increased the tensile decreased.	Morandim-Giannetti et al., 2012
Rice starch	Cellulose-derived OPMF treated with silane (10 – 40 wt%)	Increased with increment of fiber loading up to 30 wt%	Phattaraporn et al. (2011)
Polyester	EFB with 55 wt%	Flexural modulus increased from 3.2 to 3.7 GPa	Hill and Khalil (2000)

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2.5.2 Oil palm fiber/PP biocomposites

PP is a linear structure based on the monomer C_nH_{2n}. PP has higher melting temperature (T_m) and have higher modulus and tensile strength. Polypropylene is one versatile synthetic polymers which used in a variety of industries including agriculture, construction, automotive, packaging and is found in every market sector that uses plastics. In the same time, PP has excellent mechanical properties, low cost and more important is its easy processability. Polypropylene has great potential for composites because it can be processed using conventional technologies, such as extrusion, compression and injection moulding.

Jawaid et al., (2014) demonstrated in his study the production of hybrid biocomposite, with coir/EFB (50:50) consists of 30 wt% of EFB, 30 wt% of coir and 70 wt% of PP exhibits the highest mechanical properties compared to biocomposites prepared with EFB only or coir only.

Rozman et al. (2002) has reported study on the effect of maleic anhydride (MAH) on EFB with PP biocomposite. The mechanical properties of the treated fiber/PP biocomposites were improved with MAH treatment as shown in Table 2.12. MAH treatment has improved the compatibility of fiber-PP interaction by providing interaction of polar group MAH with hydroxyl group of fiber. Meanwhile, the effect of fiber size shows that the mechanical properties of the biocomposites reduce with increased of fiber size as shown in Table 2.13.

Table 2.12: Flexural and impact strength of EFB/PP biocomposite*.

Properties	MAH concentration (%)		
	5	**10**	**15**
Flexural strength (MPa)	105	123	135
Flexural modulus (GPa)	36	40	59
Impact strength (J/m)	13	42	44

* Prepared at 40 wt% fiber loading and size of Mesh 80.
Reference: Rozman et al., 2002.

Table 2.13: Mechanical properties of MAH-treated EFB/PP biocomposite*.

Properties	Mesh 60	Mesh 80	Mesh 100
Flexural strength (MPa)	52	123	82
Flexural modulus (GPa)	65	41	55
Impact strength (J/m)	76	44	27

*Prepared at 40 wt% fiber loading treated with 10% MAH.
Reference: Rozman et al., 2002.

Another study on effect of fiber loading was demonstrated by Khalid et al. (2008), shows that the tensile properties of EFB/PP biocomposite reduced with the increased

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of fiber loading. Untreated EFB at high amount will interrupt the stress transfer along the applied force. Moreover the poor adhesion with PP contributed to low tensile strength. However, it is interesting to note that addition of cellulose-derived EFB increased the tensile strength of biocomposite, where 40 wt% of cellulose-derived EFB exhibits similar strength of neat PP. The flexural modulus increased with increase the filler content, and cellulose-derived biocomposite had higher modulus compared to EFB biocomposite. In overall, cellulose-derived biocomposite demonstrated higher mechanical properties compared to original EFB/PP biocomposite.

2.5.3 Processing of natural fiber/polymer biocomposites

The processing parameters for biocomposites depend largely on the type of polymer being used as a matrix material. Appropriate temperature and pressure is needed to ensure good melt flow and polymer is coated around the fiber (Faruk et al., 2012. Biocomposite are mainly fabricated by different extrusion, compression molding and injection molding.

Challenge for processing of natural fiber biocomposites is to keep processing temperatures below 200 °C as natural fiber started to decompose above this point (Mwaikambo and Ansell, 2002; Quajai and Shanks, 2005; John and Thomas, 2008). In an extruder, a screw or twin screw rotation will mix the fiber and polymer through a heated cylinder. Solid state polymer melted and mix with the fibers as it moves through the mixing chamber. Extrusion method is widely used to fabricate short fiber reinforced biocomposites. Many researchers fabricated biocomposites by the extrusion method. Abdolmohammadi et al., (2012) fabricated polycaprolactone with chitosan, Siyamak et al., (2012) use this method to mix poly butylene adipate-*co*-terephtalate with EFB and Then et al (2014b) used melt blended extruder type to mix polybutylene succinate with OPMF.

Injection molding is a process that involves injecting a blended mixture (fiber and polymer) or plastic material into a closed mold of required shape. The molding compound is fed into injection chamber through a feeder. Then the molding compound is melted due to heat in the chamber. It is forced into the injection mold by the plunger. This method is normally used for high-volume manufacturing and suggested to short fibers biocomposites. Many studies produced biocomposites by injection molding such as molding of abaca, jute and flax with PP done by Bledzki et al., (2007) and Arzondo et al. (2005) fabricated sisal with PP.

Compression molding is one of the oldest techniques and used for mass production. It uses large presses to compress the material which is placed between two steel dies. Compression involves the pressing of deformable materials between the two heated mold. The effect of elevated mold temperature will transform the molded material to a solid product. Shubhra et al., (2010) used compression molding to fabricate silk with PP and Khan et al. (2009) with the same method blended jute with PP.

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In this study, OPMF/PP biocomposites were fabricated by melt blending using extrusion techniques. For short fibers such as OPMF, this techniques offered good mixing process and easily operated.

2.6 Surface modification of fiber

In order to improve and develop natural fiber reinforced polymer biocomposites with better tensile properties, it is necessary to increase fibers hydrophobicity by introducing treatment to the natural fibers. The fiber modification is attempted to improve fibers hydrophobic, interfacial bonding between matrix and fiber, roughness, wettability, and decrease moisture absorption, leading to the enhancement of mechanical properties of the biocomposites. Fiber treatment can be classified to chemical treatment and steam treatment.

2.6.1 Chemical treatments

Poor adhesion of fiber-polymer causes ineffective stress transfer throughout the interface of the biocomposites. Therefore, certain chemical treatments on the surface of natural fibers are needed. The followings are the review of chemical treatments on the fiber and their effects on the biocomposite properties. Table 2.14 shows the summary on effect of chemical treatment on properties of natural fibers.

Table 2.14: Effects of surface treatments on properties of natural fibers.

Chemical treatment	Effect on natural fibers
Alkaline	Reduce the diameter of the fiber due to removal of hemicellulose, wax and pectin
Sodium chlorite treatment	Delignification makes fiber more flexible band remove moisture from the fiber
Silane treatment	Impart a chemical link between fiber and matrix through siloxane bridge
Maleated coupling agents	Reduced hydroxyl groups and provide interaction with fiber and matrix
Acetylation	Remove waxy layer from the surface and improve the hydrophobicity of fiber
Peroxide treatment	Improve hydrophobicity and moisture absorption

2.6.1.1 Alkaline treatment

Alkaline treatment is one of the most popular chemical treatments of natural fibers. The fiber treatment by sodium hydroxide (NaOH) is widely used to modify the fiber surface. This method will disrupted the hydrogen bonding in the network structure of the fibers (Li et al., 2007). Figure 2.9 presents the schematic view of the natural fiber structure, before and after alkaline treatment. Treated fibers have lower lignin and hemicellulose content (Xinwen et al., 2010; Kabir et al., 2012), wax and oil are reduced (Norul Izani et al., 2013) and distension of crystalline cellulose order

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(Rozman et al., 2003). It changes the orientation of highly packed crystalline cellulose order and forming an amorphous region to provide more access to penetrate chemicals.

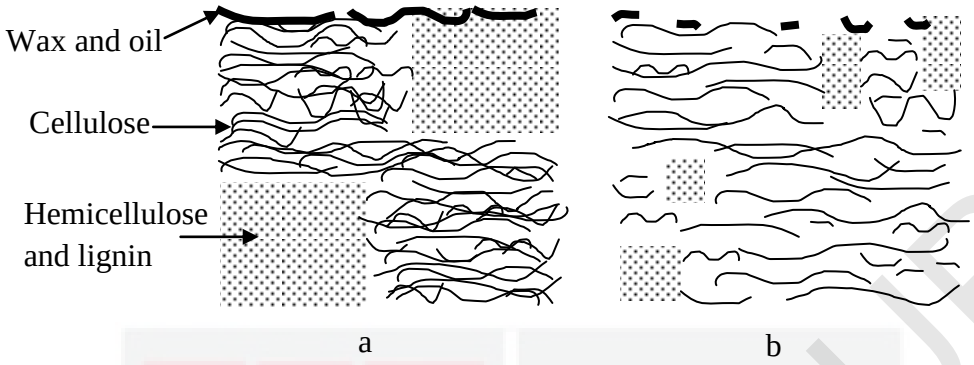

Figure 2.9: Structure of natural fiber (a) untreated and (b) alkaline treated fiber (Kabir et al., 2012).

The amorphous region makes the cellulose micromolecules separated at large distances and the spaces are filled by water molecules. The hydroxyl groups (part of alkaline) present among the molecules are broken down, which then react with water molecules (H-OH) and move out from the fiber structure. The remaining reactive molecules form fiber–cell–O–Na groups between the cellulose molecular chains (Faruk et al., 2012). The chemical reaction of the fiber-structure and NaOH is presented in Scheme 2.1. Due to this, hydrophilic hydroxyl groups are reduced and increase the fibers moisture resistance.

$$\text{Fiber-cell-OH} + \text{NaOH} \longrightarrow \text{Fiber cell-O}^{-}\text{Na}^{+} + \text{H}_2\text{O} + \text{impurities}$$

Scheme 2.1: Chemical reaction of the fiber-cell and NaOH (Kabir et al., 2012).

It also takes out a certain portion of hemicellulose, lignin, pectin, wax and oil (Xiao et al., 2001; Then et al., 2014a). As a result, the fiber surface becomes clean. Microvoids are eliminated and thus the stress transfer ability between the microfiber improves. In addition, alkaline treatment reduces fiber diameter and thereby increase the aspect ratio. This increases effective fiber surface for adhesion with the polymer matrix (Rong et al., 2001; Norul Izani et al., 2013). Mechanical and thermal properties of the biocomposites are improved significantly by this treatment (Then et al., 2015). Table 2.15 summarizes the recent results on the effect of alkaline treatments on the mechanical properties of alkaline-treated fiber.

Jacob et al., (2004) study the effect of NaOH concentration at 0.5, 1, 2, 4 and 10% w/v on sisal fiber. The authors found 4% NaOH resulted the highest tensile strength of the biocomposite. Mishra et al., (2002) demonstrated biocomposite prepared from polyester and sisal fiber treated with 5% w/v NaOH for 1 h at 30 °C had improved

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tensile strength by 20%. Treatment of sisal fiber with 2 wt% NaOH for 2 h found to improve the mechanical properties of PP based bicomposite (Kaewkuk et al., 2013).

Table 2.15: Tensile properties of alkaline-treated natural fibers.

Type of fiber	Tensile strength (MPa)		Young modulus (MPa)		Reference
	Untreated	Alkaline -treated	Untreated	Alkaline -treated	
OPEFB	248	224	2000	5000	Sreekala et al., 1997
OPEFB	52	64	2407	2625	Norul Izani et al., 2013
OPMF	80	64	500	740	Sreekala et al., 1997
Sisal fiber	56	63	33GPa	37GPa	Mohan and Kanny, 2012
Sisal fiber	329.5	372.3	21.3GPa	20.7GPa	Kaewkuk et al., 2013

2.6.1.2 Sodium chlorite treatment

Sodium chlorite ($NaClO_2$) is used for the bleaching of fibres in acid solution. $NaClO_2$ is acidified and liberates chlorous acid ($HClO_2$), which undergoes an oxidation reaction and forms chlorine dioxide (ClO_2). ClO_2 reacts with lignin constituents and lignin is removed from the fiber. It also reacts with the hydrophilic hydroxyl groups of hemicelluloses (Li et al., 2007). These combined effects remove moisture from the fiber and enhance the hydrophobic nature of the fiber. After delignification, fibres become more flexible and have lower stiffness properties.

Mishra et al., (2002) demonstrated bleached sisal-polyester biocomposite improved in flexural and impact strength due to treated sisal was more flexible after delignification.

2.6.1.3. Silane treatment

Silane is a chemical compound with chemical formula SiH_4. The composition of silane forms a chemical link between the fiber surface and the matrix through a siloxane bridge. It undergoes several stages of hydrolysis, condensation and bond formation during the treatment process of the fiber. Silanols form in the presence of moisture and hydrolysable alkoxy groups (hydrolysis). The hydrolysis process is presented in Scheme 2.2. During condensation process, one end of silanol reacts with the cellulose hydroxyl group (Si–O–cellulose) and the other end form Si – matrix bonding. This co-reactivity provides molecular continuity across the interface of the biocomposites. The reaction was shown in Scheme 2.3. As a result, fiber matrix adhesion improves and stabilizes the biocomposites properties. Sever et al., (2010) applied silane treatment on jute fiber and produced fabric biocomposite with polyester. Authors found 0.3 wt% silane treated biocomposite had 40 and 30% improvement in tensile and flexural strength, respectively. Silane treated fibers

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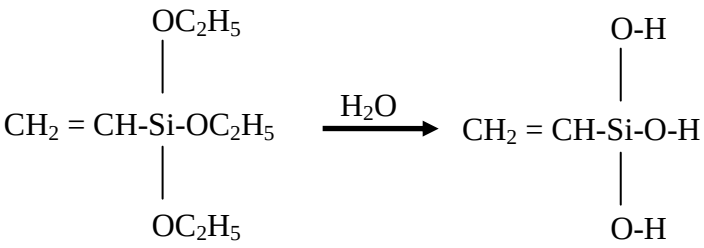
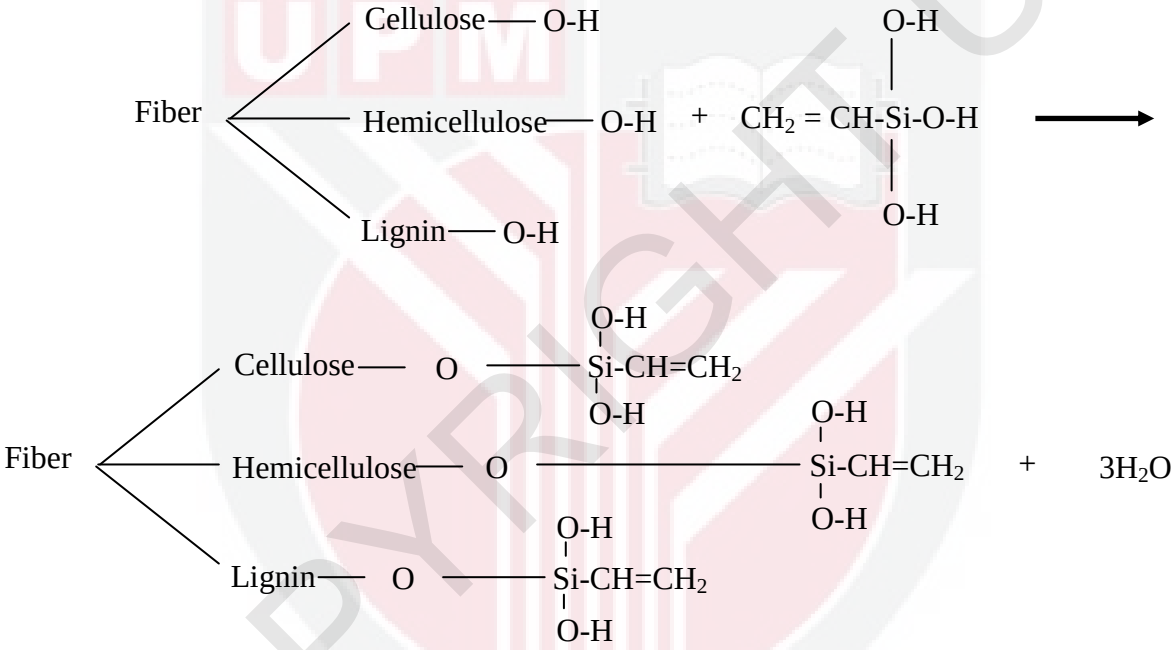
exhibit micro-pores on their surface, penetrate into the pores and develops mechanically interlocking on the fiber surface.



Scheme 2.2: Hydrolyzable alkoxy group to form silanol (Li et al., 2007).



Scheme 2.3: Reaction of silanol with natural fiber hydroxyl group (Li et al., 2007).

2.6.1.4 Maleated coupling agents

In chemical coupling method the fiber surface is treated with a compound that forms a bridge of chemical bonds between fiber and matrix. The chemical composition of coupling agents allows them to react with the fiber surface forming a bridge of chemical bonds between the fiber and matrix. Most researchers found these treatments were effective and showed better interfacial bonding (Bengtsson et al., 2007). Among different coupling agents, maleic anhydride (MAH) is the most commonly used. In general, the literature reports improvements in tensile strength and elongation at break when MAH grafted matrices are used as compatibilizers (coupling agent) (Kaewkuk et al., 2013). During grafting, MAH reacts with hydroxyl groups in the amorphous region of cellulose structure and removes the hydroxyl

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groups from the fiber cells. Long chain polymer coatings are produced on the fiber surface and reduce the hydrophilic character. Maleated coupler forms carbon-carbon bond to the polymer chain with the matrix. The covalent bonding between the hydroxyl groups of the fiber and the anhydride groups of the MAH provide balanced properties to make bridge interface for strong interlocking (Rozman et al., 2003).

MAH also can be reacted with PP matrix producing maleic anhydride grafted polypropylene (MAPP) to achieve better interfacial bonding with fibers. The reaction mechanism of MAPP and the fiber are presented in Scheme 2.4. MAPP copolymer is activated at temperature of 170 °C, followed by the esterification of fibers. This results in better wettability and good interfacial adhesion with fiber.

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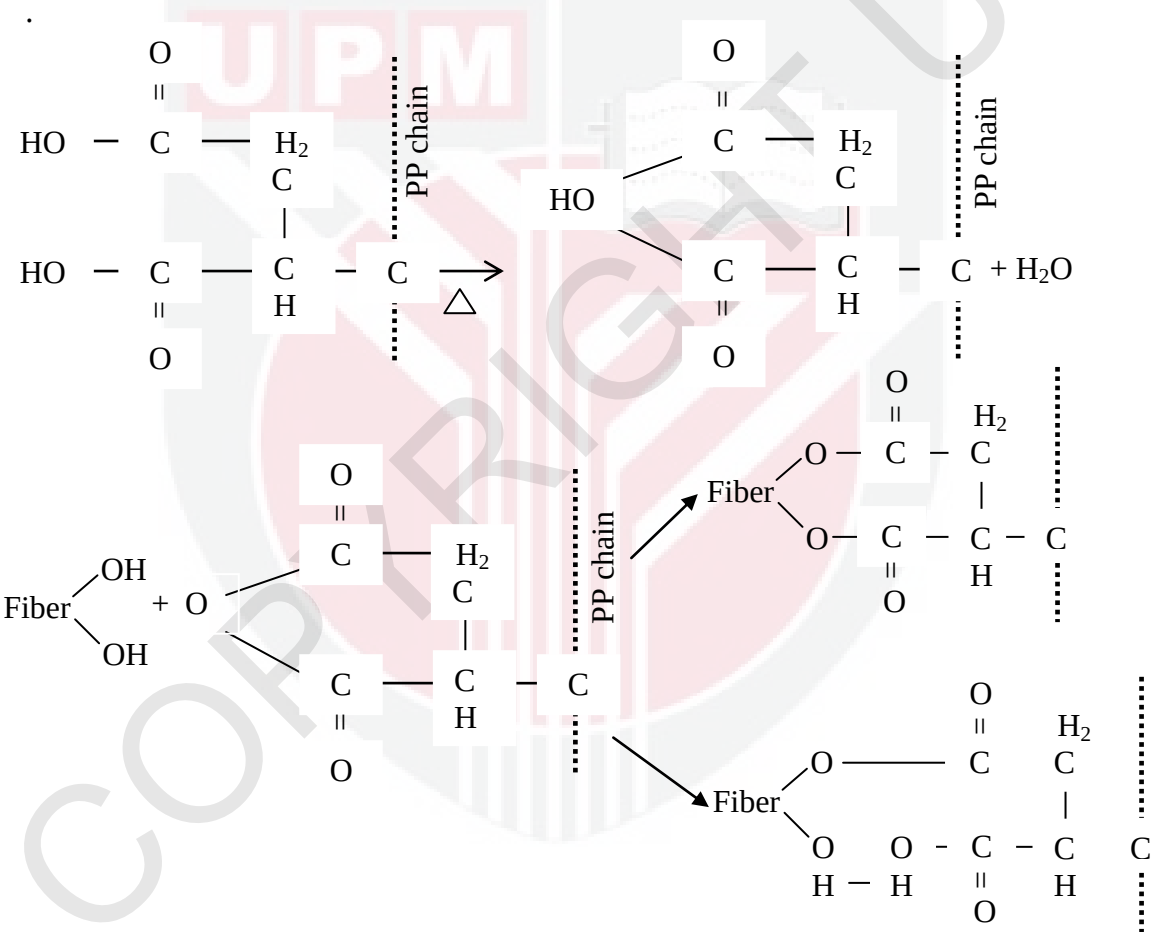

Scheme 2.4: The reaction of natural fiber with hot MAPP copolymers (Kabir et al., 2012).

Mohanty et al. (2004) used MAPP as coupling agent for the surface modification of jute fibers. The study used 30 wt% fiber treated with 0.5% MAPP concentration in toluene for 5 min and reinforced in PP matrix. The biocomposite produced had improved around 72% higher flexural properties compared to untreated biocomposite. Polypropylene biocomposite prepared from flax, hemp or sisal with

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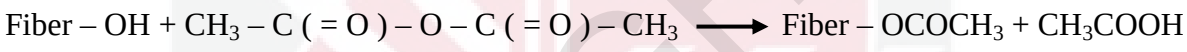
addition of MAPP in a range of 10 to 13.3 wt% had higher strength and impact (El-Sabbagh, 2014). In study conducted by Etaati et al., (2014) shows the addition of 5 wt% MAPP in hemp/PP biocomposite with 40 wt% of fiber loading gave significant improvement of tensile strength

2.6.1.5 Acetylation treatment

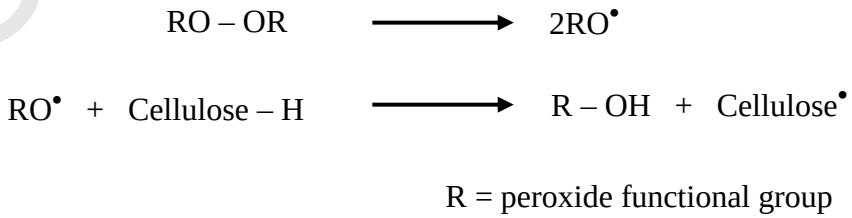
Another surface treatment for natural fibers is known as acetylation. This reaction resulted from the introduction of acetyl functional group into an organic compound. Studies shown acetylation improve interfacial bonding, tensile and flexural strength of the treated fiber biocomposite (Khalil et al., 2001; Tserki et al., 2005). Chemical modification with acetic anhydride substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, making the polymers hydrophobic (Bledzki et al., 2008). As a result, acetylation is commonly used to reduce the hygroscopic nature of natural fibers thereby improving the dimensional stability and fiber matrix interface of biocomposites. The reaction of acetylation is shown in Scheme 2.5. Bledzki et al., (2008) studied acetylation treatment at different concentration on flax fiber demonstrated improved thermal properties by 50% due to hemicellulose reduction.



Scheme 2.5: Acetylation reaction on natural fibers (Kabir et al., 2012).

2.6.1.6 Peroxide treatment

In organic chemistry, peroxide is a specific functional group or a molecule with the functional group ROOR containing the divalent ion O–O. Organic peroxides tend to decompose easily to free radicals of the form RO radical. $RO^{\bullet}$ then reacts with the hydrogen group of the matrix and cellulose fibers (Kabir et al., 2012; Li et al., 2015). The reaction is shown in Scheme 2.6. Peroxide treatment involves alkaline pre-treatment on the fiber then coated with benzoyl peroxide or dicumyl peroxide (6% concentration) in acetone solution for 30 min. Complete decomposition of peroxide can be achieved by heating at high temperature.



Scheme 2.6: The reaction between the cellulosic –OH group of the fiber and decomposition of the peroxides (Li et al., 2007).

2.6.2 Physical treatments

Physical treatments change structural and surface properties of the fiber and thereby influence the physical bonding with polymers. Physical treatments include corona, plasma and steam treatment.

2.6.2.1 Corona treatment

Corona treatment uses plasma generated by applying a high voltage to sharp electrode tips separated by quartz at low temperature and at atmospheric pressure. Gassan and Gutowski (2000) have used corona plasma and UV to treat jute fibers. Treated fiber found to increase the hydrophobicity of the fiber and increased up to 30% of flexural strength. However fiber tensile strength was reduced.

2.6.2.2 Plasma treatment

Plasma treatment is performed using a vacuum chamber with gas continuously supplied to maintain the pressure and gas composition. Study done by Sinha and Panigrahi (2009) showed the plasma treatment increased the hydrophobic of fiber and increased surface roughness. Flexural strength of biocomposite produced increased up to 30% due to better interfacial adhesion.

2.6.2.3 Steam treatment

Steam treatment is one of physical treatment which use water for heat transfer and modify the material surface (Eslam et al., 2011). Material surface exposed to steam undergo physical, chemical and mechanical changes which affected the wetting behaviour and penetration of chemical (Han et al., 2009). Studied had shown steam treatment able to improve the characteristic of natural fibers (Rowell et al., 2002; Han et al., 2009 and Acharjee et al., 2011). Some chemicals changes were reported during steam treatments which include:

i) Degradation of the hemicellulose to produce simple sugars which undergo reversion reactions to form highly branched polysaccharides.
ii) Thermal softening of the cell wall matrix, mainly lignin.
iii) Crosslinking between carbohydrate polymers and/or between lignin and carbohydrate polymers
iv) Degradation of hemicellulose to form volatile breakdown byproducts
v) Increase in cellulose crystallinity.

Several effective steam treatments have been developed such as saturated steam, steam explosion, liquid hot water and superheated steam. It was reported steam treatment resulted in degradation of hemicellulose thus decrease hygroscopicity and reduce moisture content (Rowell et al., 2002; Ramos et al., 2003). This was due to hemicellulose are much less stable to heat and undergo thermal degradation more rapidly than cellulose. Figure 2.10 shows that steam explosion treatment releases

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hemicellulose from the cell walls and makes them accessible to chemical and biochemical degradation. Rowell et al., (2002) reported that acids were formed as by-products reaction from the non-hydrolytic degradation of hemicellulose. Aoyama (1996) reported that a large percentage of the hemicellulose from bamboo was solubilized at temperatures between 170 and 206 °C. It was also found that wood treated in a pressurized steam treatment had better dimensional stability (Hosseinaei et al., 2011).

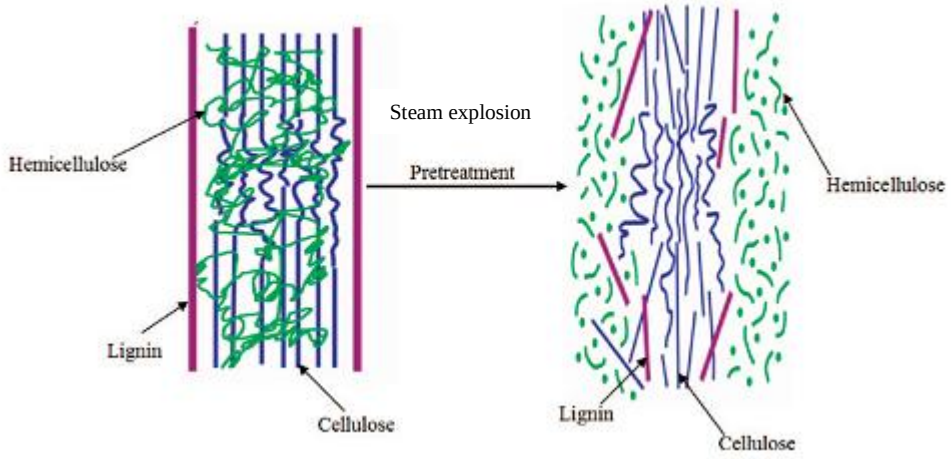
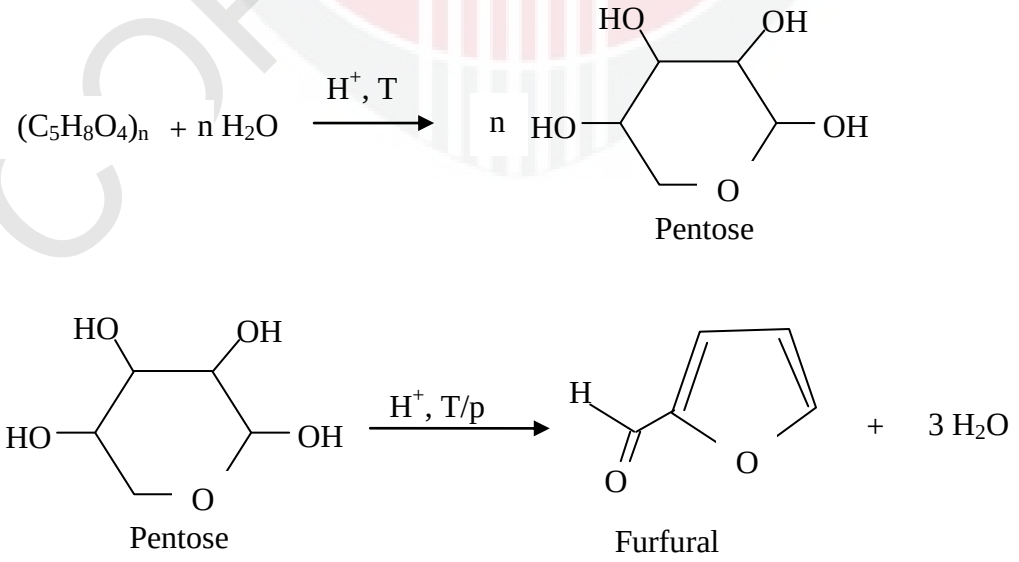


Figure 2.10: Effect of steam explosion on the fiber cell wall (Ramos et al., 2003).

