

**Department of Mechanical Engineering
Faculty of Engineering & Science**

**Mechanical Performance and Thermal Stability of Natural Fiber
Composite Using Palm Oil Biomass**

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This thesis is presented for the degree of

Doctor of Philosophy

of

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: Omid Nabinejad

Date: 4th November 2017

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Abstract

This PhD thesis aims to investigate the thermal stability of polymer composite containing palm oil biomass, and improve its mechanical performance by developing a thermoset-based (polyester, vinyl ester, and epoxy resins) natural fiber composite.

To investigate the mechanical performance of the composites, the effects of various chemical treatments, filler size, filler percentage and matrix type on the tensile and flexural properties of the composite were studied. Carbon nanotubes (CNTs), which possess an extremely high surface area, was also used in this research to improve the mechanical performance by increasing the level of polymer chain entanglement between the natural filler and the polymer matrix. Therefore, a suitable solvent mixing method, assisted with ultrasonication, was used as the methodology of natural filler-CNTs hybrid composite preparation. This method results in a significant improvement in the dispersion of CNTs, which improved the mechanical performance of the hybrid composite when compared to the natural fiber composite.

As the application of lignocellulosic fibers is limited due to their low thermal stability, the consequence of changes in the processing parameters on the thermal stability of the fiber/filler and its composite was also addressed in this thesis. Therefore, the thermal behavior of the natural filler, before and after surface treatment, was investigated by Thermogravimetric Analysis (TGA). Moreover, as the thermal degradation of the natural filler and polyester resins occurs within similar temperature ranges, the experimental method using Thermogravimetric Analysis (TGA) failed to determine the filler contents. Therefore, an empirical equation based on the TGA method was also developed in this thesis to quantify the filler percentage. The loading of natural fillers causes a significant delay in the curing reaction of thermoset resins, which is the main drawback for the application of natural fillers in NFC/WPC. Therefore, the fabrication of thermoset composites, at a high filler percentage, is another key challenge and has been addressed in this thesis. Depending on the type of thermoset resin used, the effect of filler load on the rate of curing reaction was investigated. Eventually, a model with a suitable remedial action was developed to predict the curing behavior and increase the level filler loading for thermoset resins filled with natural filler composite.

List of Publications

The following book chapter and other publications were referred to during this doctoral study.

The book chapter that was included in this thesis:

O. Nabinejad, and D.Sujan, Natural-Fiber-Reinforced Polymer Composites. Spherical and Fibrous Filler Composites, (ed. Vikas Mittal.), 2016. Wiley-VCH Verlag GmbH & Co. KGaA. p. 101-125.

Peer reviewed journals that were included in this thesis:

O. Nabinejad, D. Sujan, M. E. Rahman, Willey Y.H and Ian J Davies, “Hybrid composite using natural fiber and Multi Walled Carbon Nano Tube (MWCNTs)”.- Spriger- Applied Composite Materials, 2017, DOI : 10.1007/s10443-017-9667-8, (IF: 1.217)

O. Nabinejad, D. Sujan, M. E. Rahman, and Ian J Davies, “Effect of filler content on the mechanical and thermal performance and the kinetic of reaction of oil palm shell as a wood flour filled thermoset composites”. Elsevier- Journal of cleaner and production, 2017: 164: 1145-1156, (IF: 5.715)

O. Nabinejad, D. Sujan, M. E. Rahman, Willey Y.H and Ian J Davies, Mechanical and thermal characterization of polyester composite containing treated wood flour from palm oil biomass, Polymer composite, Wiley, 2016, DOI: 10.1002/pc.24052, (IF: 2.324)

O. Nabinejad, D.Sujan, M.E.Rahman, Ian J Davies. “Effect of oil palm shell powder on the mechanical performance and thermal stability of polyester composites. Materials & Design. 2015: 65:823-3, (IF: 4.364)

O. Nabinejad, D.Sujan, M.E.Rahman, Ian J Davies. “Determination of filler-content for natural filler polymer matrix composite by thermogravimetric analysis”. Journal of Thermal Analysis and Calorimetry. 2015: 122(1), 227-233, (IF: 1.953)

Additional publications by candidate, relevant to the thesis, but were not included in this thesis:

ISI index journals papers:

O. Nabinejad, D. Sujan and M. M Taheri, “Oil Palm Fiber Vinylester Composite; Effect of bleaching treatment”, Materials Science Forum, 2017, 882, p43

O. Nabinejad, D. Sujan, J. Y. Teh, Willey Y. H. Liew and Ian J Davies. “Influence of alkali treatment and nanoclay addition on the properties of rice husk reinforced polyester composites”, Materials Science Forum, 2017, 882, p89

O. Nabinejad, D. Sujan, M.E. Rahman, M.M .Reddy, W.Y.H.Liew, Ian J Davies “The Effect of Alkali Treatment of OPKS Filler on Mechanical Property of Polyester-Composite” - Advanced Materials Research, 2014: 980, 86-90

International conference papers and poster:

O. Nabinejad, D. Sujan, M. E. Rahman and Ian J Davies, “Thermoset Based Wood Flour Composite With High Filler Content”, International Conference and Exhibitions on Inventions by Institutions of Higher Learning (PECIPTA), -Poster- 2017, Malaysia, (Awarded az the Bronze Winner by Malaysia's Ministry of Higher Education)

O. Nabinejad, D. Sujan, J. K Beh, “Effect of Alkali Treatment and addition of Nanoclay on the Mechanical Performance and Moisture Absorption of Unidirectional Bamboo Fiber Polyester Composite”, 8th International Conference on Manufacturing Science and Technology (ICMST), 2017, Hong Kong

O. Nabinejad, D. Sujan, M. E. Rahman and Ian J Davies, Hybrid Composite Using Carbon Nano Tube and Natural Fiber, Asian Workshop on Polymer Processing (AWPP) -Poster- 2016, Melbourne, Australia

O. Nabinejad, D. Sujan, J. Y. Teh, Willey Y. H. Liew and Ian J Davies, “The Effect of Nanoclay on Rice Husk Particle Reinforced Unsaturated Polyester Composites”, 9th CUTSE International Conference, 2014, Miri, Malaysia, (Awarded for best paper)

Explanatory Overview and Organization of the Thesis

This thesis, submitted in the form of series of manuscripts published in international peer-reviewed journals in accordance with ‘Rule 10: Degree of Doctor by Research’ and approved by Curtin University of Technology.

The aim of this thesis is to develop a thermoset based wood polymer composite (WPC) containing natural filler from palm oil biomass to achieve an optimal mechanical performance. In this research, the effect of processing conditions (filler size, surface treatment and filler percentage) on the mechanical properties of the composite were investigated. Moreover, the thermal stability of the filler and the resulting composite were also analyzed to determine the temperature ranges for the processing and application of this type of composite.

Therefore, the objectives of this research are as follows:

- Objective one: Investigate the mechanical performance of the developed WPC from palm oil biomass.
- Objective two: Investigate the thermal stability of the natural filler and its composites to determine the temperature ranges for the filler processing and applications for the composite.
- Objective three: Optimize the processing conditions (including various matrices, filler size, filler percentage and the surface treatment of the filler) to develop a thermoset based WPC.
- Objective four: Develop an empirical model to estimate the filler percentages of the composite.
- Objective five: Develop a hybrid composite containing the natural filler and Carbon Nano Tube.

The contribution of each chapter and the objectives of the thesis are as follows:

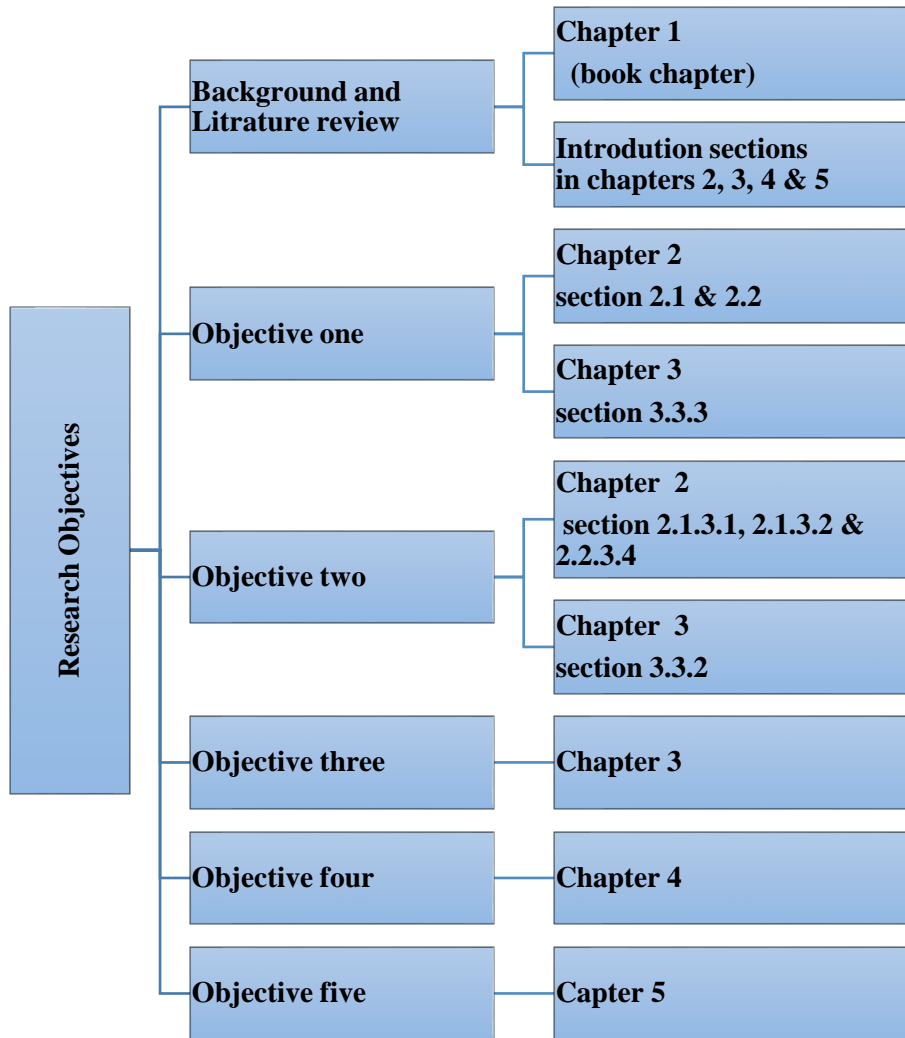


Figure 0-1. The relationships between the thesis objectives and each chapter

The contents of each chapter are summarized as follows:

Chapter 1: Introduction and literature review:

Chapter one consists of three sections including the literature review, research challenges, and the objectives and scope of the thesis.

1.1 Literature review: Natural- Fiber Reinforced Polymer Composites

This section covers the literature review with up-to-date research on natural fiber composites which has been published as a book chapter by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. It should be noted the published version of the book chapter contains three additional elements, including; dynamic mechanical performance, moisture absorption, and tribological performances. However, these features were not included in the literature review as they are not the objectives of this thesis. Instead, the current situation of nanoparticles/natural fiber based hybrid composites and a natural fiber composite from palm oil resources were addressed.

1.2 Research Challenges

In this section, the research challenges are addressed and the research questions are identified.

1.3 Objectives and Scopes of the Thesis

The research objectives and the scope of work are identified in this section.

Chapter 2: Effect of size and treatment of natural filler on the mechanical properties and thermal stability of wood flour composite;

Chapter two is divided into two parts and each part is considered as a published paper.

2.1 Effects of oil palm shell powder on the mechanical performance and thermal stability of polyester composites

This section focuses on the physical and chemical properties of oil palm kernel shell (OPS) as a natural filler and the mechanical properties of its polymer composite. It is discussed how OPS powder, as a natural filler, interacts with the polymer matrix, and this interaction influences the mechanical performance of the OPS filled with Unsaturated Polyester (UP) Composites. Moreover, the OPS powder size was optimized to achieve the maximum performance of the OPS-UP composite. The thermal stability of OPS and its composite is also investigated.

2.2 Mechanical and thermal characteristics of a polyester composite containing treated wood flour from palm oil biomass.

As a result of section 2.1, where an increase of the surface roughness of filler is shown to be the key to the improvement of filler-matrix interfacial bonding, a proper chemical treatment is developed in section 2.2. This section focused on the effects of different surface treatments on the thermal degradation and the chemical composition of the natural filler. Accordingly, the effect of treatment conditions, such as elevated temperature, concentration, and sonications on the chemical composition of fiber cells (cellulose, hemicellulose, and lignin), along with the thermal stability of the fiber, together with the mechanical performance of composite are investigated.

Chapter 3: Optimize the filler content to develop thermoset based WPC

Chapter three consists of a published paper entitled *“Effect of filler content on the mechanical and thermal stability and the kinetic reaction of oil palm shell as a wood flour filled thermoset composite.”*

This chapter investigates the loading effect of OPS as a lignocellulosic filler in the processing condition, mechanical performance, thermal behavior and shrinkage of composites. In addition, the curing reaction of thermoset resins in the presence of lignocellulosic filler was investigated in order to understand the role of filler load in the delaying of the curing reactions. Consequently, the reason for this delay is addressed and an effective mitigation action was developed to increase the level of filler load for these thermoset matrices. Furthermore, the effect of different thermoset resins on the mechanical properties is investigated in this section.

Chapter 4: Develop an empirical model to estimate the filler content of WPC.

Chapter four consists of a published paper entitled *“Determination of filler content for natural filler polymer composite by thermogravimetric analysis.”*

This chapter addresses the inability for an accurate prediction of filler content by thermogravimetric analysis (TGA) for natural filler reinforced composites, as the thermal degradation of both the filler and matrix occurs within similar temperature ranges. Therefore, a different approach to applying thermogravimetric analysis (TGA) with a semi-empirical equation was developed for the determination of filler content.

Chapter 5: Hybrid composite (effect of using nanoparticles)

Chapter five consists of a published paper entitled “*Hybrid composite using natural fiber and Multi Walled Carbon Nanotube (MWCNTs).*”

It is shown in chapter 2 section 2.1 that the polymer chain entanglement is the main mechanism in the wettability of the natural filler by the polymer matrix, which improves the mechanical performance of the composite. To increase the level of wettability, Multi-Walled Carbon Nanotubes (MWCNTs), which have an extremely high surface area, were used in this research. For this reason, a hybrid composite comprising of pristine MWCNTs and OPS reinforced in unsaturated polyester composite was developed in chapter 5 to improve the mechanical performance of WPC. Dispersion of nanoparticles in the polymer matrix, which is the main challenge in the application of these materials, is addressed and a methodology was also developed to avoid the nanoparticle agglomeration. Next, the optimum concentration of pristine MWCNTs for improved mechanical properties of the hybrid composite was determined, and the consequence of higher concentrations was addressed. Finally, the effect of MWCNTs on the thermal stability of hybrid composite was also investigated.

Chapter 6: Conclusion

The findings and the conclusions of this research, as well as possible future research regarding this study are presented in chapter six.

Research Significant

In the past few decades, NFC or WPC have been widely investigated by researchers due to their environmentally friendly behaviors and possessing high specific strength compared to synthetic fiber reinforced composites. However, development of these composite materials has some limitations. This thesis addresses three main challenges related to the development of these materials.

In terms of processing, this thesis addressed the key challenge in the fabrication of thermoset composites at a high level of natural filler content. Increasing the loading of the lignocellulosic filler was found to delay the curing reaction of all thermoset resins. A model with a suitable remedial action was developed to solve the issue by prediction the curing behavior and increasing the level of filler loading. Subsequently, the loading effect of lignocellulosic filler in the processing condition, mechanical performance, thermal behavior and shrinkage of composites was investigated. The compatibility of the natural filler with different thermoset polymers was also investigated and the most compatible thermoset polymer for this filler was suggested.

The thesis also solved an issue related to characterization of NFC or WPC. The issue arises when the experimental method using Thermogravimetric Analysis (TGA) failed to determine the filler contents. This is due to the fact that the thermal degradation of the natural filler and some polymer matrices like unsaturated polyester occurs within similar temperature ranges. To address the issue, an empirical equation based on the Thermogravimetric Analysis method was developed to quantify the filler percentage.

In terms of mechanical properties, the poor interfacial bonding between the natural fiber and matrix results in a low mechanical performance and consequently limits the range of applications for these types of composites. In this direction, the effect of different surface treatments on the quality of the bonding between natural fillers (lignocellulose) and the polymer matrix, the thermal stability and the mechanical properties of the composite were investigated. Moreover, to improve the mechanical properties of NFC, a hybrid composite comprising of a Carbon NanoTube (CNT) and a lignocellulose filler reinforced polymer composite was developed. Dispersion of nanoparticles in the polymer matrix, which is the main challenge in the application of these materials, was addressed as well as a methodology to avoid the nanoparticle agglomeration. The results revealed the dispersion of CNT in the polymer matrix was strongly enhanced by the solvent mixing method assisted ultra-sonication. Eventually, a suitable solvent was also suggested for the optimum dispersion of the nanoparticles.

Glossary

EFB	Empty Fruit Bunches
BMC	Bulk Molding Compound
CAGR	Compound Annual Growth Rate
CAT1	Cold Alkali Treatment At 1 Hr
CAT48	Hot Alkali Treatment At 48 Hr
CDW	Cold Distilled Water
CNT	Carbon Nanotube
COF	Coefficient of Friction
CVD	Carbon Vapor Deposition
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric Analysis
EP	Epoxy Resin
FRP	Fibre Reinforced Polymer
FTIR	Fourier Transform Infrared Spectroscopy
GFRP	Glass Fiber Reinforced Plastic
GS	Gamma-Aminopropyltriethoxysilane
HAT	Hot Alkali Treatment
HDPE	High-Density Polyethylene
HDW	Hot Distilled Water
HDW-US	Hot Distilled Water with Ultrasonication
LDPE	Low-Density Polyethylene
MEKP	Methyl Ethyl Ketone Peroxide
MRPS	Γ -Mercaptopropyl Trimethoxysilane
MS	Mass Spectroscopy
MWCNTs	Multi-Walled Carbon Nanotube
NFCs	Natural Fiber Composites
NFRP	Natural Fiber Reinforced Plastic
NR	Natural Rubber
ONF	Olive Nut Flour
ONP	Oil Newsprint
OPF	Oil Palm Fiber
OPS	Oil Palm Kernel Shell
OPS-CNT-UP	Oil Palm Kernel Shell – Polyester – Carbon Nanotube Hybrid Composite
OPS-UP	Oil Palm Kernel Shell – Polyester Composite
OPWF	Oil Palm Wood Flour
OSF	Olive Stone Flour

PHBV	Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate)
PLA	Poly(lactic Acid)
POEFB	Palm Oil Empty Fruit Bunches
PP	Polypropylene
PVC	Poly(vinyl Chloride)
PVC-U	Unplasticised Poly Vinyl Chloride
rHDPE	Recycled High Density Polyethylene
RTM	Resin Transfer Molding
SEM	Scanning Electron Microscopy
SMC	Sheet Molding Compound
SWCNTs	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TG-FTIR	Thermogravimetry Analysis Coupled with Fourier Transform Infrared Spectroscopy
TG-MS	Thermogravimetry Analysis Coupled with Mass Spectroscopy Coupled
UP	Unsaturated Polyester
UT	Untreated Filler /Fiber
VE	Vinylester Resin
VIP	Vacuum Infusion Process
WFC	Wood Flour Composite
WPC	Wood Plast Composite
XPS	X-Ray Photoelectron Spectroscopy

Nomenclature

d	Sliding Distance
E'	Storage Modulus
E''	Loss Modulus
F_n	Normal Applied Load
mc	Initial Composite Mass at a Temperature
md	Mass Loss of the Composite at a Temperature
mdc	Total Mass Loss for the Composite
m_f	Dried Filler Mass
mp	Dried Polymer Mass
m_{rc}	Total Mass Residue of the Composite At T_r
M	Moisture Uptake in the Composites
M_d	Dry Mass of Composite
M_{df}	The Percentage Decreases in Filler Masses at Temperature T_{df}
M_{dp}	The Percentage Decreases in Polymer Masses at Temperature T_{df}
M_{rf}	Filler Residue Percentage
M_{rp}	Polymer Residue Percentage
$M_{w(eq)}$	Wet Mass of Composite
P_f	Filler Mass Percentage
phr	Part Per Hundred Matrix
T_{df}	The Point At Which The Trend Of The DTG Curve Suddenly Plateaus
T_g	Glass Transition Temperature
t_{gel}	Gel Time
t_{peak}	Time to Peak
T_r	The Temperature Utilized to Record the Mass Residue
W_{cnt}	Weight of Carbon Nanotube
W_f	Weight of Filler
W_m	Weight of Matrix
W_s	Specific Wear Rate
α	Mass Loss Coefficient
β	Mass Residue Coefficient
ΔV	Volume Difference
ρ_{cnt}	Density of Carbon Nanotube
$\rho_{experimental}$	Experimental Density
ρ_f	Density of Filler
ρ_m	Density of Matrix

$\rho_{theoretical}$	Theoretical Density
Θ_{peak}	Peak Exothermic Temperature
ψ	Constant Related to the Mass Losses of the Filler and Matrix

Chapter 1:
Introduction and Research Background

Chapter 1

1 Introduction and Research Background

Introduction

This chapter covers an introduction, research challenges and general background information gathered during the literature review. More specific literature review, related to each topic, presented individually in the following chapters (2, 3, 4 and 5), where combined with the relevant methodologies and results. The literature review and the latest research advancements in the development of natural fibres derived from plant resources, which are not included in the subsequent chapters, are presented in section 1.1. It addresses the physico-chemical properties of natural fibers including their chemical composition, major processing concerns, mechanical properties, and the thermal stability of natural fibers and their composites. Moreover, the current situation of natural fiber composites produced from palm oil resources as well as nanoparticles/natural fiber based hybrid composites is addressed. The second and third sections of this chapter focus on the research challenges and research objectives.

1.1 Research Background

This section is the peer reviewed version of the following article: *Omid Nabinejad and Sujan Debnath, "Natural-Fiber-Reinforced Polymer Composites" in the book "Spherical and Fibrous Filler Composites", Editor V. Mittal, Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 101-125. (2016)*, which has been published in final form at <http://onlinelibrary.wiley.com/doi/10.1002/9783527670222.ch4/summary>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving. It should be noted that this is a modified version of the published version.

Natural-Fiber-Reinforced Polymer Composites

Omid Nabinejad and Sujan Debnath

Abstract: *Green composites using natural fibers from plant resources have been widely developed by researchers for a variety of applications as a result of depleting petroleum resources and increasing environmental concerns. Natural fiber reinforced composites (NFCs) are widely employed in the automotive, construction, aerospace, sport and packaging industries due to their several structural and environmental advantages. They are environmentally friendly; possess high specific strength; and are inexpensive to synthesize compared to synthetic fiber reinforced composites. This chapter introduces NFCs and discusses up-to-date research advancements in the development and characterization of NFCs. The benefits and challenges to development and applications of lignocellulosic derived fillers are discussed in addition to their complete physicochemical characteristics including chemical compositions, thermal and mechanical properties, and response to surface treatment and modifications. Also, major processing concerns, mechanical performance, moisture-induced degradation, thermal and tribological performances of NFCs are addressed.*

Keywords: chemical compositions, lignocellulose-derived fillers, moisture-induced degradation, natural-fiber-reinforced composites, surface treatment, tribological performances.

1.1.1 Introduction

Fiber reinforced polymer composites using synthetic fibers such as Glass, Kevlar, and Carbon fibers have been developed significantly in the past few decades to attain the characteristics required in engineering applications. However, in the recent years, environmental activists by nongovernment organizations and Greenpeace groups increased the pressure on the developed countries to preserve the natural resources with a focus on renewable raw materials (Nourbakhsh, 2011, Jawaid and Abdul Khalil, 2011).