Several researchers have shown that the yield of free sugars formed from hemicellulose during steaming of lignocellulosic increase in concentration and then decrease with increasing time of steaming. This indicate that free sugars released from the degradation of the hemicellulose undergo further reactions to form other products (Linde et al., 2008; Han et al., 2009; Hosseinaei et al., 2012) i.e. furfural as shown in Scheme 2.7.



Scheme 2.7: Hydrolysis of hemicellulose into xylose and further degradation into furfural (Ramos et al., 2003).

At temperature exceeded 160 °C, there was flow of lignin to block pores within the fibers structure to restrict the re-entry of moisture (Rowel et al., 2008). Inoue at al., (1991) had shown that heating natural fiber under pressure resulted in an increase in cellulose crystallinity. Therefore based on the discussion above, it is shown that there are many physical and chemical reactions taking place during steam reaction. High pressure steam and steam explosion involves heating fibers material at high pressures and temperature. It modifies the plant cell structure, yielding a dark brown material from which partially hydrolysed hemicellulose are easily recovered by water-washing, leaving a cellulose, residual hemicellulose and a modified lignin (Ramos, 2003). Zhang et al., (2008) found that a large amount of hemicellulose was destroyed with the increased pressure of steam explosion. With more hemicellulose reduction, the bond linking between lignin and hemicellulose would be affected and up to certain extent, the structure of lignin will be disrupted.

Deepa et al., (2011) explained that, natural fiber treatment with high pressure steam for short periods of time, followed by sudden decompression results in a hydrolysis of glycosidic bonds in the hemicellulose and also leads to a cleavage of hemicellulose-lignin bonds. Hydrothermolysis is a treatment method in which the raw material is cooked in liquid water at high temperatures and pressure but no steam is generated in the process. Detailed on SHS treatment is explained in next section.

2.7 Superheated steam treatment

Superheated steam (SHS) process has been a subject of research for many decades. SHS has been used as a heating medium for drying of chemical, timber and especially in food processing (Sotome and Isobe., 2011; Anto et al., 2014). The next sections provide discussion on properties, mechanism and application of SHS treatment.

2.7.1. Properties of superheated steam

SHS is ‘dry steam’ at a temperature above the saturated steam at atmospheric pressure. It is produced by the addition of heat to saturated steam which has been removed from contact with the water from which it was generated (Bahrin et al., 2012). Saturated steam cannot be superheated when it is in contact with water which is also heated and condensation of SHS cannot occurred without being reduced to the temperature of saturated steam. It has a high heat transfer coefficient, enable rapid and uniform heating (Sotome and Isobe, 2011). Drying rates with SHS are faster than that with conventional hot air. Steam in dried state or SHS it is assumed to behave like a perfect gas.

Although SHS is considered as a perfect gas, it possesses properties like those of gases namely pressure, volume, temperature, internal energy, enthalpy and entropy. The pressure, volume and temperature of steam as a vapour is not connected by any simple relationship such as is expressed by the characteristic equation for a perfect

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gas. Figure 2.11 illustrates the relationship between the enthalpy and temperature of the various states of water and steam known as a phase diagram.

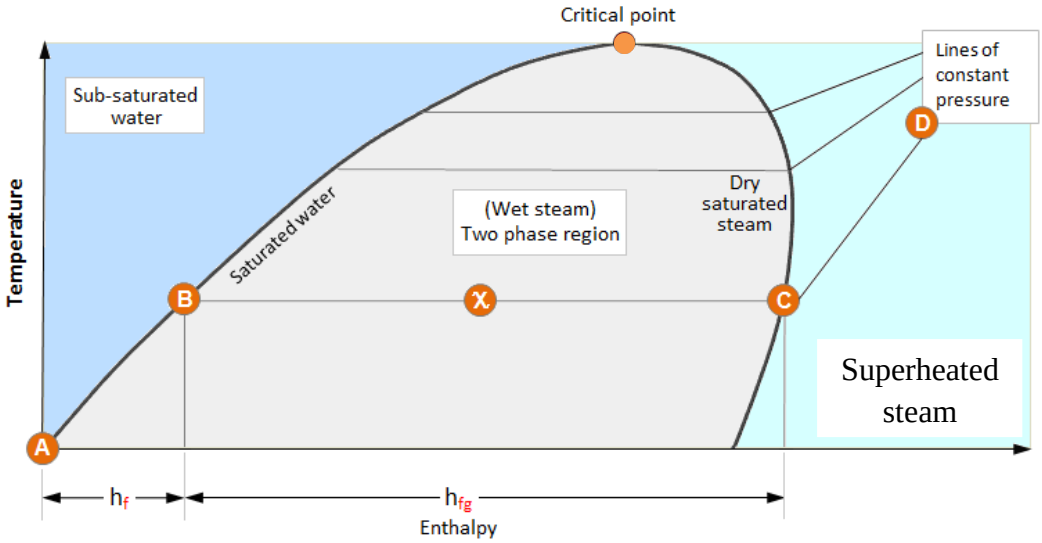

Figure 2.11: Graphical represent the formation of superheated steam.

As water is heated from 0 °C to its saturation temperature, its condition follows the saturated water line until it has received all of its liquid enthalpy, h_f (point A to B). Further heating, will changes the water phase to a water/vapour mixture and the enthalpy continues to increase at constant saturation temperature, h_{fg}; enthalpy of evaporation (point B to C). As the water/vapour mixture increases in dryness, its condition moves from the saturated liquid line to the saturated vapour line. Once it has received all of its enthalpy of evaporation (h_{fg}) , it reaches the saturated steam line. Continue to heat after this point at constant pressure will raise the steam temperature and producing superheated condition (point C to D).

The saturated water and saturated team lines enclose a region in which a water/vapour mixture exists known as wet steam. In the region to the left of the saturated water line is only water and in the region to the right of the saturated steam line is only superheated steam exists. The point at which the saturated water and saturated steam lines meet is known as the critical point.

Interesting to note, the drop in SHS temperature during processing will not results in its condensation, as long as the temperature is higher than the saturation temperature at the processing pressure. Moreover the moisture that is evaporated during treatment process need not be exhausted, as it becomes part of the drying medium (Anto et al., 2014). SHS have higher heat transfer and faster drying. It is operated at atmospheric pressure thus presents no fire hazard.

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2.7.2 Application of superheated steam

SHS is widely used in food processing due to efficient heat transfer and prevention of the nutrient oxidation in food. Studies on the application of SHS for various food processing were presented in Table 2.16.

The major advantages of using SHS for food processing are better product and reduced oxidation losses due to absence of oxygen. SHS having higher enthalpy can quickly transfer heat to the material being processed, resulting in its rapid heating.

Table 2.16: SHS drying of meat, fish products, fruits and vegetables.

Product	Drying conditions	Remarks	References
Fish cake	146 – 185 °C	High moisture and lesser loss of omega-3 fatty acids	Borquez et al., 2008
Banana slice	Low pressure SHS with radiation	Products had porous structure and higher ascorbic acid retention	Nimmol et al., 2007
Potato	SHS for drying	Samples were glossier and no remaining starch granules on the surface.	Iyota et al., 2001
Potato	SHS at 115 – 145 °C	Higher retention of ascorbic acid than air dried method.	Caixeta et al., 2002
Noodles	SHS at 110 – 150 °C	At 150 °C, noodles were partially cooked, eliminates additional cooking in oil.	Markowski et al., 2003
Tortilla chips	SHS at 115 – 145 °C	At 145 °C, samples were less shrinkage and high crispiness.	Pronyk et al., 2005

The use of SHS is advantageous to the industry as listed:

i) Promote to energy saving for about 50 to 80% compared to hot air treatment. SHS has higher heat transfer coefficients and resulted to higher drying rates. The higher drying rates will increase the efficiency of the processing leads to reduction in equipment size or increase output. Exhaust steam can be collected for recycled steam and used elsewhere in the processing.
ii) Operated at oxygen free environment compared to hot air drying. It means that there is no oxidative or combustion reactions during drying. It reduces the risk of safety such as fire and explosion.
iii) SHS treatment is designed as a closed system where the outlet (exhaust) may be collected and condensed. In this way toxic or expensive compounds are removed and collected before they reach the environment thus reducing air pollution.

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Recently, fiber treatment for surface modification involving SHS are gaining interest, as this treatment is more environmental friendly and simple in operation (Bahrin et al., 2012). Table 2.17 shows some studies on surface modification of natural fibers using SHS treatment..

Table 2.17: SHS treatment for surface modification.

Type of fiber	Nature of research	Research aim	References
OPMF	SHS treatment at 190 to 210 °C for 1 h. Reduced the hemicellulose content and increased the crystallinity of treated fiber	To improve hydrolysis of the material	Zakaria et al., 2015
OPMF	SHS treatment at 140 to 210 °C (20 – 90 min). Removal of hemicellulose and silica increased with temperature.	To improve hydrolysis of the material	Nik Mahmud et al., 2013
EFB	SHS treatment at 140 to 210 °C (20 – 90 min). Treated fiber had lower hemicellulose and silica content.	To improve hydrolysis of the material	Bahrin et al., 2012
EFB	SHS treatment at 125 to 200 °C. Treatment at 200 °C able to reduce silica.	To dry the fiber	Hasibuan and Daud, 2009

SHS pretreatment is a cost-effective method for large-scale purpose and it is one of the eco-friendly approaches due to the utilization of excess steam produced at the palm oil mill. Environmental pollution or odour emission to the atmosphere can be eliminated since drying occurs in closed chamber without air (Hamawand, 2013). SHS has been applied for drying of EFB (Hasibuan and Daud, 2009) and to enhance hydrolysis process for biosugar production (Bahrin et al., 2012; Zakaria et al., 2015). Considering the potential of SHS treatment in surface modification, thus this study was conducted moreover there were lack of studies done on characteristics of SHS-OPMF and SHS-OPMF/PP bicomposite properties

From the literature reviewed, SHS shows the potential to be used as treatment for fiber surface modification. Fiber compositions are altered after SHS treatment where the percentage of hemicellulose is reduced. By removing the unstable components, the characteristics of natural fibers could be improved which is beneficial for biocomposite production. In addition SHS consume less energy than steam explosion and reduce the fire and explosion hazard.

2.8 Recent developments in biocomposite for sustainable environment

Sustainable development means that 'The development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. Using agricultural waste such as oil palm biomass (Norul Izani et al., 2013), coir fiber, banana fiber (Sumaila et al., 2013), sisal (Mohan and Kanny, 2013) and

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other fibers as raw materials for making biocomposite products provides a renewable resources as well as generating a non-food source of economic development from agricultural and rural areas (Shinoj et al., 2011). Faruk et al. (2014) reported that primary driving force for developments of biocomposite are the cost of natural fiber is one third cheaper than glass fiber. Issues related to greenhouse gas emissions have prompted automotive manufactures to focus on the development of lightweight vehicles. Lightweight one is major components for fuel consumption is foreseen to drop as much 16 to 24% (Pervaiz et al., 2016). Since lighter objects needs less energy to get accelerated, lightweight materials provide a better opportunity to enhance vehicle's fuel economy and mitigate greenhouse gas emissions. Demand for these materials is projected to rise to 8020 million pounds in year 2018 which is 53% higher than year 2008 (Holmes, 2014). Pickering et al. (2015) reported that natural fibers may able to reduce the usage of glass fiber in fabrication of wind turbine blade and surfboard fins. In construction application, Pandey et al. (2015) reported that it was projected to rise 55% higher *i.e.* from US2530 million in year 2013 to US3924 million in year 2018. Thus, studies are conducted to improve the properties of natural fibers and to develop high performance fibers that can be used in high technology applications. With further development in improvement of treatments methods and processing techniques, new opportunities and applications may arise. Further requirement and opportunities to advance the use of biocomposite are listed below.

i) Methods of fiber preparation that able to produce consistency raw materials and do not damage the fiber (storage, degradation, moisture).
ii) Reduction in use of organic solvents for treatment of fiber surface modification
iii) Improvement in the mechanical performance, through the introduction of new hybrid biocomposite may result in an expansion in their use into more diverse and technically demand application areas.
iv) Biocomposites have excellent potential in production of products where the service lives are short and durability is not a significant factor such as casing for computer, monitor, mobile phone covers and many others which the same functionality.
v) Innovations in biocomposite recycling methods and processes will increased the amount of re-use polymer and fibers. Although the majority of biocomposite may not find their application in mechanical structures, however, implementation of these materials in packaging and similar products could lead to positive changes in today's environment.

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CHAPTER 3

MATERIALS AND METHODS

3.1 Overall research methodology

Figure 3.1 illustrates the overall experimental overview for this research. Fresh OPMF used in this study were collected from FELDA Serting Hilir Palm Oil Mill, Negeri Sembilan, Malaysia. The OPMF were cleaned and sun-dried, followed by treatments using SHS and chemicals such as NaOH, KOH or $NaClO_2$. The fibers were then ground using a Wiley mill (Model CW-1, Taiwan) with frequency of 50 Hz, 5 rotating blades and 0.5 mm screen size. Ground OPMF was sieved using a sieve shaker Minor 200 (Endecotts, UK) to pass through various mesh sizes of 355, 250 and 150 μm for 20 min. Prior to blending, untreated and treated OPMF were kept in an oven at 60 °C for 24 h. OPMF/PP biocomposite was prepared by melt blending in a twin screw internal mixer model Thermo Haake Rheomix Polydrive at 170 °C and 50 rpm rotor for 10 min. To form biocomposite sheet, the OPMF/PP blend was molded with electrically heated platen press. The sheets were used for mechanical, thermal, morphological and water absorption analyses.

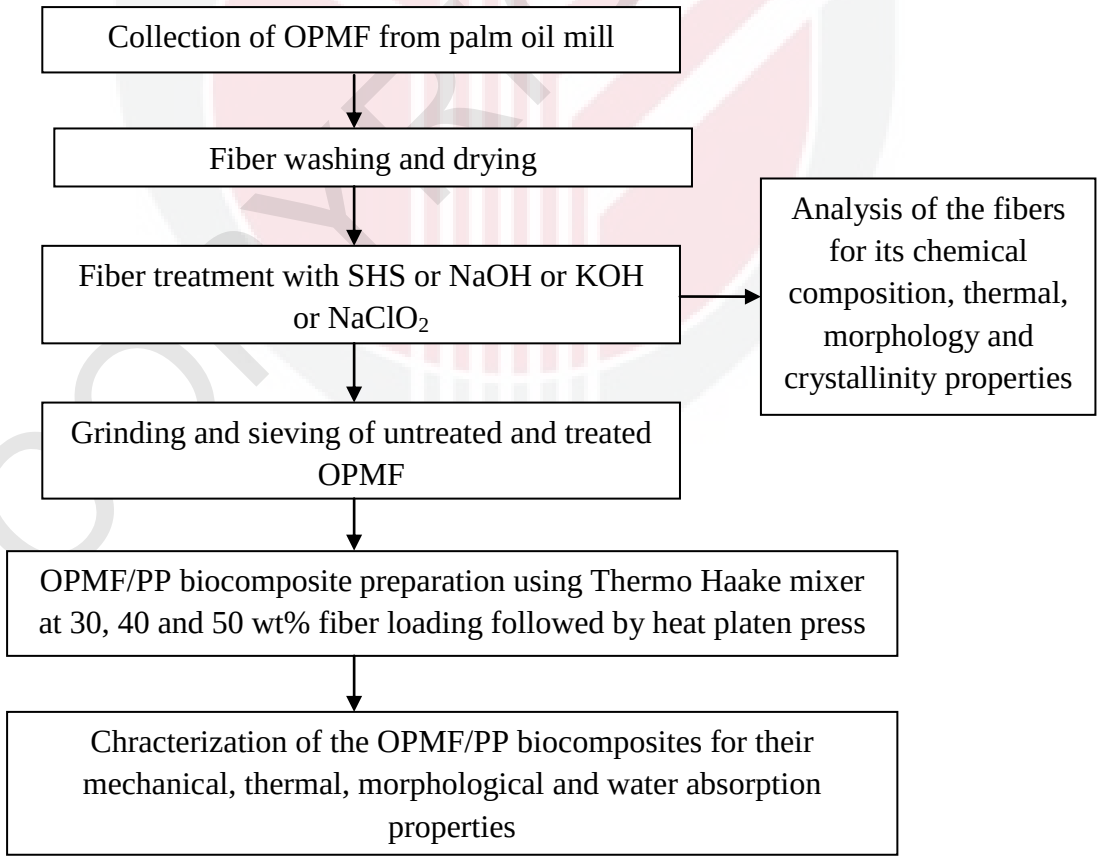

Figure 3.1: Overall experimental overview for the preparation of OPMF/PP biocomposite.

3.2 Materials

3.2.1 Biomass collection and preparation

In this study, OPMF with size ranging from 30 – 40 mm was collected from FELDA Serting Hilir Palm Oil Mill, Negeri Sembilan, Malaysia. Crude OPMF consisted of mesocarp fiber, palm kernel and crushed shell. Crude samples were washed with tap water to remove dirt and to separate kernel and crushed shell. Clean fibers were sun-dried until completely dried to prevent fungus contamination. Samples were then stored in sealed plastic bag at room temperature (±24 °C) until further use.

3.2.2 Chemicals

Sulfuric acid (H_2SO_4) (liquid, 90% purity), potassium hydroxide (KOH) and sodium hydroxide (NaOH) in pellet form were supplied by Merck, Darmstadt, Germany. Sodium chlorite ($NaClO_2$) in powder form was supplied by Acros Organics, Geel, Belgium. The selected matrix was polypropylene (PP) pellets supplied by Polypropylene (Malaysia) with a code of 606251 G 112. The Melt Flow Index (MFI) at 230 °C was 18 g/10 min and density: 0.91 g/cm^3. All chemicals are used without further purification.

3.3 Superheated steam treatment

3.3.1 Superheated steam oven specifications

SHS treatment of OPMF was done for surface modification. SHS oven (QF-5200C, Naomoto Corporation, Osaka, Japan) consists of two parts, which are a stainless steel heating chamber and a built in boiler. The boiler was operated at power of 3.3 kW with steam production of 4.95 kg/h. An electric heater, rated at 1.2 kW, was installed in the heating chamber to maintain the superheated condition. Figure 3.2 illustrates the schematic diagram of the SHS treatment. Saturated steam was produced from the boiler and injected into heating chamber where the upper and lower heating elements will further heat the saturated steam in order to achieve superheated condition.

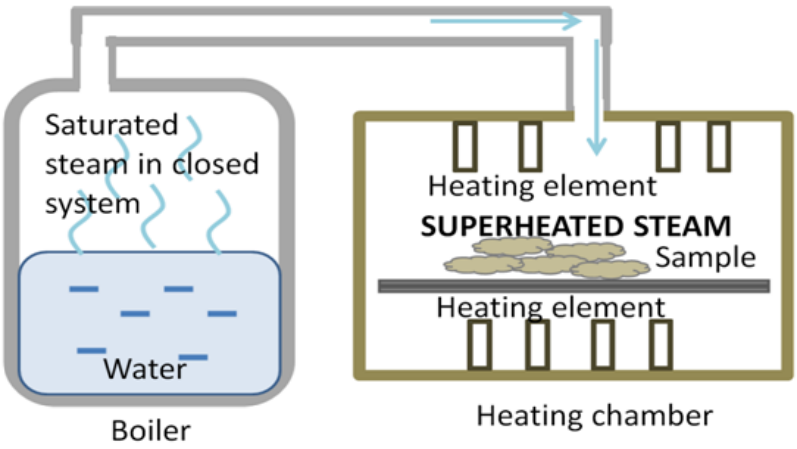

Figure 3.2: Schematic diagram of the SHS treatment.

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3.3.2 Treatment of oil palm mesocarp fiber by superheated steam

SHS oven temperature was set at designated temperature range. When stable temperature was reached, five gram of OPMF on stainless steel mesh was placed in the oven and treated for specific reaction time. For preliminary experiment, SHS temperature and reaction time was set at 160 – 220 °C and 100 min, respectively. These treatment conditions were set based on Bahrin et al. (2012).

Based on findings from the preliminary experiment, the OPMF was subsequently treated at 190, 210 and 230 °C. In order to further clarify the effect of reaction time on SHS-treated OPMF characteristics, SHS treatment was conducted for 1, 2 and 3 h. The summary of the SHS treatment conditions used in this study is summarized in Table 3.1.

Table 3.1: Treatment of OPMF sample using SHS.

No	Treatment condition	Sample
1	Untreated OPMF (control)	Untreated OPMF
2	190 °C for 1 h	SHS190-1h
3	190 °C for 2 h	SHS190-2h
4	190 °C for 3 h	SHS190-3h
5	210 °C for 1 h	SHS210-1h
6	210 °C for 2 h	SHS210-2h
7	210 °C for 3 h	SHS210-3h
8	230 °C for 1 h	SHS230-1h
9	230 °C for 2 h	SHS230-2h
10	230 °C for 3 h	SHS230-3h

3.4 Characterization of OPMF

Untreated and SHS-treated OPMF were analyzed for their chemical composition, thermal stability, silica content, morphology and crystallinity.

3.4.1 Chemical composition

Cellulose, hemicellulose and lignin content of OPMF were analyzed gravimetrically by a method described by Iwamoto et al. (2008) with some modification. About 1.5 g of OPMF sample was heated using SHIMADZU moisture balance (MOC-120H) to determine moisture content in the sample. Prepared sample was immersed in 5 wt% $NaClO_2$ solution (pH adjusted to 4 ~ 5 by adding a few drop of H_2SO_4) at 70 °C for 1½ h in order to remove lignin. Then, the solution was filtered out and washed with deionized water. Sample was left over night in a vacuum oven. After drying, sample was weighed. This was followed by hemicellulose removal by using 6 wt% KOH solution. The immersed sample was stirred for 24 h at room temperature. KOH solutions were filtered and flushed through with deionized water, leaving only

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cellulose fiber. Vacuum oven was used to ensure the final sample was dried. Finally, sample weight and moisture content were recorded. Equations 3.1 – 3.3 were used to calculate the percentage of chemical composition in the samples.

$$Lignin\ \% = \left(\frac{\left(Initial\ weight(dry,\ g) - Weight\ aft\ erextraction_{NaClO2}(dry,g)\right)}{Initial\ weight,(dry,g)}\right) \times 100 \quad (3.1)$$

$$Hemicellulose\ \% = \left(\frac{\left(Weight\ after\ extraction_{NaClO2}(dry,g) - Weight\ after\ extraction_{KOH}(dry,g)\right)}{Initial\ weight,(dry,g)}\right) \times 100\% \quad (3.2)$$

$$Cellulose\ \% = \frac{Residue\ of\ KOH\ extraction\ (dry,g)}{Initial\ weight\ (dry,g)} \times 100 \quad (3.3)$$

Ash was determined according to Varley (1966) with some modification. Firstly, the crucible and OPMF was dried at 105 °C overnight and weighed it. Then the sample was heated in the furnace at temperature 550 °C for 4 h. The crucibles were cooled in a desiccator and weighed. Equation 3.4 was used to calculate the percentage of ash in the sample.

$$Ash\ content\ \% = \frac{Weight\ of\ crucible\ with\ sample\ (dry,g) - Weight\ of\ crucible\ with\ ash\ (g)}{Initial\ weight\ (dry,g)} \times 100 \quad (3.4)$$

3.4.2 Thermal stability

Thermogravimetric Analysis (TGA) was carried out on TG analyzer (EXSTAR6000 TG/DTA6200, SII NanoTechnology Inc, Japan) to evaluate the thermal stability of the OPMF. About 6-8 mg of samples was heated from 50 – 550 °C using a nitrogen air flow of 50 ml/min and heating rate of 10 °C/min. From the analysis, degradation of cellulose, hemicellulose and lignin can be observed (Yang et al., 2007; Brebu and Vasile, 2009; Bahrin et al., 2012).

3.4.3 Functional group determination

Changes in chemical composition due to the SHS treatment were evaluated by Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectroscopy analysis of the OPMF was done on a FTIR (Model Perkin Elmer Spectrum GX FT-IR, USA) in order to determine functional groups in OPMF. Samples were scanned in a range of 280 – 4000 cm^{-1}. Attenuated total reflectance infrared spectroscopy (ATR FTIR) method was used. The spectra were the average of 16 scans at spectral resolutions of 4 cm^{-1}.

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3.4.4 Silica content

Silica content in OPMF was determined using Inductively Coupled Plasma (ICP) analysis (Perkin Elmer, 7300 DV, USA). OPMF ash samples were used for this purpose. About 0.1 g of ash sample was digested by 20% v/v nitric acid for 30 min on a boiling water bath, according to the standard methods as described in MS 677: Pt. I–VIII: Part II. The digestion solution was then filtered out. Distilled water was added to make the volume of the filtrate to 100 ml before the samples was injected into ICP.

3.4.5 Crystallinity

Crystallinity of untreated and treated OPMF was measured using Wide-angle X-ray diffraction (WAXD) (Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation source (λ = 0.154 nm) at 40 kV and 30 mA. Samples were scanned at 2θ from 5 to 50° at room temperature. The crystallinity index (CrI) was calculated from XRD data and determined based on the formula by Segal *et al*. (1959) as shown in Equation 3.5:

$$\mathrm{CrI} = \frac{\mathrm{I}_{002} - \mathrm{I}_{\mathrm{am}}}{\mathrm{I}_{002}} \times 100\% \qquad (3.5)$$

which I_{002} is the intensity for the crystalline portion of sample, *i.e.*, cellulose at about 2θ = 22 and I_{am} is the peak for the amorphous portion, *i.e.*, cellulose, hemicellulose and lignin, at about 2θ = 17.

3.4.6 Morphological analysis

Surface morphology of untreated and SHS-treated OPMF samples was observed under Scanning Electron Microscopy (SEM) with a model LEO 1455 VPSEM (LEO Electron Microscopy Ltd., Cambridge, England) with an Oxford Inca EDX (Oxford Instruments, Oxfordshire, United Kingdom). For SEM/EDX microanalysis, oven-dried OPMF samples were mounted on the stub and gold-coated for 180 sec prior to SEM/EDX observation to improve its interface conductivity. The SEM/EDX micrographs were obtained with an acceleration voltage of 20 kV.

3.5 Preparation of OPMF/PP biocomposite

Biocomposites were prepared from OPMF with PP at selected size of fiber and fiber loading. From the analysis of the biocomposite, the effectiveness of the treatment can be evaluated.

3.5.1 Grinding and sieving

OPMF samples were ground using a Wiley mill (Model CW-1, Taiwan). The mill was operated at frequency of 50 Hz with 5 rotating blades and screen size of 0.5 mm.

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Then, the ground OPMF was sieved using a vibrating screener (Sieve shaker Minor 200; Endecotts, UK) to pass through various mesh sizes of 355, 250 and 150 μm for 20 min. Prior to blending, untreated and SHS-treated OPMF were kept in an oven at 60 °C for 24 h.

3.5.2 Melt blending

Biocomposite was prepared by melt blending in a twin screw internal mixer model Thermo Haake Rheomix Polydrive at 170 °C and 50 rpm rotor speed as described by Ibrahim et al. (2011). PP pellet was first introduced into mixing chamber to melt for 2 min. Subsequently, OPMF samples were added to the mixing chamber and continued mixing for another 10 min (Abdolmohammadi et al., 2012; Then et al., 2014b). The total sample weight of the PP and fiber inside the mixing chamber was 40 g.

3.5.3 Hot compression molding

Biocomposite sheet (10 × 10 cm) was prepared by heat compressing 10 g of OPMF/PP blend (untreated and SHS-treated biocomposites) in a hot compression molding machine (Type : Electrically heated platen press, Hsin-Chi Machinery Co. Ltd., Taiwan). Biocomposite samples were preheated in the mold at 160 °C for 10 min to allow complete melting at atmospheric pressure. A pressure of 110 kg/cm^2 was then applied to the mold and held for 5 min under constant temperature to form 1 mm biocomposites sheets. The molded sheets were then transferred to a cold press and pressed for another 5 min. This form of hot-pressed sample was used for tensile test. While for flexural and impact test, about 80 g of compounded sample was used to form 3 mm thickness hot-pressed molded biocomposite. The sheets were used for mechanical, thermal, morphological and water absorption analyses.

3.6 Characterization of biocomposite

In order to evaluate the performance of biocomposite produced, analyses were done consisted of mechanical testing, thermal, crystallinity, morphological and water absorption analysis.

3.6.1 Mechanical testing

Mechanical properties of the produced biocomposites, namely tensile, flexural strengths were tested using an Instron Universal Tester (model 4302). Impact strength was tested using IZOD Impact Tester equipped with 7.5 J pendulum. Tensile tests were measured according to the ASTM Standard Method D638 on dumbbell shape specimens with 1 mm thickness at 5 mm/min crosshead speed and 1 kN of load cell. Flexural test was performed according to ASTM D790 on rectangular standard samples with dimension of 120 mm x 12.7 mm and 3 mm thickness. The support span length used was 48 mm and 1.3 mm/min crosshead

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speed. Flexural test was determined by a three-point bending test. Izod unnotched impact test was conducted according to ASTM Standard Method D256.
Seven samples were used for each test and an average of five results was taken as the resultant value. The standard deviations are expressed in error bar or stated in parenthesis.

3.6.2 Thermogravimetric Analysis

Thermal stability of biocomposites was determined by TGA. About 6-8 mg of samples were heated from 50 – 600 °C using a nitrogen air flow of 50 ml/min and heating rate of 10 °C/min in a TGA (Model: TA Instruments Q500, Waters-LLC).

3.6.3 Differential Scanning Calorimetry

Thermal analysis of the biocomposites was investigated using a DSC (Model: TA Instruments Q20, Waters-LLC). A test sample of 7 – 9 mg was used. All samples were heated from 40 to 200 °C at heating rate of 10 °C min^{-1}. Percentage of crystallinity (X_c) of the biocomposites were determined from the DSC analysis as shown in equation 3.6. X_c of the biocomposites was calculated as the ratio of the melting entalphy (ΔH_m) to the specific heat of fusion of 100% crystalline PP, taken as 190 J g^{-1} (Hristov and Vasilena, 2003):

$$X_c = \frac{\Delta H_m}{\Delta H_m^{*PP}} \times 100 \qquad (3.6)$$

3.6.4 Scanning Electron Microscopy

Surface morphology of the fractured samples after tensile test of PP/OPMF biocomposites was observed using a SEM (Model : LEO 1455 VPSEM, Electron Microscopy Ltd., Cambridge, England). For SEM analysis, oven-dried OPMF samples were mounted on the stub and gold-coated for 180 seconds prior to SEM observation. The SEM micrographs were obtained with an acceleration voltage of 20 kV.

3.6.5 Water absorption

Dumbbell shape specimens were used to standardise the sample size for water absorption test (Hosseinaei et al., 2012). The samples were oven-dried at 60 °C for 24 hours, weighed and then soaked in water at 25 °C for 90 days. Sampling was done periodically in order to check for water absorption by removing the sample from the water, weighing it and immersing it in the water again. The amount of water absorbed (M_t) was calculated as in Equation 3.7 below:

$$M_t\% = \frac{(W_t - W_o)}{W_o} \times 100 \qquad (3.7)$$

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where w_o is the initial weight of the specimens, and w_t is the weight of the specimens at *t* time.

3.7 Statistical analysis

All data were analyzed with one-way analysis of variance (ANOVA) followed by Duncan's multiple range test for comparing means. Results of five replicate for each parameter analyzed were used in performing the statistical analysis. The ANOVA was performed on Mstat software and the probability was set at 0.05 ($p < 0.05$). Means values for each set of data were compared to determine either the parameter was significant or insignificant affected. Significant differences between parameter analysed are denoted by different superscripts (A – C).

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CHAPTER 4

MODIFICATION OF OIL PALM MESOCARP FIBER CHARACTERISTICS USING SUPERHEATED STEAM TREATMENT

4.1 Introduction

The main disadvantages of natural fiber for biocomposite reinforcement are due to its low compatibility with polymer matrix and its high moisture absorption. The polar nature of lignocellulose due to the presence of hydroxyl groups in cellulose and hemicellulose causes it to be incompatible with non-polar thermoplastics (Sreekala and Thomas, 2003; Shinoj et al., 2011; Kabir et al., 2012). The incompatibility has led the biocomposite to form aggregates during extrusion (Rozman et al., 2003), difficult to homogenize (Mohanty et al., 2001; Mir et al., 2013; Ramamoorthy et al., 2015), has poor adhesion (Mishra et al., 2002; Norul Izani et al. 2013), and limited stress transfer (Li et al., 2007; Then et al., 2013), and showing fiber pull-outs in fracture surfaces (Valadez-Gonzales et al, 1999; Eslam et al., 2011; Kaewkuk et al., 2013). Several treatment methods have been introduced to modify the fiber surface either to make it more hydrophobic or to develop a new linkage between fiber and polymer matrix, which makes the fiber and polymer to have better compatibility and furthermore, better mechanical properties.

Among the treatment methods used to increase the interaction between natural fibers and thermoplastics are the use of coupling agent (Rozman et al., 2001; Lee and Wang, 2006; Wong et al., 2012; Siyamak et al., 2012), compatibilizer (Rozman et al., 2003; Yang et al., 2007), crosslinking, hydrothermal treatment (Eslam, et al., 2011; Hosseinaei et al., 2012), heat treatment (Liu et al., 1994), acetylation (Mwaikambo and Ansell, 1999; Bledzki et al., 2008), sodium hydroxide treatment (Ichazo et al., 2001; Bachtiar et al, 2013), chemical grafting, and etc. Coupling agents, compatibilizers, crosslinkers and other chemical treatments have been widely used and proven to increase the interaction between natural fiber and polymer matrix (Lee and Wang, 2006; Tajeddin et al., 2009; Ibrahim et al., 2010; Kaewkuk et al., 2013).

Recently, another approach has been introduced to modify the fiber surface that is via hydrothermal treatment (Han et al., 2009; Eslam et al., 2011; Deepa et al., 2011; Hosseinaei et al., 2011; Hosseinaei et al., 2012). Based on their results, it was found that hydrothermal treatment could remove hemicellulose, which is the most hydrophilic and thermally unstable component in wood. Removal of hemicellulose makes the fiber to be less hydrophilic and this will potentially increase the compatibility of treated wood and polymers and improves the mechanical properties and water resistance of composites (Hosseinaei et al., 2012). Apart from that, hemicellulose has low thermal resistant whereby its decomposition temperature is within the same range as melt molding temperature for common thermoplastics. Degradation of hemicellulose generates volatile substances such as acetic acid and formic acid, hence, if the fiber is melt-blended with a thermoplastic, the

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hemicellulose component will be decomposed and generates unpleasant odor at the working environment.

Looking at the potential of hydrothermal treatment as a method for increasing surface compatibility between fiber and thermoplastics, it is no doubt that steam treatment may have the same capability. To date, the use of steam treatment or steam explosion for lignocellulose has been mainly focusing on the pre-treatment to gain better substrates for enzymatic hydrolysis, which is useful for biofuel production (Kaar et al., 1998; Ohgren et al., 2007; Linde et al., 2008; Shamsudin et al., 2012). These studies showed that the use of high pressure steam treatment is able to remove hemicellulose. However, the steam treatment used by those researchers involved the use of elevated pressure, which may impose high energy consumption apart from safety issue.

SHS can be an alternative treatment method for lignocellulose. SHS treatment is advantageous over steam explosion as it is being conducted at atmospheric pressure. To date, SHS has been mainly used for drying (Schwartze and Brocker, 2002; Hasibuan and Wan Daud, 2009). Recently, there have been reports on the use of SHS for treating oil palm biomass in order to ease the enzymatic hydrolysis of the lignocellulose for sugars production (Bahrin et al., 2012; Nik Mahmud et al., 2013).

In this chapter the potential of SHS as a novel treatment for modification of lignocellulose towards biocomposite production is discussed. The treated OPMF obtained in this study was analyzed for its chemical component, thermal stability, chemical structure and morphological characteristic.

4.2 Experimental

4.2.1 Superheated steam treatment

Procedures of OPMF treated with SHS were detailed in Section 3.3.2.

4.2.2 Characterization of OPMF

Untreated and SHS-OPMF were characterized as described in Section 3.4.

4.3 Results and Discussion

4.3.1 Preliminary study of superheated steam treatment

SHS-treated fiber from preliminary experiment was characterized for its chemical composition qualitatively by thermogravimetric (TG) analysis. It has been reported that TG analysis can be used for qualitative analysis of lignocellulose components, whereby lignin, hemicellulose, and cellulose showed distinct degradation

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temperature ranges of 160–900, 220–315 and 315–400 °C, respectively (Yang et al., 2007). From the preliminary results, TG thermogram showed multi-step degradation (Appendix B1) while differential TG (DTG-Appendix B2) thermogram exhibited two peaks at temperature range of 200 – 400 °C, representing hemicellulose and cellulose. Based on the TG curves, SHS-treated fiber had slight improvement in thermal stability when the SHS temperature increased. This may indicate the removal of low thermal stability component. A clearer result can be observed from DTG curves which showed decreased area of the first peak for OPMF treated at 220 °C compared to 160 and 200 °C, which showed removal of some hemicellulose component. This may suggest that temperature 220 °C or above can be used for hemicellulose removal. Nevertheless, Ando et al. (2000) reported that at temperature over 230 °C in hot compressed water treatment, cellulose started to decompose. Therefore 230 °C should be set as maximum temperature for SHS treatment.

4.3.2 Characteristics of untreated OPMF

Chemical composition analysis showed that untreated OPMF contained cellulose, hemicellulose, and lignin at 42, 32, and 22 wt%, respectively. Cellulose, hemicellulose and lignin composition of untreated OPMF found in this study was similar to that reported by Riansa-ngawong and Prasertsan (2011).

Thermal stability of untreated OPMF was evaluated by TGA. Figure 4.1 shows TG/DTG thermogram of untreated OPMF (sample 1). It was observed that weight loss occurred at four different regions : (i) 160–220 °C, (ii) 220–320 °C, (iii) 320–390 °C, and (iv) 390–550 °C. The multi-step degradation indicates sequential degradation of multiple components: low molecular weight lignin, hemicellulose, cellulose and lignin, respectively. The weight loss at temperature less than 100 °C was due to moisture content.

This can be seen clearly in Figure 4.1, in which the DTG thermogram suggests a hidden wide peak from the gently sloping baseline. The broader degradation temperature range of lignin can be explained by the presence of various oxygen-containing functional groups in its structure (Brebu and Vasile, 2010).

These complex structures of lignin show various thermal degradation behaviors, since the scissions occurring at different temperatures. Therefore, it is suggested that the temperature range of lignin degradation overlaps with those of hemicellulose and cellulose degradation. The degradation occurred within second temperature region ranging from 220 to 320 °C was related to the degradation of hemicellulose and cellulose of the fiber. This is in agreement with a report by Sinha and Rout (2009), whereby the glycosidic linkages of cellulose in raw jute fiber started to disrupt at 290 °C. The third stage of weight loss, which occurred at temperature range between 320 and 390 °C, indicates the degradation of cellulose and other non cellulosic materials from the fiber (Kabir et al., 2010). The intense peaks at 290 and 350 °C in DTG thermogram (Figure 4.1) are attributed to the hemicellulose and cellulose decomposition, respectively.

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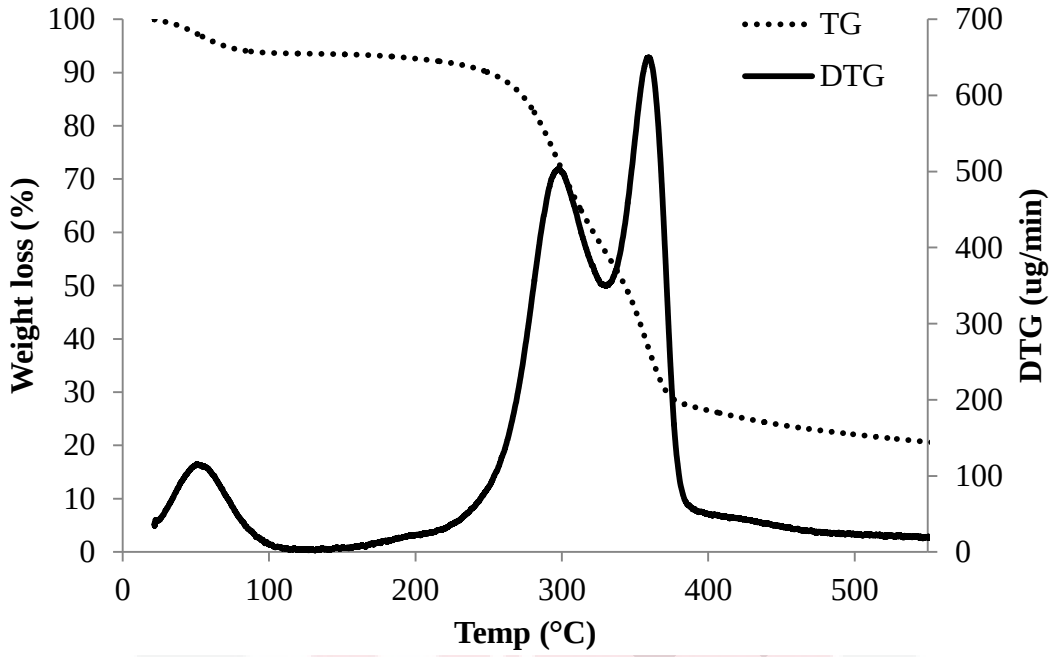

Figure 4.1: TG and DTG of untreated OPMF shows two clear peaks of hemicelluloses and cellulose.

4.3.3 Effects of SHS treatment on chemical composition of OPMF

OPMF was treated with SHS at various temperatures and treatment times. Table 4.1 shows the major components of untreated and treated OPMF. Generally, all treated OPMF had higher composition of lignin and lower composition of hemicellulose compared to the untreated OPMF. These results indicate that SHS operated at 190–230 °C for 1 to 3 h under atmospheric pressure selectively removed hemicellulose component, thereby increasing the composition of lignin. Lignin seems to be least affected by the SHS where it can be observed that percentage of lignin was increased as treatment temperature and time increased. Result found in this study was inagreement with a study done by Bahrin et al. (2012), showed that percentage of lignin in SHS-treated EFB was increased from 14.2% to 20.9% at 210 °C for 1 h. This can be explained by the complex structure of lignin which makes it difficult to be degraded. This is in contrary with hemicellulose whereby the branched structure of hemicellulose makes it easily affected by the SHS treatment. Moreover, the structure of hemicellulose is most unstable because of its amorphous structure (Hosseinaei et al., 2012).

Lignin contains polar hydroxyl groups and non-polar hydrocarbon and benzene rings making it less hydrophilic (Rozman et al., 2001). On the other side hemicellulose is hydrophilic due to the presence of abundant hydroxyl groups.

Table 4.1: Chemical composition of untreated and SHS-treated OPMF.

Sample	Treatment		Chemical composition* (%)			
	Temp (±2 °C)	Time (h)	Hemicellulose	Cellulose	Lignin	Ash
1	0	0	33.10 ± 2.01	42.81 ± 0.69	20.49 ± 3.44	3.59 ± 0.74
2	190	1	26.13 ± 0.18	41.39 ± 0.06	28.44 ± 1.27	4.04 ± 1.02
3		2	22.47 ± 1.67	40.46 ± 2.52	33.38 ± 1.34	3.69 ± 0.49
4		3	19.71 ± 0.72	37.50 ± 0.18	38.72 ± 1.04	4.07 ± 0.14
5	210	1	16.80 ± 2.15	33.75 ± 2.28	45.19 ± 4.66	4.26 ± 0.85
6		2	12.82 ± 1.75	32.85 ± 0.12	49.81 ± 1.91	4.52 ± 0.83
7		3	11.50 ± 1.19	30.75 ± 1.09	52.30 ± 0.92	5.44 ± 0.37
8	230	1	11.42 ± 0.21	33.61 ± 1.10	49.73 ± 0.70	5.24 ± 0.45
9		2	9.42 ± 1.16	34.35 ± 1.33	50.63 ± 1.76	5.59 ± 0.05
10		3	9.71 ± 0.88	28.89 ± 1.75	55.22 ± 1.87	6.18 ± 0.75

***** Data provided is mean of duplicate samples.

Therefore, by destruction of hydroxyl in hemicellulose, the percentage of lignin will be higher, thus reducing the overall hydrophilicity of the fiber (Eslam et al., 2011). In addition, treated samples will allow the interaction between the non-polar hydrocarbon chains and benzene rings of lignin with hydrophobic polymers. Besides that, hydroxyl groups of lignin will interact with the structure of the fiber (Rozman et al., 2001). This may promote the adhesion of SHS-treated OPMF to polymer and make it more compatible with the polymer matrix.

Detailed analysis on the chemical composition of SHS-treated OPMF suggested that the composition of treated fiber was affected by treatment temperature and time. It was found that the removal of hemicellulose by SHS treatment was more pronounced at temperatures above 210 °C whereby more than 50% of the hemicellulose was removed compared to the use of lower temperature when treated for 1 h. Moreover, it was also found that prolonged treatment time of up to 3 h may reduce the hemicellulose content to nearly half of the original value, even at lower temperature, *i.e.*, 190 °C. This indicates that hydrolysis of hemicellulose by SHS was affected by both temperature and retention time. However, the use of high temperature may hydrolyze the cellulose component of OPMF. This was proven when percentage of cellulose started to decrease at temperature 210 °C and higher. At temperature a 230 °C for 3 h of treatment, the cellulose content was decreased notably. This is in agreement with Ando et al. (2000) which reported that cellulose started to degrade when the temperature of hot water extraction was over 230 °C.

Furthermore, prolonged the retention time up to 3 h for SHS treatment at 230 °C did not give a marked difference in hemicellulose content. About 8 –9% of hemicellulose was still left in the treated OPMF. This could be the result of recalcitrant hemicellulose, which is closely linked to lignin through covalent bonds such as ester and ether bonds, which is known as lignin-carbohydrate complex (LCC) as shown in Figure 4.2. This kind of bonding may require more energy to break.

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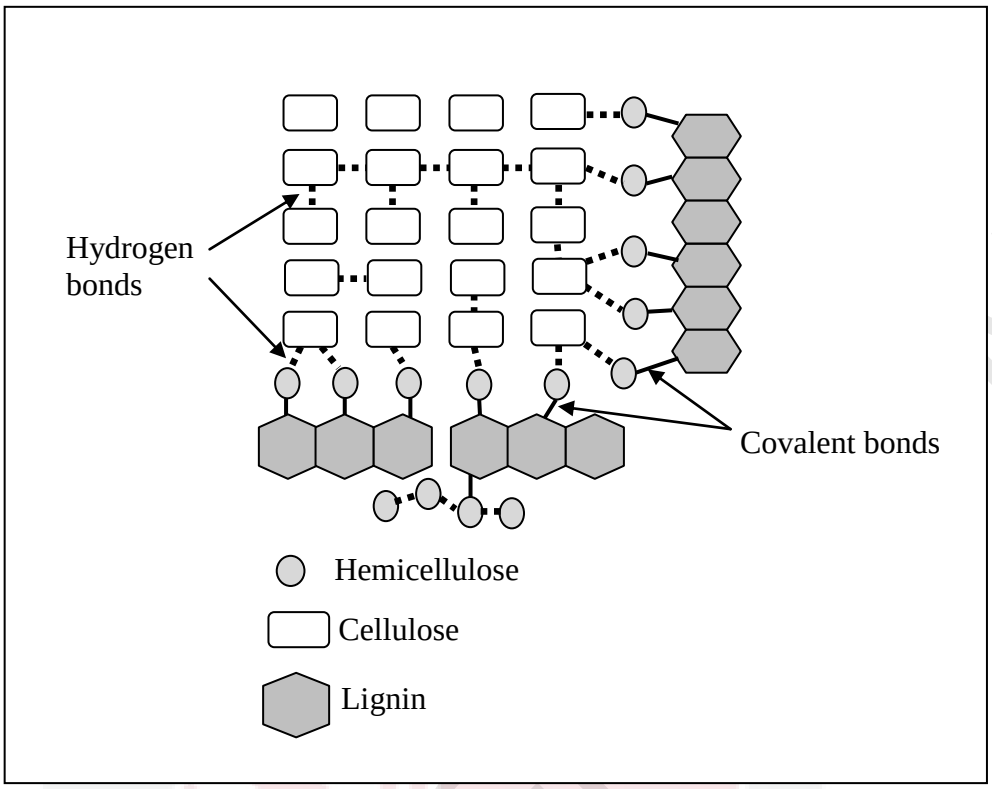

Figure 4.2: Schematic representation of lignin linked by covalent bond to hemicellulose and hemicellulose linked to cellulose through hydrogen bonding (adopted from Vaca-Garcia, 2008).

Alteration in chemical components of SHS-treated OPMF can also be shown by the changes in its chemical structure and compared with the untreated OPMF as shown in Figure 4.3. From this FTIR spectrum, it is seen that the strong absorption peaks were found at 3330 and 2950 cm^{-1}, which were attributed by the stretching vibrations of –OH groups and the C–H stretching, respectively. Peak stretching around 3330 cm^{-1} was decreased after the SHS treatment attributed to the removal of hydroxyl group and hydrogen bond reflecting that the treated sample has lower moisture content compared to untreated OPMF. The band around 2950 cm^{-1} are assigned to the C–H groups corresponds to methyl and methylene groups in lignin, cellulose and hemicellulose (Hosseinaei et al., 2011). However, this band did not show much different between the samples due to the functional groups were present in all the three components.

Meanwhile a small shoulder peak at 1730 cm^{-1} is assigned to the characteristic of carbonyl groups in hemicellulose and/or lignin (Yang et al., 2007; Hosseinaei et al., 2011; Bahrin et al., 2012). This band was decreased after the treatment which could be due to the removal of hemicelluloses, which has also been observed in the steam pretreatment of wheat straw (Zhang et al., 2008). This result corresponded well with the chemical composition analysis, which showed low percentage of hemicelluloses in SHS samples. It was also reported by Bahrin et al. (2012) that the intensity of this

band was gradually decreased after SHS treatment of oil palm empty fruit bunch (OPEFB) due to removal of hemicellulose.

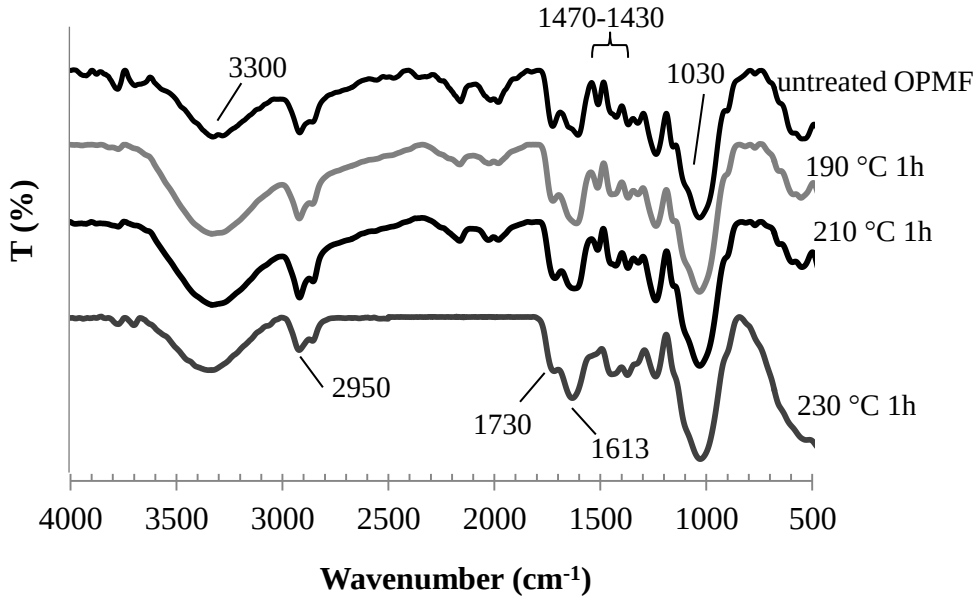

Figure 4.3: FTIR spectra of the untreated and SHS-treated OPMF.

Signals at 1613 and 1450 cm^{-1} are indicative of the aromatic C=C stretch of aromatic vibrations in bound lignin (Xiao et al., 2001). The intensity of these peaks increased in the treated OPMF and became more apparent in OPMF sample treated at 230 °C for 1 h, reflecting a higher fraction of lignin in the treated samples. The bands at 1470 – 1430 cm^{-1} portrayed the methoxyl-O-CH_3 in lignin compounds which appeared in all the samples. The band at 1370 cm^{-1}, which is from cellulose and hemicelluloses, did not show change after the treatment. The intensity of the band at 1158 cm^{-1} originate from C–O stretching vibrations are due to partial acetylation of hydroxyl groups in both polysaccharides and residual lignin (Sun et al., 2000). The decreased of the respective peaks revealed a higher percentage of lignin after SHS treatment which corroborates the earlier statement.

The intensity of the band related to C-O-C pyranose ring skeletal vibration and C-O anti-symmetric stretching, around 1030 cm^{-1}, increased after the treatment, which also shows the higher lignin ratio in treated samples (Yang et al., 2007). From the FTIR result, it was suggested that during the SHS treatment, reactions occurred randomly on the entire OPMF surface. The functional groups and the IR signal with the possible compounds are listed in Table 4.2 for a reference (Xiao et al., 2001; Yang et al., 2007; Fahma et al., 2010; Hosseinaei et al., 2011; Bahrin et al., 2012).

Partial removal of hemicellulose and elimination of low degradation temperature lignin may cause the SHS-treated OPMF to be more ductile (Rong et al., 2001). The removal of both hemicellulose and lignin which are considered as internal constraints may lead to a closer packing of the cellulose chain. It is also expected that the

removal of hemicellulose and low degradation temperature lignin may cause improvement in fiber strength and its mechanical properties.

Table 4.2: The main functional groups in the OPMF.

Transmittance peak (cm^{-1})	Functional groups	Peaks intensity after SHS treatment
3330	O-H stretching (holocellulose and lignin)	Decreased contributed by reduced content of hemicellulose
2950	C-H stretching (methyl and methylene groups)	Present in lignin, hemicellulose and cellulose
1730	C=O stretching (carbonyl groups in hemicelluloses)	Decreased devoted due to removal of hemicellulose
1613, 1450	C=C stretching (aromatic skeletal mode)	Increased as prominent lignin content
1470 - 1430	O-CH_3 (methoxyl-O-CH_3)	Devoted to lignin compounds
1370	C-H bending (ester)	Devoted to cellulose and hemicellulose
1158	C-O-C asymmetric stretching (cellulose and hemicelluloses)	Decreased due to reduced of hemicelluloses component
1030	C-O and C-C stretching (cellulose), aromatic C-H in plan deformation, C-O deformation (lignin)	Increased as higher percentage of cellulose and lignin

4.3.4 Effects of SHS treatment on thermal stability of OPMF

A study on thermal properties of OPMF is very important in order to estimate the fiber's degradation behaviour during biocomposite processing. Processes such as melt blending, injection molding and hot-pressing for many polymeric materials are mostly done at high temperature, exceeding 170 °C. Some components in the fiber *i.e.* lignin and hemicellulose start to degrade at temperature of 160 °C. The degradation of these components will affect the mixing process such as it will cause the formation of void during heating process and subsequently producing a low quality blended product. Therefore, treatment is required in order to improve thermal stability of the natural fiber.

Thermal stability of untreated and SHS-treated OPMF are shown as TG and DTG thermograms, as in Figures 4.4 and 4.5. Degradation at temperature below 110 °C was contributed by moisture content in the samples. Based on magnified thermogram in Figure 4.4, it is seen that moisture content of SHS-OPMF samples was lower compared to untreated-OPMF. At temperature above 180 °C multi-step degradation

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of untreated OPMF (sample 1) gradually changed to single step degradation for treated OPMF (samples 2, 5 and 8) as seen in the TG thermogram, indicating that the component in the treated OPMF gradually changed with the SHS treatment.

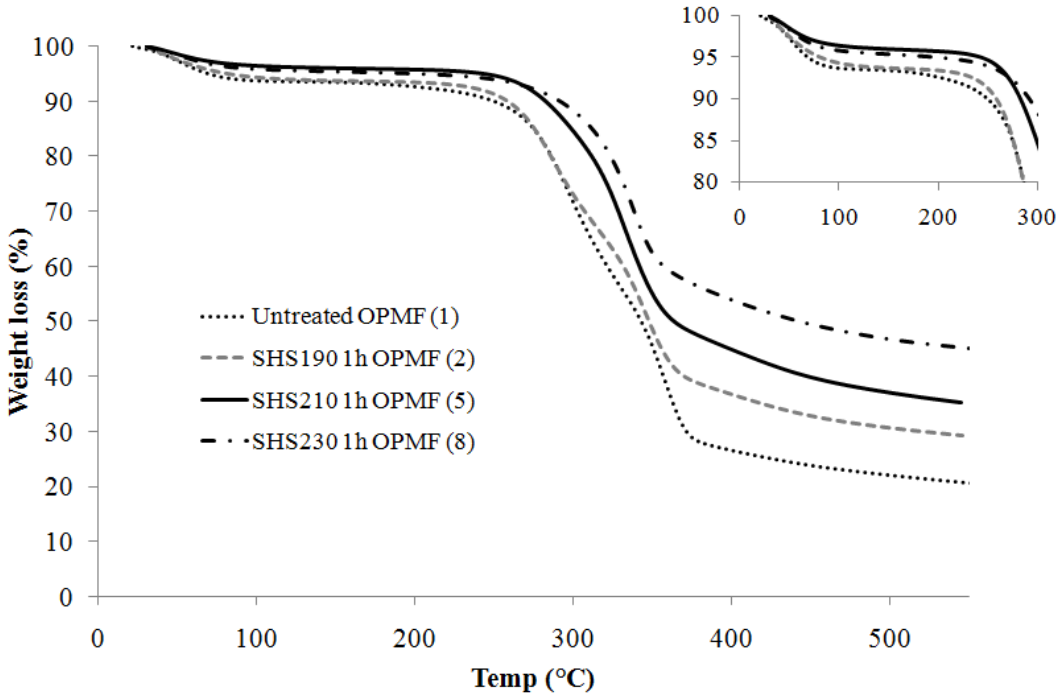

Figure 4.4: TG thermogram of untreated OPMF (sample 1), SHS-treated OPMF; at 190 °C (sample 2) , 210 °C (sample 5) and 230 °C (sample 8), for 1 h treatment.