In order to answer the environmental concerns, green composites from renewable resources are being proposed for the reinforcement phase as well as the matrix phase (Fowler et al., 2006). The concept of using natural fibers has come throughout the world history when various civilizations utilized plant fibers as the reinforcement phase in composite materials (Fuqua et al., 2012). Currently, the demand of natural fibers is increasing rapidly, where the market size for natural fiber reinforced composites is expected to reach up to \$5.83 billion by 2019, at a compound annual growth rate (CAGR) of 12.31% between 2014 and 2019 (Markets and Markets 2015).

Natural-fiber-reinforced composites in short natural fiber composite (NFCs) offer several advantages such as renewability, less abrasiveness to equipment, bio-degradability, high specific strength, low cost, noncorrosive, nonhazardous nature and flexibility during manufacturing compared to the synthetic fiber reinforced composites (Mokhothu and John, 2015, Fiorelli et al., 2015). Currently, NFC are widely used in the aerospace, sport, packaging, construction and automotive industries. In the transport industry, the application of this material can prevent the adverse health effects on the passengers by reducing the hazardous toxic elements in the interior air of the cabin (Ahmed Ali et al., 2015). The production of biocomposites (WPC and NFC) in the European Union 2012 and forecast for 2020 are listed inTable 1-1.

Table 1-1. Production of biocomposites (WPC and NFC) in the European Union 2012 and forecast for 2020 (Nova Institute for Ecology and Innovation, 2015).

	Biocomposites	Production in 2012	Forecast production in 2020	
			without incentives for bio-based products	without incentives for bio-based products
WPC	Construction, extrusion	190,000 t	400,000 t	450,000 t
	Automotive, compression moulding & extrusion/thermoforming	60,000 t	80,000 t	300,00 t
	Technical applications, furniture and consumer goods, mainly injection moulding	15,000 t	100,000 t	>200,000 t
	Traded granulates, for extrusion and injection moulding	40,000 t	200,000 t	>300,000 t
NFC	Automotive, compression moulding	90,000 t	120,000 t	350,000 t
	Granulates, injection moulding	2,000 t	10,000 t	>20,000 t

1.1.2 Overview of Natural Fiber from Plant Resources

Natural fibers derived from plant resources can be categorized as primary plants and secondary plants. The primary plants such as flax, mesta, cotton, kenaf, hemp, jute and sisal are the plants that are cultivated mainly to obtain the fibers. The natural fibers from secondary plants such as rice, pineapple, and oil palm are the fibers which are produced as a by-product from the industries (Faruk et al., 2012). Depending on the part of the plant from which they are extracted, the natural fibers are categorized as the bast/stem fiber, leaf fiber, and seed/core fiber. The other types of fibers can be classified as the stalk fiber, grass and reed fiber and wood fiber (John and Thomas, 2008a, Jawaid and Abdul Khalil, 2011, Faruk et al., 2012).

1.1.2.1 Advantages of Natural Fiber

Natural fibers have low density, high toughness, high strength and stiffness, good thermal and acoustic insulating properties, high electrical resistance. They also have less adverse effects on the cutting tools (Satyanarayana et al., 2009, Singha and Thakur, 2008). Less environmental side effects are generated during the production of natural fiber when compared to the synthetic fiber, due to the decreased dependency on fossil fuels in the process of these materials from cultivation to harvest and extraction (Joshi et al., 2004). It has been reported that by replacing 30% glass fiber with 65% hemp fiber, approximately 50,000 MJ (equivalent to 3 tons of carbon dioxide emission) per ton of thermoplastic can be saved (Pervaiz and Sain, 2003). Table 1-2 presents a comparison between natural fibers to synthetic fiber in technical, economical and ecological perspectives.

Table 1-2. Comparison between common natural fibers and two synthetic fibers from economy, technical, and ecological points of view. (Shah, 2013).

Properties	Plant fibres (Bast, leaf and seed fibres)	Glass fibre (E- and S-glass)	Carbon fibre (Polyacrylonitrile (PAN)- and pitch-based)
Technical	Density (gcm ⁻³)	Low (~ 1.35-1.55)	High (2.50-2.70)
	Tensile stiffness (GPa)	Moderate (~30–80)	Moderate (70–85)
	Tensile strength (GPa)	Low (~0.4–1.5)	Moderate (2.0–3.7)
	Tensile failure strain (%)	Low (~1.4–3.2)	High (2.5–5.3)
	Specific Tensile Stiffness (GPa/gcm ⁻³)	Moderate (~20–60)	Low (27–34)
	Specific Tensile Stiffness (GPa/gcm ⁻³)	Moderate (~0.3–1.1)	Moderate (0.7–1.5)
Economy	Abrasive to machines	No	Yes
	Annual global production of fibres (tonnes) at 2010	31000000	4000000
	Cost of raw (£/kg)	Low (~0.5–1.5)	Low (~1.3–20.0)
Ecological	Energy consumption /kg of raw fibre (MJ)	Low (4–15) cultivation only	Moderate (30–50)
	Renewable source	Yes	No
	Recyclable	Yes	Partly
	Biodegradable	Yes	No
	Hazardous/toxic (upon inhalation)	No	Yes

1.1.2.2 Disadvantages of Natural Fibres

The major disadvantage of natural fibers in biocomposite is their large variation in properties and characteristics due to the a number of variables, including the fiber type, fiber location on the plant, processing methods, environmental conditions, soil quality, fertilization, seed density, field location, climate, and harvest timing. Further limitations, which can lead to the variation in the fiber quality, come from the processing conditions of natural fiber such as the extraction methods, damage incurred in harvesting and processing, variation in the cross-sectional area and the differences in drying process. In addition, the processing of natural fibers are generally restricted below 180–200 °C or below than 175 °C for prolonged periods (Faruk et al., 2012, Dittenber and GangaRao, 2012). However, the poor compatibility between hydrophilic surface groups on the fiber or filler and the hydrophobic groups in the matrix is the another major concern of using natural filler in polymer composites (Hassan et al., 2010). The poor compatibility between

the reinforcement and matrix results in weak interface bonding, which prevents adequate stress transfer and limits the mechanical strength of NFC.

1.1.2.3 Chemical Constituents of Natural Fiber

Plant fibers, which are also called lignocellulosic structures, mainly consist of cellulose, hemicelluloses, and lignin (Fuqua et al., 2012). Among all chemical compositions in fiber cell, cellulose with a general formula of $C_6H_{10}O_5$, is a non-branched macromolecule with 1–4 linked β -d-anhydroglucopyranose units (Akil et al., 2011, John and Thomas, 2008a). The cellulose content in the plant fiber can significantly influence the market value, performances, and the usefulness of the fiber for various applications (Reddy and Yang, 2005). For instance, bast and jute are highly preferable in textile and paper applications due to their higher cellulose content (John and Thomas, 2008a). Hemicellulose, also known as misnomer, a multiple branched polysaccharide polymer, is soluble in alkali and hydrolyzed in acids due to its hydrophilic nature (John and Thomas, 2008a). Hemicellulose, which consists of sugars such as glucose, xylose, galactose, mannose, and arabinose, acts as the binder between cellulose and lignin and contributes to strength and stiffness of fibres or individual cells to some extent (Reddy and Yang, 2005). Lignin, the second most abundant natural polymer after cellulose in the plant cell wall, is unique as a highly branched and amorphous biomacromolecule due to its heterogeneity, lack of defined primary structure and aromatic functionality (Liff et al., 2007). Lignin provides rigidity and compressive strength to plant tissue and individual fibers. It also acts as a protective barrier by stiffening the cell wall of fibers in order to prevent the physical damage of carbohydrates or sugars from chemical and microbiological attack (Reddy and Yang, 2005, Ho et al., 2012, Hameed et al., 2011). Figure 1-1 presents the molecular structure of the ingredients of natural fiber and their configuration in fiber cell.

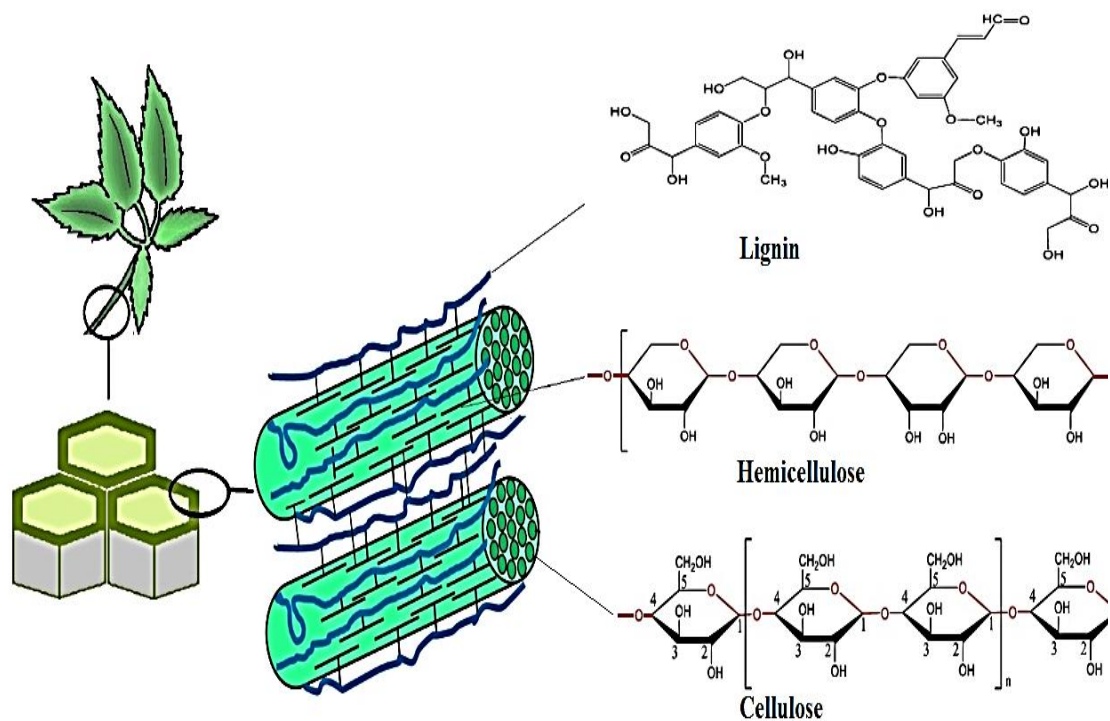


Figure 1-1 Microstructure and molecular structures of natural fiber.

Natural fibers also contain some minor components such as pectin, wax, protein, tannins, ash, and inorganic salts (Fuqua et al., 2012). Pectin, with the chemical name of heteropolysaccharides, offers flexibility for the plants. Pectin must be partially neutralized with ammonium hydroxide or alkali in order to make it soluble in water. Waxes, which consist of a few different types of alcohols, can be obtained from the plant by using organic solution but are not soluble in water and some acids such as stearic acid, palmitic acid and oleaginous acid (Bledzki and Gassan, 1999, John and Thomas, 2008a). The chemical composition and structural parameters of common lignocellulosic fiber which are significantly affected by the maturity, soil conditions, climate, and the extraction process are presented in Table 1-3.

Table 1-3. Chemical composition percentage (wt%) of common lignocellulosic fiber (Gurunathan et al., 2015)

	Fiber	Cellulose	Hemicellulose	Lignin	Pectin	Wax	Water soluble
Bark/Stem fiber	Flax	71–78	18.6–20.6	2.2	2.3	1.7	3.9–10.5
	Hemp	70.2–74.4	17.9–22.4	3.7–5.7	0.9	0.8	2.10
	Jute	61–71.5	13.6–20.4	12–13	0.2	0.5	1.2
	Kenaf	45–57	21.5	8–13	3–5	N.S.	N.S.
	Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9	0.3	6.1
	Banana	63–64	10	5	N.S.	N.S.	N.S.
	Nettle	86	4.0	5.4	0.6	3.1	2.1
	Sisal	67–78	10–14	8–11	10	2	1.3
Leaf fiber	Curaua	73.6	9.9	7.5	N.S.	N.S.	N.S.
	Pineapple	80–83	15–20	8–12	2–4	4–7	1–3
	Abaca	56–63	21.7	12–13	1.0	0.2	1.6
	Henequen	77.6	4–8	13.1	N.S.	N.S.	N.S.
Fruit/Seed fiber	Cotton	85–90	5.70	0.7–1.6	0–1	0.6	1.0
	Coir	36–43	0.15–0.25	41–45	3–4	N.S.	5.2–16.0
	Oil palm	65	0–22	19	N.S.	N.S.	N.S.
Wood	Hardwood	43–47	25–35	16–24	N.S.	N.S.	N.S.
	Softwood	40–44	25–29	25–31	N.S.	N.S.	N.S.

1.1.2.4 Properties of Natural Fiber

The high cellulose content, high degree of cellulose polymerization, high aspect ratio and low microfibrillar angle are the key contributing factors for the improvement of mechanical performances of plant fiber (Satyanarayana et al., 1986, Reddy and Yang, 2005). On the other hand, the thermal and biological protection of the natural fiber depends on the lignin structure and the content of the lignocellulose fiber (Jacob et al., 2005). The properties of natural fiber and their dependence on lignocellulose composition are summarized in Figure 1-2 suggests that any modification on the constituents of fiber cell can have a significant effect on the overall performance of natural fiber. The average density, moisture absorption and tensile property of common natural fibers present in Table 1-4.

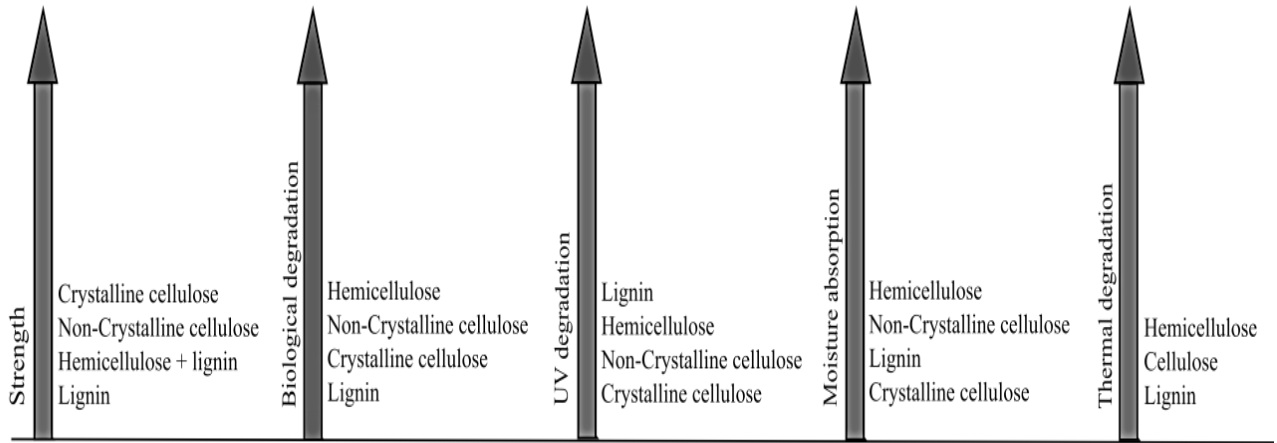


Figure 1-2. The influence of chemical composition of natural fiber on the performance of fiber. (Reproduced from Sain and Panthapulakkal ([Sain and Panthapulakkal, 2004](#)), with permission of Elsevier.)

In general, the electrical, thermal and chemical properties of composites are influenced by the polymer matrix whilst the mechanical characteristic of the composites are affected by the reinforcement phase ([Ghosh, 2002](#)). The interfacial bonding between matrix and fiber must be strong enough to minimize fiber pull-out. Therefore, the fiber and matrix combination should be chosen appropriately in order to ensure sufficient bonding strength ([Callister, 2007](#)). However, the poor compatibility between hydrophobic groups in the matrix and hydrophilic groups on the surface of fiber/filler results in poor interfacial bonding, which prevents adequate stress transfer between the reinforcement and matrix. Consequently, it leads to poor physical, chemical and mechanical performance of natural fiber reinforced polymer composites. In order to improve the compatibility between the fiber and the matrix, researchers developed a variety of surface treatment techniques to apply on the surface of natural fiber which are discussed in the section surface treatment.

Table 1-4. Physical and mechanical properties of plant fibre (Ahmad et al., 2015, Pickering et al. 2015)

Fibre	Density (g/cm ³)	Length (mm)	Diameter [μ m]	Tensile strength (MPa)	Specific tensile strength (MPa/g cm ⁻³)	Stiffness/Young's modulus (GPa)	Specific Young's modulus (GPa/g cm ⁻³)	Failure strain (%)
Ramie	1.5	900–1200	50	220–938	147–625	44–128	29–85	2.0–3.8
Flax	1.5	5–900	–	345–1830	230–1220	27–80	18–53	1.2–3.2
Hemp	1.5	5–55	–	550–1110	370–740	58–70	39–47	1.6–4.4
Jute	1.3–1.5	1.5–120	40–350	393–800	269–610	10–55	6.9–39	1.5–1.8
Harakeke	1.3	4–5	–	440–990	338–761	14–33	11–25	4.2–5.8
Sisal	1.3–1.5	900	50–300	507–855	362–610	9.4–28	6.5–20	2.0–7.0
Alfa	1.4	350	–	188–308	134–220	18–25	13–18	1.5–2.4
Cotton	1.5–1.6	10–60	–	287–800	179–530	5.5–13	3.4–8.4	3.0–10
Coir	1.2	20–150	–	131–220	110–180	4–6	3.3–5	15–30
Kenaf	1.45	–	70–250	930	641	53	36.55	1.6
Abaca	1.5	–	–	400	267	12	8	3–10
Bamboo	1.1	–	240–330	500	454	35.91	32.6	1.40
Banana	1.35	–	50–250	600	444	17.85	13.2	3.36
Coconut	1.15	–	100–450	500	435	2.5	2.17	20
Curauá	1.4	–	170	158–729	113–521	–	–	5
Softwood	1.5	–	–	1 000	667	40	26.67	4.4

1.1.2.5 Surface Treatment

Surface treatment of the reinforcement phase is a technique that enhances the physical and mechanical properties of the resulting composites by improving the quality of interfacial bonding between the reinforcement and the matrix phases (Xie et al., 2010). These techniques also reduce the moisture absorption of the composite when exposed to water or humid atmosphere (Azwa et al., 2013). Two main surface modification techniques that are typically applied on the natural fiber, are physical treatment and chemical treatment (Gurunathan et al., 2015).

1.1.2.5.1 Physical Treatment

Physical treatments by ionized gas (corona or plasma), steam explosion, and laser or γ -ray modify the structure and surface properties of natural fibers which can enhance the mechanical bonding between the fiber and the polymer (Faruk et al., 2012, Majeed et al., 2013). However, a very shallow surface of cell walls is modified by these treatments; thus

no significant influence applies on the hygroscopic characteristic of fibers (Xie et al., 2010).

In corona discharge treatment, the surfaces of natural fibers create new functional groups which clean the surface of the fiber and modify the free surface energy, polarity and wettability of the fiber and matrix (Majeed et al., 2013, Gassan and Gutowski, 2000). However, the polarity of treated yarns is not significant due to the difficulties in the effective treatment of three-dimensional objects with corona discharge (Faruk et al., 2012). A research study showed that the corona treatment affected the surface roughness and morphology of the hemp fiber, which improved the stiffness and elastic density energy and Young's modulus of the Polypropylene (PP) composite (Ragoubi et al., 2010).

The plasma discharge treatment applies an ionized gas, which contains an equal quantity of positively and negatively charged molecules, to the surface of the materials (Majeed et al., 2013). In general, larger plasma power results in greater interfacial adhesion, and the quality of fiber adhesion is sensitive to the atmosphere and the matrix type. For instance, plasma treatments on the flax-reinforced polyester composite indicated that the air treated flax fiber exhibit a better interfacial adhesion compared to the argon-treated flax fiber. On the other hand, argon plasma treatment was more effective than the air plasma treatment of flax fiber reinforced in high-density polyethylene (HDPE) (Bozaci et al., 2013). The tensile properties and the storage modulus in the dynamic mechanical properties of wood fiber-PP composite improves by plasma treatment. Moreover, the increment of oxygen/carbon ratios of wood fibers, in plasma treatment, can be confirmed by X-ray photoelectron spectroscopy (XPS) on the composite (Yuan et al., 2004).

1.1.2.5.2 Chemical Treatment

In chemical modification technique, the hydroxyl groups on the surface of the natural fiber cell wall are replaced by coupling agents with a chemical covalent bond. This replacement prevents the generation of hydrogen bonding between water molecules and hydroxyl groups on the cell wall, thus converts the hydrophilic nature of fiber to hydrophobic

nature. Figure 1-3 presents the schematic presentation of some of the common chemical surface treatments of natural fiber.

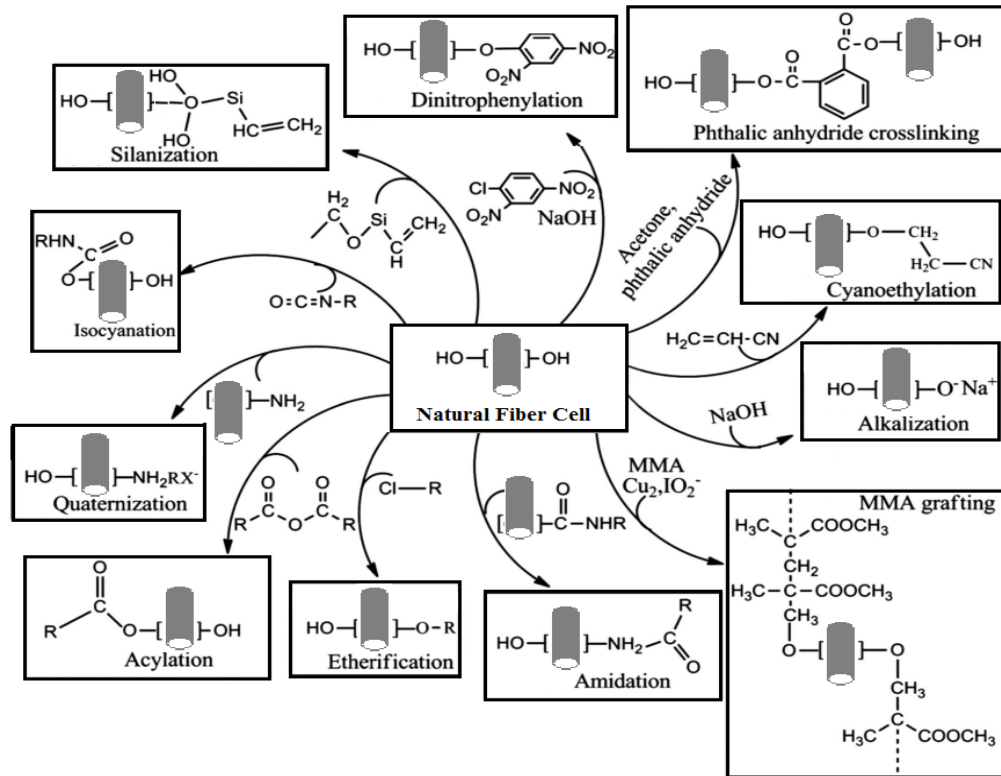
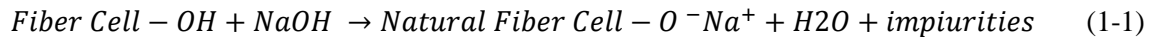


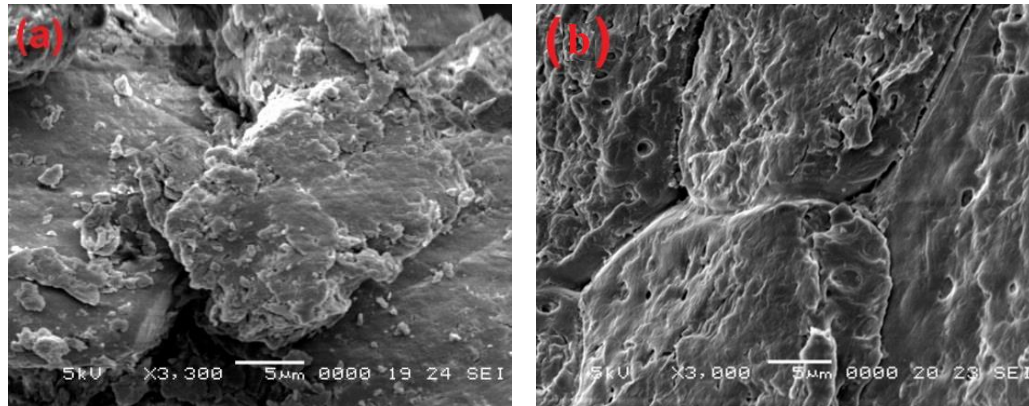
Figure 1-3. Common chemical surface modifications of natural fiber. (Adapted from (Gurunathan et al., 2015))

1.1.2.5.2.1 Alkali Treatment (Maceration)

The Alkali treatment or maceration changes the orientation of highly packed crystalline cellulose order to an amorphous region, which provides easy access to chemicals penetration. In this process, the Alkali sensitive hydroxyl (OH) groups on the cell wall react with alkali molecule which convert natural fiber cell to fiber-cell-O⁻Na⁺ as shown in Equation 1-1. Moreover, this treatment removes some portion of other component in the cell wall such as hemicelluloses, lignin, wax, pectin and oil-covering materials from the natural fiber structure. As a result, the fiber surface becomes clean by removing the impurities and the aspect ratio (length/diameter) of fiber increases due to the reduction of the fiber diameter (Kabir et al., 2012).



High crystalline fibers such as hemp fiber have the least tendency to react with an alkali solution as this treatment is more effective on the low crystalline fiber, which has high amorphous regions. The effect of the removal of chemical groups by alkali treatment can be identified by Fourier Transform Infrared (FTIR) spectroscopy (Mwaikambo and Ansell, 2002). The fiber shrinkage during treatment significantly improves the mechanical properties including fracture performance of fiber. For instance, the alkali treatment (20nmin at 20°C in 25% NaOH solution) of jute yarn improved the tensile strength and modulus of the fiber by 120% to 150% respectively (Gassan and Bledzki, 1999). Figure 1-4 illustrates the influence of removing the impurities and waxy materials from the surface of Palm Oil Shell (OPS) powders by alkali treatment on the bonding quality of OPS filled Unsaturated Polyester (UP) composite.



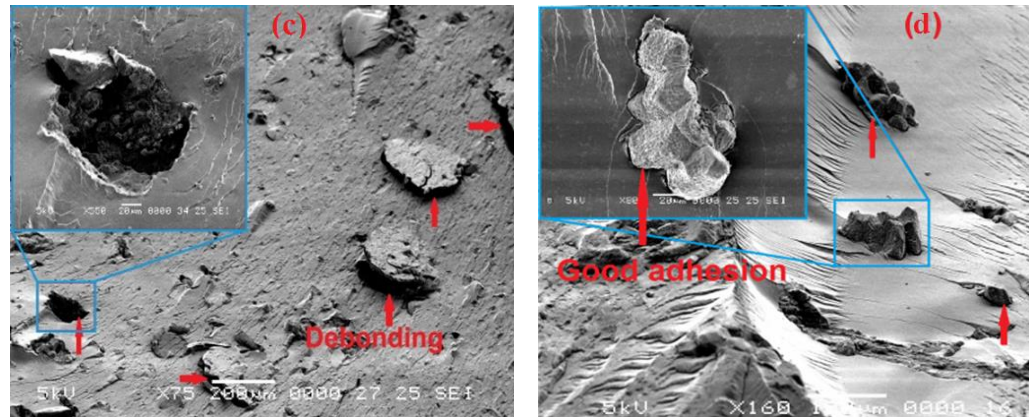


Figure 1-4. Scanning electron microscope (SEM) image of (a) Untreated OPS, (b) Alkali treated OPS, (c) Untreated OPS-UP composite, (d) Alkali treated OPS-UP (Nabinejad et al., 2014).

1.1.2.5.2.2 Silane Treatment

Surface treatment of natural fibers with silane coupling agents may mainly proceed through four steps; including (i) Hydrolysis in the presence of water and catalyst, (ii) Self-condensation during the hydrolysis process, (iii) Adsorption and (iv) Grafting under heating conditions. Figure 1-5 illustrates the interaction of silane with natural fibers by hydrolysis process.

In this treatment, the matrix characteristics and the organofunctionality of silane are the two critical factors for the interaction of the polymer and silane group. For instance, the functional groups of matrices in thermoset resins can react with the organofunctionalities of silanes in the presence of resin catalysts. On the other hand, a free radical process is required in order to couple the matrices and the vinylsilane-treated fiber in the case of inert thermoplastic polymers (Xie et al., 2010). It has been shown that the silane treatment enhanced the tensile and dynamic properties of jute fiber reinforced PP composites due to the improvement of interfacial adhesion between the fiber and the matrix (Hong et al., 2008). On another note, pretreatment of natural fiber using alkali or gamma-aminopropyltriethoxysilane (GS) treatment increased the performance of silane uptake by the increase of the mechanical interlocking between fiber and composite (Pickering et al., 2003).

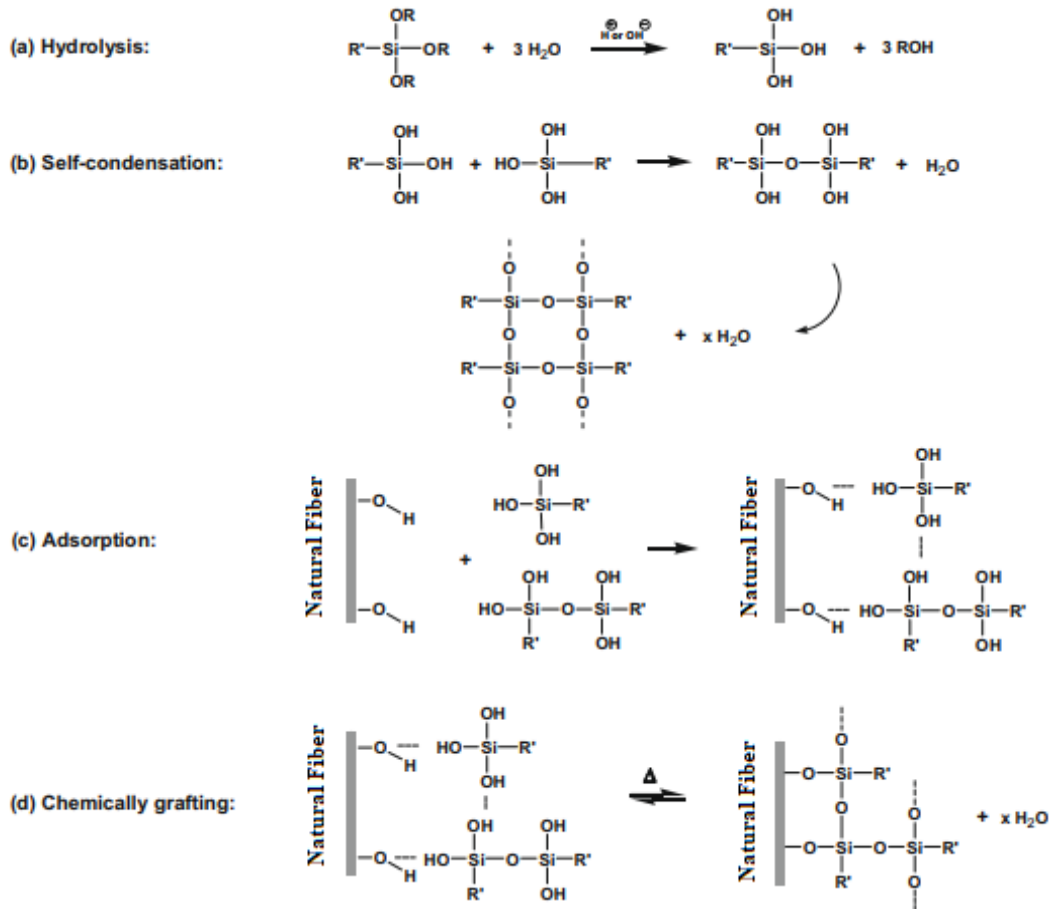


Figure 1-5. Silane treatment of natural fibers via hydrolysis process (Xie et al., 2010).

1.1.2.5.2.3 Other Chemical Treatments

In peroxide treatment, the hydroxyl group of the fiber reacts with the polymer matrix by initiating the free radicals of peroxide. Peroxide treatment improved the thermal stability and reduced the moisture absorption tendency of natural fiber and also enhances the fiber-matrix adhesion (Kabir et al., 2012). In acetylation treatment, the dimensional stability of composites increases due to the reduction of the hygroscopic nature of natural fibers (Li et al., 2007). In benzoylation treatment using benzoyl chloride, the hydrophilic nature of the fiber decreases which results in a better interfacial bonding between fiber and matrix and consequently increases the strength of the composite. During benzoylation treatment,

alkali pretreatment is required to remove extractable materials such as lignin, waxes, and oil covering materials to expose reactive hydroxyl (OH) groups of the fiber surface. In the second step, the hydroxyl group on the cellulose backbone will be replaced with benzoyl chloride as shown in Figure 1-6 (Kabir et al., 2012). Treatment of natural fiber by maleated coupling agents provides an efficient interfacial bonding between the functional group of the fiber and matrix. This is due to the grafting reaction of maleic anhydride with the hydroxyl groups (OH) in the amorphous region of cellulose structure, which results in long chain polymer coating on the fiber surface (Geroge et al. 2001). In isocyanate treatment an strong covalent bond (urethane linkage) generates between natural fiber and matrix as a result of a reaction between the functional groups of isocyanate and the hydroxyl groups of cellulose and lignin constituents of the fibres. Moreover, the moisture present on the fiber surface also reacts with the isocyanate and forms Urea. The Urea can further react with the hydroxyl groups of the celluloses which results in higher moisture resistance properties of the fiber (Kabir et al., 2012). Other chemical treatments namely permanganate, acrylonitrile grafting, sodium chlorite (NaClO₂) and thermal pre-treatment in wet or dry environments are also used by the researchers to modify the composition and the structure of the natural fiber.

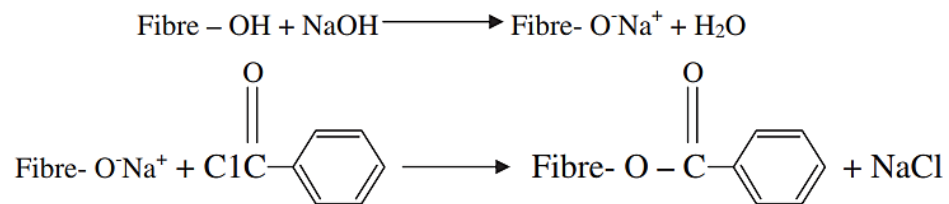


Figure 1-6. Treatment of natural fiber by benzylation treatment using benzoyl chloride (Joseph et al., 2003)

1.1.3 Natural-Fiber Composites

Green composites made of natural fibers, which called natural fiber composite (NFC), are used by researchers to develop eco-friendly materials, due to depleting nonrenewable petroleum resources and increasing environmental concerns. Natural fibers have a huge

potential to replace synthetic fibers in polymer composites. However, fabrication of green composites with 100% natural products is not cost-effective. Therefore, a combination of petroleum and natural based resources is a feasible way to fabricate green composite materials (John and Thomas, 2008b). In terms of matrix selection, thermoset polymers offer advantages such as easy processing, low temperature and low pressure requirement, easy wetting and higher loading of the fibers compared to the thermoplastics polymer. On the other hand, thermoset matrix is non-recyclable and have high curing time. Nevertheless, due to the outstanding mechanical properties of thermoset polymers, they are frequently used in different areas (Thakur and Thakur, 2014).

1.1.3.1 Processing of Natural Fiber Composites (NFCs)

Traditional polymer composite processing techniques can be utilized to manufacture the NFCs. The main limitation, which affects the processability of the NFC is the rapid increase of the viscosity of the mixture by fiber loading. Consequently, the filler percentage hardly reach more than 50–60 wt.% due to the increase of viscosity, although, the fiber volume fraction can be increased in sheet molding compound (SMC) process (for thermoset NFC) and film staking process (for thermoplastic NFC) up to 60–65% and 70% respectively. Due to the hydrophilic nature of natural fiber, the fibers absorb moisture. The moisture changes to water vapor and generates voids during the processing of composites, which lead to poor mechanical properties of NFC. Therefore drying technique such as hot air jets, rotating driers, ventilated ovens are recommended to reduce the moisture content at a minimum level (2–3%) (La Mantia and Morreale, 2011, Fuqua et al., 2012).

The low degradation temperature of natural fiber limits the maximum processing temperature (up to 200°C) of these materials. Therefore, a wide number of polymer matrixes which have higher processing temperature than the thermal stability of fibers cannot process with these fibers. Thus, thermoset resins with low and moderate curing temperatures such as unsaturated polyester, vinyl ester and epoxy, and thermoplastics with

low melting temperature like polyethylene and polypropylene are widely used for processing with natural fiber.

Another important factor which should be considered during the processing of natural fiber is the inconsistency in physical, chemical and mechanical properties due to the plant variation, weathering, harvesting and extraction conditions. The fiber and matrix interfacial bonding is also a critical factor in the processing of these materials. As the surface treatment improves the wettability of fiber and matrix, it facilitates the process and generates the strong interfacial bonding during the processing of natural fiber-polymer composite.

Injection molding process generally provides improved fiber dispersion in the matrix which has a significant effect on the tensile and flexural properties of composite (Mohanty et al., 2004). However, injection molding and extrusion process changes the length and diameter distribution of the fibers due to the screw motion, which deteriorates the properties of natural fibers. On the other hand, the isotropic properties of the composites are preserved and the physical properties are unaffected during the compression molding process (Liu et al., 2007). In terms of fiber length, compression SMC, Bulk Molding Compound (BMC) and hot press molding can process both long and short fibers whereas injection molding can be applied only for short fibers.

Other common processes such as Resin Transfer Molding (RTM) and Vacuum Infusion Process (VIP), which are widely used for synthetic fiber, can also be processed with natural fiber. It has been reported (Rouison et al., 2006) that the injection pressure and the fiber concentration in RTM process were the critical parameters to achieve proper mold filling. Moreover, pre-pressing of natural fiber at 100°C can increase the fiber content of NFC in RTM process which also leads to an easier process with high-quality and low-voids content of the product.

1.1.3.2 Mechanical Performance of Natural Fiber Composites (NFCs)

The mechanical performance of natural-fiber-reinforced thermosetting polymers, similar to synthetic fiber composite, is extremely dependent on the fiber source, volume fraction, fiber orientation, and interfacial interaction between fiber and matrix phases. In general, the traditional theory of composite material with a heavy emphasis on the effects of fiber treatment can be applied to determine the mechanical performance of NFC. Thermoplastic composites with continuous natural fiber are still relatively uncommon due to the difficulty in processing. Moreover, for short and randomly orientated natural fiber thermoplastic composite, the surface treatment of fiber does not have a significant effect on the strength of NFC. As filler loading increases, the strength of NFC decreases due to the surface void formation in high viscous molten polymers. Although the surface treatment of fibers can alleviate this issue, it has been reported that the strength of these composites is nearly comparable with the neat thermoplastic polymer even at high filler loading level ([Fuqua et al., 2012](#)).

1.1.3.2.1 Tensile Properties

The tensile strength and modulus of NFC, which indicate the average properties through the thickness, are measured by the universal testing machine. In general, using untreated fiber with low aspect ratio can decrease the tensile strength of thermoplastics. The tensile strength of treated NFC experiences a peak due to the addition of the fiber loading up to a certain percentage, while the tensile modulus keeps on increasing with a further increase of fiber content. To predict the tensile modulus of NFC, the rule of mixture can be used while Halpin–Tsai equation is the most effective to estimate the tensile strength ([Ku et al., 2011](#), [Fuqua et al., 2012](#)). As the effects of voids content and the low interfacial shear strength, which hinder the effective load transfer, were not considered in the theory, the predicted tensile modulus of NFC can be higher than the experimental value. Moreover, the lower tensile strength in experimental value might be due to the improper alignment of fiber and void content in NFC ([Arib et al., 2006](#)).

1.1.3.2.2 Flexural Properties

By definition, flexural strength indicates the ability of the structure to resist deformation. The elastic modulus and moment of inertia are two important characteristics in order to determine the flexural strength of material (Faruk et al., 2012). In general, the flexural strength and flexural modulus of NFC are highly influenced by the fiber content, fiber length, and its orientation. The flexural properties similar to tensile strength, experiences a peak with the increment of fiber content and declines by a further fiber loading. Moreover, the inadequate wetting of the natural fiber due to the insufficient amount of matrix prevents the formation of the void-free composite at high fiber content. It should be noted that the flexural strength and flexural modulus of NFC also increase with the increment of the fiber length, similarly to synthetic fiber composite (Sathishkumar et al., 2012). A study on an alfa polypropylene composites showed that the flexural modulus of NFC was almost constant from 5 to 20% of fiber loading. However, any further increment in fiber content resulted in a drastic increase in the flexural modulus of the composite. This was attributed by the sufficient wettability of fiber with the matrix which resulted in a good stress transfer from the low-modulus polymer matrix to the high-modulus treated fibers (Arrakhiz et al., 2013).

1.1.3.2.3 Impact Properties

The energy absorption in impact test of composite materials strongly depends on the fiber and matrix properties together with their interfacial bonding strength. Thus, the surface treatment of natural fiber has a significant effect on the impact strength of NFC (Mylsamy and Rajendran, 2011). The effect of flax fiber on polypropylene (PP) showed that impact strength increased by filler loading and hit the peak at 30% and then decreased at 40% (John and Anandjiwala, 2009). In another study, the energy absorption of cabuya fiber and sisal fiber-reinforced HDPE and oil palm fiber-reinforced unplasticised poly vinyl chloride (PVC-U), however, decreased by increasing natural fiber loading and the thermoplastic composite become more brittle (Torres and Aragon, 2006, Bakar and

Hassan, 2003). An investigation on the low-velocity impact energy absorption of the hemp- fiber-reinforced unsaturated polyester composite confirmed that the peak load and energy absorption improved significantly at various fiber volume fractions. Moreover, by increasing the volume fraction of hemp fiber the contact time was also increased which led to the higher peak load. The brittle fracture behavior of composite at lower fiber volume fractions was converted to the ductile behavior at higher fiber volume fractions (Dhakal et al., 2007).

1.1.3.3 Thermal Stability of Natural Fiber Composite (NFCs)

Thermal analysis such as differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) are techniques where heat flow and mass losses of the sample are monitored respectively against temperature or time while the temperature is programmed. In order to achieve a deep understanding of the thermal decomposition mechanisms, FTIR Spectrometry and Mass Spectroscopy (MS) can be coupled with thermal analysis. These coupled techniques are helpful not only to get the on-line analysis of the volatile products but also to clarify different steps during fiber decomposition at DSC and TGA, which are known as TG-FTIR and TG-MS respectively (Pielichowski and Njuguna, 2005, Benítez-Guerrero et al., 2014).

1.1.3.3.1 Thermal degradation of fiber

Lignocellulosic fibers exhibit similar trends in DSC and TGA analysis. Table 1-5 illustrates the three main stages of thermal decomposition of the natural fiber where the main decomposition occurring in the range of 200-400°C (Nabinejad et al., 2015b, Nabinejad et al., 2015a). The thermal analysis depends on the atmosphere involved. For instance, the endothermic peak in DSC test for cellulose under inert atmosphere changes to exothermic peak at oxidative (air or oxygen) atmosphere (Martin et al., 2010).

Table 1-5. The three main stages of mass loss of natural fiber (Nabinejad et al., 2015b)

Stage1		Stage2		Stage3	
Temperature (°C)	Correspond	Temperature (°C)	Correspond	Temperature (°C)	Correspond
220–315	Hemicellulose pyrolysis	315–400	Cellulose pyrolysis	160–900	Lignin pyrolysis
50–300	Moisture evaporation	200–300	Hemicellulose decomposition	400–500	Lignin and cellulose degradation
300	Hemicellulose and glycosidic link of cellulose decomposition	360	α -cellulose decomposition	200–500	Lignin decomposition with max at 350 °C and two other peaks
250–300	Hemicellulose decomposition	300–400	Cellulose decomposition	420	Lignin decomposition
97	Moisture evaporation	325	Protein degradation	Major at 260 and slow at 390	Major decomposition for silk fiber gelatin composite
186–401	Hemicellulose decomposition	207–404	Cellulose decomposition	174–600	Lignin decomposition

(Reproduced from Nabinejad et al. (Nabinejad et al., 2015b), with permission of Elsevier.)

The DSC and TGA curves of hemp fiber and its ingredients are presented in Figure 1-7. The first mass loss in TGA and heat absorption in DSC curve in 10-150°C is referred to the moisture evaporation, where the linked water molecules evaporate in higher temperature (about 100°C) compared to the free water molecules. Hemicellulose exhibits an endothermic peak/mass loss at the range of 10-200°C together with an exothermic peak/mass loss at 200-320°C in DSC/TGA curve, which are referred to linked water evaporation and hemicellulose molecule degradation respectively. The third step decomposition of natural fiber at 340°C is referred to the cellulose section which generates a sharp mass drop in TGA curve. The DSC curve of cellulose shows an endothermic peak referred to depolymerisation followed by generation of cellulose char residue via exothermic reactions. The figure also shows that the lignin decomposition happens at the temperature range of 250-450°C where the peak is hidden beneath peaks associated with cellulose and hemicellulose (Kabir et al., 2013, Nabinejad et al., 2015b).

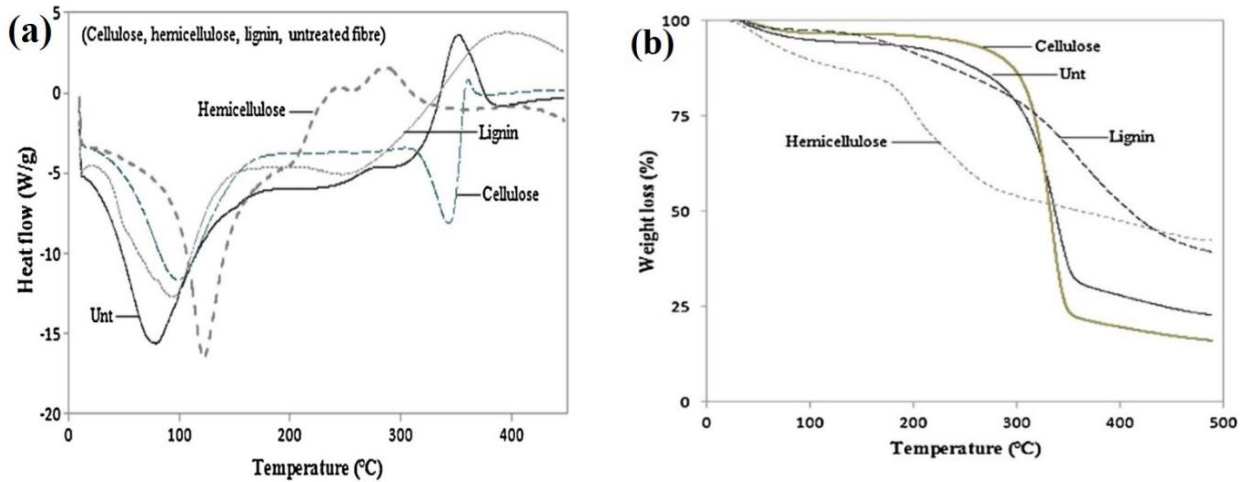


Figure 1-7. (a) DSC and (b) TGA curve of fiber constituents and untreated fiber. (Reproduced from Kabir et al. (Kabir et al., 2013), with permission of Elsevier.)

The TGA is a reliable method to measure the effectiveness of removing the impurities from the surface of the natural filler (Nabinejad et al., 2015b). In general, non-cellulosic polysaccharides and mineral matters change the thermal behavior of the cellulose as the main component of natural fiber. Moreover, the temperature of pyrolysis and combustion of natural fiber are influenced by the hemicelluloses, pectins, and inorganic elements (Benítez-Guerrero et al., 2014). Figure 1-8 shows the TGA and derivative thermogravimetric analysis (DTG) curves of untreated and alkali treated oil palm fiber. It is clear that the hemicellulose peak in DTG was partially removed and the cellulose decomposition peak shifted to the lower temperature. Moreover, the mass residue of fiber was decreased in TGA curve due to the alkali treatment.