This can be clearly seen from the DTG thermogram (Figure 4.5). Peak at around 300 °C which represents hemicellulose decomposition was rapidly decreased and nearly disappeared in the SHS-treated sample at high temperature, *i.e.*, 230 °C (sample 8). In other words, the thermally unstable hemicellulose content was removed during the SHS treatment.

It has been reported that pretreatment of wood chip with hot-water extraction reduced the hemicellulose content resulting in increased in the degradation starting point (Hosseinaei et al., 2012). In addition, the ratio of cellulose and lignin to hemicellulose in SHS-treated OPMF were increased, causing the formation of higher thermal stability fiber. However as discussed earlier, at high temperature cellulose will also partially degraded, therefore, the disappearance of a broad peak at 160–340 °C for untreated samples can be assumed as a thermal degradation of both hemicellulose and cellulose.

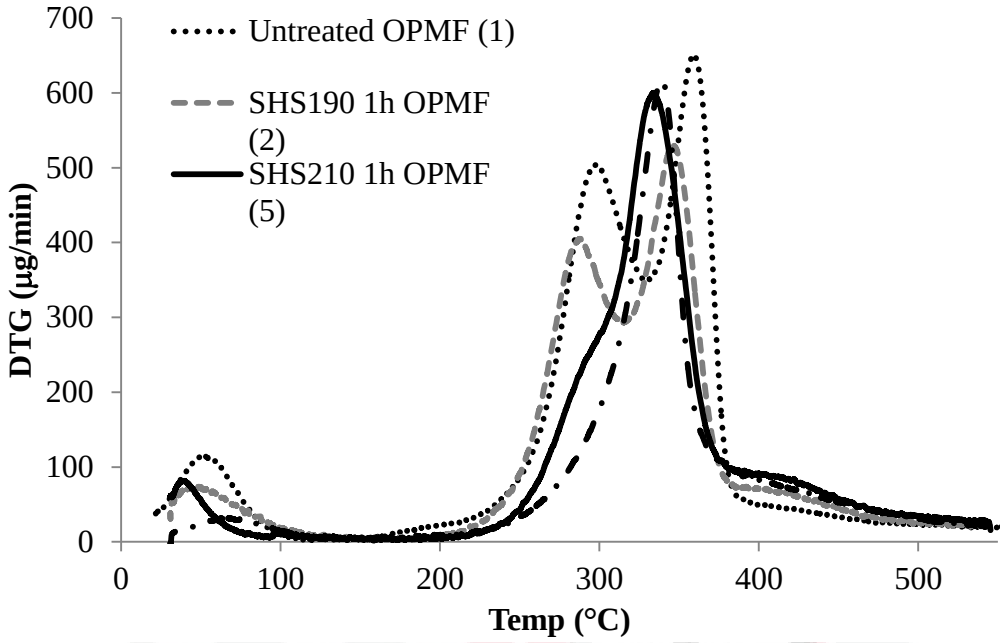

Figure 4.5: DTG thermogram of untreated OPMF (sample 1), SHS-treated OPMF; at 190 °C (sample 2), 210 °C (sample 5) and 230 °C (sample 8), for 1 h treatment.

There was distinct observation in the amount of carbonaceous residue for untreated and SHS-treated OPMF, which is attributed by lignin and inorganic compounds. Samples treated at higher temperature had more residue after TG analysis. This is in agreement with the results shown in Table 4.1, whereby lignin and inorganic compounds (ash) was higher for samples treated at higher temperature. As being mentioned earlier, lignin has a wide degradation temperature range (160–900 °C), and lignin is less prone to degradation due to its complex structure. This explains why lignin is less affected during superheated steam treatment and hence, contributed to the large amount of residue after TG analysis of treated OPMF.

Increased in thermal stability of treated OPMF is shown in detail in Table 4.3. The table shows decomposition temperature of fiber at 5, 20 and 50% weight loss ($T_{5\%}$, $T_{20\%}$, and $T_{50\%}$) and peak temperature (T_P) of DTG. The temperatures of decomposition were determined after moisture content was vaporized. $T_{5\%}$ of untreated OPMF was recorded at 258 °C. The value was increased to 261, 276 and 285 °C when the OPMF was treated for 1 h at 190, 210 and 230 °C, respectively.

Overall, these results suggested that the high temperature of thermal decomposition and high residual mass of the OPMF obtained after SHS treatments is attributable to the selective removal of hemicellulose. These results are consistent with the results obtained from the FTIR and chemical analysis as discussed in the earlier section.

Table 4.3: Decomposition temperature at 5, 20 and 50% fiber degradation, obtained by TGA of untreated and SHS-treated OPMF.

Sample	Temp (°C)	Time (h)	$T_{5\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_p (°C)	Residue at 550 °C (%)
1	0	0	257.7	294.8	348.1	299.6, 359.9	22.01
2	190	1	260.9	295.1	352.5	287.7, 346.6	31.11
5	210	1	276.0	317.9	374.3	334.1	36.63
8	230	1	285.3	329.5	476.9	339.2	47.14

Note : - T_p represents peak temperature of DTG.
- Decomposition temperature refers to decomposition of fiber after moisture loss (above 110 °C).

4.3.5 Effect of SHS treatment on the morphology of OPMF

Apart from modifying the chemical composition and thermal stability of the OPMF, SHS treatment also resulted in morphological changes as well as chemical changes on the OPMF surface. Figure 4.6 (a) shows the surface morphology of untreated OPMF, whereby silica bodies were observed to deposit on the entire fiber surface. There has been a report which shows that silica bodies were observed to be present on the entire surface of OPMF strands (Chua et al., 2009). The result is also in agreement with SEM image of OPEFB, where silica bodies are found to be spread at the entire fiber surface (Shinoj et al., 2011).

Figures 4.6 (b, c and d) show the morphology of OPMF after SHS treatment at 190 °C, 210 °C and 230 °C for 1 h. Based on these figures, it was found that SHS treatment was able to remove silica bodies on the OPMF surface. Figure 4.7 (a) shows the image of SEM mapping, whereby silver particles observed in the figure represent silica bodies. The finding is supported by EDX analysis, which is shown in Figure 4.7 (b). The spectrum of the elements present in the fiber surface demonstrated that the particles were silica. Mapping of SEM micrographs for SHS-treated samples are shown in Figures 4.7 (c, d and e). It can be clearly seen that the amount of silica bodies was decreased after SHS treatment.

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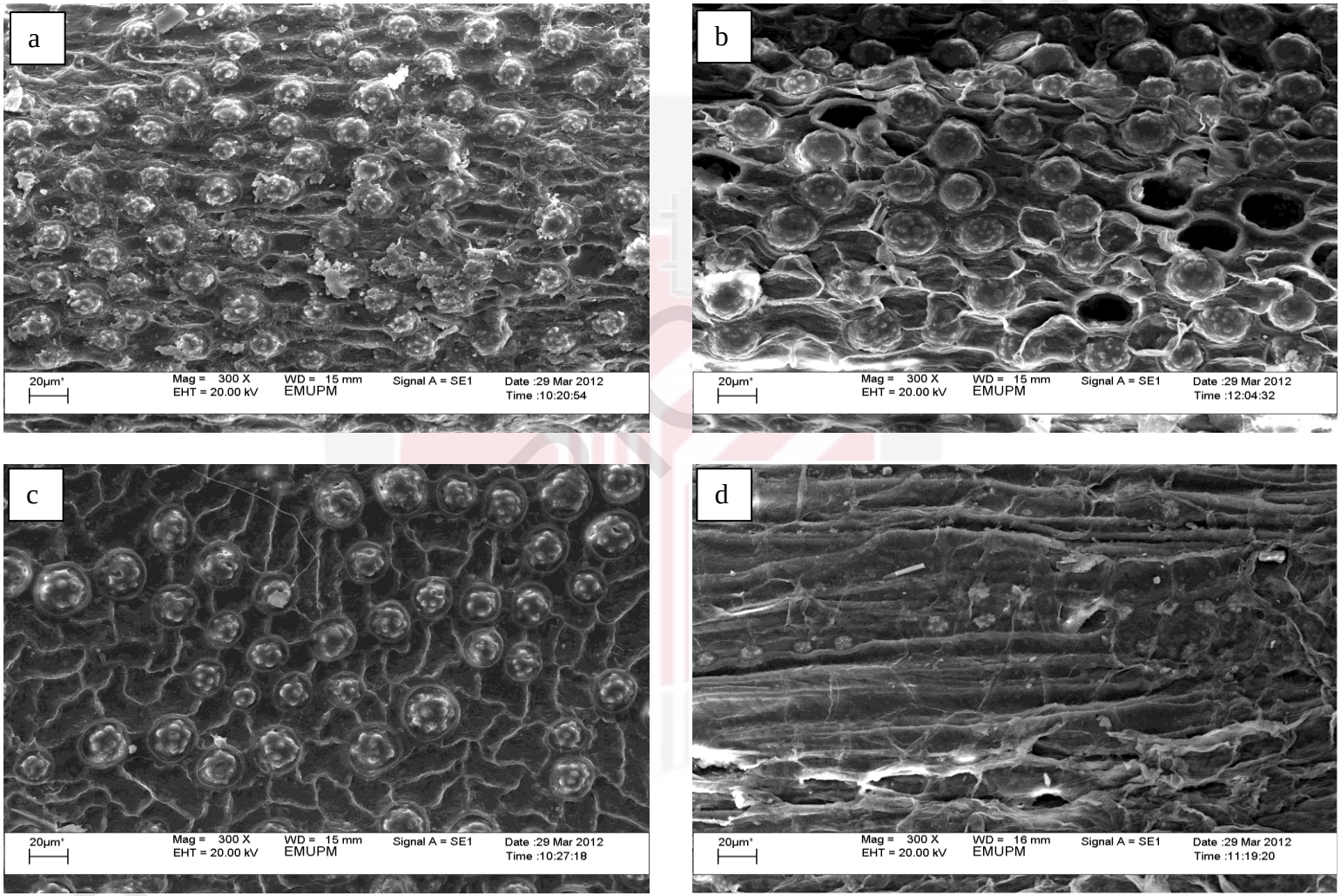

Figure 4.6: SEM images of (a) untreated OPMF, (b) SHS-190, (c) SHS-210 and (d) SHS-230 for 1 h of treatment.

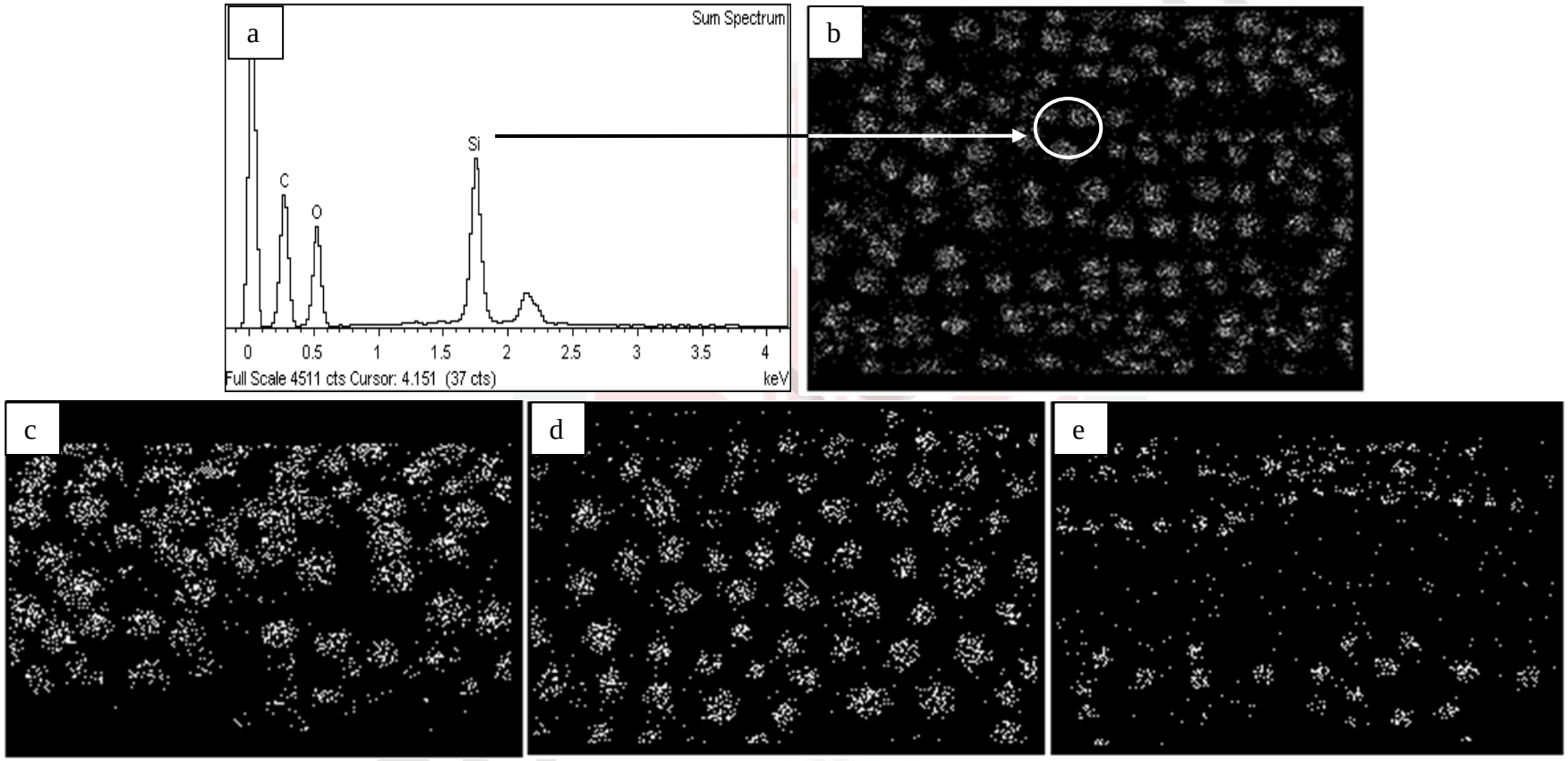

Figure 4.7: (a) Microanalysis spectrum by SEM/EDX. SEM mapping identified silver particles as silica. (b) untreated OPMF; SHS treated OPMF at: (c) 190 °C, (d) 210 °C and (e) 230 °C; for 1 h, show reduction of silica bodies after SHS treatment.

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Silica content in the untreated and SHS-treated OPMF was measured quantitatively and the results are shown in Table 4.4. From the analysis, it was found that silica content was reduced after the SHS treatment. The results obtained were in agreement with the SEM micrographs which show the decrement in silica bodies after SHS treatment.

Table 4.4: Silica content in untreated-OPMF and SHS-treated OPMF.

Sample	Treatment		Silica (ppm)
	Temp (±2 °C)	Time (h)	
1	0	0	224.8
6	210	1	203.9
9	230	2	198.3
10	230	3	93.4

Figures 4.8 (a-c) show SEM micrographs of SHS-treated OPMF at different SHS treatment temperature and duration. Significant reduction of silica bodies can be seen in sample treated at 230 °C compared to sample treated at 190 °C. This observation is similar to that reported by others studies (Hasibuan & Wan Daud, 2009; Bahrin et al., 2012), whereby it was shown that SHS treatment removed silica bodies from OPEFB.

It is interesting to note that at high temperature (230 °C) as shown in Figure 4.8 (c-i and c-ii), the loose structure of fiber can be clearly observed. This is closely related to the removal of hemicellulose, since hemicellulose together with lignin (as LCC) constitute the bonding matrix of the cellulose microfibers to assemble the microfibrils into macrofibrils (Vaca-Garcia, 2008). On the other hand, hemicellulose linked to cellulose through hydrogen bonding. Therefore when hemicellulose is removed, cellulose macrofibrils will collapse, the tightly packed cellulose microfibrils tend to become loose and leave the loose structure as seen in Figures 4.8 b and c. Loosening of OPEFB structure was also observed after steam pretreatment at 240°C (Ariffin et al., 2008).

Silica bodies removal after SHS treatment caused the OPMF to have perforated surface as shown in Figures 4.6 (b to d) and 4.8. Based on the observation of SEM micrographs in Figures 4.6 and 4.8, the average diameter of massive silica bodies is about 10–20 μm for the untreated OPMF. The perforated and rough surface of SHS-treated OPMF is an advantage as the scar-like surface of fiber obtained after dislodging of silica bodies will provide a good anchor for polymer which will subsequently improve the interaction between the two materials (Shinoj et al., 2011). Moreover, the uneven surface of fiber is more advantageous to help the diffusion and penetration of melt polymer chains into the fiber (Shinoj et al., 2011).

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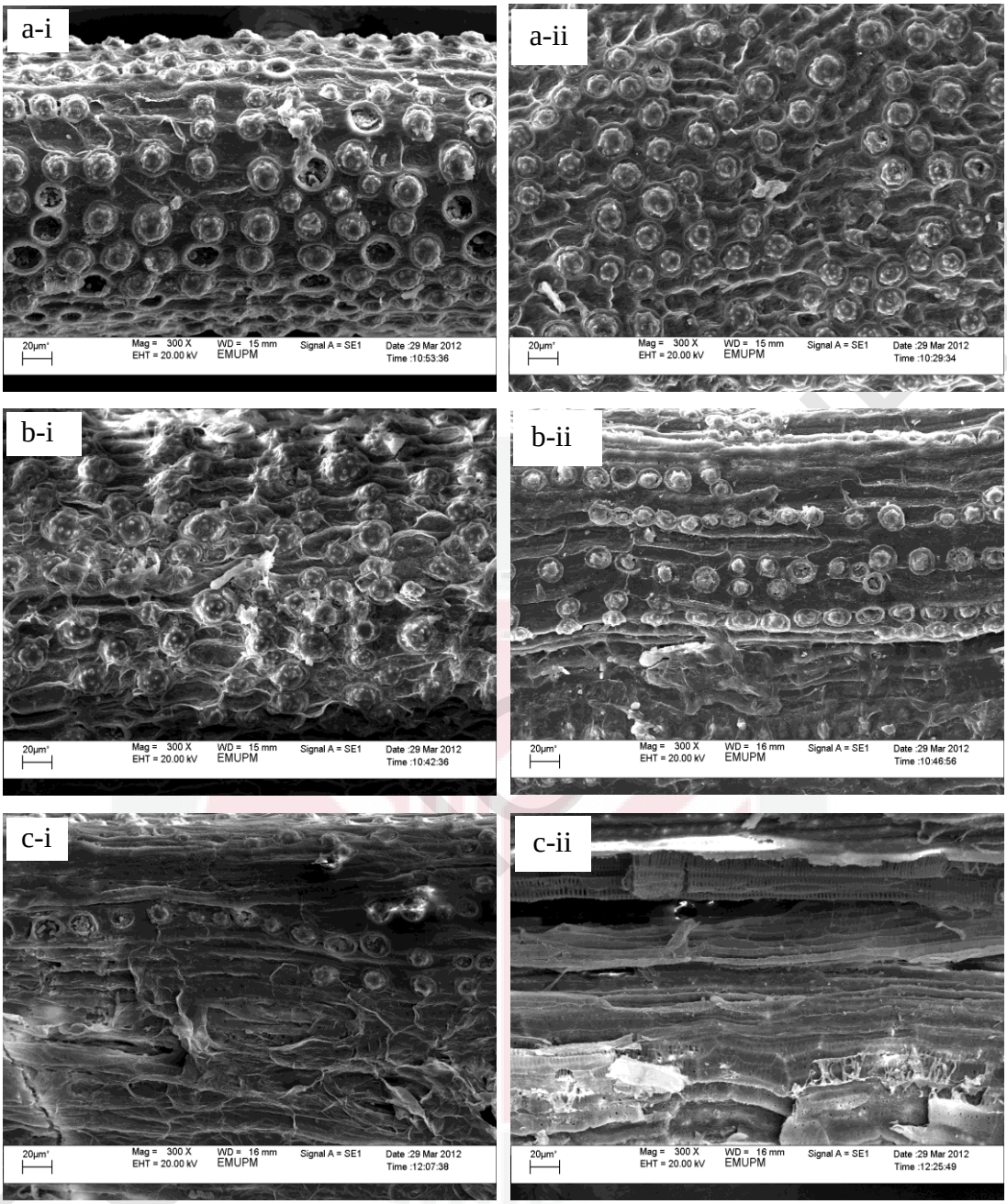

Figure 4.8: SEM micrographs of SHS-treated mesocarp fiber (a) 190 °C, (b) 210 °C and (c) 230 °C; (i) – 2 h and (ii) - 3 h of treatment.

4.3.6 Crystallinity of SHS-treated OPMF

WAXD patterns of untreated and SHS-treated OPMF in Figure 4.9 show the natural occurring cellulose form known as cellulose I (John and Thomas, 2008). It was reported that the peak at about 2θ = 22 is the peak for the crystalline portion of biomass (*i.e.*, cellulose) and the peak at about 2θ = 17 corresponds to the amorphous region (Segal et al., 1959; Muller et al., 2009). It can be seen that the diffraction peak at 22° (0 0 2) is wide and broad for untreated OPMF, however, the peak was sharper and narrower in SHS-treated OPMF, hence indicating a higher degree of crystallinity

in the treated fibers. The crystallinity index for untreated OPMF was 76.3% and this was increased to 84.0% after treatment at a temperature of 210 °C for 1 h. However after prolonged treatment *i.e.*, 3 h, the sample shows a decrease in crystallinity index (to 76.4%). This might be due to the long treatment that disrupts the structure of cellulose. The crystallinity index of OPMF decreased to 73.1% at a higher temperature, 230 °C after 2 h. The increased of crystallinity in treated samples can be attributed to the removal of cementing amorphous component, which was hemicellulose as discussed in Section 4.3.3. This finding is supported by Hosseinaei and colleagues (2012) in their report which mentioned that increased crystallinity of wood flake was observed after hot-water treatment compared to untreated wood flake. Fiber with high crystallinity might improve the mechanical properties of the composite. It will promote the resistance to cracks which may contribute to better mechanical properties.

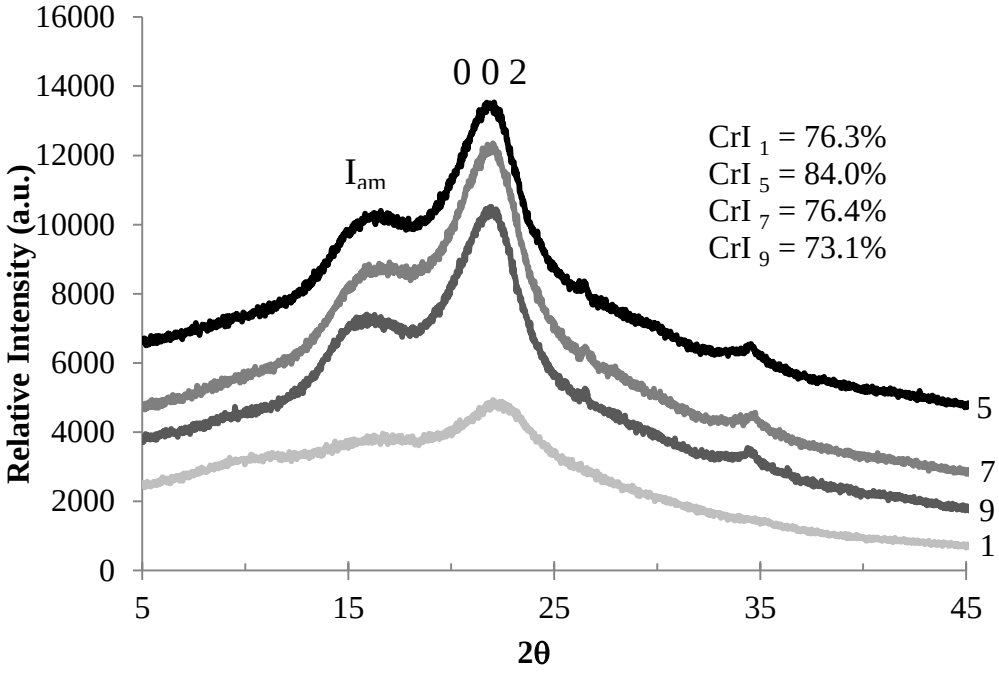

Figure 4.9: X-ray diffraction patterns of (1) untreated OPMF, SHS-treated OPMF; at (5) 210 °C for 1 h, (7) 210 °C for 3 h and (9) 230 °C for 2h of treatment.

4.4 Summary

In this chapter, the use of SHS treatment for surface modification of lignocellulose fiber for biocomposite production is discussed. Based on the results, it was shown that chemical composition, thermal stability and morphological property of OPMF were greatly affected by SHS treatment. Chemical composition and FTIR analysis of the SHS-treated OPMF revealed that there was selective removal of hemicellulose, indicating the success of SHS treatment as a treatment method for preparing less hydrophilic lignocellulose fiber for biocomposite production. Moreover, SHS-treated OPMF also exhibited improved thermal stability property, whereby the thermal degradation temperature at $T_{5\%}$ increased from 258 °C for untreated OPMF to 285 °C

for SHS-treated OPMF at 230 °C for 1 h, and thus making the fiber as promising candidate for polymer composite processing. Morphological analysis revealed that the SHS-treated OPMF had rougher surface due to the removal of silica bodies. From the results obtained SHS treatment conducted at 210 °C for 1 h was sufficient to successfully improve the characteristics of OPMF. Higher treatment temperature may disrupt the cellulose content. It was noted, further treatment only gave almost no changes to the hemicellulose content. Overall, it can be concluded that SHS treatment has great potential application in reinforced-polymer composite processing as it may provide lignocellulose fiber with better physical, chemical and thermal properties which in turn could produce biocomposite with enhanced characteristics. Moreover, the non-chemical and environmental friendly characteristics give extra value to this novel and green treatment method.

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CHAPTER 5

EFFECT OF SUPERHEATED STEAM TREATMENT AND FIBER LOADING ON PROPERTIES OF OIL PALM MESOCARP FIBER / POLYPROPYLENE BIOCOMPOSITE

5.1 Introduction

In recent years, attention has been given on the development of hybrid materials which combine petroleum-based polymers with biodegradable (Mohan and Kanny, 2012), low cost (Hosseinaei et al., 2012; Then et al., 2013) and renewable natural fibers (Gomes et al., 2007).

In Malaysia, palm oil industry is the biggest contributor for agricultural waste. EFB and OPMF are two important fibrous materials generated as biomass at palm oil mill, where OPMF is generated after the oil was extracted. At present, OPMF is used as biomass fuel and inefficiently burnt for energy generation by steam boiler (Chua et al., 2009; Riansa-ngawong and Prasertsan, 2011; Zakaria et al., 2015). OPMF in nature has similar characteristics with EFB in term of chemical composition, therefore OPMF may have the potential for other use such as biosugar production (Bahrin et al., 2012; Nik Mahmud et al., 2013; Zakaria et al., 2015) and as reinforced material in biocomposite production (Sreekala and Thomas, 2003; Thawien, 2009; Phattaraporn et al., 2011; Then et al., 2013).

OPMF, like other natural fiber has low compatibility with polymer matrix due to its hydrophilic property. Research have shown that surface modification of fiber such as silane treatment (Herrera-Franco & Valadez-Gonzalez, 2005; Sawpan et al., 2011;), alkaline treatment (Gomes et al., 2007; Sgriccia et al., 2008; Mohan & Kanny, 2012) and addition of compatibilizer (Arbelaiz et al., 2005; Hosseinaei et al., 2012) can improve the interaction between the two materials and hence, improving mechanical properties of the biocomposites.

In lignocellulosic material, hemicellulose is the most hydrophilic and thermally unstable polymer (Herrera-Franco & Valadez-Gonzales, 2005; Arbelaiz et al., 2005; Sgriccia et al., 2008). It has been reported that interfacial bonding of fiber-polymer can be improved by diminishing hemicellulose component in the fiber (Han et al., 2009; Eslam et al., 2011; Hosseinaei et al., 2012; Kaewkuk et al., 2013). Several studies have shown that hydrothermal and steam treatments such as SHS (Bahrin et al., 2012; Nik Mahmud et al., 2013; Then et al., 2014) hot-water extraction (Eslam et al., 2011; Hosseinaei et al., 2012) and steam explosion (Ando et al., 2000; Han et al., 2009;) can reduce hemicellulose content in the fiber.

In chapter 4, it was shown that OPMF became more hydrophobic after SHS treatment due to reduced content of hydroxyl groups. SHS-OPMF also exhibited

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fiber with higher crystallinity and thermal stability. In this chapter the effect of SHS treatment and fiber loading on the characteristics of OPMF/PP biocomposite were clarified. This study will reveal the potential of SHS-OPMF as biocomposite and data provided in this report is important for further evaluation of OPMF as filler material for biocomposite production.