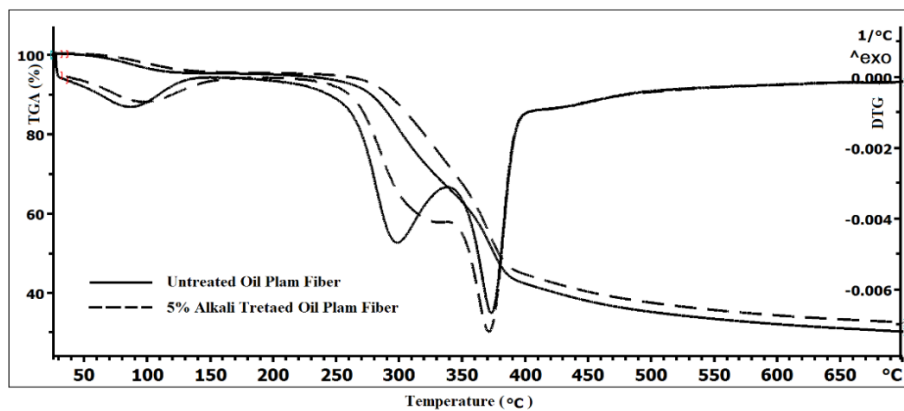


Figure 1-8. TGA and DTG Curves of untreated alkali treated oil Palm empty fruit bunch fiber

1.1.3.3.2 Thermal Degradation of Composite

Thermal analysis of NFC can provide useful qualitative and quantitative information. In general, thermal stability of polymer composite depend on the thermal stability of fiber and polymer, the moisture content, the dispersion quality of the fiber and other particles in the matrix (Ray and Cooney, 2012). The surface treatment enhances the thermal stability of natural fiber, which increases the thermal stability of NFC (Li et al., 2007). Basically, polymer degrades easier and faster in the air or oxygenated atmosphere such as air compared to an inert atmosphere like nitrogen (Doan et al., 2007). The thermal stability of some NFCs such as jute fiber reinforced polypropylene showed that it was higher than its individual reinforcement and matrix phases. Moreover, the thermal resistance of this composite increased in air atmosphere while the reverse trend recorded in nitrogen atmosphere (Monteiro et al., 2012). It appears that the formation of char residue in the earlier stage of thermal degradation at oxidative environment is the key factor for shifting the thermal degradation peak of the NFC to the higher temperature (Nabinejad et al., 2015b, Sliwa et al., 2012).

Use of natural fillers limits to compounds made of polymers that exhibit lower processing temperature compared to the degradation temperature of natural fillers. Moreover, the filler loading have significant effect on the thermal stability of NFC. Figure 1-9 presents the effect of oil palm shell as a natural filler on the thermal degradation of LDPE in different filler loading at TGA curves under the nitrogen atmosphere. The figure indicates that natural fillers change the degradation temperature range of NFC, which starts at a lower temperature and it completes at a higher temperature in an inert atmosphere.

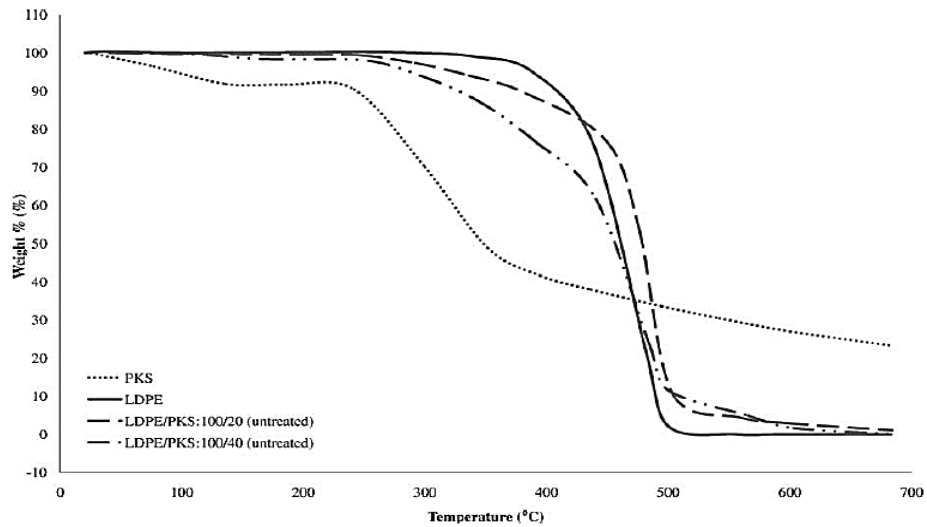


Figure 1-9. TGA curves of different percentages of oil palm shell (OPS) in LDPE composite. (Reproduced from H. Salmah et al. (Salmah et al., 2012), with permission of SAGE Publishing Company.)

1.1.3.4 Nano Particles and Natural Fiber Based Hybrid Composites

Hybrid composites are defined as a system, where two or more reinforcements/fillers are present in a single matrix, or the reinforcement/filler is added to a blend of matrices (a mixture of different matrices), or as both approaches combined (Saba et al., 2014). Natural fiber plastic composites have been commercialized nowadays, however, the potential application of these materials has been limited in many industries due to their low mechanical performance (Saba et al., 2014). Nanoparticles such as nanoclays, metal oxides, carbon nanotubes and carbon nanofibres offer an opportunity to enhance the performance of composites beyond that established in conventional materials (Dewan et al., 2013). Only a small quantity of these nanoparticles have been reported to enhance physical, thermal and mechanical properties of composites (Alamri and Low, 2013).

Although many research studies have included nano-composite and natural fiber composites individually, hybrid composites of natural fiber and nanoparticles need more attention. The majority of the research published on natural fiber and nanoparticle hybrid composites were conducted with nanoclay, and the effect of other nanoparticles such as carbon nanotube, on the performance of hybrid composites are the least understood.

presents the updated research studies on hybrid composites using natural fiber/filler and carbon nanotubes. As can be seen from Table 1-6, all the studies were limited to the wood flour composite and thermoplastic polymers.

Table 1-6. Reported works on natural fiber - carbon nanotube hybrid composites.

Natural Fiber	Matrix	Reference
Wood Flour	Polypropylene (PP)	(Nabinejad and Sujan, 2016)
Wood flour	Polypropylene (PP)	(Fu et al., 2010)
Wood flour	Low density polyethylene (LDPE)	(Kordkheili et al., 2013)
Wood flour	polyvinyl chloride (PVC)	(Farsheh et al., 2011)
Old newsprint (ONP)	Polypropylene (PP)	(Asgary et al., 2013)
Bagasse	High density polyethylene (HDPE)	(Ashori et al., 2013)

1.1.3.5 Natural Fiber Composite from Palm Oil Biomass

In the past few decades, the global production of palm oil, the highest yielding edible oil crop, has steadily increased, as shown in Figure 1-10 ([Shean, 2014](#)). Currently, nearly 80 % by volume of the harvested fruit bunches are discarded as waste material. This significant amount of waste material causes an emerging environmental and economic challenge in the 43 countries involved in cultivating a total of 14.4 million hectares of Palm oil ([Yan et al., 2014](#), [Chong et al., 2013](#)). For example, it was estimated in Malaysia only, with 4.69 million hectares in cultivation in 2009, had 77.24 million tons of palm oil biomass ([Abdul Khalil et al., 2013](#)), which had been simply discarded onto the environment.

The large amount of waste material produced by the oil palm industry has led to calls for an improvement in recycling these materials. Natural fiber extracted from palm oil biomass has been proven ([Hassan et al., 2010](#)) to provide some specific properties that are comparable to conventional synthetic fibers used in composite materials. In general, a typical fresh fruit bunch (FFB) produces 21–23% empty fruit bunches (EFB), 12–15% oil palm fiber (OPF) and 6–7% oil palm kernel shell (OPS) by weight as waste materials ([Hossain et al., 2016](#)).

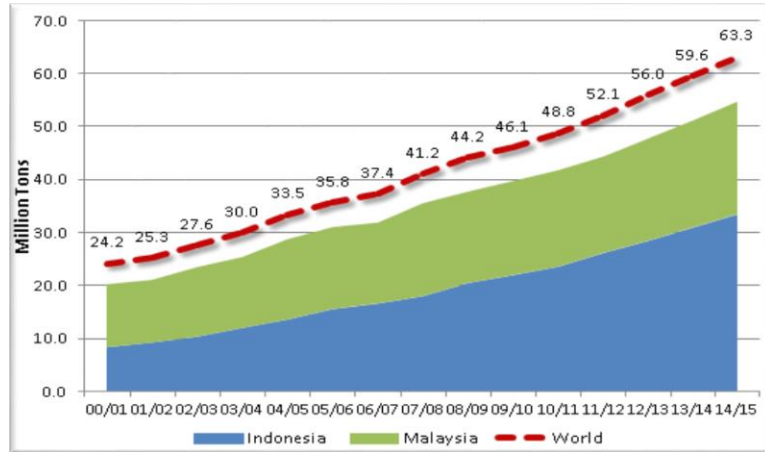


Figure 1-10. Global palm oil production. (Shean, 2014)

Figure 1-11 presents the OPF and OPS as a byproduct of palm oil industry. According to the study carried out by Hassan and co-workers, most researchers have focused their studies on OPEFB fiber as a reinforcing material in various polymer matrixes. Physical and mechanical properties, water absorption, and the effect of OPEFB fiber treatment were the main issues researchers analysed to confirm the suitability of OPEFB and OPF with the polymer matrices (Mahjoub et al., 2013, Hassan et al., 2010). However, no significant research has been carried out until now (2017) on the performance of other lignocellulose biomass from the palm oil industry.



Figure 1-11. Palm oil biomass (palm oil fiber and palm oil kernell shell)

Table 1-7 presents the current history of research related to OPS polymer composite. As can be seen from Table 1-7 there is lack of research on the application of these materials in thermoset resins. Moreover, a comprehensive study should also be conducted on the effect of other parameters with different surface treatments on the OPS polymer composite.

Table 1-7. Research studies conducted on OPS polymer composites

Matrix	Parameters	Properties	Reference
low-density polyethylene (LDPE)	filler loading	tensile properties, thermal analysis, water absorption	(Salmah et al., 2013)
Polylactic acid (PLA)	filler loading, treatment with Butyl methacrylate treatment	Tensile strength and thermal stability	(Hasnan et al., 2016)
Polypropylene (PP)	Treatment with PP-POSS ¹ and PP-g-MAH ²	Mositure absorption, Tensile and impact peroperties	(Mohaiyiddin et al., 2016)
Natural Rubber (NR)	filler carbonization at different temperature	Tensile properties, abrasion resistance hardness, density, fatigue properties	(L.Ekwueme et al., 2016)
Recycled high density polyethylene (rHDPE)	filler loading	Rheological properties and thermal stability	(A. Nadiatul Husna, 2016)
Polypropylene (PP)	Filler loading and treatment with 3-aminopropyltriethoxysilane	Tensile and flexural properties	(H. L. Ong, 2016)

1 polypropylene methyl polyhedral oligomeric silsesquioxanes
2 polypropylene-grafted maleic anhydride compatibilizers

1.1.4 Conclusion

The advantages and disadvantages of using lignocellulosic fillers as reinforcement in polymer composites were reviewed in this chapter. Despite their many advantages, the large variation in properties and characteristics of the natural fiber, and their poor compatibility within a matrix limit their processing and application. Various physical and chemical surface treatment methods to improve their compatibility were also discussed in this chapter. Due to the inherent low degradation temperature of the natural fiber, their application in polymer resin is limited by temperature constraints. In addition, the rapid increase of the viscosity of the mixture limits the fiber loading, and traps voids in the composite. As a result, the voids formed during the processing of composites results in poor mechanical performance.

The chapter also addressed the effects of fiber loading, surface treatment and filler size on the tensile and flexural properties, impact strength and dynamic mechanical performance of the composite. Furthermore, the thermal degradation of fibers together with the thermal degradation of their composite was investigated in order to determine the thermal stability of the composite. Moreover, an investigation into the potential application of by-products from palm oil biomass revealed that natural fibers, using palm oil shell filled in thermoset polymer needs more attention. Equally important, it has been shown the addition of nano particles such as carbon nano tube; to enhance the mechanical performance of NFC was limited to thermosplastic composites.

1.2 Research Challenges

It has been stated in section 1.1.3.2 that the mechanical performance of natural fiber composite (NFC) is limited to low mechanical properties when compared to synthetic fiber. Wood floor composites (WFC) are natural fiber composite materials in which wood particles are dispersed in the polymer matrix instead of the longer fibers in NFC. Generally, particulate composites have very low mechanical properties compared to fibrous composites. However, particulate composites are relatively lower in cost and easy to produce which leads the researcher to try to improve the mechanical performance of these composites. Equally important, the majority of studies in the field of WFC were conducted to improve the mechanical properties of thermoplastic resins. While thermoset resins, in general, possess a higher mechanical performance compared to thermoplastic composites, thermoset based WPC was not fully developed. This is because the loading of lignocellulosic filler in thermoset resins (such as polyester, vinylester, and epoxy) are limited to very low filler content. Thus, this issue is one of the crucial parameters, which should be considered when working with thermoset based natural fiber composite (Osman E et al., 2012, Kosar and Gomzi, 2010).

It has also been discussed in section 1.1.3.3 that the low degradation temperatures of natural fibers/fillers limit the maximum processing temperature and the operating temperature range of NFC or WPC. Surface treatments, which can improve the

mechanical performance of these composites, affect the thermal stability of the fiber/filler. Therefore, the influence of surface treatment on the thermal stability of natural fibers/fillers and their composites needs to be considered when the improvement of the mechanical performance of NFC/WPC is the focus of the research.

In terms of thermal analysis, Thermogravimetric analysis (TGA) is a method which measures the mass losses of composite as a function of increasing temperature (with a constant heating rate), or as a function of time (with constant temperature). As the thermal degradation of the natural filler and some polymer matrix occur within similar temperature ranges, this method is not capable of accurately predicting the filler percentage for natural fiber composites (Fuad et al., 1994).

From the above discussion, which addressed the research challenges, the research questions are given as below:

- 1) How to improve the mechanical performance of WPC?
- 2) What is the consequence of improving the mechanical properties of WPC?
- 3) How to increase the loading of natural filler in thermoset based natural fiber or wood flour composites?
- 4) How to determine the filler contents of WPC?

1.3 Scopes of Thesis

The overall objective of this research study was to develop a thermoset based wood flour composite to achieve an optimal mechanical performance and investigate the thermal stability of the wood polymer composite (WPC). In this regard, the scope of this research study is given as below:

I. OPS powder will be used in this study as an example of other wood powders from palm oil biomass (OPEFB fiber and oil palm fiber) in order to study the potential application of these materials in WPC.

II. Unsaturated polyester resin will be selected to fabricate the thermoset resin based WPC.

III. To identify the mechanical performance of composites, the samples will be prepared and the tensile strength, tensile modulus, flexural strength and flexural modulus of the composite will be measured according to ASTM D638 and ASTM D790.

IV. The effect of filler size, filler content and filler treatment on and the mechanical performance of composites will be measured.

V. FTIR and SEM tests will be carried out to investigate the effect of surface treatments on the functional groups of natural filler and the quality of interfacial bonding of filler and matrix in the composite.

VI. The effect of filler content on the fabrication and processing parameter will be investigated and a mitigation action will be developed to overcome any limitations of using natural filler at high filler loading in thermoset resins.

VII. An empirical model based on the thermogravimetric analysis (TGA) will be developed to quantify the filler percentage in the developed wood polymer composite.

VIII. The effect of surface treatment of the natural filler on the thermal stability of the natural filler and its composite will be investigated. Moreover, the effect of filler loading on the thermal stability composite will be investigated.

IX. The barriers to expanding the potential application of Carbon Nano Tubes (CNT) to fabricate OPS-CNT polyester hybrid composites will be analyzed.

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Chapter 2

Effect of Size and Treatment of Natural Filler:

Chapter 2

2 Effect of Size and Treatment of Natural Filler:

Introduction

As stated earlier, OPS has been selected as an example of a natural filler from palm oil biomass, to be used in this thesis. As mentioned in the previous chapter, surface treatment of natural fillers enhances the physical and mechanical performance of composites by improving the quality of interfacial bonding between the filler and the polymer matrix.

This chapter presents an introductory discussion of the physical and chemical properties of OPS and its unsaturated polyester (UP) composite, which is the foundation of this thesis. To investigate the mechanical performances of an OPS filled unsaturated polyester (UP) composite, OPS powder has been analyzed on how it interacts with the polymer matrix, and how this interaction influences the mechanical performance of the OPS-UP composites. Moreover, the size of the OPS powder was optimized to achieve the maximum performance of the composite. To improve the filler-matrix bonding, the effect of the chemical surface treatment of OPS on the mechanical properties of the composite was investigated.

In order to measure the consequences of improvement in the mechanical property of composite by surface treatment, the thermal stability of OPS will be discussed in detail through the thermogravimetry analysis (TGA). Then, the effects of different surface treatments on the chemical composition of fiber cells (cellulose, hemicellulose, and lignin), the thermal stability of OPS and the mechanical performance of the composites were investigated.

As mentioned earlier, this chapter is divided into two parts, and each part is considered as a published paper.

2.1 Filler and Matrix Interaction and Effect of Filler Size

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Effect of Oil Palm Shell Powder on the Mechanical Performance and Thermal Stability of Polyester Composites.

O. Nabinejad, D. Sujan, M. E. Rahman and Ian J. Davies

Abstract: *This paper presents an experimental study on the development of polymer bio-composites. The composites were fabricated from unsaturated isophthalic polyester resin containing powdered oil palm shell (OPS) as a function of powder particle size. The influence of washing OPS powder in methanol to remove surface impurities was also investigated with the tensile and flexural strengths and moduli improving significantly (between 22.9~61.4 %) for the composites containing washed OPS powder compared to the unwashed case. It was observed that the composite tensile and flexural strength generally increased with decreasing powder size with the strength of the composite containing 75~150 μm OPS powder being similar to that of the pure matrix. However, the tensile and flexural moduli of the composites were found to be essentially independent of powder size. Thermogravimetric analysis (TGA) in flowing oxygen indicated that the addition of OPS powder shifted the thermal degradation peak of the bio-composite from 370 °C to 418 °C.*

Keywords: Polyester Composite, Oil palm shell, Strength, Modulus, Thermal Analysis

2.1.1 Introduction

The twenty first century has seen notable achievements in the field of bio-material science due to a rapid increase in industrial applications of green composites containing either natural reinforcement or bio-polymers or else a combination of both. Natural fiber or filler reinforcements that have been used in bio-composite materials have included renewable sources such as cotton, flax, hemp, kenaf or else by-products from crops such as banana, coconut, rice husk and palm oil empty fruit bunches. According to recent studies, the burning of composite components with natural fibers produces lower air emissions due to their reduced energy consumption when compared to equivalent synthetic fiber composites (Cicala et al., 2010). The main advantages of these natural or cellulose based fibers or fillers compared to man-made fibers such as glass, carbon or aramid include their low cost, low density, ease of separation, carbon dioxide sequestration, non-corrosiveness, reduced tool wear and reduced respiratory irritation (Mohanty et al., 2004). However, the major disadvantage of natural filler reinforced polymer composites is the poor compatibility between hydrophobic groups in the matrix and hydrophilic surface groups on the fiber or filler (Hassan et al., 2010). Consequently, the weak interface due to this poor compatibility prevents adequate stress transfer between the reinforcement and matrix, therefore limiting the mechanical strength of composite materials containing natural fiber or filler.

Oil palm is the highest yielding edible oil crop in the world and a total of 14.4 million hectares are currently cultivated in 43 countries where Indonesia, Malaysia and Nigeria being responsible for approximately 83 % of the worldwide production (Yan et al., 2014). Palm oil and palm kernel oil are two types of oil found in palm nuts which are extracted from the outer and inner core of the nut, respectively. The palm kernel is covered by a hard endocarp which is also known as oil palm shell or oil palm shell (OPS) (Basri et al., 1999) as shown in Figure 2-1. One emerging environmental and economic issue related to the oil palm industry is that nearly 80 % of the volume is removed as waste material from processing of the fresh fruit bunches. At the present time approximately 6.89 million tons of OPS are produced annually with this amount being expected to increase rapidly in the coming years (Chong et al., 2013). Whilst OPS has been used occasionally as a boiler

fuel, researchers have suggested its use as lightweight aggregates to replace conventional aggregates in structural elements and road construction with use of OPS in concrete being expected to lead to cost reductions on the order of 40 % (Basri et al., 1999, Dai and Fan, 2014). A study adding OPS in polymer materials showed that it improved the mechanical properties of the composite (Nabinejad et al., 2014). In spite of this, relatively little work has been carried out on the development of polymer matrix composites containing OPS as a reinforcement. In the present work the authors have therefore investigated the mechanical and thermal properties of bio-composites comprising of unsaturated polyester reinforced by OPS filler.



Figure 2-1. Oil palm shell

2.1.1.1 Physical Properties and Chemical Composition of OPS

With the exception of water, plant cell walls comprise mainly of sugar based polymers, e.g., cellulose and hemicellulose, which are combined with lignin and lesser amounts of extracts, protein, starch and inorganic phases. Table 2-1 shows the main chemical constituents and lignocellulose composition of several raw OPS specimens (Hoseinzadeh Hesas et al., 2013, Idris et al., 2010, Lahijani et al., 2012, Rowell et al., 2000) with

variations in the individual plants, climatic conditions, age of the plants and processing methods being known to have a significant effect on the total lignocellulose content.

Table 2-1. Chemical composition of raw OPS ([Hoseinzadeh Hesas et al., 2013](#), [Idris et al., 2010](#), [Lahijani et al., 2012](#))

Ultimate analysis (wt.%)				Proximate analysis (wt.%)				Lignocellulose composition (%)			
C	H	N	O	Moisture	Ash	Volatile%	Fixed Carbon%	Cellulose	Hemicellulose	Lignin	Extractives
54.7	7.49	2.03	35.6	4.7	7.2	74.3	13.8				
41.33	4.57	0.99	53.02	0.0	10.5	69.2	16.0				
46.65	6.43	8.25	35.67	7.0	1.8	69.9	21.3	32.6	22.1	42.3	3.0

The functional groups found on the surface of OPS have been investigated using Fourier transform infrared spectroscopy (FTIR) ([Lahijani et al., 2012](#)) with the presence of stretching O-H bonds found in carbonaceous materials, stretching C-O bonds, vibrations for ketones and quinones and a peak attributed to aromatic rings being noted. Similar to other natural reinforcements, it is expected that the hydroxyl group plays an important role in absorbing moisture onto the OPS surface with the surface water molecules acting to separate the interface between the matrix and OPS reinforcement. This absorption of water will tend to produce poor adhesion between the filler and polymer ([Ray and Rout, 2005](#)) and subsequently reduced mechanical properties. Further to this, the density of OPS has been reported to be $1.53 \text{ g}\cdot\text{cm}^{-3}$ ([Guo and Lua, 2002](#)) with a porosity of 3.9 % and specific surface area of $1.6 \text{ m}^2\cdot\text{g}^{-1}$.

A scanning electron micrograph (SEM) showing the irregular shape of raw OPS together with the presence of pores is shown in Figure 2-2. Also noted is the presence of surface impurities which are attributed to various waxy and oily materials left as a byproduct of the oil extraction process when the oil, kernel and kernel shell were separated. To investigate the effect of porosity and surface roughness of the OPS on the mechanical properties of polyester composites, the mechanical properties of polyester composite before and after removing impurities from the surface of OPS were studied. Following this, the influence of OPS powder particle size on the mechanical and thermal properties of polyester composites containing 5 wt.% of OPS powder was investigated

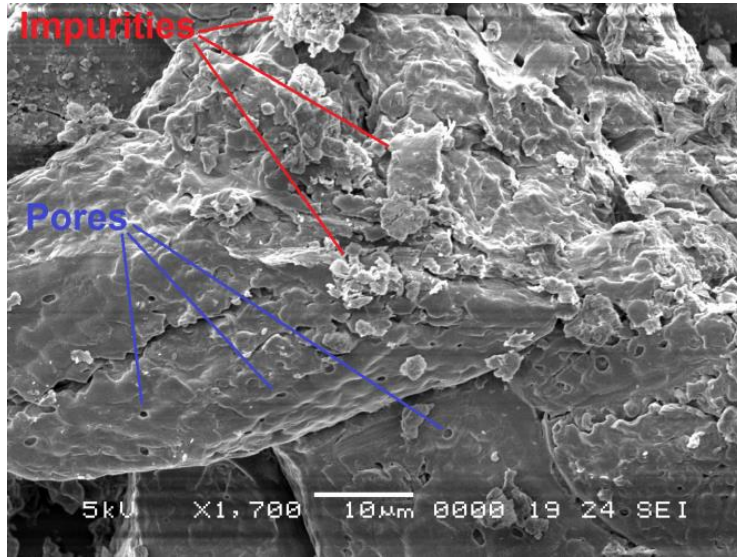


Figure 2-2. The pore distribution and impurities on the surface of raw OPS

2.1.2 Sample Preparation

Raw OPS material (Lambir Oil Palm Company, Sarawak, Malaysia) was first ground in a ball mill to produce OPS powder and then separated by mechanical sieving into different particle size distributions as shown in Table 2-2. Following this, the powdered OPS was optionally soaked in methanol for 1 hour at room temperature and then washed with distilled water in order to remove impurities and dried in an oven at 100 °C for 2 hours – this was referred to as “washed” OPS powder. In contrast to this, the “unwashed” OPS powder was dried in an oven at 100 °C for 2 hours without being subjected to the methanol washing treatment.

Table 2-2. Composite samples with different sizes of OPS powder

No	OPS size	Material name	Filler percentages	Composite name
1	--	Pure Resin	0%	PR00
2	600µm < size <1.18 mm	OPS 1200	5%	TPG1200
3	300µm < size <600 µm	OPS 600	5%	TPG600
4	150µm < size <300 µm	OPS 300	5%	TPG300
5	75µm < size <150 µm	OPS 150	5%	TPG150
6	50µm < size <75 µm	OPS 075	5%	TPG075
7	size <50 µm	OPS 050	5%	TPG050

In the first stage of testing the influence on washing with methanol on the resulting composite properties was investigated by manufacturing composite specimens containing 5 wt.% of either washed or unwashed OPS powder in the size range 75~150 μm in isophthalic unsaturated polyester (UP) resin (selected for its combination of low cost and good mechanical properties). Subsequently, 1.5 wt.% of methyl ethyl ketone peroxide (MEKP) was added MEKP to initiate the polymerization reaction in unsaturated polyester. The mixture was gently mixed and then placed under weak vacuum to carefully remove excess air bubbles. Following this the mixture was poured into molds via casting method in order to produce dumbbell and bar specimens according to ASTM: D638-10 and ASTM: D760-10 for tensile and flexural testing, respectively. The specimens were left overnight to cure at room temperature and then post cured at 80 °C for 1 hour prior to being removed from the molds. In the second stage of testing, the influence of OPS powder size was investigated by manufacturing composites containing 5 wt.% of washed OPS powder with varying powder sizes (as shown in Table 2-2) using the procedure outlined above with the designations of the OPS powder and resulting composite specimens are presented in Table 2-2.

2.1.3 Characterization Techniques

2.1.3.1 Thermal Analysis

The thermal behavior of the OPS powders and their resulting polyester composites was investigated using thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis (Mettler Toledo TGA, Model; TGA/DSC1) between 25 °C and 700 °C with a heating rate of 10 °C \cdot min⁻¹. The OPS powder specimens were analyzed in a flowing nitrogen atmosphere whereas the composite specimens were analyzed in flowing oxygen atmosphere with the flow rate being 80 ml \cdot min⁻¹ for all cases.

2.1.3.2 Mechanical Characterization

The mechanical behavior of the composite specimens under tensile and flexural loading were investigated using a universal tensile testing machine (Lloyds instrument model LR10K Plus Digital Control Testing). Specimens for tensile testing were evaluated according to the ASTM: D638-10 standard using a 10 kN load cell and a crosshead rate of 2 mm·min⁻¹ with the tensile strength, tensile modulus at failure being evaluated. The flexural properties of composites were measured using the three-point bend configuration according to the ASTM: D790-10 standard with a 500 N load cell and crosshead speed of 2 mm·min⁻¹. The specimens were tested with a nominal span to depth ratio of 20 with the flexural strength, σ_f , flexural modulus, E_f being calculated from the following equations:

$$\sigma_f = \left(\frac{3PL}{2bd^2}\right)\left[1 + 6\left(\frac{D}{L}\right)^2 - 4\left(\frac{d}{L}\right)\left(\frac{D}{L}\right)\right] \quad (2-1)$$

$$E_f = \left(\frac{L^3m}{4bd^3}\right) \quad (2-2)$$

Where P is the load, L is the span, b is the specimen width, d is the specimen depth, D is the deflection of the specimen at its center and m is the slope of the initial linear portion of the force-displacement curve. A minimum of five specimens for each composite composition were tested for the tensile and flexural configurations with the mean and standard deviations being presented in this work.

Investigation of the OPS powder morphology and fracture surfaces of composite tensile specimens was carried out by using scanning electron microscopy (SEM; JEOL JSM-5610LV).

2.1.4 Result and Discussion

2.1.4.1 Effect of Methanol Washing on the Thermal Degradation of OPS Powder

It has been previously been reported that natural fibers tend to exhibit similar trends in their TGA and DTG curves as a result of the base cellulose contained within the fibers.

For example, it has been noted that natural fibers generally decompose in three main stages as shown in Table 2-3 ([Methacanon et al., 2010](#), [Martin et al., 2010](#), [Basri et al., 1999](#), [Alvarez and Vázquez, 2004](#), [Suardana et al., 2011](#), [Manfredi et al., 2006](#), [Shubhra et al., 2011](#), [Lee and Wang, 2006](#)) with most of the thermal decomposition occurring in the range of 215 °C to 310 °C ([Yao et al., 2008](#), [Methacanon et al., 2010](#), [Martin et al., 2010](#)). The three decomposition stages for OPS powder have been previously reported by ([Methacanon et al., 2010](#)) with almond shell being investigated by ([Font et al., 1991](#)).

Table 2-3. Three main stages of weight loss of natural fibers

Stage 1		Stage 2		Stage 3		Ref
Temperature	Correspond	Temperature	Correspond	Temperature	Correspond	
220-315 °C	Hemicellulose pyrolysis	315-400 °C	Cellulose pyrolysis	160- 900 °C	Lignin pyrolysis	(Suardana et al., 2011)
50-300°C	Moisture evaporation	200-300 °C	Hemicellulose Decomposition	400-500 °C	Lignin and cellulose degradation	(Methacanon et al., 2010) (Basri et al., 1999 ,
300 °C	Hemicellulose and glycosidic link of cellulose decomposition	360 °C	α-cellulose decomposition	200-500 °C	Lignin decomposition with max at 350 °C and two other peaks	Manfredi et al., 2006 , Alvarez and Vázquez, 2004)
250-300 °C	Hemicellulose decomposition	300-400 °C	Cellulose Decomposition	420 °C	Lignin decomposition	(Lee and Wang, 2006)
97 °C	Moisture evaporation	325 °C	Protein degradation	Major at 260 & slow at 390 °C	Major decomposition for silk fiber gelatin composite	(Shubhra et al., 2011)
186-401 °C peak at 348 °C	Hemicellulose decomposition	207-404 °C peak at 353 °C	Cellulose Decomposition	174-600 °C peak at 367 °C	Lignin decomposition	(Martin et al., 2010)

The first stage in the present work was to investigate the influence of methanol washing on thermal decomposition with the TGA and DTG curves of washed and unwashed OPS powder is shown in Figure 2-3. The weight loss noted in the temperature range from 30 °C to 155 °C is attributed to evaporation of moisture within the fiber (intra and intermolecular dehydration reactions) with the degradation of lignin starting from 155 °C. The DTG curve exhibits two distinct peaks with maxima at 288.7 °C and 359.7 °C for

unwashed OPS and 292.4 °C and 365.4 °C for the washed OPS. The first peak is a shoulder of the main degradation peak which occurs between 248~340 °C for unwashed OPS and 254~345 °C for washed OPS and this was attributed to hemicellulose degradation. In contrast to this, thermal degradation of cellulose occurs at higher temperatures with a faster degradation rate compared to hemicellulose with the main peak attributed to cellulose degradation occurring between 340~394 °C (maximum at 359 °C) for the unwashed OPS and between 345~400 °C (maximum at 365 °C) for the washed OPS sample. This result is in good agreement with previous research (Methacanon et al., 2010, Lee and Wang, 2006, Martin et al., 2010) as shown in Table 2-3.

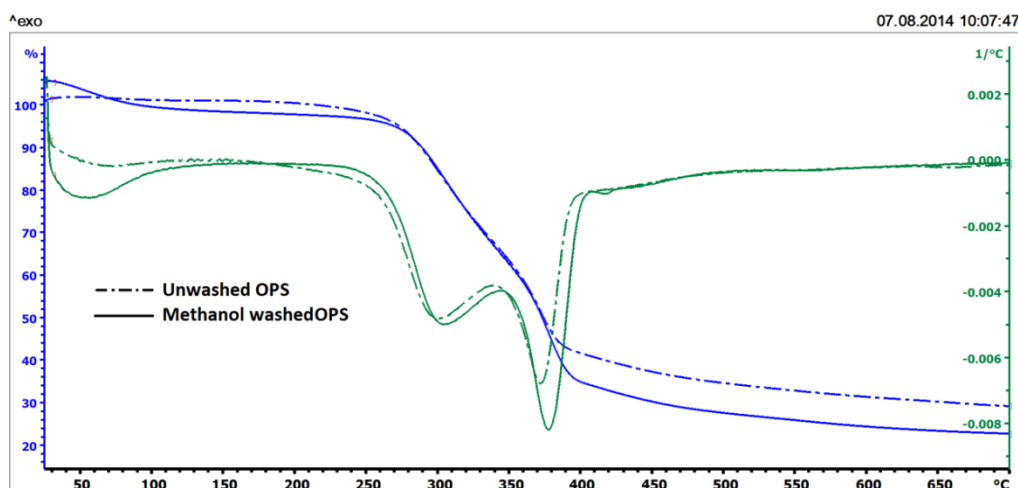


Figure 2-3. Thermal analysis of unwashed and methanol washed OPS under nitrogen purge

Based on Figure 2-3, it appears that lignin pyrolysis for the unwashed OPS started at 155 °C with a 2.68 % mass loss to 248 °C whereas for washed OPS it started at 200 °C with a 1.86 % mass loss up to 254 °C. For both cases the lignin pyrolysis continued up to 510 °C indicating that degradation occurred over a wide range of temperatures.

The sequence of events outlined is consistent with (Nada and Hassan, 2000) who reported that the pyrolysis of lignin ranged between 155 and 900 °C. According to (Martin et al., 2010) the pyrolysis peak for pure lignin occurred at 367 °C although the peak was hidden beneath peaks associated with hemicellulose and cellulose. Therefore, it is suggested that weight losses in the range of 248~394 °C and 254~400 °C for the unwashed and washed

samples, respectively, can be attributed to hemicellulose, cellulose and also partially lignin. It is also observed from the DTG curves in Figure 2-3 that the decomposition peaks became narrower and shifted to higher temperatures for the washed OPS. This is attributed to the methanol washing procedure removing impurities from the surface of the OPS powder as shown in Figure 2-4.

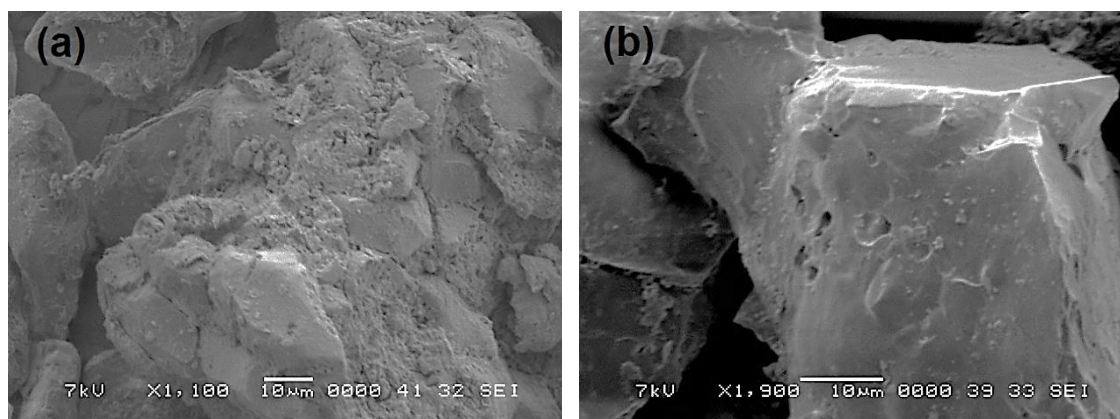


Figure 2-4. SEM micrograph of washed and unwashed OPS, (a) Impurities on the surface of unwashed OPS (b) Pores and surface roughness on methanol washed OPS

In order to explain the above phenomenon and the types of materials removed; five different stages of decomposition for the washed and unwashed OPS are listed in Table 2-4. Due to the wide range of decomposition of lignin, lignin decomposition was analyzed in Stage 1 and Stage 4 with the char yield being reported at 700 °C for dry samples. Previous researchers ([Albano et al., 1999](#)) have attributed the char yield to condensation of the lignin parts in the natural fibers together with the formation of aromatic molecules in inert atmosphere. According to Table 2-4 the char yield for the unwashed and washed samples is 27.9 % and 18.42 %, respectively, which suggests that 9.48 wt.% of material was removed from OPS by the washing procedure. It can be concluded from Table 2-1 and Table 2-4 that the total degradation percentage for pure OPS can be estimated at 80.8 %, which is close to the value (81.58 %) for the methanol washed OPS sample as shown in Table 2-5. It would appear that the major impurities in the OPS were removed by washing without serious damage to the structural component. It should be noted that any slight variation in chemical composition shown in Table 2-5 is

likely due to the plant variation. It is concluded that methanol washing is an easy and quick method to remove impurities from the OPS surface.

Table 2-4. Analysis of OPS weight loss in five stages with its chemical constituents

OPS Sample	Stage1		Stage2		Stage3		Stage4		Stage5		Char% dry Sample
	Moisture evaporation		Lower molecules lignin decomposition		Hemicellulose decomposition		Cellulose decomposition		Longer molecule Lignin decomposition		
	T (°C)	Wt. loss%	T (°C)	Wt. loss%	T (°C)	Wt. loss%	T (°C)	Wt. loss%	T (°C)	Wt. loss%	
Unwashed	30-155	2.68	155-248	2.68	248-340 Peak at 289	30.71	340-394 peak at 359	25.45	394-700	13.5	27.90
Methanol Washed	30-155	7.2	155-254	1.86	254-345 peak at 294	31.16	345-400 Peak at 365	30.43	400-700	12.25	18.42

Table 2-5. The comparison of methanol washing efficiency with other references

OPS component	Estimate degradation from the references			Degradation in this study*	
	Components in each 100 g of OPS (Lahijani et al., 2012)	Degradation for each components (Martin et al., 2010)	OPS Degradation	Unwashed	Methanol washed
Hemicellulose	22.10	91.0%	20.11	30.827	33.58
Cellulose	32.60	99.5%	32.44	25.527	32.80
Lignin extractive	42.30	58.0% →	24.53	15.774**	15.202*
	3.00	100%	3.00	--	--
Sum	100.0	---	80.08	72.128	81.58

* The values were reported according each stage in Table 2-4

** Stage1 and stage4 were added together

2.1.4.2 Effect of OPS Powder on the Thermal Degradation of Composite Specimens

Figure 2-5 displays the influence of OPS powder on thermal properties of polyester composites. It can be observed that thermal degradation of the pure polyester occurs in two stages with the first stage comprising of a broad peak between 320 and 425 °C with a maximum at 374 °C (attributed to the unsaturated polyester) and the second stage comprising of a sharp peak between 472 and 490 °C with a maximum at 484 °C (associated

with the styrene component). The addition of OPS powder was noted to shift the maximum value of the first stage polyester component peak to a higher temperature (from 370 °C to 418 °C) whereas the second stage styrene component peak shifted to a lower temperature (from 484 °C to 462 °C). Therefore, it would appear that initial thermal degradation of the composite shifted to higher temperatures due to the incorporation of OPS powder. In addition, the presence of an additional small peak in the first stage of polyester decomposition can be noted in Figure 2-5 which was also attributed to the addition of OPS powder.

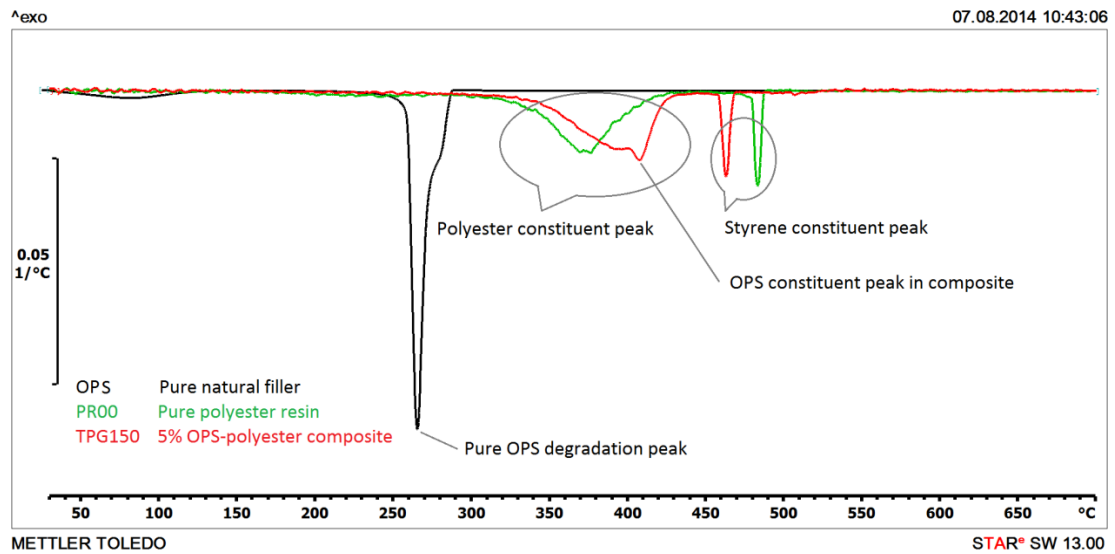


Figure 2-5. DTG curves on pure polyester resin, OPS filler and their composite under oxygen purge

From the above discussion, it can be summarized that the addition of OPS powder to the polyester resulted in an increased decomposition temperature in oxygen atmosphere for the composite when compared to either the pure polyester or pure OPS powder. A similar outcome reported by (Doan et al., 2007) for the addition of jute fiber in polypropylene where thermal degradation of the composite in air atmosphere also shifted to higher temperatures.

2.1.4.3 Effect of Fillers and Matrix Attraction on Mechanical Performance of Composite

As previously shown in Figure 2-2, the surface of the OPS powder was noted to be rough with the presence of porosity. According to (Gomes et al., 2007) the vital parameters which influence bonding between the polymer matrix and particle reinforcement in composites are the processing method, fiber aspect ratio, fibre treatment and the nature of the polymer and fiber components. The surface roughness of powder particles enhances the interfacial force of attraction between two contact surfaces (Packham, 2003) whereas (Traina, 2008) indicated that powder with high surface area had a positive effect on the mechanical performance of composites by restricting the polymer chain mobility. Furthermore, (Bigg, 1987) reported that the interfacial bond strength depends on the efficiency of wetting ability and use of coupling agents. The tensile strength of powder composites is known to strongly depend on the degree of interfacial bonding between the powder and polymer matrix. For example, (Akinci, 2010, Nielsen, 1966) stated that good wettability of powder particles with polymer molecules could be attributed to effective polymer chain pinning between the matrix and reinforcement which enhanced the resulting composite mechanical performance. In addition, (Mansfield and Theodorou, 1991, Baschnagel and Binder, 1995) reported that the filler particle porosity will improve the effective polymer chain pinning in the composite by generating a relaxation zone on the filler in the composite. This will ultimately improve the mechanical properties of the composite.

Based on the above discussion, the noted porosity and roughness of the hydrophilic OPS surface would be expected to increase its wettability by the hydrophobic polymer matrix. When the composite stretches under load, the polymer chains would be expected to transfer stress to the OPS powder by polymer chain pinning and relaxation zone. As a result, the ultimate fracture stress of the composite would be expected to increase when compared to powder with low surface roughness and porosity.

2.1.4.3.1 Micro-Structural Observation

According to the previous result and discussion the methanol washing procedure was noted to increase the surface roughness of the OPS powder by removing the impurities and thus improving bonding between the powder and matrix. The influence of removing impurities on the wettability of polyester resin by OPS powder is presented in Figure 2-6. It would appear that the bonding between matrix and powder in the methanol washed OPS composite sample (Fig 6(b)) is superior to that of the unwashed sample (Fig 6(a)) due to its higher surface roughness and porosity which was promoted by removing the impurities with methanol.

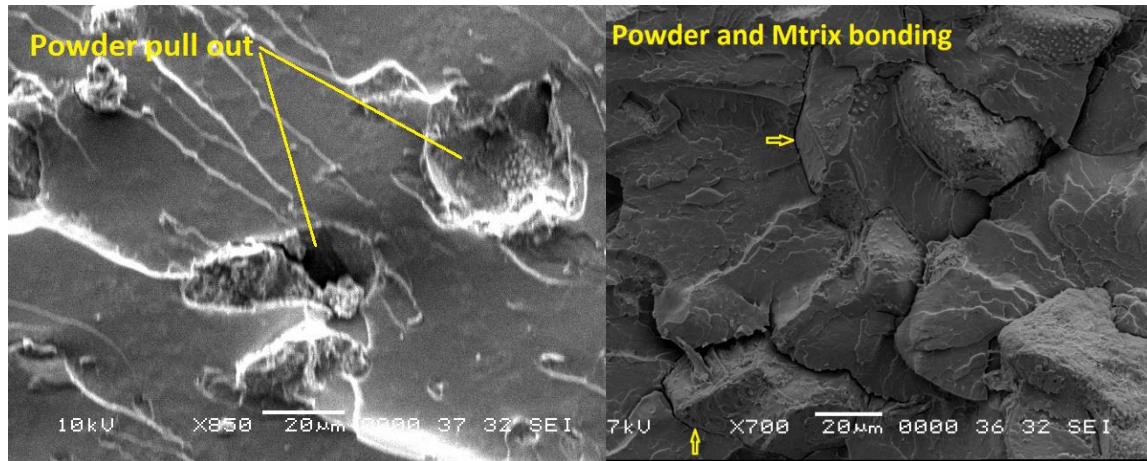


Figure 2-6. SEM micrograph of washed and unwashed OPS filled polyester composites after tensile fracture (a) Poor bonding on unwashed OPS/composite (b) Respectable bonding on methanol washed OPS/composite

2.1.4.3.2 Influence of Surface Impurities on Mechanical Properties

2.1.4.3.2.1 Tensile and Flexural Strength

The influence of methanol washing of OPS powder on the tensile and flexural strength of resulting composites are presented in Figure 2-7 with the tensile strength of the washed OPS powder composite being 27 % higher (40.18 MPa) compared to that of the equivalent unwashed powder composite (31.62 MPa). A similar trend was noted for the flexural strength with the washed powder composites being 26.8% greater (60.34 MPa) compared to the washed powder composite (47.58 MPa). From these results it is clear that washing

of the OPS powder produces a significantly stronger composite and this was attributed to improved filler-matrix bonding by polymer chains as mentioned previously. However, it should be noted that the tensile and flexural strength of the washed powder composites were still slightly below those of the pure matrix (43.41 MPa and 63.4 MPa, respectively).