5.2 Experimental

5.2.1 Superheated steam treatment

SHS oven (QF-5200C, Naomoto Corporation, Japan) was used to perform the extraction of hemicellulose at different temperatures (190, 200, 210, 220 and 230 °C) over a time period of 60 minutes which was selected based on results obtained in Section 4.3.3.

5.2.2 OPMF/PP biocomposite

5.2.2.1 Preparation of biocomposite samples

Grinding of untreated and SHS-treated OPMF was done as described in Section 3.5.1. Melt blending and hot compression molding of OPMF/PP biocomposite was conducted as previously explained in Sections 3.5.2 and 3.5.3, respectively.

5.2.2.2 Determination of suitable fiber size for OPMF/PP biocomposite

A preliminary study on suitable fiber size for OPMF/PP biocomposite production was conducted as there was not much information on OPMF biocomposites. For this purpose, various particle sizes of untreated OPMF were used: 355 – 250, 250 – 150 and <150 μm. Each of the fiber size was mixed with PP at fiber loading of 30 wt%.

5.2.2.3 Effect of SHS treatment temperature on biocomposite characteristics

Section 4.3.3 gives that the temperature of SHS treatment affected the chemical composition of OPMF. The changes in chemical composition of OPMF may affect the properties of biocomposite produced. To clarify that, untreated OPMF and SHS-treated OPMF (varies from 190 to 230 °C for 1 h) were mixed with PP to produce six biocomposite samples as shown in Table 5.1.

For this purpose, fiber loading and particle size used were based on the results from previous experiment (section 5.2.2.2), *i.e.* 30 wt% of fiber loading with particle size of <150 μm.

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Table 5.1: Designation of OPMF/PP[a] biocomposites.

OPMF sample[b]	Designation
Untreated OPMF	untreated-OPMF/PP
SHS 190 °C	SHS190-OPMF/PP
SHS 200 °C	SHS200-OPMF/PP
SHS 210 °C	SHS210-OPMF/PP
SHS 220 °C	SHS220-OPMF/PP
SHS 230 °C	SHS230-OPMF/PP

[a] Fiber with size of <150 μm and 30 wt% fiber loading
[b] Treatment time fixed for 1 h

5.2.2.4 Effect of fiber loading on biocomposite characteristics

Fiber loading is an important parameter which can influence the properties of a biocomposite. In order to determine the effect of fiber loading, two types of biocomposite samples were prepared *i.e.* untreated OPMF/PP and 210-OPMF/PP. Each of the biocomposite samples were prepare with different fiber loadings: 30, 40 and 50 wt% as shown in Table 5.2.

Table 5.2: Composition of prepared biocomposites.

Sample	Fiber loading (wt%)	PP (wt%)
Untreated-OPMF/PP :	30	70
	40	60
	50	50
SHS210-OPMF/PP :	30	70
	40	60
	50	50

5.2.3 Analyses

Biocomposite samples were subjected to several analyses such as mechanical testing, TGA, DSC, SEM and water absorption as previously explained in Section 3.6.

5.2.4 Statistical analysis

The significant effect of the mechanical properties of the biocomposites was performed on Mstat software. The detailed was described in Section 3.7.

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5.3 Results and discussion

5.3.1 Effect of fiber size on tensile properties of untreated-OPMF/PP biocomposites

It has been reported that maximum stress transfer could be achieved by choosing suitable fiber size in biocomposite production (Sumaila et al., 2013). Figure 5.1 shows the tensile strength of untreated-OPMF/PP biocomposite prepared from different size of fiber at 30 wt% of fiber loading. The tensile strength decreased with a corresponding increased of fiber size. There were marked different in tensile strength for biocomposite prepared from fiber size of <150 μm and 250 – 355 μm, respectively. Biocomposite prepared with fiber size of <150 μm had tensile strength of 16.32 MPa, which is 35% stronger compared to the biocomposite with fiber size of 250 – 355 μm.

The decrease in tensile strength of the biocomposite has been attributed to two situations, namely agglomeration and poor dispersion of the fiber in the matrix, thus increasing fiber/fiber interaction which acts as stress risers and propagations sites for crack initiation (Khalid et al., 2008; Sumaila et al., 2013; Then et al., 2013).

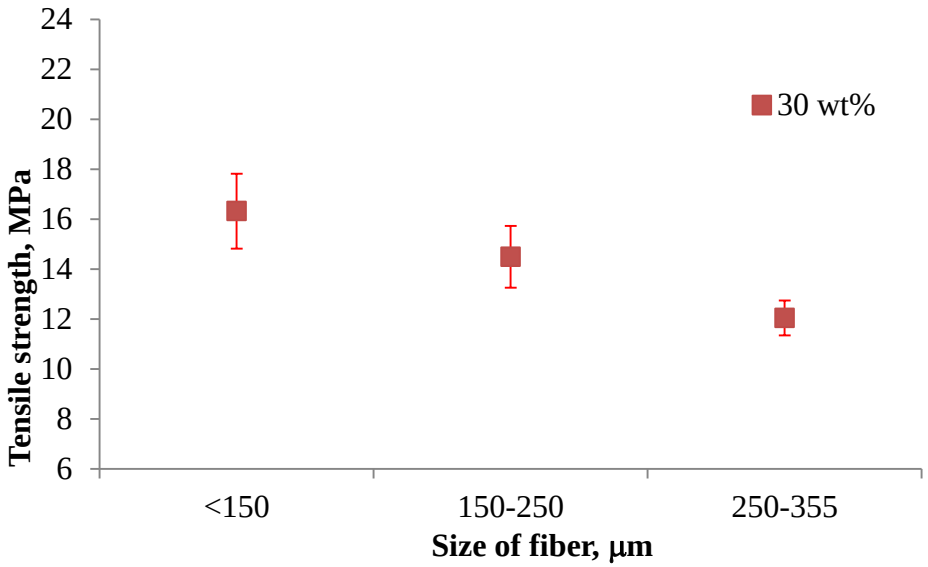

Figure 5.1: Tensile strength of untreated-OPMF/PP at different fiber size.

SEM images of biocomposite prepared from fiber size of <150 μm and 250 – 350 μm are shown in Figure 5.2 (a) and (b). Smaller size fiber had better arrangement (Figure 5.2a) compared to larger size of fiber (Figure 5.2b) which had random orientation. Voids and fiber pull-outs can easily observed from biocomposite prepared from fiber size of 250-350 μm. It was reported that void content increased with the increase in fiber size (Sumaila et al., 2013; Etaati et al., 2014). This could be attributed to improper fiber wetting and inability of the matrix material to coat at higher fiber length (Takagi and Ichihara, 2004; Shinoj et al., 2011), as can be seen in

Figure 5.2 (b). Smaller fiber size gave higher surface area per volume hence improved the surface contact between fibers and polymer matrix and subsequently, improved the physical adhesion between the two materials. Additionally, small size of OPMF may improve the stress transfer between polymer matrix and fibers compared to longer fibers.

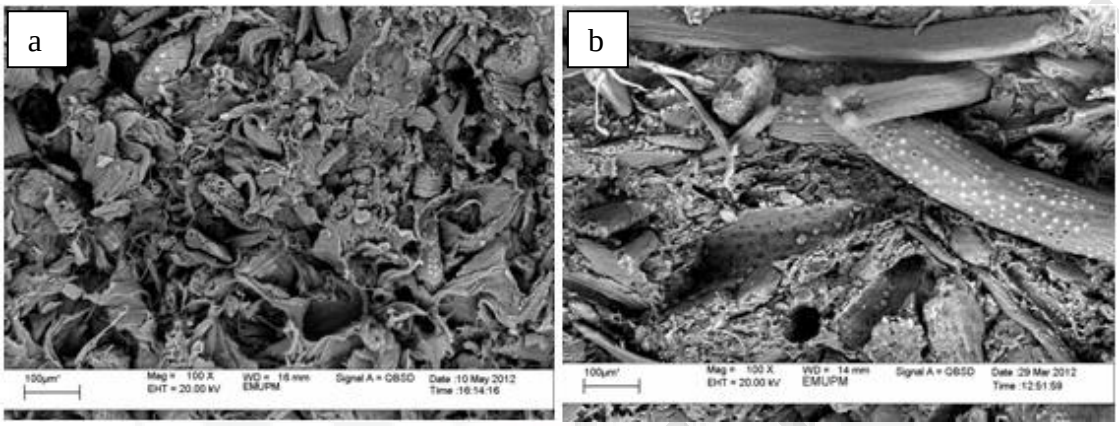

Figure 5.2: SEM micrographs of biocomposite prepared from different fiber size. (a) <150 μm - better fiber distribution and orientation, (b) 250 – 350 μm - fiber agglomeration and randomly orientated.

5.3.2 Effect of SHS treatment temperature on properties of OPMF/PP biocomposites

Effect of SHS temperature on the mechanical properties of OPMF/PP biocomposites was determined and the results are shown in Table 5.3. Overall results showed that the mechanical properties of SHS-OPMF/PP biocomposites were improved compared to untreated-OPMF/PP biocomposite, up to treatment temperature of 210 °C.

The mechanical properties of SHS-OPMF/PP were improved by 25% for tensile properties, 18% for tensile modulus, 45% for flexural strength, 3% for flexural modulus and 83% for impact strength when compared to untreated-OPMF/ PP. From Table 5.3, it is seen that SHS210-OPMF/PP biocomposite gave the highest tensile strength at 20.5 MPa. In term of tensile modulus, the increment was significant for SHS-OPMF/PP biocomposites compared to untreated-OPMF/PP biocomposite regardsless of the temperature used. Statistical analysis showed that there was no significant difference in flexural modulus for all samples. On the other hand, it was seen that the impact strength of SHS-OPMF/PP biocomposites (*i.e.* 190 °C sample) increased at almost one time higher than untreated biocomposites. However, upon addition of fiber treated at temperature over 220 °C, the impact strength was decreased to as low as 47 J/m.

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Table 5.3: Mechanical properties of OPMF/PP biocomposite samples[a, b].

Treatment temperature (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
Untreated	16.32 (1.87)^{B}	448.56 (10.49)^{B}	23.02 (2.27)^{C}	1329 (283)^{A}	44.10 (7.34)^{C}
190	17.45 (0.54)^{B}	524.94 (23.58)^{A}	30.90 (1.55)^{AB}	1327 (130)^{A}	86.85 (10.35)^{A}
200	17.72 (1.03)^{B}	522.92 (48.70)^{A}	32.15 (1.54)^{AB}	1428 (103)^{A}	82.52 (6.35)^{A}
210	20.47 (1.44)^{A}	531.46 (44.91)^{A}	33.44 (0.91)^{A}	1370 (112)^{A}	80.92 (5.37)^{A}
220	19.92 (0.29)^{A}	539.08 (9.62)^{A}	29.67 (1.26)^{AB}	1338 (142)^{A}	61.17 (7.54)^{B}
230	19.28 (0.75)^{A}	540.36 (13.97)^{A}	29.15 (1.18)^{B}	1273 (107)^{A}	46.55 (8.27)^{C}

[a] Standard deviation shown in parentheses.
[b] In superscripts, different letters in the same column indicate a statistical difference ($p < 0.05$) among the sample

Fiber-polymer physical interaction can be explained further by SEM micrographs of fractured samples from the tensile test (Figure 5.3).

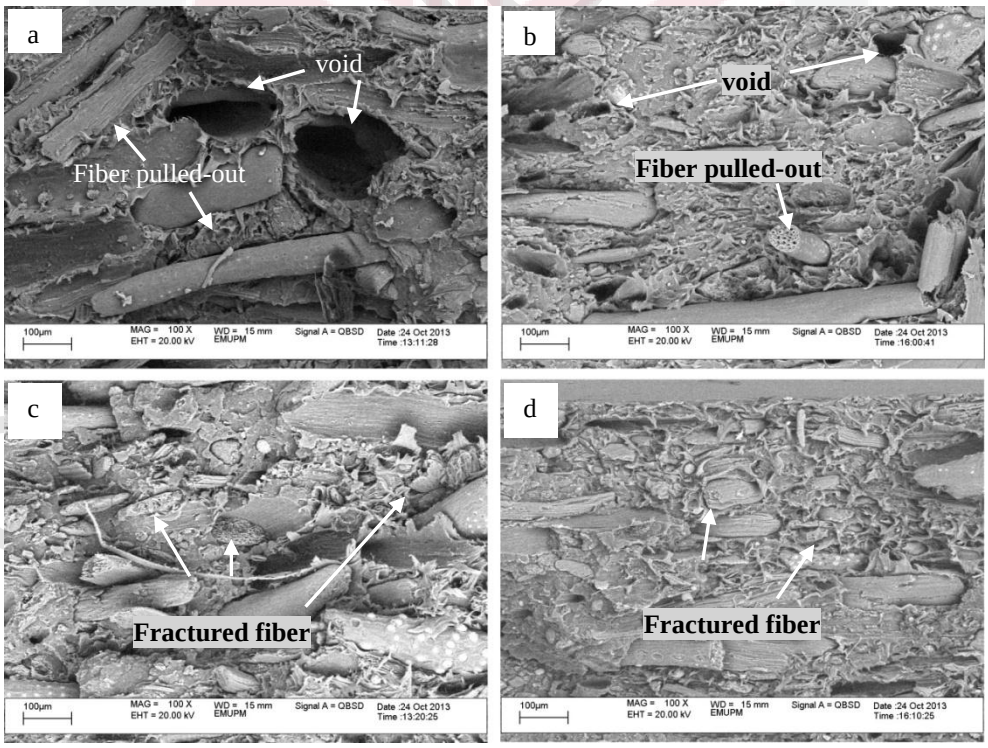

Figure 5.3: Fractured samples after tensile test of (a) untreated-OPMF/PP, fiber pulled-out, voids and gap between the fiber and PP easily can be observed; (b) SHS190-OPMF/PP, less fiber pulled-out and voids; (c) SHS210-OPMF/PP, fractured fiber can be observed; and (d) SHS230-OPMF/PP, showed less voids and gap.

It was observed that untreated OPMF in PP matrix was easily visible, and many of them were pulled out from the PP matrix during tensile test (Figure 5.3a). This implies that there was poor interfacial adhesion between polymer and untreated fiber which explains low mechanical properties of the biocomposites. It is also possible to observe distinct gaps between the fiber and the matrix that may explain low mechanical properties of biocomposites.

In contrast to SHS-treated fiber, there was less fiber pull-out as can be observed in Figures 5.3 (b – d). Figure 5.4a shows untreated biocomposite failure caused by matrix tearing only. However, for SHS-OPMF/PP biocomposites shown in Figure 5.4b, massive failures of both fibers and matrix in the form of fiber splitting and tearing could be observed.

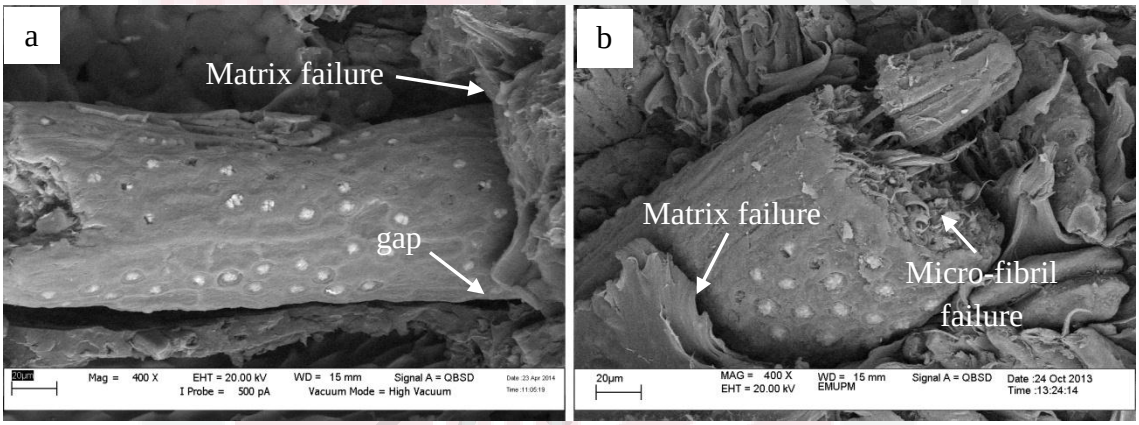

Figure 5.4: (a) Untreated-OPMF/PP biocomposite showed only matrix failure and (b) SHS-OPMF/PP biocomposite has good fiber-matrix adhesion indicated by micro-fibril and matrix failure.

The improved and decreased trends of the mechanical properties of the biocomposite can be contributed mainly by the alteration of the fiber chemical composition after SHS treatment. In previous chapter, it was shown that SHS treatment removed some hemicellulose, silica bodies and moisture from the fiber (Section 4.3.3). The reduction of hemicellulose content increased hydrophobicity of the fiber. Improved hydrophobicity of the fiber increased the mechanical properties of the biocomposite due to stronger physical interaction between fiber and polymer matrix (Khalid et al., 2008; Sinha and Rout, 2009; Then et al., 2014a). This explains why SHS-treated-OPMF/PP biocomposites had higher mechanical properties compared to untreated-OPMF/PP. Removal of silica bodies on the other hand would give rougher surface topography of the fiber which consequently increases the effective surface area for PP to adhere on the fiber surface. This is in agreement with Kaewkuk et al., (2013) where in their report the term ‘mechanical interlocking’ was used to explain the phenomenon. In order to further explain this, Figure 5.5 is drawn to show fiber-polymer interaction as the silica bodies were removed. As shown in the figure, silica removal causes the formation of crater which eventually provides space for polymer interlocking. This will result in stronger adhesion between polymer and fiber.

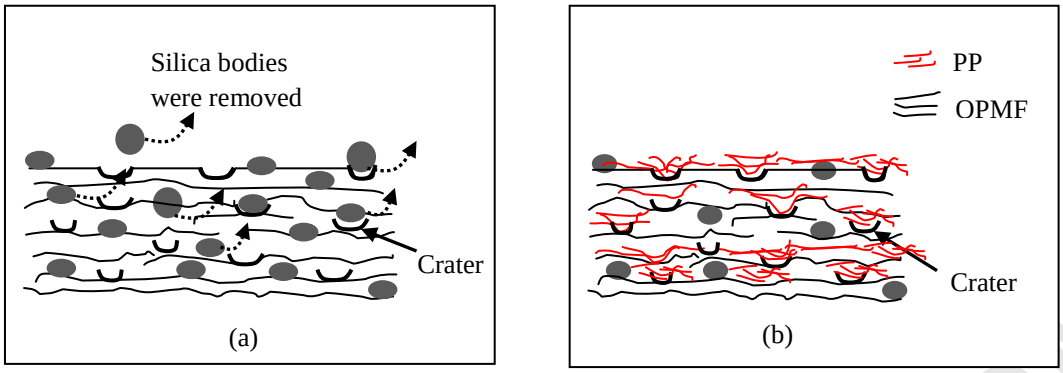

Figure 5.5: (a) During SHS treatment, silica bodies were removed and the crater formed. (b) During melt blending, crater acted as anchor for PP, hence improve the adhesion with fiber.

Another explanation for improved mechanical properties of SHS-treated biocomposites can be related to fiber dispersion within polymer matrix. Fiber with improved hydrophobicity is more compatible with the polymer, causing it to be easily dispersed within the matrix (Hosseinaei et al., 2012). Hydrophilic untreated-OPMF tends to agglomerate due to fiber-fiber interaction, causing it to be difficult to disperse in hydrophobic polymer matrix. Poor fiber dispersion results in the biocomposite to have uneven strengths, which is shown by untreated-OPMF biocomposite in Table 5.3. Figure 5.6 illustrated the possibility of fiber dispersion in SHS-treated and untreated biocomposite samples.

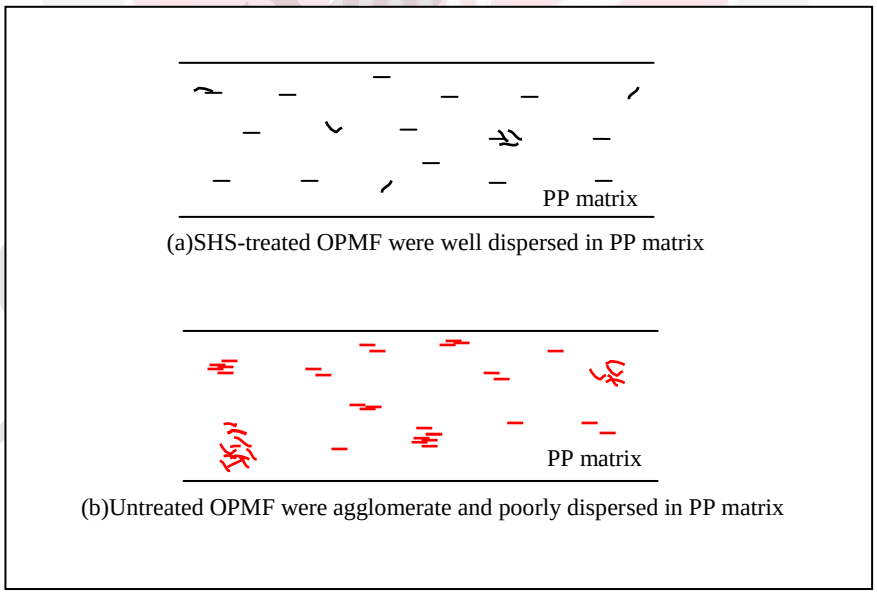

Figure 5.6: (a) SHS-treated OPMF were well dispersed, while (b) untreated-OPMF was easily agglomerated and poorly dispersed in PP matrix.

Table 5.4 shows melting point and crystallinity of the OPMF/PP biocomposites. An increased trend of biocomposites melting point can be seen from the table, and the

value eventually reached 169.2 °C which is near to the T_m of neat PP (169.5 °C). This shows that SHS-treated OPMF had better compatibility with PP compared to untreated-OPMF. It is interesting to note that the increment in melting point is consistent with the increased in SHS treatment temperature. This can be explained by improved compatibility between fiber and PP at higher SHS temperature, as more hemicellulose was removed at higher temperature as shown in Table 4.1 (Chapter 4).

Crystallinity of OPMF/PP biocomposite was increased when the samples were prepared from SHS-OPMF up to treatment temperature of 210 °C. The highest crystallinity was devoted to SHS200-OPMF/PP biocomposites where an improvement of almost 20% was recorded compared to that of untreated-OPMF/PP biocomposites. Increased in the crystallinity can be contributed by the removal of amorphous hemicellulose and low molecular weight lignin due to SHS treatment. On the other hand, biocomposites prepared from OPMF treated with SHS at high temperature (above 210 °C) had reduced crystallinity. This finding is in agreement with the results reported in Figure 4.9 (Chapter 4) suggesting the alteration of cellulose crystalline region at high treatment temperature, which subsequently affecting the biocomposite crystallinity.

Table 5.4: Melting point (°C) and crystallinity (%) of OPMF/PP biocomposite.

Sample	T_m(°C)	ΔH_m (J g^{-1})	X_c (%)
Untreated-OPMF/PP	162.9	49.7	24.3
SHS190-OPMF/PP	164.6	51.7	27.2
SHS200-OPMF/PP	165.1	55.0	28.9
SHS210-OPMF/PP	166.7	53.3	28.0
SHS220-OPMF/PP	167.0	45.5	23.9
SHS230-OPMF/PP	169.2	44.3	23.3

5.3.3 Effect of fiber loading on mechanical properties of OPMF/PP biocomposite

Effect of fiber loading (30 – 50 wt%) on mechanical properties of SHS-OPMF/PP biocomposites was conducted using sample of untreated OPMF and sample treated at 210 °C for 1h (SHS210-treated OPMF) and the results are shown in Table 5.5. Overall, it was seen that increased in fiber loading decreased the tensile strength, tensile modulus, flexural strength and impact strength of biocomposites prepared from both untreated and SHS210-treated OPMF. However, flexural modulus was improved for both samples as the fiber loading was increased.

Low mechanical properties for both biocomposites at high fiber loading can be explained by insufficient fiber wetting of PP matrix leading to poor stress transfer. Similar results were also reported by other studies which shows that the mechanical properties of biocomposites decreased when more fiber was added (Yang et al., 2007; Bengstsson et al., 2007; Islam et al., 2010; Mir et al., 2013; Etaati et al., 2014).

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Table 5.5: Mechanical properties of untreated-OPMF/PP and SHS210-OPMF/PP biocomposites at different fiber loading[a, b].

Sample	Fiber loading (wt%)	Tensile strength (MPa)	Tensile modulus (Mpa)
Untreated-OPMF/PP	30	16.32 (1.87)^{A}	449 (10)^{A}
	40	14.89 (0.89)^{B}	429 (15)^{B}
	50	13.43 (1.26)^{B}	375 (18)^{B}
SHS210-OPMF/PP	30	20.47 (1.44)^{A}	531 (45)^{A}
	40	16.92 (1.27)^{B}	525 (71)^{B}
	50	13.99 (1.06)^{C}	442 (26)^{C}

Table 5.5: (Cont.)

Sample	Fiber loading (wt%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
Untreated-OPMF/PP	30	23.02 (2.27)^{A}	1329 (283)^{B}	44.10 (7.34)^{A}
	40	22.58 (4.27)^{A}	1596 (133)^{A}	46.60 (6.61)^{A}
	50	20.97 (0.81)^{B}	1706 (69)^{A}	44.18 (4.80)^{A}
SHS210-OPMF/PP	30	33.44 (0.91)^{A}	1370 (112)^{B}	80.92 (5.37)^{A}
	40	27.63 (0.92)^{B}	1382 (49)^{B}	72.64 (11.02)^{B}
	50	23.83 (0.62)^{C}	1737 (58)^{A}	69.32 (5.30)^{B}

[a] Standard deviation shown in parentheses.
[b] In superscripts, different letters in the same column indicate a statistical difference ($p < 0.05$) among the samples. Statistical differences were analyzed between the fiber loading only for the same group of OPMF/PP biocomposite.

Additional explanation to the lower mechanical properties of biocomposites at high fiber loading is due to fiber agglomeration which creates void in the biocomposites. Fiber agglomeration at high fiber loading is the result of strong fiber-fiber interaction (Then et al., 2013; Kaewkuk et al., 2013). Based on these results, it is seen that effect of fiber loading on biocomposites mechanical properties is similar for both untreated and SHS-treated biocomposites. Even though compatibility of the PP-fiber was increased after SHS treatment but at higher fiber loading, agglomeration and poor wettability will be the strongest reason which provides a site for failure.

Flexural modulus was improved for both untreated and SHS-treated biocomposites when fiber content was increased. When fibers were incorporated into the polymer matrix, the biocomposites became stiffer and their flexural moduli were improved (Lee et al., 2013). Other studies also showed an increment of flexural modulus as fiber content was increased due to the stiffness of the fiber which may positively contribute to the overall stiffness of the biocomposite (Rozman et al., 2003; Bengstsson et al., 2007; Khalid et al., 2008; Then et al., 2013).

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5.3.4 Water absorption of OPMF/PP biocomposites

Untreated-OPMF/PP and SHS-OPMF/PP biocomposites were examined for their water absorption and the results presented in Figure 5.7. Overall, it is seen that percentage of water absorption was the highest for untreated OPMF biocomposite, followed by SHS190-OPMF/PP and SHS200-OPMF/PP biocomposite. A trend can be observed for SHS-treated OPMF biocomposites, whereby biocomposites contained OPMF treated at lower temperature range showed higher water absorption compared to biocomposites with OPMF treated at higher temperature.