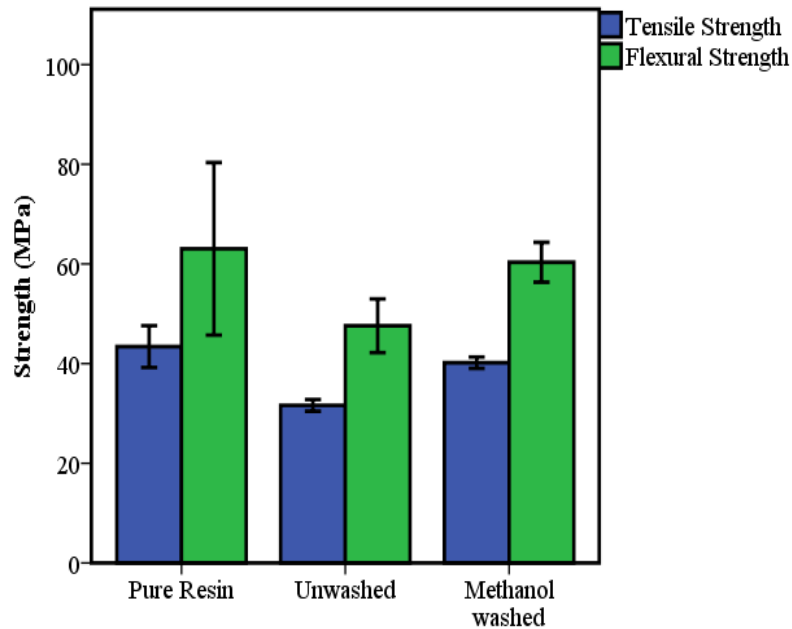


Figure 2-7. Tensile and flexural strength of 5 wt.% unwashed and methanol washed OPS filled composites with particle size in the range of 75~150 μm

2.1.4.3.2.2 Tensile and Flexural Young's Modulus

Figure 2-8 illustrates the tensile and flexural moduli of washed and unwashed OPS powder composites with both moduli being significantly improved by methanol washing. For example, the tensile modulus of the unwashed OPS powder composite was 940 MPa (approximately 30 % lower compared to the pure matrix) which increased by 40 % to 1326 MPa for the washed composite which was comparable to that of the pure matrix (1342 MPa). A similar result was noted for the flexural modulus with values for the unwashed and washed composite and pure matrix being 1781 MPa, 2910 MPa and 2951 MPa, respectively. Similar to the case of the strength data, these results indicate improved interfacial bonding between the OPS powder and matrix following methanol washing which is believed to have removed impurities from the OPS surface.

In summary, such a result has been noted in many powder reinforced polymer composites, the strength and moduli values for the washed composite were still slightly below that of the pure matrix with this being attributed to poor compatibility between the hydrophobic and hydrophilic groups in the polyester matrix and OPS powder reinforcement, respectively.

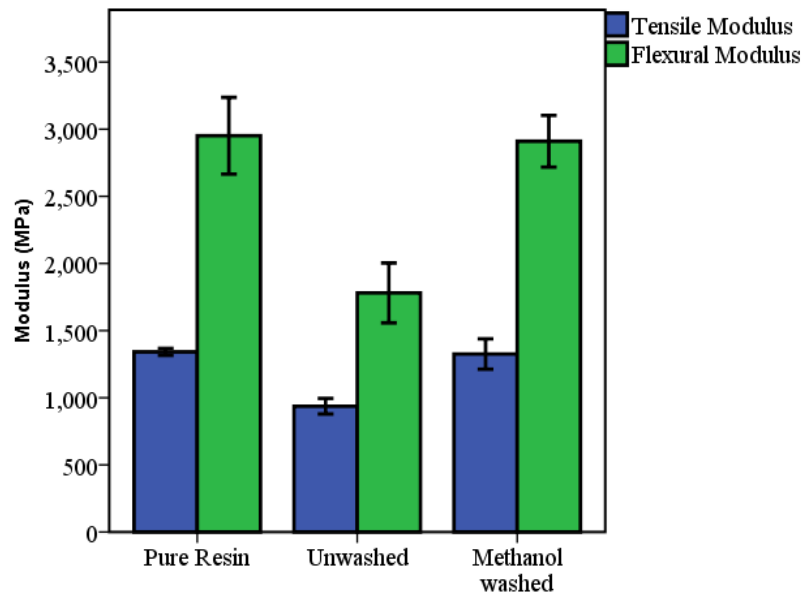


Figure 2-8. Tensile and flexural modulus of 5 wt.% unwashed and methanol washed OPS filled composites with particle size in the range of 75~150 μm

It has been reported that the methanol treatment improved in the permeability of jute fiber by 10%. The permeability is known as a measure of the ability of porous materials to allow fluids to pass through them (Mateusz et al., 2013). Therefore, it can be concluded that wettability or absorbability of OPS powder by polyester resin was improved by methanol treatment, which resulted in a better mechanical performance of the composite.

2.1.4.3.3 Effect of Powder Size on Mechanical Properties

2.1.4.3.3.1 Tensile and Flexural Strength

The effect of OPS powder size on the tensile and flexural strength of resulting composites is presented in Figure 2-9. For both cases the general trend was for the strength of the largest powder size composite (TPG1200) to decrease approximately 40~50 % when compared to the pure matrix. This can be explained in terms of the powder particles acting as a defect which leads to a substantial decrease in strength. However, it was also noted that the strength tended to increase as the powder size decreased, which again could be explained in terms of the smaller powder sizes acting as smaller flaw sizes and thus increasing the strength. Indeed, the tensile strength of the TGP150 composite was only 7 % lower than that of the pure matrix (40.2 MPa compared to 43.3 MPa) whereas the flexural strength of the same composite was approximately 10 % greater than that of the pure matrix (80.2 MPa compared to 74.3 MPa). Therefore, it was shown that through the use of small powder sizes it was able to produce composites with tensile and flexural strengths comparable to that of the pure matrix.

From the above discussion, it would appear that OPS powder with a size smaller than 150 μm possesses significant interfacial bonding with the polymer. This was attributed to factors such as the high surface area, high powder roughness, increased porosity and additional polymer chain pinning between the OPS powder which resulted in improved interactions between the smaller OPS powder and the polyester matrix. However, it should be noted from Figure 2-10 that the composite containing the smallest powder size (TPG050) exhibited a slight decrease in strength compared to the TPG150 and TPG075 composites. This was attributed to the effects of agglomeration due to poor dispersion of the smaller powder sizes within the matrix.

The trends shown above have been supported by (Leidner and Woodhams, 1974, Maiti et al., 2013) who indicated that smaller sized reinforcement particles tend to increase the tensile strength of composites. However, other studies by (Zaini et al., 1996) on the influence of powder size for oil palm wood flour (OPWF) reinforced polypropylene have

reported contradictory results in higher filler content which may be attributed to enhanced agglomeration of smaller sized powder. Furthermore, (Fu et al., 2008) reported that the tensile strength of composite could only be improved significantly through use of micro-sized powders although it has been suggested that further reductions in powder size to the nano-scale will deteriorate the tensile strength.

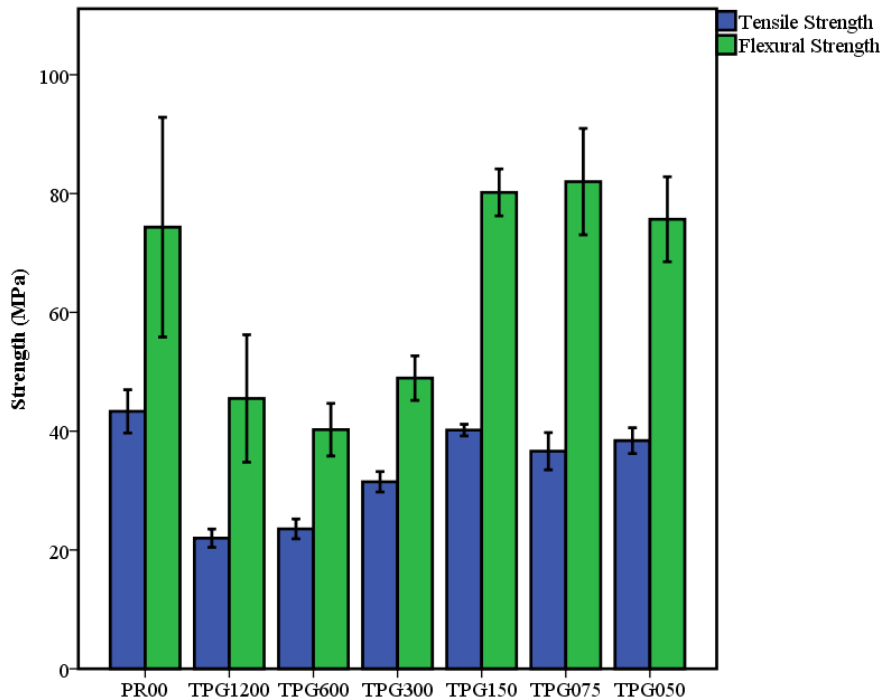


Figure 2-9. Effect of OPS size on tensile strength and flexural strength

2.1.4.3.3.2 Tensile and Flexural Young's Modulus

The effects of powder size on tensile and flexural moduli are presented in Figure 2-10. In contrast to the trend for strength, no significant influence of powder size was noted for the composite moduli with the possible exception of the TPG1200 composite which showed a significantly higher value. Overall it could be seen that composite strength tended to increase with decreasing OPS powder size whereas the composite modulus was essentially independent of powder size.

A study (Nakamura et al., 1992) on the effect of spherical and irregular-shaped silica powder size on the elastic modulus of epoxy/silica composites showed the composite

modulus to be independent of both powder size and shape and whereas (Spanoudakis and Young, 1984) found the modulus of spherical glass powder/epoxy composites to be independent of powder size for below a threshold amount (18 vol.%) and then a small decrease in composite modulus with increasing powder size above this threshold. Thus, the above findings on the effect of non-organic powder size on composite elastic modulus are in good agreement with the current work.

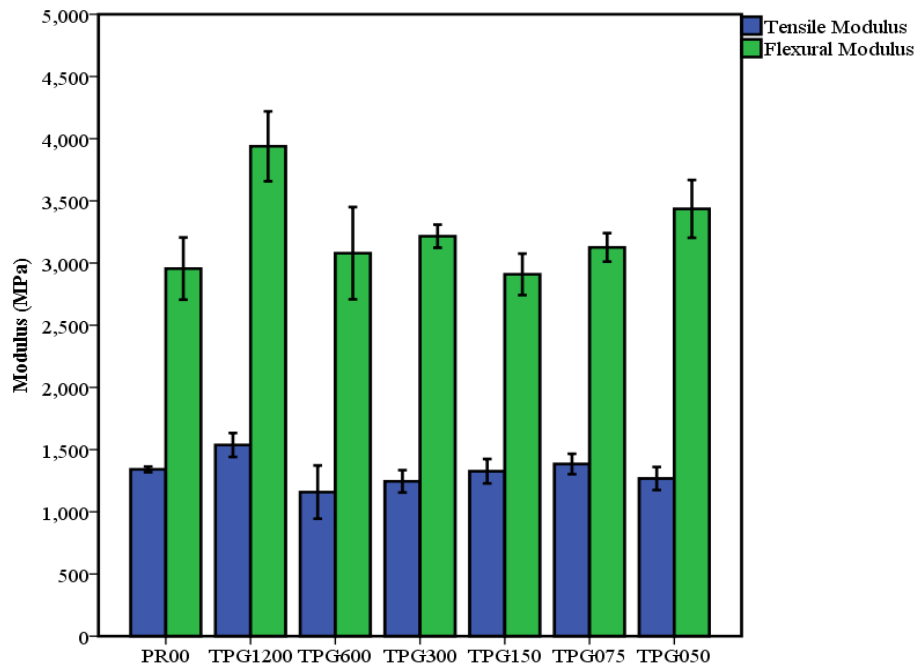


Figure 2-10. Effect of OPS size on tensile modulus and flexural modulus

2.1.5 Conclusions

This paper presented an experimental study on the development of polymer bio-composites using unsaturated polyester resin reinforced with oil palm shell (OPS) powder. The following observations and conclusions can be made on the basis of the current experimental results:

Adding OPS powder was noted to shift the thermal degradation of the composite to higher temperatures when compared to the pure matrix. From TGA tests it was noted that using OPS powder as a natural reinforcement in polyester composites shifted the thermal degradation peak of the bio-composite from 370 °C to 418 °C.

Washing OPS powder by methanol has a significant effect on mechanical properties. The tensile and flexural strengths and moduli exhibited significant improvements of between 22.86 % (flexural strength) and 61.36% (flexural modulus) compared to the composite containing unwashed OPS powder.

The composite tensile and flexural strength were found to generally increase with decreasing OPS powder size and this was explained in terms of the powder acting as defects within the composite. The maximum strength values were recorded for powder sized between 75 μm and 150 μm .

The composite tensile and flexural moduli were found to be essentially independent of OPS apart from the OPS 1200 sample.

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2.2 Effect of Filler Treatment

This section is the peer reviewed version of the following article: *Omid Nabinejad, D. Sujan, M. E. Rahman, Willey Y. H. Liew and Ian J. Davies, "Mechanical and thermal characterization of polyester composite containing treated wood flour from palm oil biomass" in a peer reviewed journal – Wiley, Polymer Composite, DOI: 10.1002/pc.24052, 2016., which has been published in final form at <http://onlinelibrary.wiley.com/doi/10.1002/pc.24052/full>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving. It should be noted that this is a modified version of the published version.*

Mechanical and Thermal Characterization of Polyester Composite Containing Treated Wood Flour from Palm Oil Biomass.

Omid Nabinejad, D. Sujan, M. E. Rahman, Willey Y. H. Liew and Ian J. Davies

Abstract

The effect of water and alkali treatment on the thermal decomposition of Oil Palm Shell (OPS) together with the mechanical performance of polyester composites reinforced with treated OPS has been presented in this work. Treatment of OPS with cold/hot distilled water and cold alkali treatment were found to improve the tensile and flexural strength of the resulting composites although the highest mechanical performance was noted with the use of sonication in hot distilled water. On the other hand, hot alkali treatment was found to produce a composite mechanical performance similar to that of the hot distilled water treatment with sonication. FTIR tests indicated that adsorbed water molecules together with some parts of the hemicellulose and lignin were removed by the treatments. Thermogravimetric analysis and scanning electron microscopy of the treated OPS with hot alkali (1~9% concentration) showed that the mechanical performance reach a peak at 7% alkali concentration with a further increase in concentration resulting in a

significant lignin mass loss and decrease in mass residue of the OPS. This trend was attributed to the higher alkali concentration removing hemicellulose as a binder for the cellulose and lignin which resulted in debonding between the filler and matrix components of the OPS and hence a deterioration in fiber structure and resulting poor composite mechanical performance. Therefore, it was concluded that the optimum concentration of alkali treatment required for maximum mechanical performance of natural filler reinforced polymer composites can be obtained simply from thermogravimetric analysis.

Keywords: Natural Fiber Composite, Polyester, Oil Palm Shell, Chemical Treatment, Mechanical Performance, Thermogravimetric Analysis

2.2.1 Introduction

Oil palm shell is an agricultural solid waste produced from the palm oil industry in tropical regimes ([Shafiqh et al., 2010](#)) with the significant amounts of waste material produced by the oil palm industry having led to calls for an improvement in recycling. It is estimated that 6.89 million tons of oil palm shell (OPS) are produced annually as a byproduct of the oil palm industry with this number being expected to increase further ([Chong et al., 2013](#)). Whilst the majority of this byproduct is currently utilized as boiler fuel, other candidate applications include the use of OPS as a natural filler for the reinforcement of concrete and other composite materials ([Nabinejad et al., 2015b](#)). The main advantages of utilizing OPS as a natural filler in polymer composite materials, in comparison to synthetic filler and fiber, are its low cost, low carbon dioxide emissions, reduced tool wear, low density, high specific properties, non-corrosiveness, ease of separation and reduced dermal and respiratory irritation ([Hassan et al., 2010](#)).

In contrast to this, a main disadvantage of OPS as a natural filler within reinforced polymer composites is the low surface free energy of both the filler and polymer which tends to result in poor interfacial bonding between the filler and polymer matrix ([Sreekala et al., 1997](#)). Physical and chemical treatment of the natural filler are common methods utilized to improve interfacial bonding between filler and matrix with physical treatment being known to alter the surface properties and structure of the filler without any change to

chemical composition (Yan et al., 2014). With regards to chemical treatment, water treatment of flax fibers has been noted to significantly increase interfacial shear strength with only a marginal decrease in tensile properties (le Duigou et al., 2012) whereas alkali treatment (also known as mercerization) is known to be an effective treatment for the removal of surface impurities together with the majority of lignin, wax and oils covering the reinforcement surface (Kim and Pal, 2011). The increase in composite mechanical properties due to alkali treatment of the natural reinforcement has been attributed to better mechanical interlocking as a result of the increase of fiber surface roughness together with an increase in potential chemical reaction sites due to the increased amount of cellulose being exposed on the fiber surface (Valadez-Gonzalez et al., 1999). It has been reported that the surface porosity and roughness of hydrophilic OPS particles could be enhanced by washing with methanol, which led to improved wettability by the hydrophobic polymer matrix (Nabinejad et al., 2015b). The porosity and other physical properties of OPS are presented in Table 2-6.

Table 2-6. The physical properties of Oil Palm Shell (OPS) (Alengaram et al., 2013, Yap et al., 2013)

Properties	specific gravity	bulk density kg/m ³	Porosity %	Fineness modulus	Water absorption (24 h) (%)	Aggregate impact value (AIV) (%)	LA abrasion value (%)	Flakiness index (FI) (%)	Elongation index (EI) (%)
Value	1.14 - 1.62	590 - 740	28 - 37	6.41	24.3	2.11	5	41	59

It has also been reported that mercerization effects the degree of polymerization and cellulosic fibril due to removal of hemicellulose and lignin together with a reduction in amorphous hydroxyl groups according to the following reaction (le Duigou et al., 2012, Li et al., 2007):



The thermal performance of natural fiber is a serious concern, especially in the case of the processing of natural fiber composites at elevated temperature, with this issue being attributed to the limited thermal stability of natural fibers (Xie et al., 2010). Based on results previously obtained by the authors, chemical treatment had a significant effect on

the thermal behavior of OPS. In addition to this, thermogravimetric analysis (TGA) in flowing oxygen revealed that the addition of OPS powder in isophthalic unsaturated polyester (UP) composites shifted the thermal degradation peak of the bio-composite to a higher temperature (from 370 to 418 °C) (Nabinejad et al., 2015b).

In light of the above information, in the present work the authors have investigated the influence of chemical treatment on the thermal behavior of OPS and the mechanical properties of unsaturated polyester composites reinforced with OPS filler.

2.2.2 Sample Preparation

Raw OPS material from Palm Oil biomass was utilized as the natural filler in this work with the OPS being first pulverized in a ball mill and then separated by mechanical sieving to produce OPS powder with a particle size in the range of 75 to 150 µm. Following this, the powdered OPS was chemically treated using distilled water and/or sodium hydroxide (NaOH) solution according to Table 2-7 and finally dried in an oven at 100 °C for 2 hours.

Table 2-7. Preparation conditions for the oil palm shell (OPS) powder specimens.

Sample Name	Step1		Step2	
	Solution	Conditions	Solution	Conditions
UT	--	Untreated	--	--
CDW	Distilled Water	1 hr at 25 °C	--	--
HDW	Distilled Water	1 hr at 90 °C	--	--
HDW-US	Distilled Water	1 hr at 90 °C	Distilled Water	High frequency ultrasonic 30 min at 60°C then neutralize
CAT1	5% Sodium Hydroxide	1 hr at 25 °C	Distilled Water	Neutralize
CAT48	5% Sodium Hydroxide	48 hr at 25 °C	Distilled Water	Neutralize
HAT	5% Sodium Hydroxide	1 hr at 90 °C	Distilled Water	Neutralize

In the first stage of testing the influence of different washing methods for OPS on the resulting composite properties was investigated by manufacturing isophthalic unsaturated polyester composites containing 5 wt% of OPS filler. The UP resin and OPS filler were gently mixed with 1.5 wt% of methyl ethyl ketone peroxide (MEKP). MEKP was added to initiate the polymerization reaction in the resin. Then the mixture was placed under

vacuum to remove excess air bubbles. Following this, the mixture was poured into molds in order to produce five dumbbell and bar specimens according to ASTM D638 and ASTM D760 for tensile and flexural testing, respectively. The specimens were left to post cure at 80 °C for 1 hour prior to being removed from the molds. In the second stage of testing, the influence of alkali treatment on OPS filler was investigated by manufacturing UP composites containing 15 wt% of OPS powder treated with NaOH (1~9% concentration) at 90 °C. In order to neutralize the aqueous system, all alkali treated samples were washed several times with distilled water until a pH of less than 8 had been achieved.

2.2.3 Characterization Techniques

2.2.3.1 Mechanical Characterization

The mechanical behavior of the composite specimens under tensile and flexural loading was investigated using a universal tensile testing machine (Lloyds instrument model LR10K Plus Digital Control Testing) at a crosshead rate of 2 mm·min⁻¹. Tensile and flexural tests were carried using 10 kN and 500 N load cells, respectively, with the span to depth ratio for the 3 point bend flexural specimens being nominally 21.

2.2.3.2 Thermal Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis of OPS powder were used to measure the weight loss and thermal behavior of untreated and alkali treated OPS as a function of temperature. The analysis was conducted for a temperature range of 35~700 °C with a heating rate of 20 °C·min⁻¹ in an 80 ml·min⁻¹ flowing nitrogen atmosphere (Mettler Toledo TGA, Model; TGA/DSC1).

2.2.3.3 Surface Characterization

The FTIR spectra of OPS powder were obtained using an Agilent Cary 630 FTIR spectrometer. The FTIR tests were carried out between 650 and 4000 cm^{-1} with a resolution of 4 cm^{-1} .

2.2.3.4 Microscopic Observation

Investigation of the OPS morphology and fracture surfaces of composite specimens was carried out using scanning electron microscopy (SEM; Hitachi S-3400N) with the surface roughness of the OPS and the quality of bonding between filler and matrix being determined.

2.2.4 Result and Discussion

2.2.4.1 Mechanical Properties

2.2.4.1.1 Effect of Different Treatments

In the present work, the influence of various washing treatments (as shown in Table 2) on the flexural strength and modulus of UP composites containing 5 wt% of OPS has been presented in Figure 2-11. As shown in Figure 2-11 the cold distilled water (CDW) washing method improved the flexural strength from 42.6 to 47.6 MPa (*i.e.*, 11.7% increase) and flexural modulus from 1.56 to 1.78 GPa (*i.e.*, 14.1% increase) compared to the untreated (UT) case. This result is in good agreement with previous research (Valadez-Gonzalez et al., 1999) which indicated that water-soluble polysaccharides on the surface of hemp fiber could be effectively removed through the use of a cold water treatment. Figure 2-11 also indicates that the flexural strength could be further increased to 65.1 MPa using a hot distilled water (HDW) treatment – an improvement of 36.8% compared to the CDW case, whilst the flexural modulus exhibited an even greater increase of 114% compared to the CDW treatment. Based on Figure 2-11 and results previously obtained by the authors (Nabinejad et al., 2015b) it can be concluded that HDW washing is more effective than

methanol with the flexural strength and modulus being 8.00% (60.3 MPa to 65.13 MPa) and 30.9% (2.91GPa to 3.81 GPa) higher, respectively, compared to methanol washed samples. The finding in the improvement of mechanical properties of WPC via surface treatment at high temperature is in good agreement with the finding of other researchers where Silane treatment of wood fiber at high temperature resulted in a better flexural strength of the HDPE composites ([Feng et al., 2017](#)).