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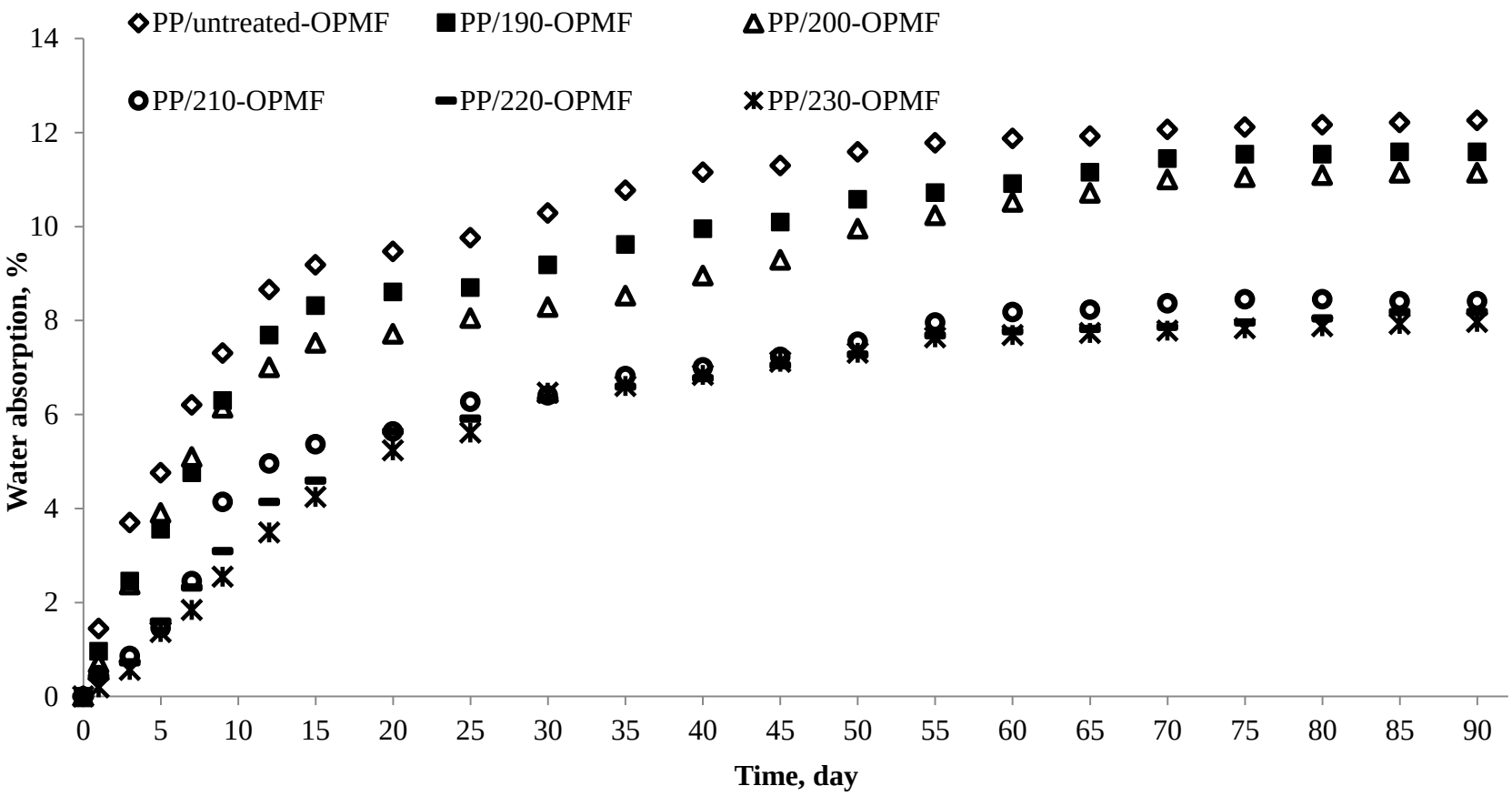

Figure 5.7: Water absorption of untreated-OPMF/PP and SHS-OPMF/PP biocomposites with addition of 30 wt% fiber loading at different SHS temperature.

To see the trend better, data for maximum water absorption results are tabulated in Table 5.6. This observation can be related to hemicellulose content in the OPMF. Hemicellulose has hydroxyl groups which caused the OPMF to be hydrophilic and able to absorb water. Untreated OPMF is generally hydrophilic, due to the presence of hydroxyl groups in hemicellulose. However, OPMF samples treated with SHS had less hemicellulose content (as shown in section 4.3.3), which may cause the biocomposite samples to be less hydrophilic and hence the results in Table 5.6.

Table 5.6: Maximum water absorption (%) of OPMF/PP* biocomposites after 90 days of soaking in water.

Biocomposite	Water absorption$_{max}$ (%)
untreated-OPMF/PP	12.26
SHS190-OPMF/PP	11.59
SHS200-OPMF/PP	11.14
SHS210-OPMF/PP	8.41
SHS220-OPMF/PP	8.18
SHS230-OPMF/PP	7.97

*Fiber size of <150 μm and 30 wt% fiber content

In order to better understand the relationship between hemicellulose content and water absorption (%), Figure 5.8 is drawn below.

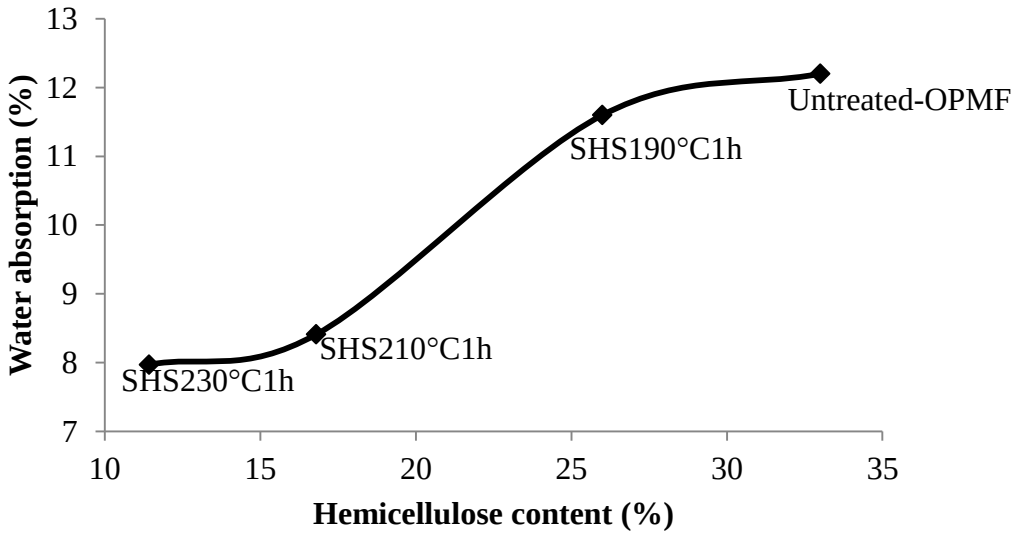

Figure 5.8: Relationship between hemicellulose content (%) and water absorption (%).

Based on Figure 5.8, it is clearly shown that higher hemicellulose content resulted in higher water absorption. Water molecules can easily attach to the hydroxyl groups of fiber through hydrogen bonding (Hosseinaei et al., 2012). Additionally, higher water absorption for untreated OPMF biocomposite can be explained by the poor adhesion

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between polymer and untreated fiber, resulted in void in the biocomposite and subsequently causing higher water absorption.

5.3.5 Thermal stability of untreated-OPMF/PP and SHS-OPMF/PP biocomposites

Biocomposite decomposition temperature was analyzed in order to determine its thermal stability as shown in Figure 5.9. The TG curve shows multiple degradation steps indicating the difference in decomposition temperature of components in the biocomposites. PP decomposition temperature range is from 350 °C until 450 °C (Morandim-Giannetti et al., 2012) as shown in Figure 5.10, the DTG thermogram of the biocomposites. Meanwhile, as being discussed in section 4.3.2 lignocellulosic components *i.e.* hemicellulose, cellulose and lignin degraded at temperature range of 160–900, 220–315 and 315–400 °C, respectively. These contributed to the multiple degradation steps of the biocomposites. Overall, TGA results showed that 210-OPMF/PP biocomposite had higher thermal stability compared to untreated-OPMF/PP. The comparison can be seen clearly from the magnified TGA curve in Figure 5.9. Untreated OPMF biocomposite started to degrade at 150 °C while 210-OPMF/PP biocomposite degraded later at temperature around 250 °C.

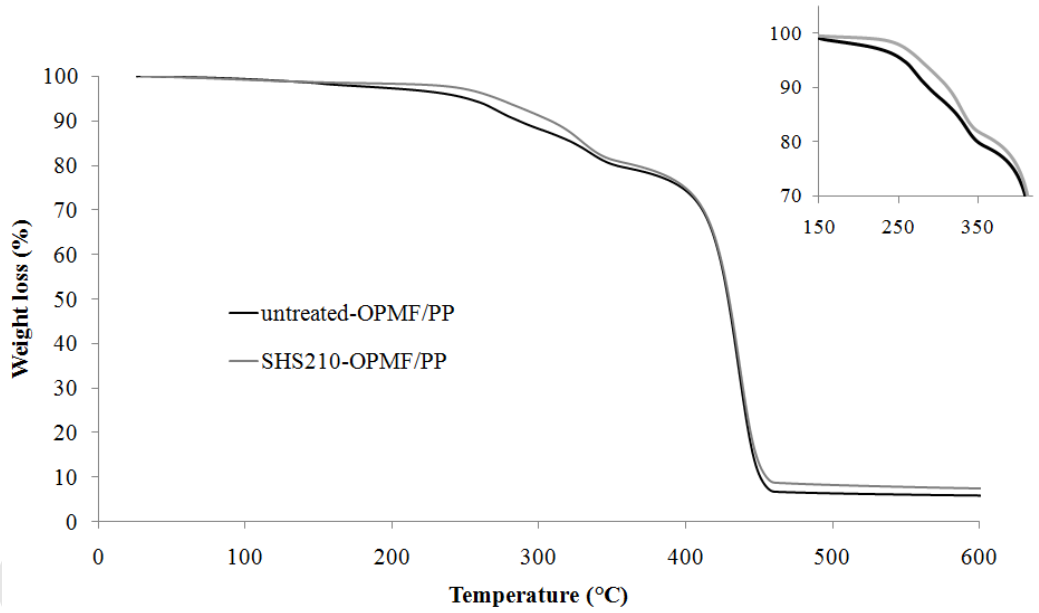

Figure 5.9: TGA of untreated-OPMF/PP and SHS210-OPMF/PP biocomposite (30 wt% of fiber loading).

This observation can be explained by thermally unstable hemicellulose content in the biocomposite. It was also demonstrated that 210-OPMF/PP biocomposite had higher residue at 550 °C, which is contributed by increased lignin composition in SHS-OPMF due to hemicellulose removal.

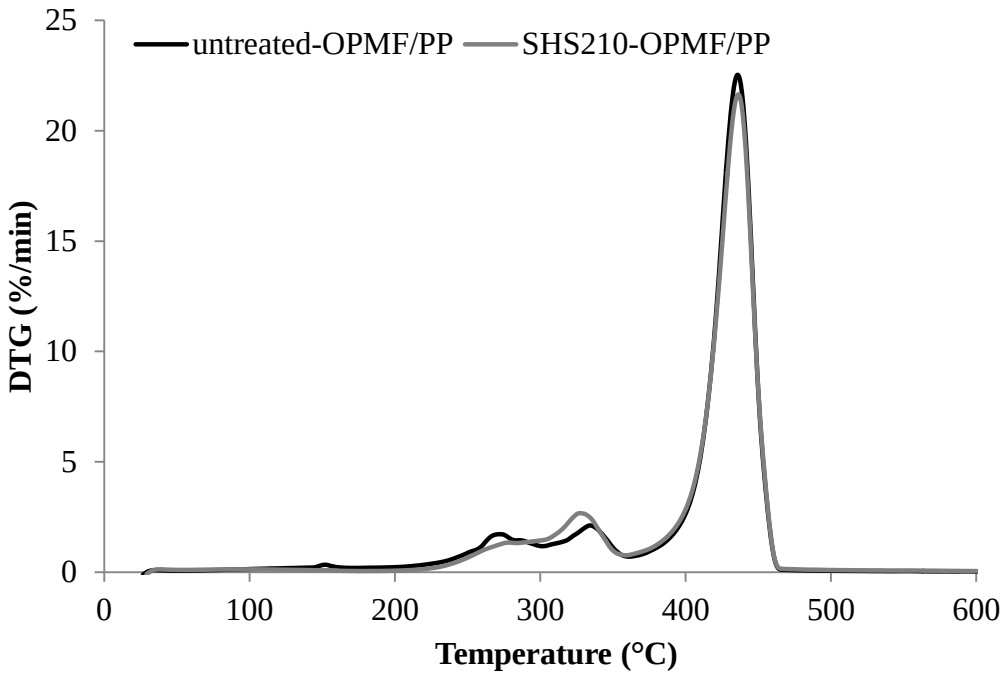

Figure 5.10: DTG thermogram of untreated-OPMF/PP and SHS210-OPMF/PP biocomposite.

5.4 Summary

Initial work conducted on effect of fiber size showed that fiber with size <150 um gave the highest tensile strength compared to fiber having higher particle size. SHS oven temperature during OPMF treatment was found to influence mechanical, thermal, crystallinity and water absorption properties of biocomposites produced. This is due to the effect of SHS on OPMF which contributed to the removal of hemicellulose and silica bodies. Removal of hemicellulose improved hydrophobicity of the fiber and hence, provided fiber surface which had higher compatibility with PP matrix compared to untreated OPMF. Removal of hemicellulose also caused the biocomposite to have better thermal stability and absorbed less water. On the other hand, silica removal caused the formation of crater and provided rough surface on the fiber for PP to anchor on the fiber. This will lead to better surface interaction between PP and OPMF. Overall biocomposite produced from SHS-treated OPMF (SHS210-OPMF/PP) had higher tensile strength, tensile modulus, flexural strength and impact strength by 25%, 19%, 43% and 84%, respectively, compared to untreated-OPMF/PP. Mechanical properties of OPMF/PP biocomposites were affected by the percentage of fiber loading. The higher fiber loading will reduced the overall mechanical properties of SHS-OPMF/PP and untreated-OPMF/PP biocomposite.

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CHAPTER 6

FEASIBILITY OF SUPERHEATED STEAM TREATMENT FOR IMPROVED BIOCOMPOSITE MECHANICAL PROPERTIES IN COMPARISON TO CHEMICAL TREATMENT

6.1. Introduction

As discussed in Chapter 4 and 5, the hydrophilic characteristic of natural fiber has caused them to be incompatible with hydrophobic polymer which may lead to weak fiber-matrix interfacial adhesion and poor mechanical properties (Rozman et al., 2001). Treatment of fiber for its surface modification has been widely studied, such as physical (Gassan and Gutowski, 2000; Sinha and Panigrahi, 2009), hydrothermal treatment (Robin and Breton, 2001; Rong et al., 2001; Then et al., 2014) and chemical treatment (Mishra et al., 2002; Bledzki et al., 2008; Alix et al., 2009; Bachtiar et al., 2013). The most common methods used for surface modification of fiber is chemical treatment due to its rapidity and effectiveness in modifying fiber surface. Among the methods used in chemical treatment of natural fiber are grafting with different monomers (Doan et al., 2006; Cantero et al., 2003), silanization (Rong et al., 2001; Valaaez-Gonzalez et al., 1999), alkalization (Gassan and Bledzki, 1999; Sreekala and Thomas, 2003; Mohanty et al., 2004; Arbelaiz et al., 2005; Alvarez and Analia, 2006; Taha et al., 2007) and acetylation (Bledzki et al., 2008). Of all of these treatments, alkalization is the most commonly used as it is an economical treatment method for natural fibers (Alvarez and Analia, 2006). It has been reported that alkaline treatment of fiber improved thermal stability, water permeability and mechanical properties of the biocomposites (Alix et al., 2009; Islam et al., 2012). Sodium hydroxide (NaOH) is one of the mostly used alkali. Treatment of fiber with NaOH causes hemicellulose and lignin components to be extracted out and thus revealing reactive functional groups like hydroxyl groups. NaOH reacts with accessible hydroxyl groups, hence the hydrophilic hydroxyl groups are reduced and increase the resistance of the fiber towards moisture (John and Anandjiwala, 2008; Islam et al., 2012).

In previous chapters, it has been shown that SHS treatment could be an effective treatment method for modification of OPMF which lead to improved properties of biocomposites. It is hence in this chapter, feasibility of SHS for surface modification of OPMF is studied in comparison with chemical treatment methods. Four chemical treatments were selected, *i.e.* treatment with NaOH, KOH, $NaClO_2$ and combined treatment of $NaClO_2$ and KOH. Each treatment has its own effect on natural fiber composition. It is therefore, this study was aimed at investigating the effect of lignocellulose composition on mechanical and thermal properties of OPMF/PP biocomposite. Results obtained were compared with those of SHS-treated OPMF in order to determine the feasibility of SHS treatment for surface modification of natural fiber.

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6.2. Experimental

Different fiber treatments were done to investigate the influence of fiber components on the properties of biocomposites. Three different chemicals were used *i.e.* NaOH, KOH and $NaClO_2$. NaOH (4 wt%) and KOH (6 wt%) were aimed for hemicellulose removal (Mohan and Kanny, 2012; Kaewkuk et al., 2013) while $NaClO_2$ (5 wt%) functions to remove lignin (Kabir et al., 2012; Li et al., 2007). The fourth treatment involved two-stage treatment *i.e.* $NaClO_2$ followed by KOH treatment which was expected to remove both lignin and hemicellulose. The summary of chemical treatments conducted is listed in Table 6.1.

Table 6.1: Chemical treatment used to treat OPMF.

Treatment	Designation
NaOH	NaOH-HR OPMF
KOH	KOH-HR OPMF
$NaClO_2$	$NaClO_2$-LR OPMF
$NaClO_2$ + KOH	($NaClO_2$+KOH)-OPMF

Note:
HR- hemicellulose removed
LR-lignin removed

6.2.1 Sodium hydroxide treatment

OPMF were soaked and stirred in a 4% NaOH solution at room temperature for 3 h with ratio of fiber to solution of 1:50 (Jacob et al., 2004). Treated OPMF was then filtered and washed several times with tap water until the pH of the water reached pH 7. The treated fiber was then dried in an oven at 60 °C and kept in sealed bag at room temperature prior to use.

6.2.2 Potassium hydroxide treatment

The OPMF was treated in 6 wt% KOH solution at a ratio of 1:50 (Fahma et al., 2010). The immersed sample was stirred for 24 h. The treated OPMF was then filtered and washed with tap water until the water pH became neutral. The fiber was then oven dried at 60 °C. Dried fiber was then kept in a sealed bag at room temperature prior to use.

6.2.3 Sodium chlorite treatment

OPMF was immersed in 5 wt% $NaClO_2$ solution (pH adjusted to 4 ~ 5 by adding a few drops of 98% H_2SO_4) at 70 °C for 1½ h to remove lignin (Fahma et al., 2010). The treated OPMF was then filtered and washed with tap water until the water pH became neutral. Sample was then dried in an oven and kept in a sealed bag.

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6.2.4 Two-stage treatment : $NaClO_2$ followed by KOH

To isolate cellulose fiber from OPMF, chemical treatment was done in two steps. The first step was $NaClO_2$ treatment for lignin removal conducted as described in section 6.2.3. The dried $NaClO_2$-treated OPMF was then treated with KOH to obtain cellulose fiber as detailed in section 6.2.2. Finally, the cellulose fiber was oven dried at 60 °C.

6.2.5 Characteristics of chemically-treated fiber

Chemically treated-OPMF were analyzed by using FTIR and SEM as described in Section 3.4.3 and 3.4.6, respectively.

6.2.6 Biocomposites preparation

Biocomposites of chemically-treated fiber were prepared according to the procedure stated in Section 3.5. Fiber size and loading were fixed to <150 μm and 30 wt%, respectively. This was based on the finding from Chapter 5 where fiber size of <150 μm and at 30 wt% fiber loading resulted in the best mechanical properties. Table 6.2 lists the biocomposites prepared from chemically-treated samples.

Table 6.2: Biocomposite samples of chemically-treated OPMF and PP.

Sample	Biocomposite
NaOH-HR OPMF	NaOH-OPMF/PP
KOH-HR OPMF	KOH-OPMF/PP
$NaClO_2$-LR OPMF	$NaClO_2$-OPMF/PP
($NaClO_2$+KOH)-OPMF	($NaClO_2$+KOH)-OPMF/PP

Note:
Prepared with fiber size <150 μm and 30 wt% fiber loading

6.2.7 Analyses of chemically-treated OPMF/PP biocomposites

Biocomposites were analyzed for their mechanical, crystallinity and morphological properties. Detailed procedures were explained in Section 3.6.

6.2.8 Statistical analysis

The significant effect of the mechanical properties of the biocomposites was performed on Mstat software. The detailed was described in Section 3.7.

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6.3. Results and Discussion

6.3.1 Characteristics of biocomposites from chemically-treated OPMF

Different treatments were conducted to evaluate the influence of changes in fiber chemical composition on biocomposites properties. Biocomposites from chemically-treated OPMF were tested for their mechanical, morphological properties and crystallinity.

Table 6.3 shows mechanical properties of biocomposites prepared from chemically-treated OPMF with PP. Treatment with NaOH and KOH reduced hemicellulose component in OPMF. While treatment by $NaClO_2$ and two-stage ($NaClO_2$+KOH) treatment were aimed to reduce lignin and lignin+hemicellulose component, respectively.

Results showed that NaOH and KOH biocomposites gave similar mechanical strength and in overall, the properties were better compared to those of untreated-OPMF biocomposite (Chapter 5). Flexural strength, flexural modulus and impact strength of ($NaClO_2$+KOH)-OPMF/PP was similar with alkaline-treated OPMF. The lowest mechanical properties were demonstrated by $NaClO_2$-OPMF/PP biocomposite and was significantly different with others biocomposite.

Table 6.3: Mechanical properties of chemically-treated OPMF/PP biocomposites[a,b].

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
NaOH-OPMF/PP	18.91^{A} (1.17)	515.50^{A} (57.36)	32.75^{A} (1.16)	1336.4^{B} (69)	78.95^{A} (5.19)
KOH-OPMF/PP	19.64^{A} (1.26)	515.10^{A} (28.88)	29.34^{A} (1.35)	1311.2^{B} (60)	77.96^{A} (6.25)
$NaClO_2$-OPMF/PP	15.38^{C} (0.88)	424.46^{B} (35.8)	24.88^{B} (2.53)	1330.2^{B} (166)	49.30^{B} (2.79)
($NaClO_2$+KOH)-OPMF/PP	16.77^{B} (1.44)	451.38^{B} (45.96)	32.37^{A} (2.84)	1549.4^{A} (71)	76.50^{A} (6.35)

[a] Standard deviation shown in parentheses.
[b] In superscripts, different letters in the same column indicate a statistical difference ($p < 0.05$) among the samples.

Removal of hemicellulose by alkaline treatment led to the improvement in the characteristic of lignocellulose and subsequently demonstrated an increment in mechanical properties of the biocomposites (Martins et al., 2006; Xinwen et al., 2010; Ibarra et al., 2010).

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Equivalent mechanical properties showed by both NaOH and KOH treatments indicate that the treatments had similar effect on hemicellulose removal from OPMF. Crystallinity of NaOH-OPMF and KOH-OPMF biocomposites were also tested and the X_c recorded was almost similar at 25% and 26%, respectively.

It was demonstrated that alkaline treatment of sisal fiber led to fibrillation of fiber, where the packed untreated fiber splitted after the fiber treatment (Cao et al. 2006). The fibrillation of fiber provided more space for PP-fiber contact (Norul-Izani et al., 2013). Additionally, Kaewkuk et al. (2013) reported that removal of surface impurities and wax after alkaline treatment were advantageous for fiber and matrix adhesion as it facilitated the physical interlocking. Based on these discussions, it is concluded that fiber treatment with either NaOH or KOH could lead to better fiber and polymer interaction and hence, improved in biocomposite mechanical properties.

Cellulose-OPMF derived by two-stage treatment had significant effect on mechanical properties of the biocomposite. Studies done by Xu and colleague (2013) reported that cellulose fibril tends to entangle in the matrix. Interestingly, these entanglements play an important role in stress transfer from matrix to cellulose fibrils, and from fibrils to fibrils which gave higher flexural and impact strength to the biocomposites. These explained the high flexural and impact strength of the ($NaClO_2$+KOH)-OPMF/PP, where the cellulose fibril contributed to the stress transfer between fiber and matrix. In term of crystallinity, X_c it was found that ($NaClO_2$+KOH)-OPMF/PP biocomposite had 29% crystallinity which was higher than alkaline-treated OPMF biocomposites, which could contribute to high flexural and impact strength. ($NaClO_2$+KOH)-OPMF/PP biocomposite demonstrated low tensile strength and modulus might because of hydrophilic character of cellulose. This caused poor compatibility of fiber with the polymer.

$NaClO_2$-OPMF/PP biocomposite on the other hand gave lower mechanical properties. It was reported by Sun et al. (2004) and Pejic et al. (2008) that $NaClO_2$ treatment was efficient to reduce lignin content. Lignin contains non-polar hydrocarbon and benzene rings making it to be less hydrophilic (Rozman et al., 2001, Mishra et al., 2002). Without lignin the fiber has less ability to adhere with hydrophobic polymer (Then et al., 2015).

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Physical interaction between OPMF and PP can be observed by examining fiber pull-out of fractured fiber-matrix interface regions after tensile test. Figure 6.1 shows the micrographs of the NaOH-OPMF/PP and KOH-OPMF/PP biocomposite.

It was clearly observed that the alkaline-treated OPMF were fractured, showing that the fiber had good adhesion with the PP (Mohan and Kanny, 2012; Norul Izani et al., 2013). Failure of the matrix which coated the fiber was also observed, where it was found that the matrix was stretched and broke off as observed in Figure 6.1 (a-ii) and (b-ii). On top of that, there was less void presence in the biocomposites.

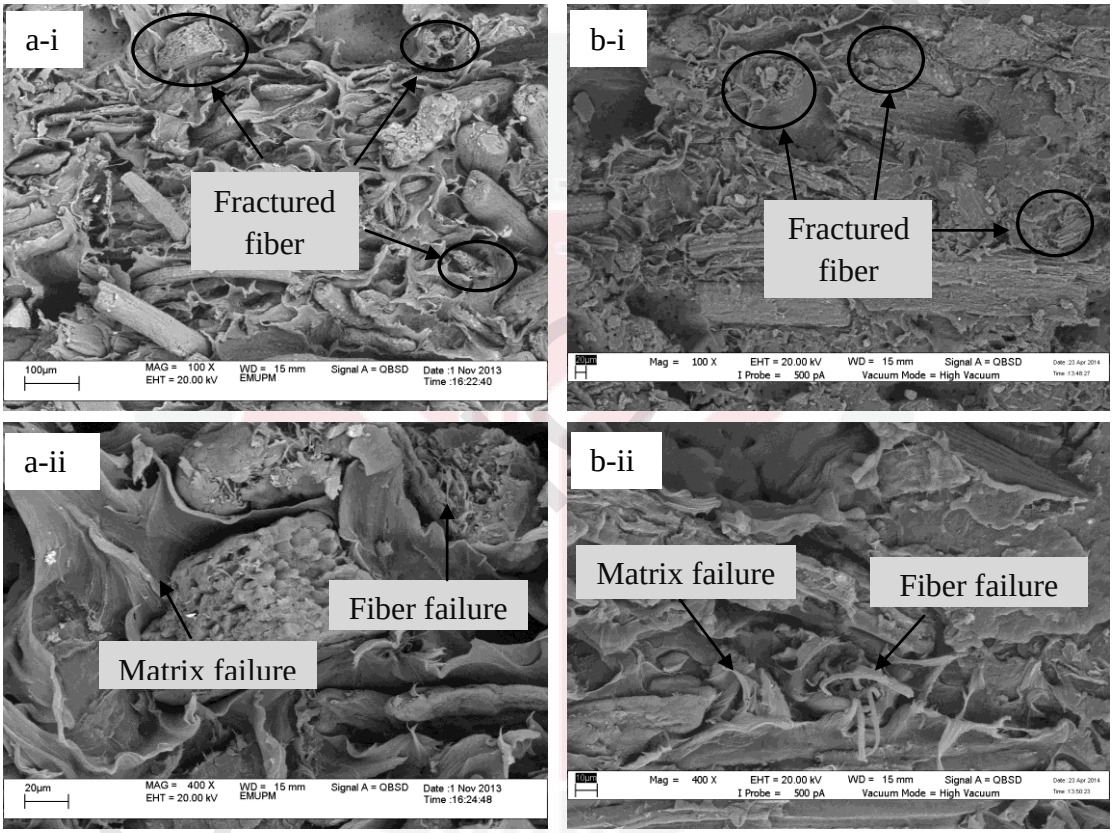

Figure 6.1: Fractured samples from tensile test of (a-i,ii) NaOH-OPMF/PP biocomposite and (b-i,ii) KOH-OPMF/PP biocomposite, shows good fiber-PP interaction by observing the failure of fiber and matrix.

Figure 6.2 (ai-ii) shows SEM images of $NaClO_2$-OPMF/PP biocomposite where fiber pull-outs and voids formation were clearly observed. ($NaClO_2$+KOH)-OPMF/PP biocomposite in Figure 6.2 (b i-ii) show the presence of cellulose fibril contributed to higher flexural and impact properties.