Furthermore, sonication was noted to improve the flexural strength of the HDW-US composites by 10.0% (71.4 MPa) compared to the HDW case with a similar trend being observed for flexural modulus with an 8.4% increase to 4.13 GPa. These results were attributed to enhanced removal of surface impurities from the OPS powder through a combination of hot distilled water and sonication. This is in good agreement with the finding by ([M.R. Islam et al., 2013](#)) where the sonication treatment of Kenaf fiber improved the flexural properties of maleic anhydride-grafted polypropylene (MAPP) composite.

Figure 2-11 also illustrates the effect of time and temperature of alkali treatment of OPS powder on flexural properties of the resulting composites. For example, although the flexural strength and modulus following 1 hr in 5% NaOH solution (CAT1) exhibited a slight improvement (1.9% for flexural strength and 5.2% for flexural modulus) compared to the HDW treated composite, the results were still lower than for the HDW-US case. Increasing the alkali treatment time to 48 hrs for the CAT48 composite decreased flexural strength by 2.72% (from 63.9 to 62.2 MPa) compared to the CAT1 composite although flexural modulus recorded a slight improvement to be comparable with the value of HDW-US case. In addition to this, flexural strength could be further increased to 70.6 MPa using a hot alkali treatment (HAT) with an improvement of 10.5% compared to the CAT1 case whilst the flexural modulus increased to 5.02 GPa (an improvement of 24.5% compared to the CAT1 treatment). In conclusion, the hot distilled water (HDW and HDW-US), cold alkali treatment (CAT1 and CAT48) and hot alkali treatment (HAT) all provided significant improvements in flexural properties compared to the cold distilled water treatment. It was also evident that effective washing by hot distilled water, which is

promoted by sonication, provided flexural results similar or slightly higher than those obtained by alkali treatment (apart from the higher flexural modulus of the HAT composite).

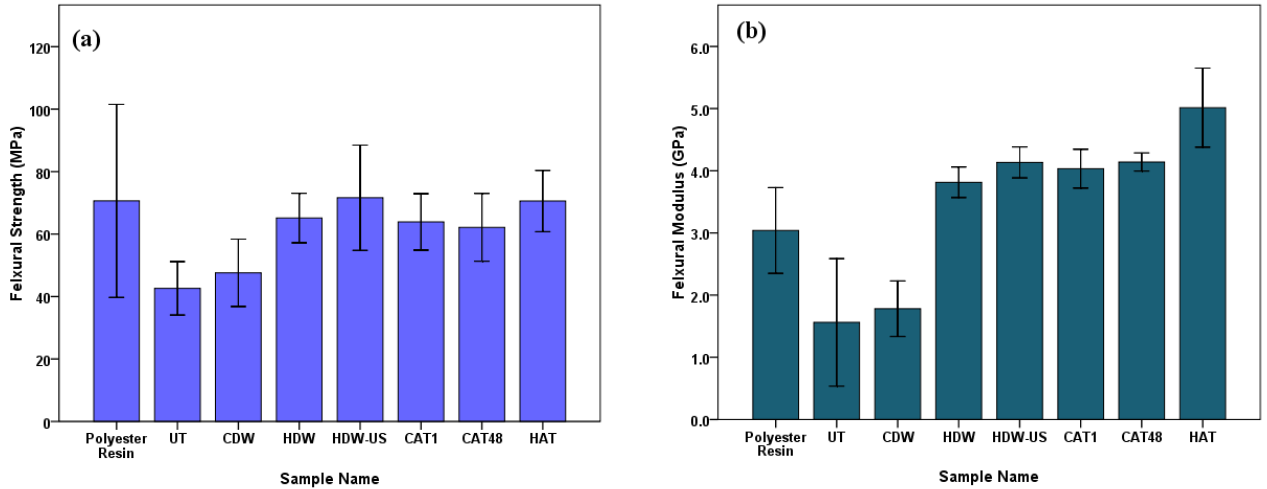


Figure 2-11. Effect of oil palm shell (OPS) powder treatment on the flexural properties of isophthalic unsaturated polyester (UP) reinforced with 5wt% of OPS: (a) strength and (b) modulus.

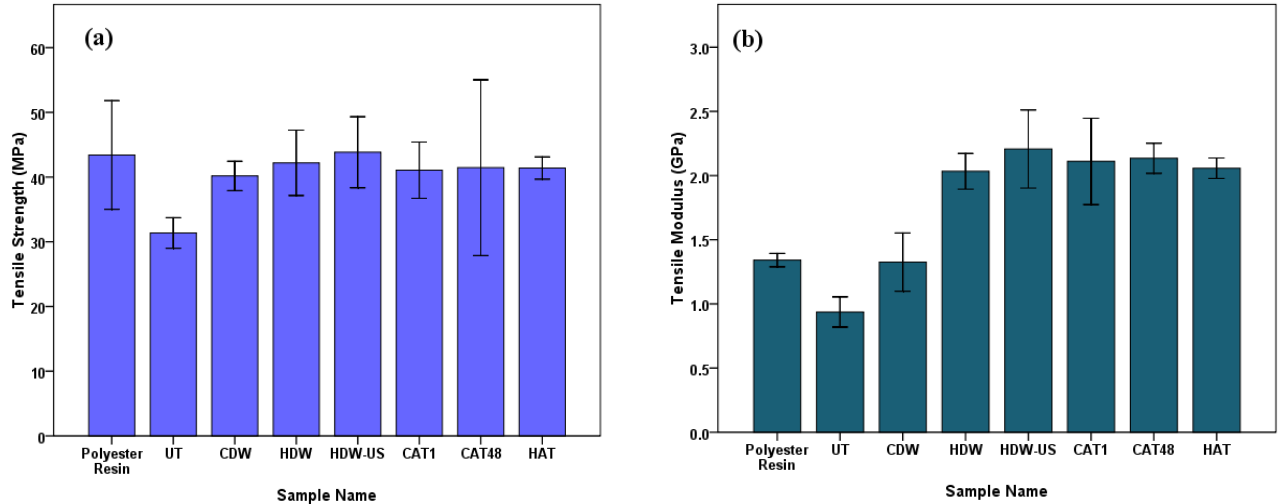


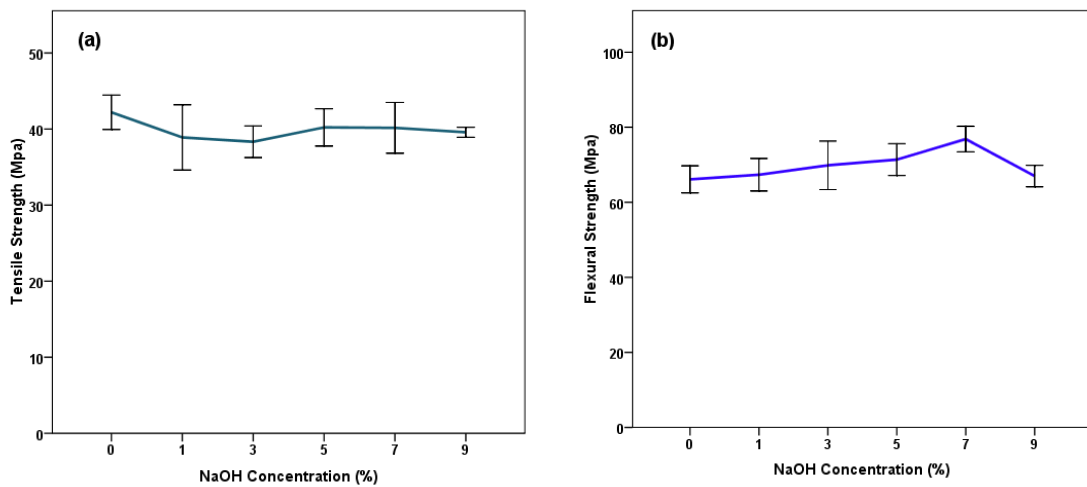
Figure 2-12. Effect of oil palm shell (OPS) powder treatment on the tensile properties of isophthalic unsaturated polyester (UP) reinforced with 5wt% of OPS: (a) tensile strength and (b) tensile modulus.

The influence of OPS treatment on the tensile properties of resulting UP composites reinforced with 5 wt% of OPS has been presented in Figure 2-12. However, compared to the flexural results, the variation in tensile strength for all OPS treatments was relatively

minor (in comparison to the untreated case), although there is a suggestion that the alkali treatments were slightly less effective compared to the hot distilled water (with and without sonication) cases. This latter finding is in agreement with previous work on the tensile properties of wood plastic composites (WPC) (Kim and Pal, 2011) where the tensile strength and Young's modulus of the fibers deteriorated by alkali treatment due to a reduction in the degree of crystallinity and crystalline orientation.

2.2.4.1.2 Effect of Hot Alkali Concentration

The effect of hot alkali (NaOH) concentration (1~9%) on the tensile and flexural properties of isophthalic unsaturated polyester composites reinforced with 15 wt% of treated OPS powder has been presented in Figure 2-13.



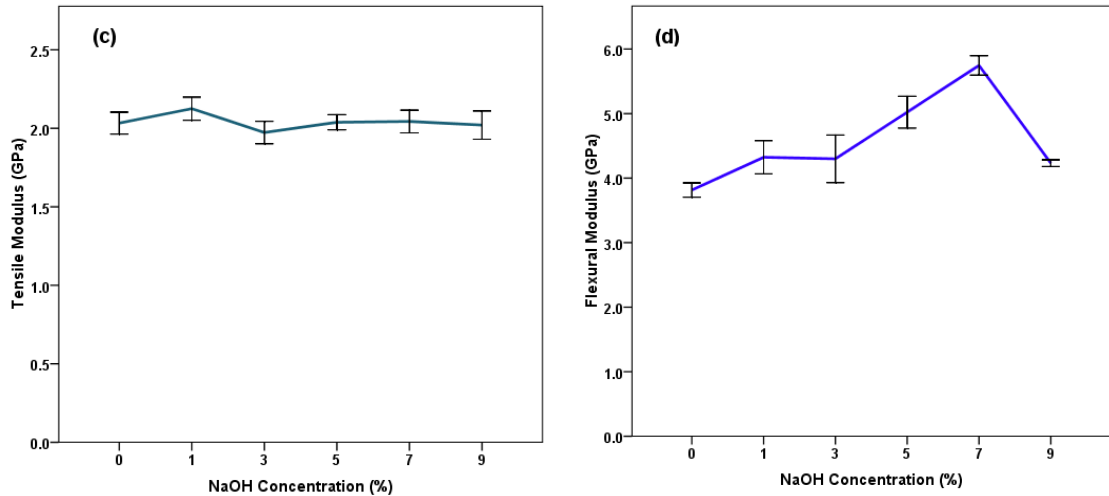


Figure 2-13. Effect of sodium hydroxide (NaOH) concentration on the mechanical properties of an isophthalic unsaturated polyester (UP) composite reinforced with 15 wt% of hot alkali treated oil palm shell (OPS) powder: (a) tensile strength, (b) flexural strength, (c) tensile modulus and (d) flexural modulus

It is clear from the results that the flexural strength (Figure 2-13(b)) and modulus (Figure 2-13(d)) reach their maximum values for the case of 7% NaOH concentration with the flexural strength increasing slightly from 66.1 MPa for the untreated (UT) composite to 76.7 MPa for 7% NaOH but then decreasing to 67.0 MPa for the 9% NaOH case. Flexural modulus exhibited a similar trend with a significant increase from 3.81 GPa for the untreated (UT) composite to 5.75 GPa for the 7% NaOH concentration composite and then followed by a decrease to 4.21 GPa for the 9% NaOH case. This finding is in good agreement with previous research ([Hairul Abral et al., 2013](#)) which indicated 7% NaOH treated natural fibers provided a better flexural properties on polyester composites in comparison with other alkali concentrations. In contrast to this, the tensile strength (Figure 2-13(a)) and modulus (Figure 2-13(c)) did not appear to be improved by hot alkali treatment with an overall general decline in tensile strength and modulus with increasing hot NaOH concentration.

2.2.4.2 Morphological Study by SEM

2.2.4.2.1 Effect of Different Treatments

As mentioned earlier, it has been reported that the existence of surface impurities on OPS powder, as shown in Figure 2-14, has a significant effect on reducing the mechanical properties of OPS-UP composites. It has been previously noted that the surface porosity and roughness of hydrophilic OPS particles could be enhanced by washing with methanol, which led to improved wettability by the hydrophobic polymer matrix (Nabinejad et al., 2015b).

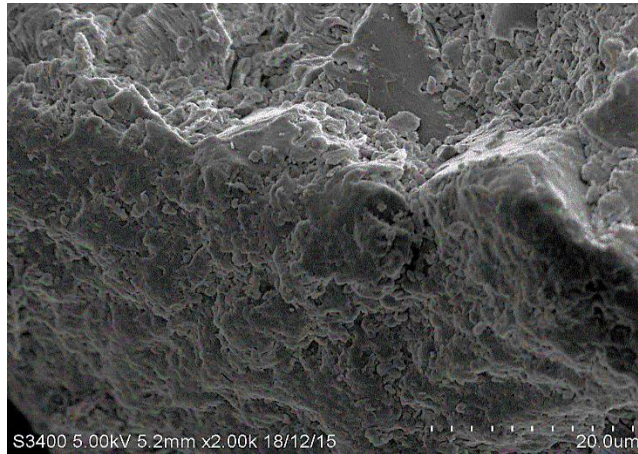


Figure 2-14. Scanning electron micrograph of unwashed oil palm shell (OPS) powder.

Figure 2-15 illustrates the effect of different treatments on the surface morphology of OPS powder. From these micrographs it appeared that hot distilled washing (Figure 2-15(a)) increased the amount of solubility impurities, waxes, oils and water-soluble polysaccharides present on the surface of OPS powder compared to the cold distilled water OPS (Figure 2-14). Figure 2-15(b) illustrates that sonication has a significant effect on the removal of the rest of the impurities and waxy materials from the surface of OPS in hot distilled water process, which increases the surface roughness as high as CAT1 (Figure 2-15(c)). In addition, it is evident that the surface roughness in the HAT sample (Figure 2-15(d)) is superior to that of the CAT1 treated powder (Figure 2-15 (c)) with this being attributed to increased removal of hemicellulose and lignin.

It has previously been suggested that improved bonding between the OPS filler particles and UP matrix was due to effective polymer chain pinning (Nabinejad et al., 2015b). Figure 2-16 illustrates fracture micrographs of UP composites reinforced with 5 wt% of washed OPS powder with obvious debonding between filler and matrix being noted in the cold distilled water composite (Figure 2-16(a)) whereas interfacial bonding improved for the hot distilled water case (Figure 2-16(b)) and it was superior for the hot distilled water with sonication (Figure 2-16(c)). Thus, it is suggested that the mechanical performance of these composites can be improved due to better wettability between filler and matrix molecules as a result of eliminating impurities together with a portion of the hemicellulose and lignin.

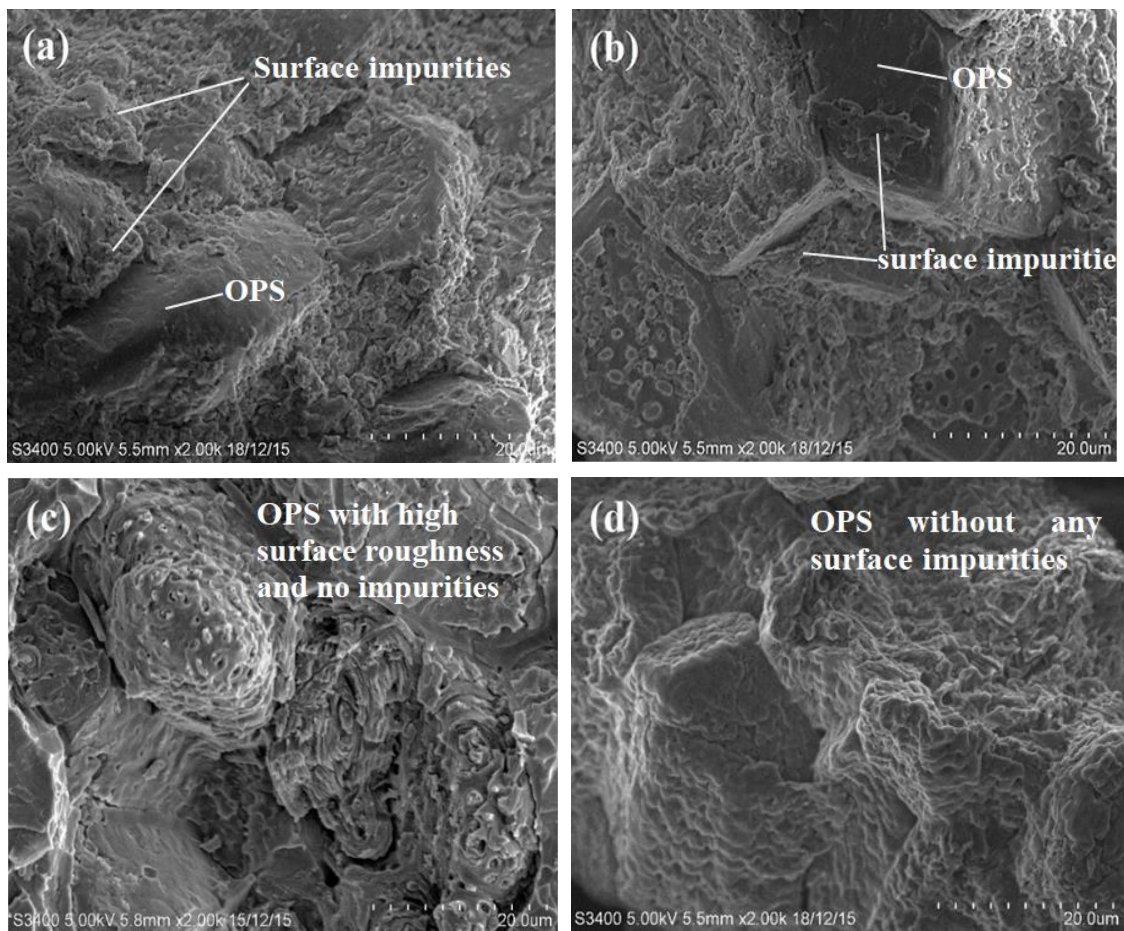
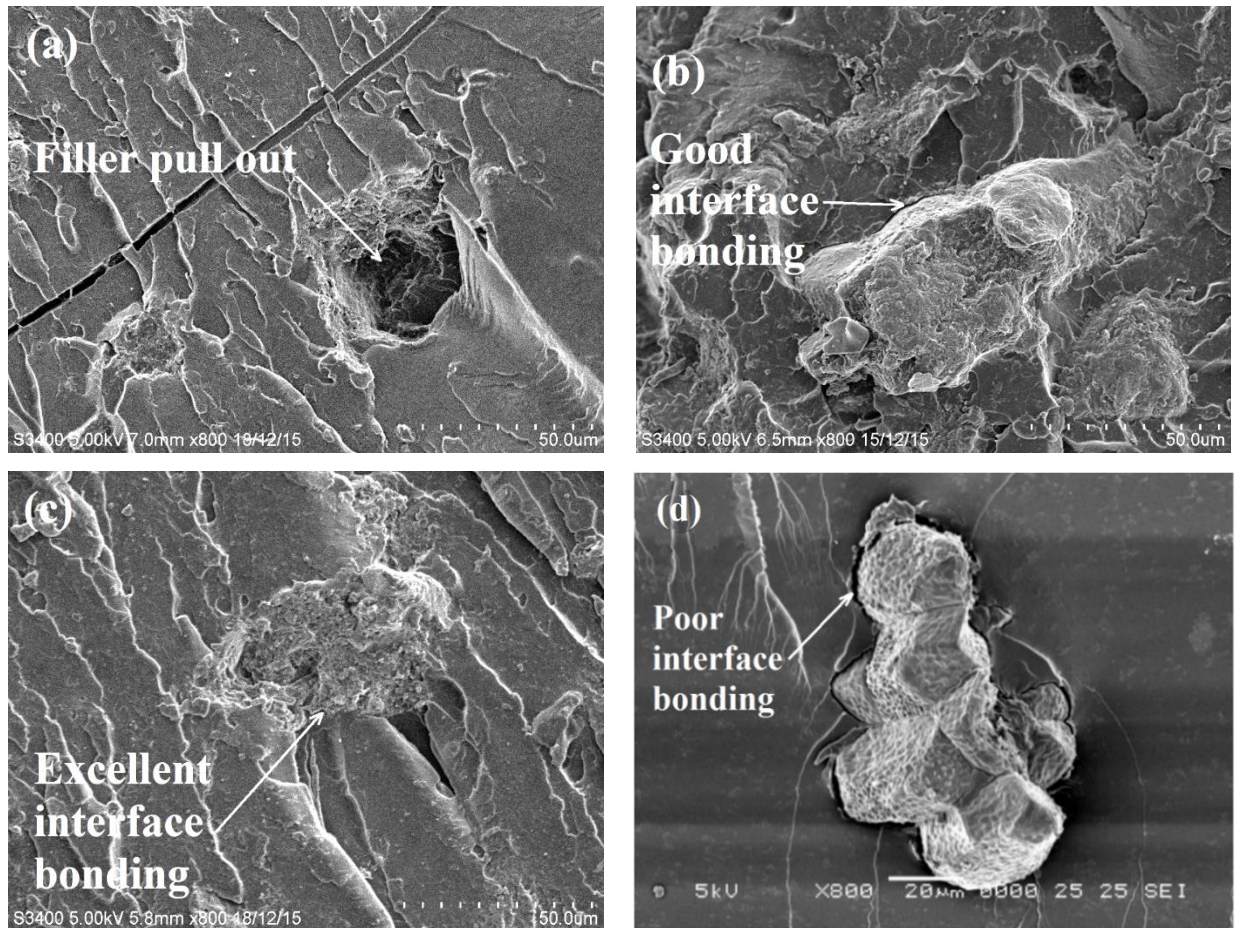


Figure 2-15. Scanning electron micrographs showing the effect of washing treatment on the surface morphology of oil palm shell (OPS) powder: (a) hot distilled water (CDW), (b) hot distilled water with sonication (HDW-US), (c) cold alkali treated for 1 hr (CAT1) and (d) hot alkali treated for 1 hr (HAT).

Whilst the surface roughness at the interface of filler and matrix was improved due to alkali treatment (Figure 2-16 (d) and (e)), it would appear that alkali treatment does not significantly improve interfacial bonding further than that already obtained using a hot distilled water treatment, especially for the case of the CAT1 treatment. Therefore, the mechanical properties of the composites were not improved significantly by alkali treatment when compared to hot distilled water treatment.



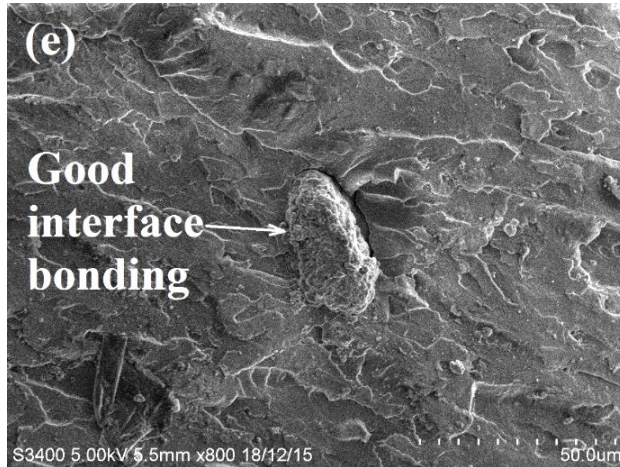


Figure 2-16. Scanning electron micrographs showing the effect of washing treatment on the fracture morphology of isophthalic unsaturated polyester (UP) reinforced with 5wt% of oil palm shell (OPS) powder: (c) cold distilled water (b) hot distilled water (HDW), (c) hot distilled water with sonication (HDW-US), (d) cold alkali treated for 1 hr (CAT1) and (e) hot alkali treated for 1 hr (HAT).