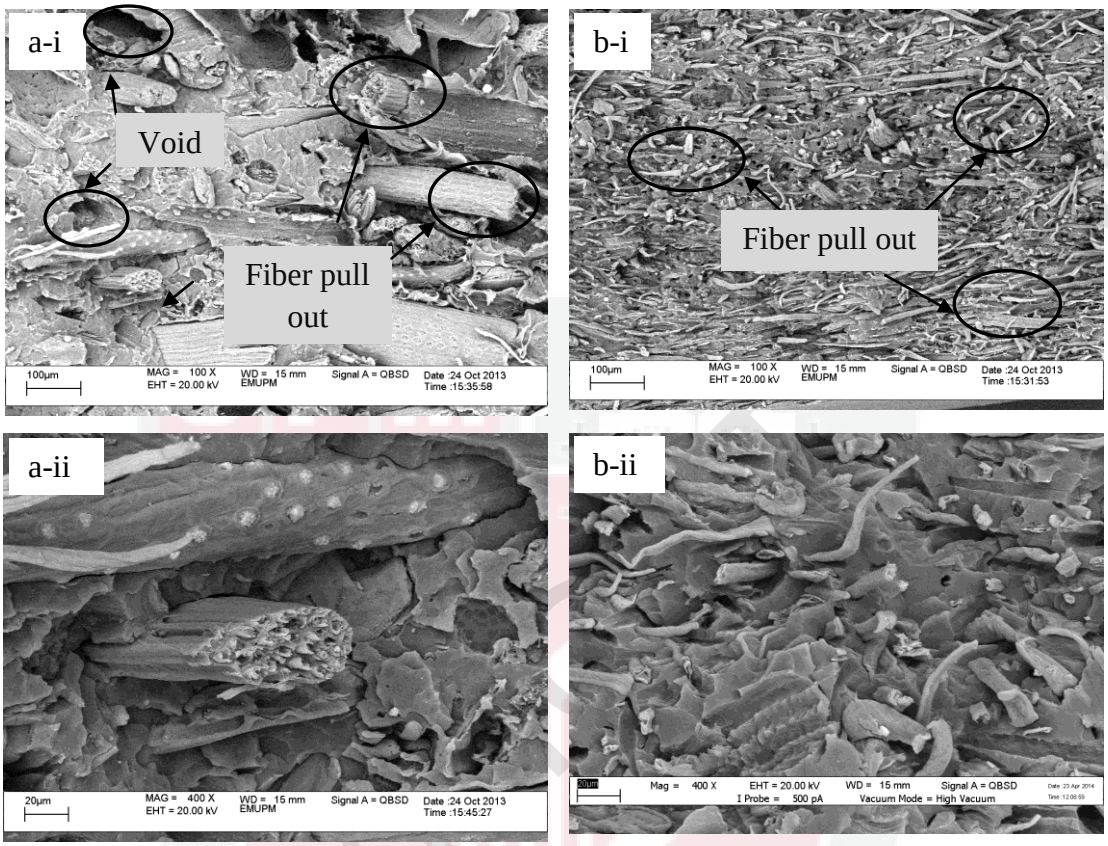

Figure 6.2: Fractured samples from tensile test of (a-i,ii) $NaClO_2$-OPMF/PP biocomposite and (b-i,ii) ($NaClO_2$+KOH)-OPMF/PP biocomposite, shows fiber pull-out and voids existed between the fiber and matrix.

Figure 6.3 illustrates the peaks of chemically-treated OPMF from FTIR analysis. The strong peak at 3330 cm^{-1} was characterized by the hydrogen bonded hydroxyl group (OH) mostly present in remaining hemicellulose and cellulose (Hosseinaei et al., 2012). The peak at 2950 cm^{-1} was due to C-H stretching vibration of all hydrocarbon constituents of the fibers.

Peak at 1730 cm^{-1} was portrayed due to C=O stretching mainly in hemicellulose. The low intensity of the peak reflects the low content of hemicellulose presence in the alkaline-treated OPMF and ($NaClO_2$+KOH)-OPMF sample. On the other hand, the 1730 cm^{-1} peak was clearly seen for $NaClO_2$-OPMF sample shows that the pronounced components in the sample were cellulose and hemicellulose. The appearing peaks at 1450 and 1613 cm^{-1} were due to C=C symmetric (aromatic skeletal) in lignin (Chen et al., 2014). The FTIR results reflected that the major components presence in alkaline-treated OPMF were cellulose and lignin.

Based on the results, it can be concluded that fiber treatment by $NaClO_2$ (lignin removal) caused the biocomposite to have lower mechanical properties compared to biocomposites prepared from fiber treated with ($NaClO_2$+KOH) and alkali. This shows the importance to retain lignin component during treatment prior to biocomposite production to ensure good mechanical properties of biocomposites produced.

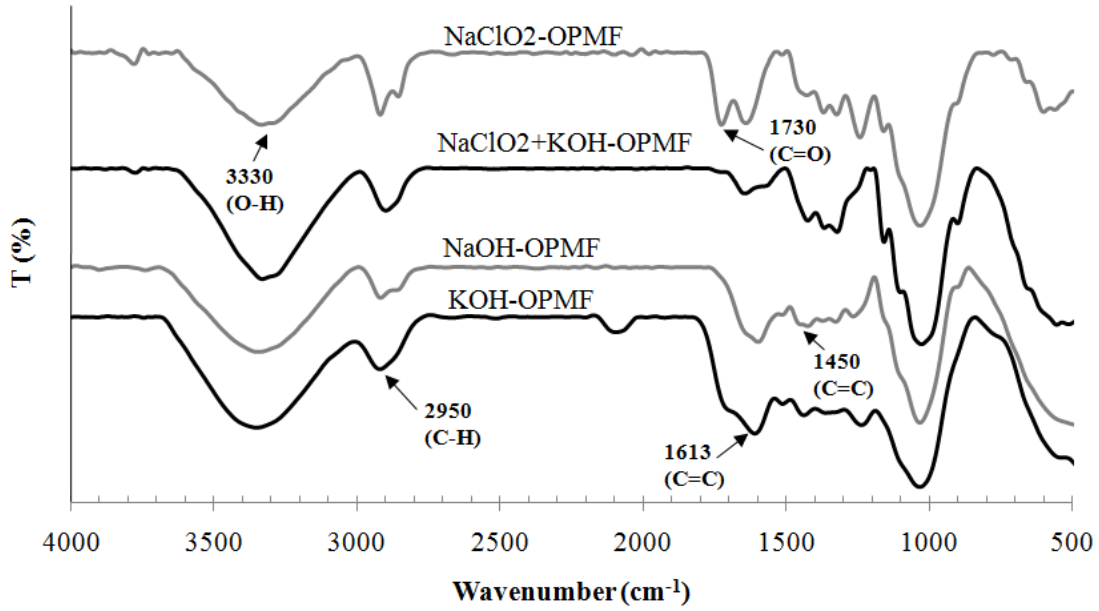

Figure 6.3: FTIR spectra of chemically-treated OPMF.

6.3.2 Comparison of NaOH and SHS treatments for biocomposite production

6.3.2.1 Biocomposite properties

In earlier section, it has been shown that chemical treatment contributed to the characteristics of biocomposites produced. It was shown that alkaline treatment by both KOH and NaOH showed almost similar results in term of mechanical properties, indicating that both of the chemicals had similar effect on lignocellulose treatment. It was also discussed that alkaline treatment is generally used for surface modification of natural fiber, aimed at hemicellulose removal to make the fiber to be more hydrophobic.

In Chapter 4, the use of SHS treatment for hemicellulose removal was discussed. Results showed that SHS has the capability in removing hemicellulose from fiber, indicating that SHS can be an option for surface modification of fiber other than alkaline treatment. In this section, comparison of alkaline and SHS treatment methods is discussed in order to further justify the potential of SHS as an additional option for surface modification of fiber aiming at hemicellulose removal.

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Comparison of the two methods is discussed in terms of mechanical properties and crystallinity of biocomposites prepared from SHS210-OPMF and NaOH-OPMF, and the results are shown in Table 6.4. Overall results showed that biocomposites prepared from SHS210-OPMF/PP and NaOH-OPMF/PP exhibited remarkable improvement in mechanical properties and crystallinity compared to untreated-OPMF/PP biocomposite. It is interesting to note that there was no significant difference in term of mechanical properties tested between SHS- and alkaline- treated samples. This proves that both SHS and alkali gave similar effect on OPMF in term of hemicellulose removal.

Table 6.4: Mechanical properties and crystallinity of OPMF/PP biocomposites[a,b].

Treatment	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)	Crystallinity (%)
Untreated	16.32^{B} (1.87)	448.56^{B} (10.49)	22.57^{B} (2.24)	1328.8^{A} (283)	44.10^{B} (7.34)	24.3
SHS210-OPMF	20.47^{A} (1.44)	531.46^{A} (44.91)	33.40^{A} (0.91)	1370.4^{A} (111)	80.92^{A} (5.37)	28.0
NaOH-HR OPMF	18.91^{A} (1.17)	515.50^{A} (57.36)	32.75^{A} (1.16)	1336.4^{A} (69)	78.95^{A} (5.19)	25.2

[a] Standard deviation shown in parentheses.
[b]In superscripts, different letters in the same column indicate a statistical difference ($p < 0.05$) among the samples.

From Table 6.4, it is seen that SHS210-OPMF biocomposite had higher crystallinity compared to NaOH-OPMF. This can be explained by the disruption of crystalline region in lignocellulose sample during NaOH treatment (Norul Izani et al., 2013). Even though it was shown in section 4.3.3 that SHS also had similar effect, however the disruption occurred only at high temperature, *i.e.* above 210 °C. This gives an advantage to SHS treatment as compared to NaOH treatment.

6.3.2.2 Treatment methods

In order to compare alkaline and SHS treatment methods, six criteria were taken into consideration: effectiveness of treatment, treatment agent, green technology, energy consumption, safety level and environmental aspect. The criteria are summarized in Table 6.5.

Criteria used in this comparison were selected based on the common issues discussed on treatment of lignocellulosic materials for biocomposite production (Han et al., 2009; Hosseinaie et al., 2011; Bahrin et al., 2012; Then et al., 2014b). Overall, SHS treatment scored higher compared to NaOH treatment, despite the effectiveness of

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both treatment methods for surface modification of natural fiber. SHS treatment method is considered as a green technology as it does not involve the use of hazardous chemicals. Moreover, the method meets five of twelve principles of green chemistry (Francesca, 2008).

Table 6.5: Comparison of SHS and alkaline treatment methods.

Criteria	SHS treatment	NaOH treatment
Treatment agent	Steam	Alkali (NaOH)
Effectiveness of treatment (hemicellulose removal)	1	1
Green technology (non-chemical)	1	0
Energy consumption	0 (High energy)	1 (Low energy)
Safety level	1	0
Waste generation	1	0
Total score	**4/5**	**2/5**

Note: 1 – Yes (positive impact)
0 – No (negative impact)

Principle number 1 stressed on waste prevention issues. Under this principle, it is mentioned that waste prevention is better than waste treatment. The use of SHS will prevent generation of wastewater, in contrary with the use of NaOH treatment. The use of NaOH will lead to the generation of wastewater containing degradation products of lignocellulose which need to be treated.

The next principle listed in green chemistry that is related to the study is the Principle number 3 highlighted on less hazardous treatment. SHS is less hazardous treatment method as it does not involve the use of hazardous chemicals. Principle number 5 mentioned on the usage of safer solvents / agents. As SHS does not involve the use of chemicals, it is relatively safer to the operator and environment to use SHS compared to chemical.

SHS treatment also meets Principle number 8 of green chemistry which is reduced derivatives. Degradation of hemicellulose due to SHS or alkaline treatment will cause the formation of hemicellulose degradation products such as acids and furfural. The derivatives concentration will be reduced in SHS treatment as in SHS treatment, the products will be diluted by steam, while in NaOH, more chemical elements are found due to the presence of NaOH.

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Safety issues which are stated in Principle number 12 related to accident prevention: SHS treatment is conducted at atmospheric pressure and hence is it safe to be operated. On the other hand, NaOH treatment involves the use of corrosive chemical.

Even though SHS treatment seems to be more advantageous compared to NaOH treatment, there is one shortcoming of SHS treatment *i.e.* it involves high energy consumption. In the next section (section 6.3.3.3), an integrated process is proposed in order to overcome the shortcoming.

All in all, it is demonstrated that SHS treatment method is effective, safe and environmentally friendly and could be an alternative treatment for modification of fiber prior to biocomposite production.

6.3.3 Potential of SHS-OPMF for biocomposites production

This section discusses the feasibility of OPMF as a feedstock for biocomposite production.

6.3.3.1 Properties of biocomposite from SHS-OPMF

OPMF treated with SHS had improved hydrophobicity due to reduction in hemicellulose content. It has been shown in Chapter 5 that changes in chemical composition of OPMF due to SHS treatment improved the overall properties of the OPMF. Table 6.6 shows the summary of SHS-treated OPMF properties. From the table, it is exhibited that SHS-treated OPMF had better hydrophobicity, higher thermal stability, reduced silica content and higher crystallinity compared to untreated OPMF.

Table 6.6: Summary of SHS-treated OPMF and untreated-OPMF properties.

Properties	Untreated OPMF	SHS210-OPMF	Remark*
Hemicellulose content (%)	33	17	48% reduced
Lignin content (%)	20	45	120% increased
$T_{5\%}$ (°C)	258	276	7% improved
Residue at 550 °C (%)	22	37	68% higher
Silica bodies (ppm)	225	204	9% reduced
Crystallinity (%)	76	84	11% higher

*Note : Comparison between SHS210-OPMF and untreated-OPMF.

It was also demonstrated in Chapter 5 that biocomposite prepared from SHS-treated OPMF had better mechanical properties compared to untreated-OPMF/PP biocomposite. The summary is shown in Table 6.7.

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Table 6.7: Improvement of SHS210-OPMF/PP biocomposite* compared to untreated-OPMF/PP biocomposite.

Mechanical properties	Untreated-OPMF/PP	SHS210-OPMF/PP	Remark
Tensile strength (MPa)	16.32	20.47	25% improved
Tensile modulus (MPa)	448.56	531.46	18% improved
Flexural strength (MPa)	22.57	33.40	48% improved
Flexural modulus (MPa)	1328.8	1370.4	3% improved
Impact strength (J/m)	44.10	80.92	83% improved

*Fiber size <150 μm, 30 wt% fiber loading

Generally, mechanical properties of SHS210-OPMF/PP biocomposite improved from 3 to 83%. A remarkable improvement was shown by flexural and impact strength by 48 and 83%, respectively. The result is in agreement with Eslam et al. (2011) who reported that biocomposite prepared from saturated-steam-treated cotton flour with PP had flexural strength improved by 40%. Another study showed that tensile strength of biocomposite from wood fiber treated with hot water improved by 12% (Hosseinaei et al., 2012).

There are various applications of natural fiber, such as in automotive industry, construction, industrial engineering, sports and recreation, packaging and electric-electronics industries. The advantage of natural fiber biocomposites is due to its unique properties that can be suited to desirable application. SHS-OPMF/PP biocomposites demonstrated good mechanical properties especially in term of impact strength. Thus, the most suitable application would be for non-structural application. Non-structural appliances do not require biocomposite with high tensile and flexural strengths (Hughes, 2000). Based on finding obtained from this study, it is suggested that SHS-OPMF/PP bicomposites adequately suitable for non-structural applications as listed:

- Automotive industries : Door panel, boot and roof liner
- Construction : Floor panel
- Electric and electronic : Computer, projector, audio and handphone casing
- Consumer products : Toys, stationary casing

6.3.3.2 Availability of OPMF in Malaysia

Malaysia is one of the world's largest palm oil exporters. With the growth of palm oil production in Malaysia, the amount of residues generated shows a corresponding increment. Approximately 445 palm oil mills are currently operating in Malaysia (MPOB, 2016).One hectare of oil palm plantation can produce about 50 – 70 tonnes of biomass fiber (Shinoj et al., 2011) which appears to be a very promising alternative as a source of raw material in Malaysia (Shuit et al., 2009). It was reported that for every tonne of FFB processed, it will produce about 7 - 15% (w/w) of OPMF and 8% of palm kernel shell (Zakaria et al., 2014). It is expected the

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biomass fiber might reach 100 million dry metric tonnes (MT) per annum by 2020 with the total solid biomass increment of 26 million metric tonnes (dry) (Hassan and Shirai, 2003; Agensi Inovasi Malaysia, 2013).

From the same report, the largest biomass generation is from oil palm plantation *i.e.* frond and trunk. Oil palm frond (OPF) is left at the plantation for soil conditioning while oil palm trunk (OPT) is only obtained once in every 25 years during replanting. Although empty fruit bunch (EFB) has been widely researched for its use in biocomposite, however it is also useful for other sectors such as biobriquette, biofuel, compost and fermentation feedstock. Pressed OPMF which has very similar structure to shredded EFB may have the same characteristics with EFB, and its potential use for biocomposite has been proven in this study. OPMF was not on the research limelight as it is widely known that OPMF is used almost exclusively for steam boiler ignition (Ng et al., 2010; Neoh et al., 2011; Nasrin et al., 2011; Zakaria et al., 2015). At present, OPMF is used inefficiently as solid fuel for boiler, causing excessive power generation at the palm oil mill. One of the reasons for more-than-sufficient OPMF burning is to dispose of the OPMF. Realizing this issue, it is hence OPMF is proposed as potential reinforce material for biocomposite, in order to efficiently use the bioresource generated daily from palm oil mill.

6.3.3.3 Availability of excess steam at the palm oil mill

As being mentioned earlier, power produced from steam boiler is normally more than sufficient to be used in the palm oil mill (Nasrin et al., 2011). Burning of OPMF in boiler produces high pressure saturated steam at 17 – 20 bar and is then expanded through the turbine blades for mechanical works (Nasrin et al., 2011). Residual steam that leaves the steam turbine at lower pressure (3 bar) will be stored in the backpressure receiver or vessel. Due to inefficient burning of OPMF, steam will be continuously entering backpressure receiver which causes the pressure to increase > 3.5 bar and has to be released to the atmosphere. This excess steam has been currently wasted at the palm oil mill. Inefficient steam utilization and biomass generated are among the major concerns in the palm oil mills (Ali et al., 2015; Abdullah et al., 2016). Availability of low pressure excess steam (>3.5 bar) provides opportunity for steam utilization, for example in the modification of lignocellulose prior to biocomposite production.

To be specific on the actual amount of excess steam, Abdullah et al., (2016) demonstrated that a palm oil mill generally generated about 299 000 tonnes of high pressure steam at 20 bars with boiler efficiency of 77%. This amount of steam would generate 7.72 GW h of electricity. Approximately 4.08 GW h/y of electricity would be required in FFB processing. Thus, this shows that 3.64 GW h/y energy is in excess which is equivalent to 140 000 tonnes of steam.

On top of energy from steam generation, palm oil mill produces tonnes of palm oil mill effluent (POME) annually. The current treatment method for POME is anaerobic digestion which produces methane as by-product. If controlled anaerobic

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digestion can be done and that methane produced can be collected, it is proposed that 3 MW can be generated (Ali et al., 2015). This will produce sufficient energy not only for the palm oil mill, but also to the surrounding areas. With the available alternative energy, OPMF can be eventually freed for other uses, *i.e.* biocomposite.

Based on the above, there will be no issue to use OPMF as raw material for biocomposite production, while excess steam generated at palm oil mill can be used for treatment of fiber. Low pressure excess steam produced at palm oil mill is highly potential to be converted to superheated steam since SHS does not require a high pressure steam for the system. The proposed concept is shown in Figure 6.4.

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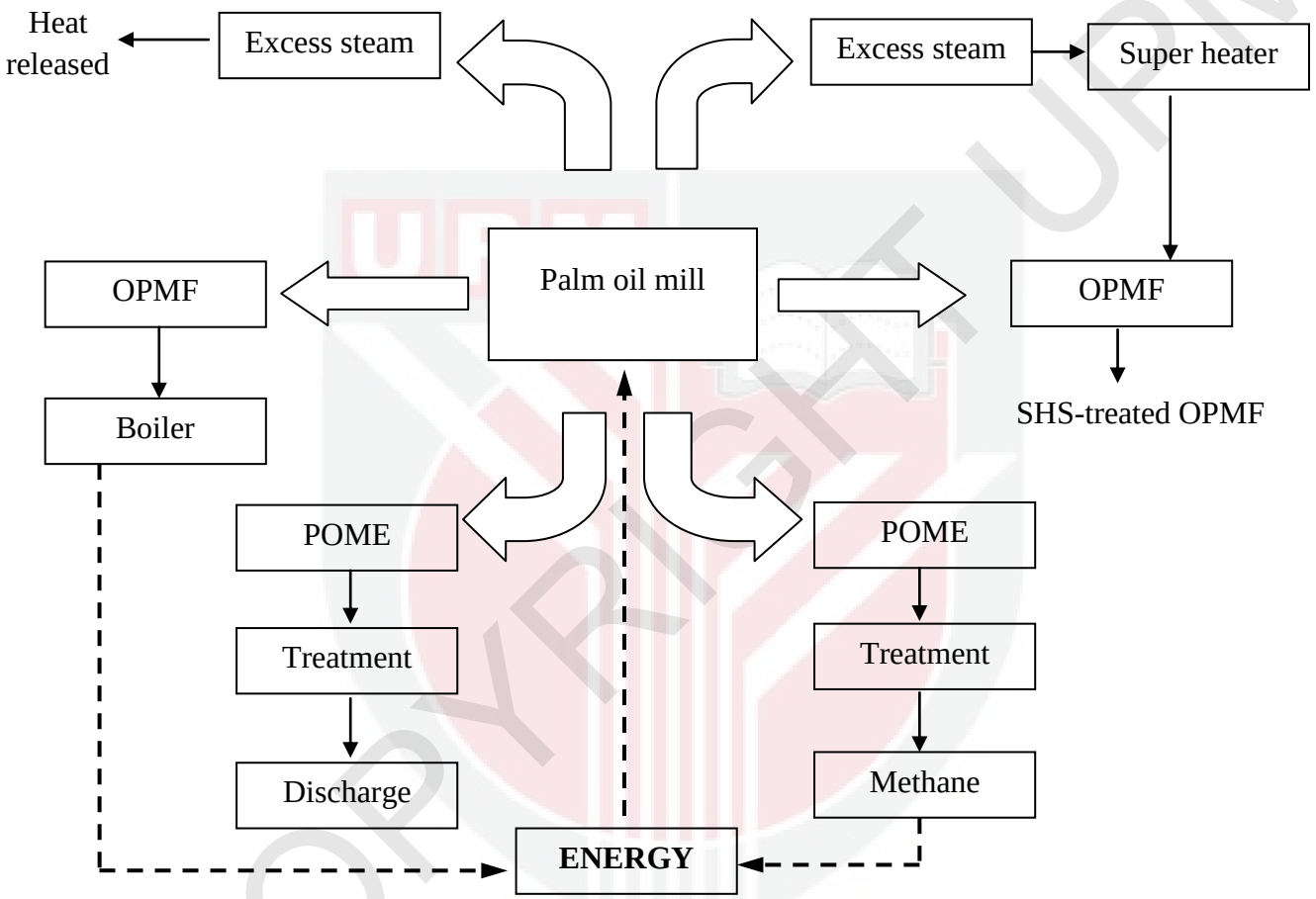

(a) Conventional palm oil mill processing (b) Proposed green palm oil mill processing

Figure 6.4: Conventional and proposed green palm oil mill processing.

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6.4 Summary

Different chemical treatments namely NaOH, KOH and $NaClO_2$ treatments were conducted on OPMF. Alkaline treatment by NaOH and KOH was aimed at hemicellulose removal, while $NaClO_2$ treatment was done for lignin removal. Two-stage treatment of OPMF ($NaClO_2$+ KOH) yielded cellulose. It was demonstrated that alkaline-treated OPMF/PP biocomposites had the highest mechanical properties, followed by ($NaClO_2$+KOH)-OPMF/PP biocomposite and $NaClO_2$-OPMF/PP biocomposite. Alkaline-treated OPMF exhibited better compatibility with polymer compared to $NaClO_2$-OPMF due to the reduction of hydrophilic component (hemicellulose) in the OPMF. On the other hand, removal of lignin in $NaClO_2$-OPMF caused the fiber to lose hydrophobic region and hence led to the poor interaction between fiber and polymer.

Both SHS and alkaline treatments have the same purpose: to remove hemicellulose. Comparison study made for alkaline and SHS treatments showed that SHS treatment is superior to alkaline treatment, based on five criteria tested. SHS treatment meets green chemistry principles such as waste prevention, does not involve the use of hazardous chemicals, safe treatment agent and produces less chemical by-products. It is therefore concluded that SHS could be an effective treatment option for lignocellulosic material treatment prior to biocomposite production.

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CHAPTER 7

SUMMARY, GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Conclusions

OPMF is one of the solid biomass produced from palm oil industry. It is inefficiently burnt in boiler at the palm oil mill as a matter of waste disposal and hence, excess energy in the form of steam is available at the palm oil industry. Integration of excess steam and abundantly produced OPMF is an interesting idea for biocomposite making. In this research, the feasibility of superheated steam for OPMF treatment prior to biocomposite production is clarified. Overall, it was found that SHS treatment is superior in altering the chemical composition of OPMF especially in hemicellulose removal, consequently producing OPMF/PP biocomposite with enhanced mechanical, thermal, crystallinity and water absorption properties. The effect of SHS treatment in alteration of OPMF chemical composition was almost similar to that of alkaline treatment. Interestingly SHS-OPMF/PP biocomposite exhibited better characteristics compared to alkaline-OPMF/PP biocomposite. This shows that SHS treatment could be an alternative treatment method to alkaline treatment for biocomposite preparation.

The specific conclusions drawn from the results of this study are:

1. Treatment of OPMF by SHS conducted at temperature range of 190 – 230 °C for 1 to 3 h showed alteration in chemical composition of OPMF in terms of hemicellulose and silica content. Increased in both treatment temperature and time was found to increase hemicellulose and silica removal. The best treatment temperature and time to alter chemical composition of OPMF was at 210 °C, 1 h. At treatment temperature above 210 °C, alteration in OPMF chemical composition was extended to cellulose component where it was exhibited that cellulose started to degrade. This caused lignin composition to be the highest in OPMF. Removal of hemicellulose resulted in the SHS210-OPMF to have better thermal stability and crystallinity by 7% and 11%, respectively compared to untreated OPMF.

2. Alteration of OPMF chemical composition due to SHS consequently improved the mechanical, thermal, crystallinity and water absorption properties of SHS-OPMF/PP biocomposites. Improvement in mechanical and water absorption properties was mainly contributed by the removal of hemicellulose and silica which caused the fiber to have better interaction with PP. This is supported by SEM images which showed less fiber pull-out and voids for SHS-OPMF/PP biocomposites. SHS-OPMF/PP biocomposites also exhibited better thermal stability compared to untreated-OPMF/PP biocomposite by 8%. SHS treatment

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temperature was found to affect the mechanical and crystallinity properties of biocomposites. The mechanical properties of SHS210-OPMF/PP were higher by 6% for tensile properties, 14% for flexural strength, 7% for flexural modulus and 73% for impact strength when compared to SHS230-OPMF/PP. This can be explained by disruption in cellulose structure at higher SHS treatment temperature. In term of water absorption, all SHS-OPMF/PP biocomposites showed lower water absorption compared to untreated-OPMF/PP biocomposite, which is contributed by improved hydrophobicity of SHS-OPMF. Overall properties of SHS210-OPMF/PP biocomposite is as following : tensile strength (20.47 MPa), tensile modulus (531.46 MPa), flexural strength (33.44 MPa), flexural modulus (1370 MPa), impact strength (80.92 J/m), crystallinity (28%) and maximum water absorption (8.41%).

3. The effect of fiber loading on mechanical properties of OPMF/PP biocomposites was studied and it was found that increasing fiber loading from 30 to 50 wt% caused reduction in the mechanical properties of both SHS210-OPMF/PP and untreated-OPMF/PP biocomposites. The reduction in the properties was due to poor wettability of PP and high tendency of fiber agglomeration.

4. Different chemical treatments namely NaOH, KOH, $NaClO_2$ and ($NaClO_2$+ KOH) treatments were conducted on OPMF. It was demonstrated that NaOH-OPMF/PP and KOH-OPMF/PP biocomposites had the highest mechanical properties, followed by ($NaClO_2$+KOH)-OPMF/PP and $NaClO_2$-OPMF/PP biocomposite. Alkaline-treated OPMF exhibited better compatibility with polymer compared to $NaClO_2$-OPMF due to the reduction of hemicellulose component in the OPMF. Removal of lignin in $NaClO_2$-OPMF caused the fiber to lose hydrophobic region and hence led to the poor interaction between fiber and polymer.

5. Comparison between alkaline and SHS treatments showed that SHS treatment is advantageous than alkaline treatment, based on five criteria selected. SHS treatment does not involve the use of hazardous chemicals, safe, produces less chemical by-products and most importantly is effective in fiber surface modification. SHS-treated biocomposite exhibited slightly better properties compared to alkaline-treated biocomposite despite of the same treatment effect, *i.e.* hemicellulose removal. It is suggested that SHS treatment could be an alternative method to treat lignocellulosic materials prior to biocomposite production.

The impacts of the findings of this research can be addressed from different point of view which benefits to community, country and include the conservation of environment. Foremost, the finding can provide a useful solution in managing biomass (waste) generated from the palm oil mill. With the proposed solution as being presented in Chapter 6 it is hoped that the OPMF can be utilized more efficiently. Additionally, the excess steam at the palm oil mill currently produced from the current practice can be utilized as SHS treatment for biomass treatment.

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OPMF is a raw material that is available throughout the year. There are no costs for planting, farming, harvesting and processing as this material is generated as a waste from the oil extraction. On top of that, OPMF is available throughout Malaysia and easily obtained.

7.2 Recommendations for Future Work

The following is a list of recommendations for further research:

1. SHS treatment was proven as an effective method for natural fiber surface modification. Scale up study of SHS treatment will provide useful results and open up the opportunity of SHS to be applied in the palm oil industry.

2. Feasibility of large scale SHS treatment which includes the scientific and economic analysis is an important topic to explore/discuss. It must consider the conventional business currently operated versus the proposed emerging business. The study may provide a solution for palm oil industry to fully utilize their resources.

3. Life cycle assessment is a system analysis for evaluating environmental impacts over the whole life cycle of products, process or activity from the 'cradle' (raw material acquisition) to the 'grave' (disposal or recycling). From LCA study, complete assessments of environmental impact from all stages of the life cycle of the OPMF/PP biocomposite can be used to evaluate its environmental attributes. Typically, LCA study comprises activities of extraction of raw materials, design, formulation, processing, manufacturing, packaging, use (reuse) and disposal.

4. The results discussed in this thesis were limited to only one type of natural fiber (OPMF) and one type of polymer matrix (PP). Future work should consider extending the treatments and assessments to other types of natural fiber and polymer. It is suggested to use biodegradable polymer such as PHA to produce 100% biodegradable and green biocomposite. Therefore soil biodegradable study can be conducted and provide comprehensive information on production of biocomposite from SHS-treated fiber.

5. Production of nanofiber from OPMF is a promising study. OPMF has higher contact surface and easier to grind. These will opened up a new alternative to utilize abundant OPMF generate inside the palm oil mill. Nanofiber has good potential in high technology application such as medical appliances.

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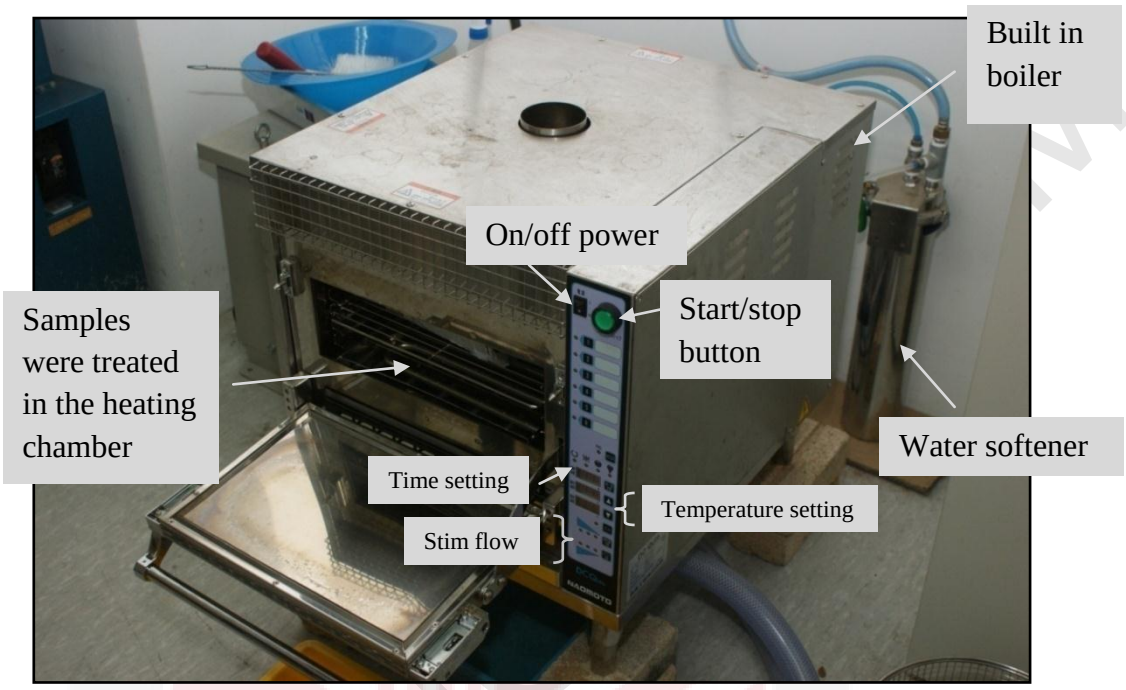
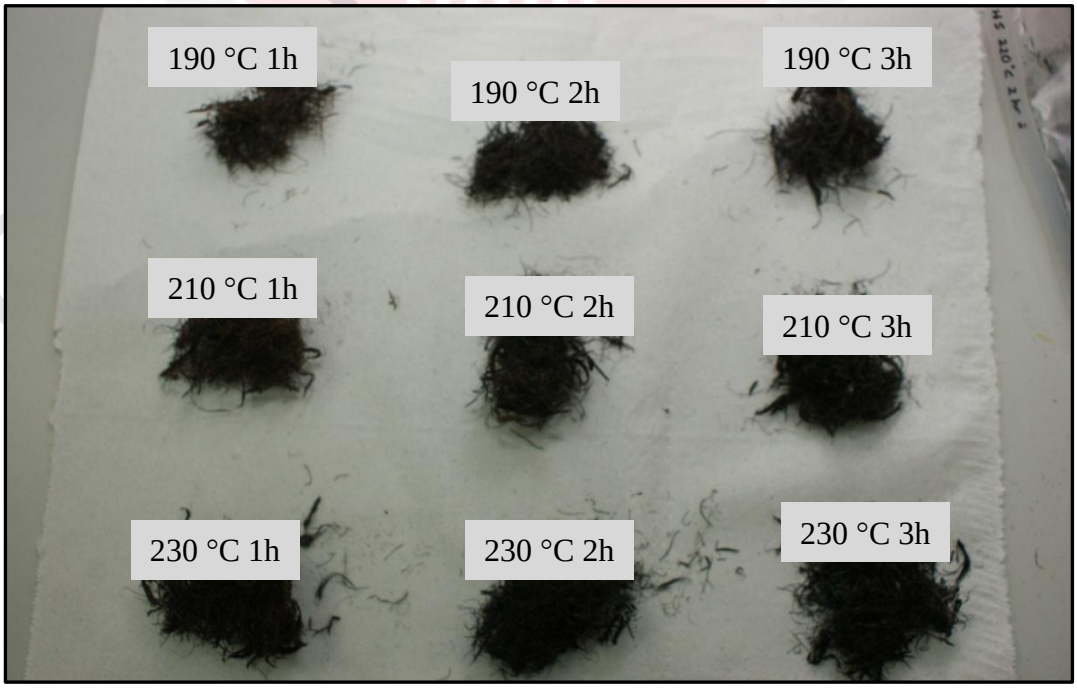
APPENDICES

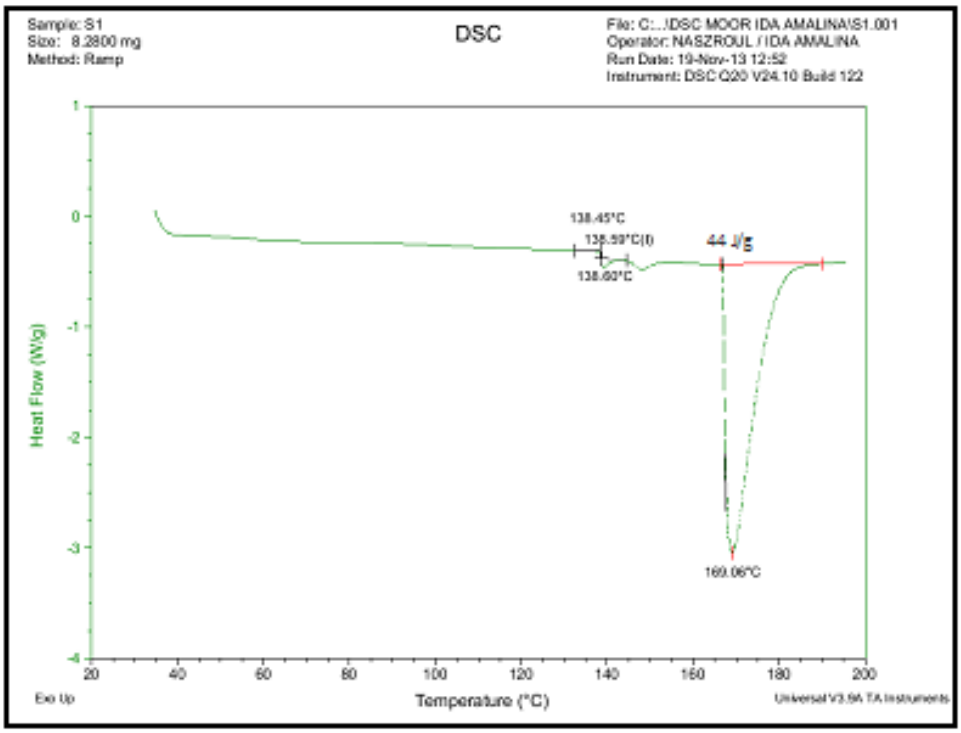
APPENDIX A



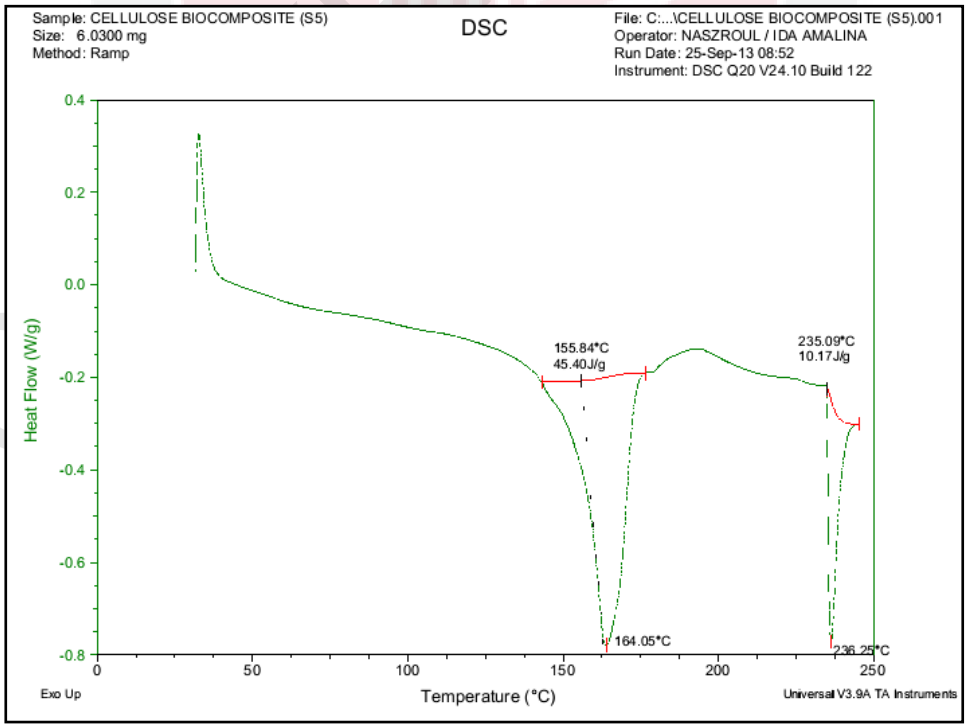
Appendix A1: Superheated steam machine.



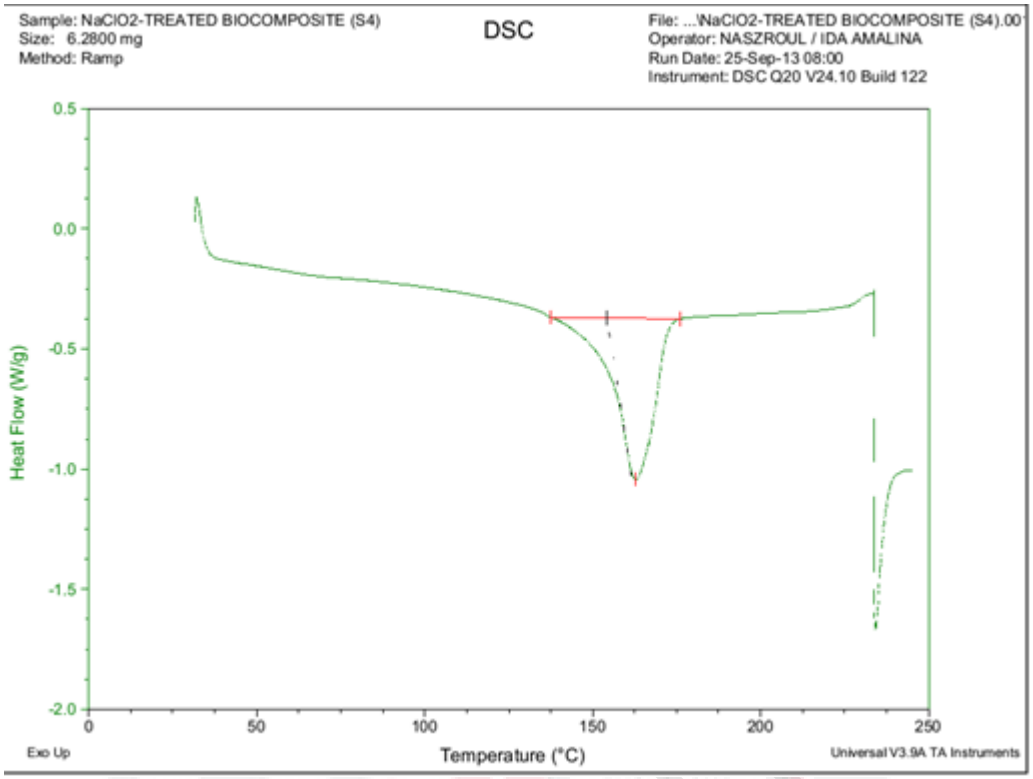
Appendix A2: SHS-treated OPMF.



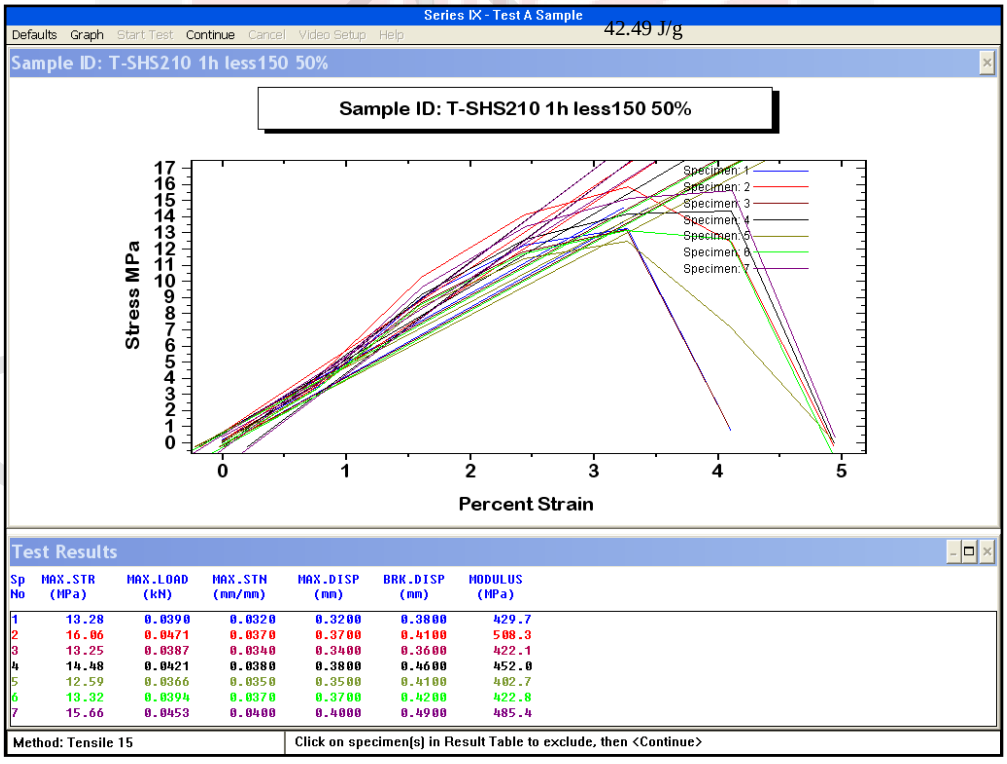
Appendix A3: DSC thermal profile of SHS-treated OPMF/PP biocomposite.



Appendix A4: DSC thermal profile of ($NaClO_2$+KOH)-OPMF/PP biocomposite.

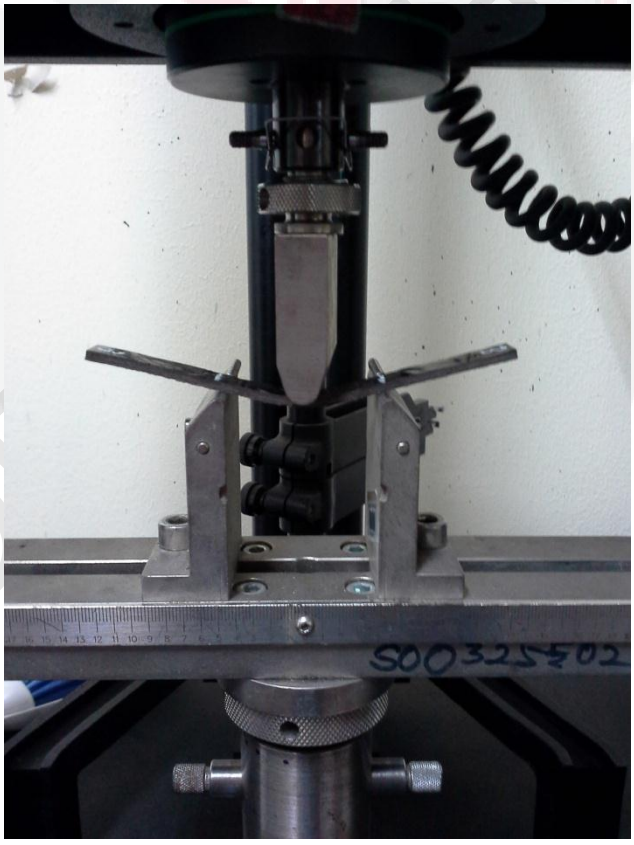


Appendix A5: DSC thermal profile of $NaClO_2$-OPMF/PP biocomposite.

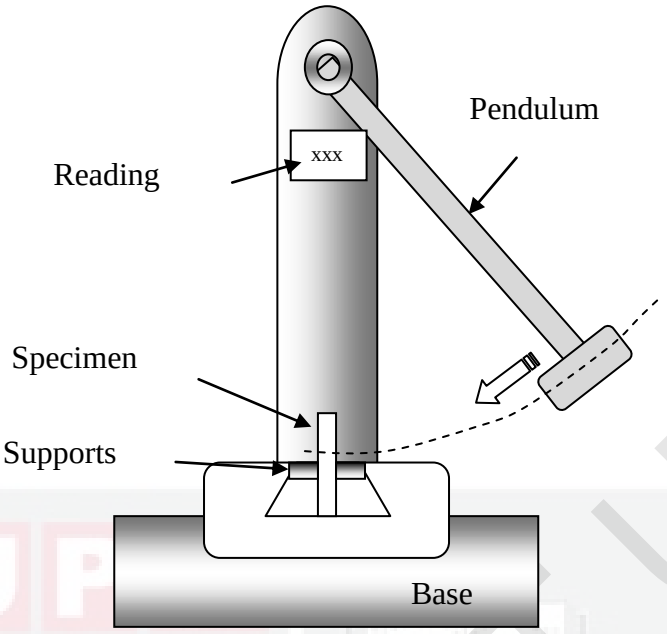


Appendix A6: Example of tensile test result.

Appendix A7:Tensile test conducted using Instron Universal Tester.



Appendix A8: Three-point bending test conducted using Instron Universal Tester.



Appendix A9: Schematic diagram of impact test pendulum. The pendulum impacts the specimen at the bottom of its swing.

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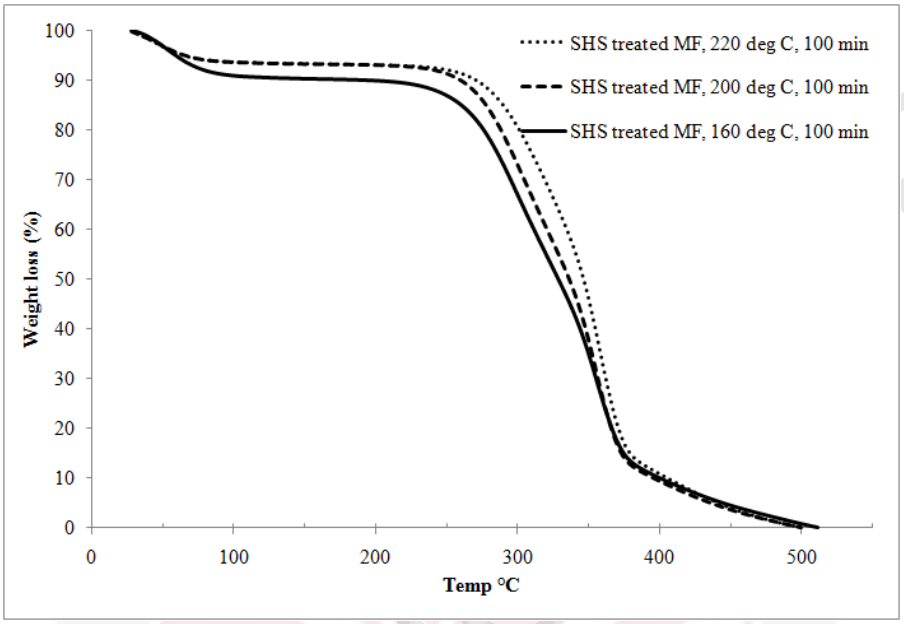
APPENDIX B

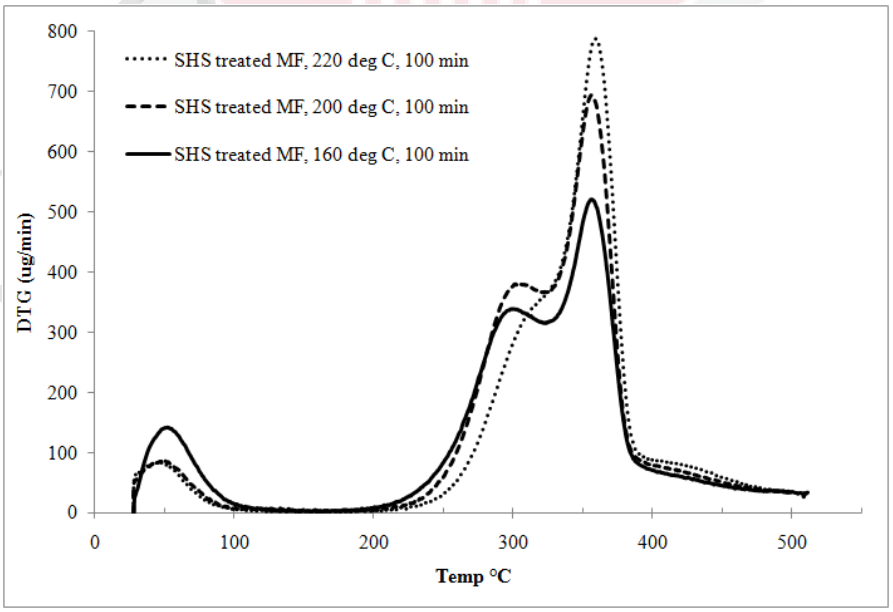
PRELIMINARY DATA AND CALCULATIONS

B1 : Preliminary Study – TG analysis



Appendix B1: Preliminary results of TG thermogram of SHS-treated OPMF.

B2 : Preliminary Study – DTG thermogram



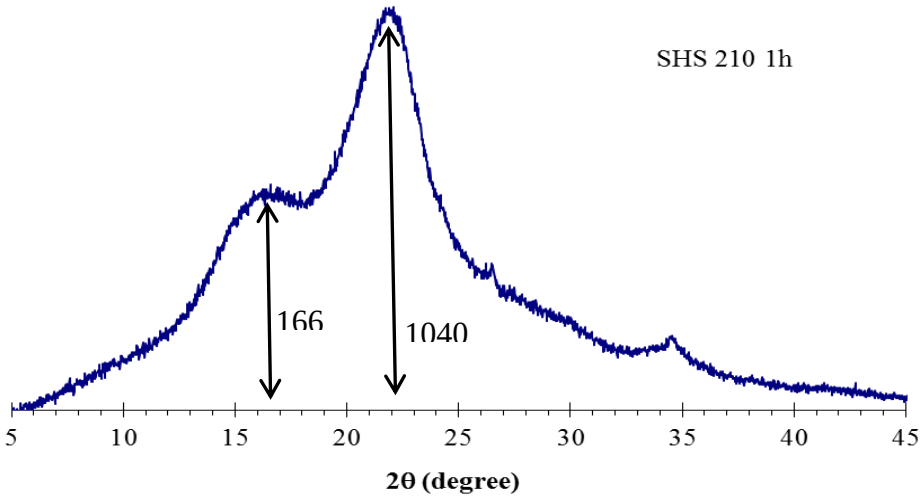
Appendix B2: Preliminary results of DTG thermogram of SHS-treated OPMF.

B3 :Determination of Crystallinity Index, CrI for OPMF

The crystallinity index (CrI) was calculated from XRD data and determined based on the formula by Segal *et al*. (1959) as shown in equation below:

$$\mathrm{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

which I_{002} is the intensity for the crystalline portion of sample at about 2θ = 22 and I_{am} is the peak for the amorphous portion (second highest peak) at about 2θ = 17.



$$\mathrm{CrI} = \frac{1040 - 166}{1040} \times 100\% \quad = \quad 84\%$$

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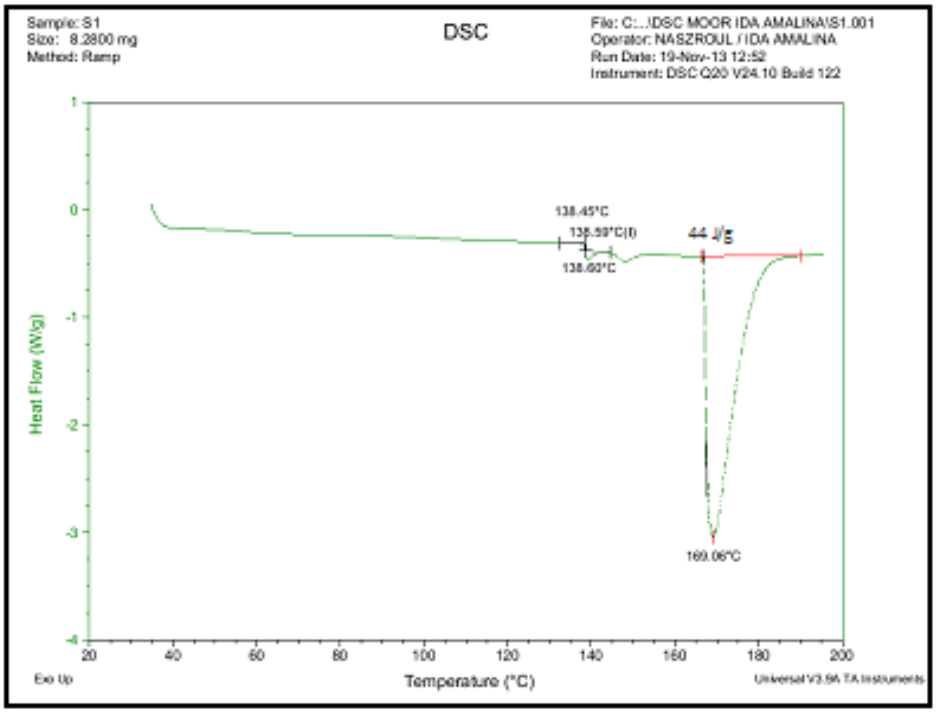
B4 : Determination of degree of crystallinity (X_c) for the OPMF/PP biocomposites



X_c for the biocomposites was calculated as the ratio of the melting entalphy (ΔH_m) to the specific heat of fusion of 100% crystalline PP, taken as 190 J g^{-1}:

$$X_c = \frac{\Delta H_m}{\Delta H_m^{*PP}} \times 100$$

$$X_c = \frac{44}{190} \times 100\% = 23.2\%$$

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APPENDIX C

C1 : The Twelve Principles of green Chemistry

	Principle	
1	Prevention	: It is better to prevent waste than to treat or clean up waste after it has been created.
2	Atom Economy	: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3	Less Hazardous Chemical Syntheses	: Whererever practicable, synthetic methods should be designed to use and generate substances that posses little or no toxicity to human health and the environment.
4	Designing Safer Chemicals	: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5	Safer Solvents and Auxiliaries	: The use of auxiliary substances (*e.g.*, solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6	Design for Energy Efficiency	: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7	Use of Renewable Feedstocks	: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8	Reduce Derivatives	: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9	Catalysis	: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10	Design for Degradation	: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11	Real-time Analysis for Pollution Prevention	: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12	Inherently Safer Chemistry for Accident Prevention	: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

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BIODATA OF STUDENT

The student, Noor Ida Amalina binti Ahamad Nordin was born on 23rd August 1979 in Pasir Putih, Kelantan, Malaysia. She completed his primary education at Sekolah Rendah Kebangsaan Batu Tiga, Kuantan, Pahang (from 1986–1991) and continued her secondary school at Sekolah Menengah Convent, Johor Bahru, Johor. Then in 1997, she furthers her study at Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia and obtained a Bachelor degree in Bioprocess Engineering in 2002.

She worked as research assistant and involved herself in projects related to biology and green technology. Working in research and university environment has motivated her to further study and obtained Master in Civil Engineering (Environmental Management) at Universiti Teknologi Malaysia in 2006. For her Master project, she had treated landfill leachate by plant uptake using wetland treatment concept. She able to reduce the heavy metal concentration in the leachate up to regulation set by the Department of Environment before release it to the river. After finished her Master study, she joined Universiti Malaysia Pahang as a lecturer in 2006. She started her Doctor of Philosophy study under the supervision of Dr Hidayah Ariffin in December 2010.

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LIST OF PUBLICATIONS

Published

Nordin, N.I.A.A., Ariffin, H., Hassan, M.A., Ibrahim, N.A., Shirai, Y., Andou, Y. (**2015**). Effects of milling methods on tensile properties of polypropylene / oil palm mesocarp fibre biocomposite. **Pertanika Journal Science & Technology**, 23, 325 – 337. (Indexed by Scopus)

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Award:

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