2.2.4.2.2 Effect of Alkali Concentration

The influence of hot alkali treatment on the wettability of UP matrix by OPS powder has been presented in Figure 2-17. It would appear that the quality of bonding between the powder and matrix was similar for the 1% hot NaOH treated composite (Figure 2-17 (a)) as for the hot distilled water treated composite (Figure 2-16(b)). As expected from the mechanical property data (Figure 2-13) the 7% hot NaOH composite (Figure 2-17(b)) exhibited the best interfacial bonding behavior when compared to the 1% (Figure 2-17(a)) and 9% (Figure 2-17(c)) cases. These results are consistent with a previous study on the effect of alkali concentration on the mechanical properties of Borassus fruit fibers ([John and Anandjiwala, 2008](#)) which indicated that the maximum tensile properties of the fibers were attained with the maximum amount of α -cellulose, which itself was achieved for an optimum period of time (8 hr) at 5% alkali treatment with the properties subsequently decreasing at more than the optimum time. This could also be attributed to the fact that the existence of surfaces impurities on the OPS powder, which has a significant effect on reducing the mechanical properties of OPS-UP composites, were removed by chemical treatment ([Nabinejad et al., 2015b](#), [Nabinejad et al., 2014](#)). This result is in good agreement with that of another study ([Chowdhury et al., 2013](#)) where the 5 wt%

concentration of alkali treatment of oil palm empty fruit bunch fibers increased the aspect ratio of the natural fiber.

The effect of chemical treatment on the removal of chemical molecules is investigated further in Sections 2.2.3.3 and 2.2.3.4.

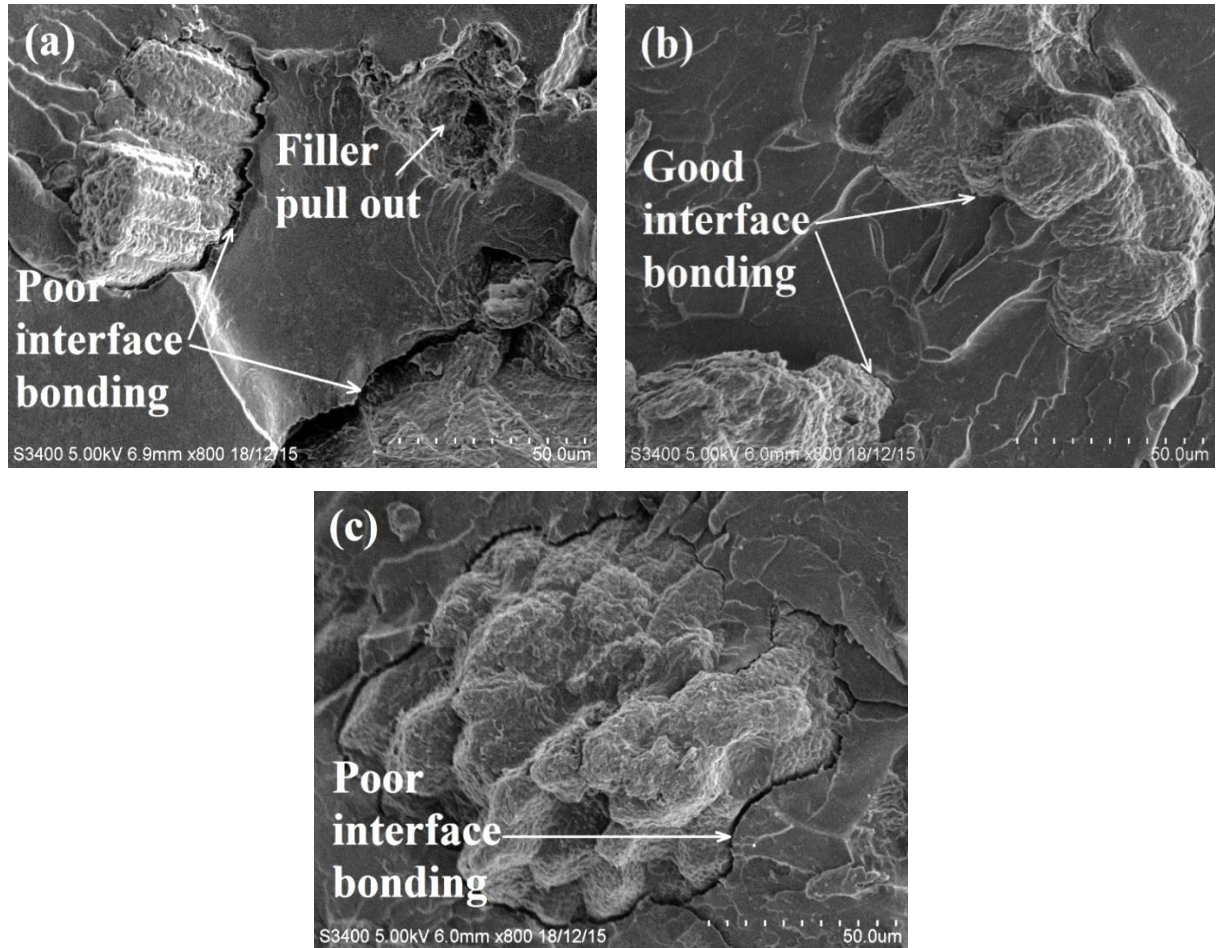


Figure 2-17. Scanning electron micrographs illustrating the effect of sodium hydroxide (NaOH) concentration on the quality of interfacial bonding in an isophthalic unsaturated polyester (UP) composite reinforced with 15 wt% of hot alkali treated oil palm shell (OPS) powder: (a) 1 %, (b) 7% and (c) 9%.

2.2.4.3 Fourier Transform Infrared Spectroscopy (FT-IR)

Lignocellulose materials are made of cellulose, hemicellulose and lignin as the three main ingredients of natural fiber/filler from plant resources (Fuqua et al., 2012). Cellulose with a general formula of $C_6H_{10}O_5$ is a linear and non-branched macromolecule with 1–4 linked

β -d-anhydroglucopyranose units which contains carbonyl, carboxyl and aldehyde groups (Akil et al., 2011, John and Thomas, 2008, Kabir et al., 2013). In contrast to this, lignin consists of aromatic syringyl, guaiacyl, methoxyl, hydroxycinnamic and methylene groups as highly branched aliphatic and phenolic structures. Hemicellulose contains different polysaccharides such as glucose, arabinose, xylofuranose, xylose, galactose, mannose and ketone groups and is responsible for the generation of suitable linkages between cellulose and lignin by ether bonds of xylene molecule (Kabir et al., 2013).

The functional groups of natural fiber can be identified by FTIR. The FTIR spectra of OPS before and after treatment are presented in Figure 2-18. As shown in Figure 8, some well-defined peaks show a slight difference after treatment in the fingerprint region between 1718 and 770 cm^{-1} . Based on Figure 2-18 the peaks in the fingerprint region, which indicate related functional groups of OPS, are assigned in Table 2-8.

It has been shown that the characteristic peak at 1030 cm^{-1} was designated as the C-H in plane deformation of Guaiacyl in lignin and C-O stretch of primary alcohol and syringyl ring (Pandey and Pitman, 2003). The intensity of the peak at 1030 cm^{-1} decreased by 17.3% (from 11.95 to 10.5) by hot water washing. This reduction was continued (by 26.7%) with sonication in hot water washed (HDW-US) OPS where the result was comparable with HAT treatment at the optimum concentration. This reduction indicates that sonication in hot distilled water was effective in removing Guaiacyl, Syringyl elements and primary alcohol molecules of lignin. Removal of Syringyl and Guaiacyl elements were confirmed by the reduction of peak intensities at 1239 and 1508 cm^{-1} respectively. The removal of lignin parts were also observed by a 55.8% reduction in peak intensity at 1594 cm^{-1} which is attributed to C-C stretching of the aromatic rings of lignin. The carbonyl of aldehydes, ketones and acetyl group in hydroxycinnamic acids associated with the alcoholic polysaccharides in lignin exhibit a peak at 1718 cm^{-1} (Kabir et al., 2013, Hoseinzadeh Hesas et al., 2013). The intensity of this peak decreased by 21% in HDW-US and completely disappeared following hot alkali treatment. Consequently, it can be concluded that HDW and HAT are able to remove some chemical elements in lignin parts of OPS.

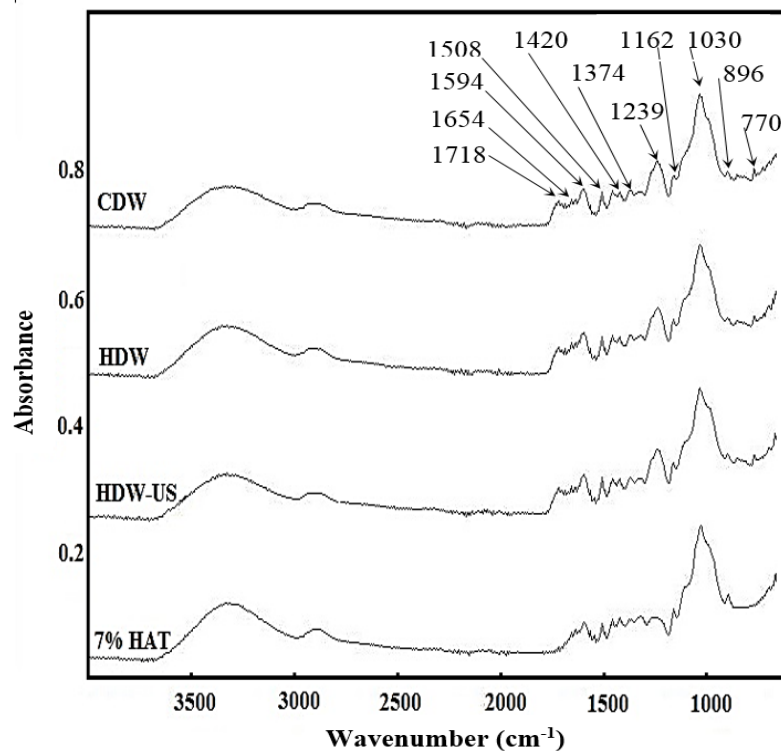


Figure 2-18. FTIR spectra of untreated and treated OPS in different condition

Xylans are polysaccharides made from units of xylose and are a group of hemicelluloses (Koch, 2008). Significant changes in FTIR spectra could be seen after treatment in the intensities of the unconjugated C = O (carbonyl) band in Xylan at 1239 and 1374 cm^{-1} (Xu et al., 2013, Pandey and Pitman, 2003). The intensities of the 1239 and 1374 cm^{-1} peaks decreased significantly with hot alkali treatment by 92.2 and 52.2%, respectively, with the peak positions shifting to 1244 and 1368 cm^{-1} . Furthermore, the intensity of the minor peak at 1654 cm^{-1} reduced significantly by hot alkali treatment, which is attributed to the C-H banding and C=O stretching frequency of Quinine, Quinine methides and adsorbed water in hemicellulose. The peak value at 1162 cm^{-1} is attributed to C-O-C symmetric stretching of hemicellulose and $\beta(1,4)$ -glycosic linkage for cellulose I and cellulose II (Xu et al., 2013). The intensity of this peak was reduced at 7% HAT by 34%. Contrary to this, the relative intensities of the bands at 896 and 1420 cm^{-1} , which are refer to the C-H bending of amorphous and crystalline cellulose respectively (Kabir et al.,

2013), get stronger by hot alkali treatment. This indicates that hot alkali treatment did not remove any cellulose molecules. Thus, the reduction in intensity at 1162 cm^{-1} could be due to removing C-O-C symmetric stretching of hemicellulose only. As a result, the lower content in Xylan, Quinine, Quinine methides elements and adsorbed water in hemicellulose in hot alkali treated OPS compared to the untreated case indicates that hot alkali treatment was effective in removal some parts of the hemicellulose.

Table 2-8. Assignment of major absorption FTIR spectra peaks in untreated OPS

Wave number (cm-1)	Absorbance	Functional group	Assignment	Reference
896	0.115	C-H	C-O-C,C-C-O and C-C-H deformation and stretching	(Dai and Fan, 2010.)
1030	11.95	C-H & C-O	C-O stretch of primary alcohol, C-H stretch of Guaiacyl, aromatic C-H in plan deformation of lignin	(Pandey and Pitman, 2003, Sinha and Rout, 2009)
1162	0.319	C-O-C	C-O-C symmetric Stretching of $\beta(1,4)$ -glycosic linkage for cellulose I & II and hemicellulose	(Xu et al., 2013, Dai and Fan, 2010.)
1239	2.870	C-O	C-O syringyl ring and C-O stretch in lignin and Xylan (hemicellulose)	(Pandey and Pitman, 2003)
1374	0.270	C=O C-OH	Carbonyl band of xylan, The C-OH in plane stretching of cellulose and aliphatic C-H stretching in methyl and phenol OH	(Kabir et al., 2013, Xu et al., 2013, Shi et al., 2012)
1420	0.125	C-H C-OH	C-H bending and OCH of crystalline cellulose	(Kabir et al., 2013, Dai and Fan, 2010.)
1508	0.523	C=C	Aromatic ring (lignin), Guaiacyl & Syringyl elements	(Shi et al., 2012)
1594	0.901	C=C	C=C stretching of aromatic ring (lignin)	(Hoseinzadeh Hesas et al., 2013)
1654	0.013	-OH C-H & C=O	-OH bending mode for the presence of water in hemicellulose and the C-H banding and C=O stretching frequency of Quinine and Quinine methides	(Kabir et al., 2013, Xu et al., 2013)
1718	0.223	C=O (-COOH)	Conjugated carbonyl groups of aldehydes and ketones and hydroxycinnamic acids (lignin)	(Kabir et al., 2013, Hoseinzadeh Hesas et al., 2013)

2.2.4.4 Thermal Behavior Study of OPS by Thermogravimetric Analysis

2.2.4.4.1 Effect of Different Treatment

Figure 2-19 illustrates the influence of washing treatment on the results of thermal analysis for OPS powder, *i.e.*, not in the composite. It has been previously reported ([Nabinejad et al., 2015b](#), [Methacanon et al., 2010](#), [Nabinejad et al., 2015a](#)) that OPS, a cellulose based material, tends to degrade in three main stages according to the TGA/DTG curves as follows: (i) evaporation of moisture (35~155 °C), (ii) hemicellulose degradation between 248 and 340 °C (maximum at 288.7 °C) and (iii) cellulose degradation between 345 and 400 °C (maximum at 359.7 °C). The effect of water and alkali treatment on the onset, endset and peak positions of oil palm shell (OPS) powder have been presented in Table 2-9.

Lignin pyrolysis was believed to occur in the range of 160~900 °C with an associated peak at 367 °C which was obscured beneath the hemicellulose and cellulose peaks ([Suardana et al., 2011](#)). Thus, except for the case of HDW-US the lignin peak was not apparent in the DTG curves. Consequently, lignin decomposition information was reported in two separate regions, *i.e.*, first and second parts of lignin decomposition, as shown in Table 2-9. The step analyses of all samples based on the dry mass have been listed in Table 2-10. Note that the mass loss values of the hemicellulose or cellulose in Table 2-10 refer to the mass losses in hemicellulose or cellulose decomposition regions together with the main part of the lignin decomposition section. Therefore, the main region of lignin decomposition has been left out of Table 2-10 with only the first and second parts of the mass loss of lignin being presented.

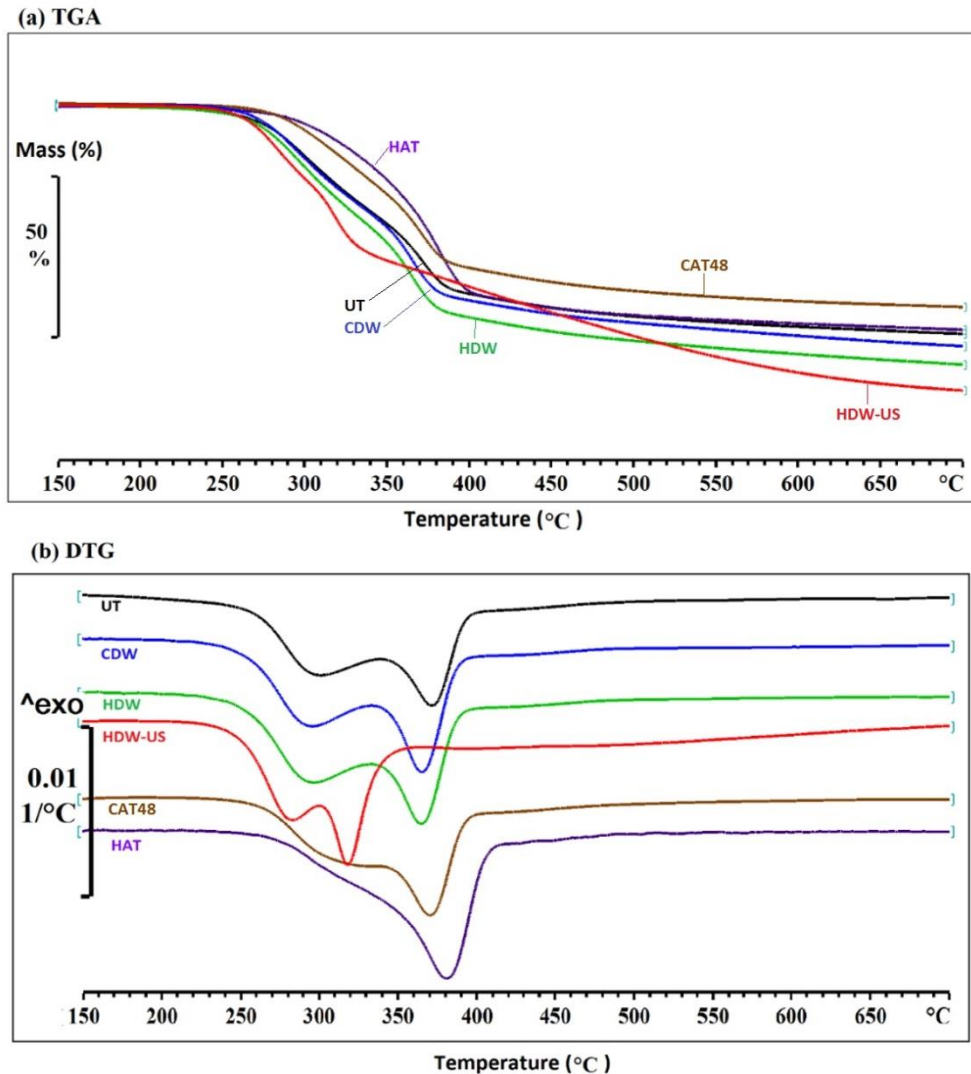


Figure 2-19. Effect of water and alkali treatment on the thermal properties of oil palm shell (OPS) powder: (a) thermogravimetric analysis (DTA) and (b) derivative thermogravimetric (DTG) analysis.

It has been previously reported ([Nabinejad et al., 2015b](#), [Stefani et al., 2005](#)) that the decrease in mass residue for washed natural filler is attributed to the removal of impurities and water-soluble polysaccharides present on the surface of the filler. In light of this, mass residue in the char yield may be an effective indicator of impurity removal due to washing. It should be noted that, for the non-degradable components, which remain as char yield, hot distilled water (HDW) decreased the char yield from 25.5% (for CDW) to 13.8% with the addition of sonication (HDW-US) reducing the char yield to only 2.29%. These results clearly indicate that, for the HDW-US OPS powder, the peak position shifted to a lower temperature with the temperature range (onset and endset) of decomposition for

hemicellulose and cellulose being decreased significantly due to sonication as shown in Table 2-9. Consequently, due to the significant displacement of the hemicellulose (291 to 284 °C) and cellulose (358 to 321 °C) peaks in the HDW-US treated powder, a peak attributed to lignin decomposition was also apparent in the DTG curve which indicated a significant increase in mass loss (from 16.8% to 44.0%) in the second stage of lignin mass loss.

Table 2-9. Effect of water and alkali treatment on the onset, endset and peak positions of OPS powder.

Sample		UT	DW	HDW	HDW-US	CAT24	HAT24
Moisture Evaporation	Onset (°C)	38.0	40.0	39.0	41.7	36.0	32.0
	Peak (°C)	69.0	61.0	63.0	71.6	90.0	68.0
	Endset (°C)	141	121	150	157	150	146
Lignin First Part Decomposition	Onset (°C)	244	263	246	252	249	251
	Endset (°C)						
	Ondset (°C)						
Hemicellulose Decomposition	Peak (°C)	290	290	291	284	Partially removed	Almost removed
	Endset (°C)	327	334	326	310	333	330
	Ondset (°C)						
Cellulose Decomposition	Peak (°C)	360	359	358	321	358	359
	Endset (°C)	382	382	381	370	381	390
	Ondset (°C)						
Lignin Second Part Decomposition	Peak (°C)	*	*	*	395	*	*
	Endset (°C)	680	680	680	680	680	675

* beneath the hemicellulose and cellulose peaks

Table 2-10. Effect of water and alkali treatment on the mass losses of OPS powder (dry based analysis).

Sample	Lignin Mass Loss		Hemicellulose	Cellulose	Char
	First Stage (%)	Second Stage (%)	Mass Loss (%)	Mass Loss (%)	Mass Residue (%)
UT	3.21	13.0	29.9	25.2	28.7
DW	2.72	15.2	27.8	28.8	25.5
HDW	2.50	16.8	34.7	32.3	13.8
HDW-US	2.15	41.0	27.9	26.6	2.29
CAT48	1.23	13.4	26.3	25.2	33.9
HAT	2.14	11.1	23.0	38.4	25.3

In contrast to this, the peak attributed to hemicellulose decomposition was almost absent in the hot alkali treatment specimen (Figure 2-19(b)) with this peak also being significantly reduced in the CAT1 specimen. The thermal analysis results also indicated that both the cold and hot alkali treatments reduced the mass loss attributed to hemicellulose decomposition when compared to the water treatments and thus increased the amount of cellulose present in the treated OPS powder. Looking at the results it was not clear how much of the hemicellulose or lignin had been removed (as a result of the various treatments) within the hemicellulose decomposition region during thermal analysis with this being attributed to the wide temperature range of lignin decomposition. It has previously been reported ([Martin et al., 2010](#)) that mass residues for the lignin, hemicellulose and cellulose components are 42%, 9% and 0.5%, respectively, which indicates that most of the char yield in natural filler is due to lignin. Consequently, the larger mass residue for the CAT48 treated powder (33.9%) compared to HAT (25.3%), together with the smaller mass drop in the second stage of lignin decomposition, appears to suggest that hot alkali treatment may be able to remove a portion of the lignin, together with the majority of the hemicellulose, which are difficult to thermally degrade under normal circumstances.

2.2.4.4.2 Effect of Alkali Concentration

Figure 2-20 illustrates the effect of NaOH concentration on the thermal properties of hot alkali treated OPS powder. Both the TGA (Figure 2-20(a)) and DTG (Figure 2-20 (b)) data indicate that increasing the NaOH concentration up to 7% did not significantly change the thermal analysis features. However, further increasing the concentration to 9% produced thermal analysis curves indicative of a substantial change in the OPS structure. For example, the main DTG peak, which is attributed to cellulose decomposition, had its maximum shifted from 322 °C for the 7% hot alkali treated OPS to 303 °C for the 9% case. Subsequently, the 9% hot alkali specimen also exhibited a lignin decomposition peak between 393 and 626 °C with a maximum at 478°C. The trend in these results is consistent with a previous study ([Kim and Pal, 2011](#)) that reported higher concentrations of alkali

solution to have produced extensive damage in wood fibers in wood plastic composite (WPC).

The effect of NaOH concentration on the lignin mass loss and mass residue obtained from TGA curves for hot alkali treated OPS powder has been presented in Figure 2-21. The data indicates a steady decline in mass residue and slight increase in lignin mass loss for increasing alkali concentrations up to 7%. However, the 9% alkali concentration OPS powder exhibited an additional substantial increase in lignin mass loss combined with a significant decrease in mass residue.

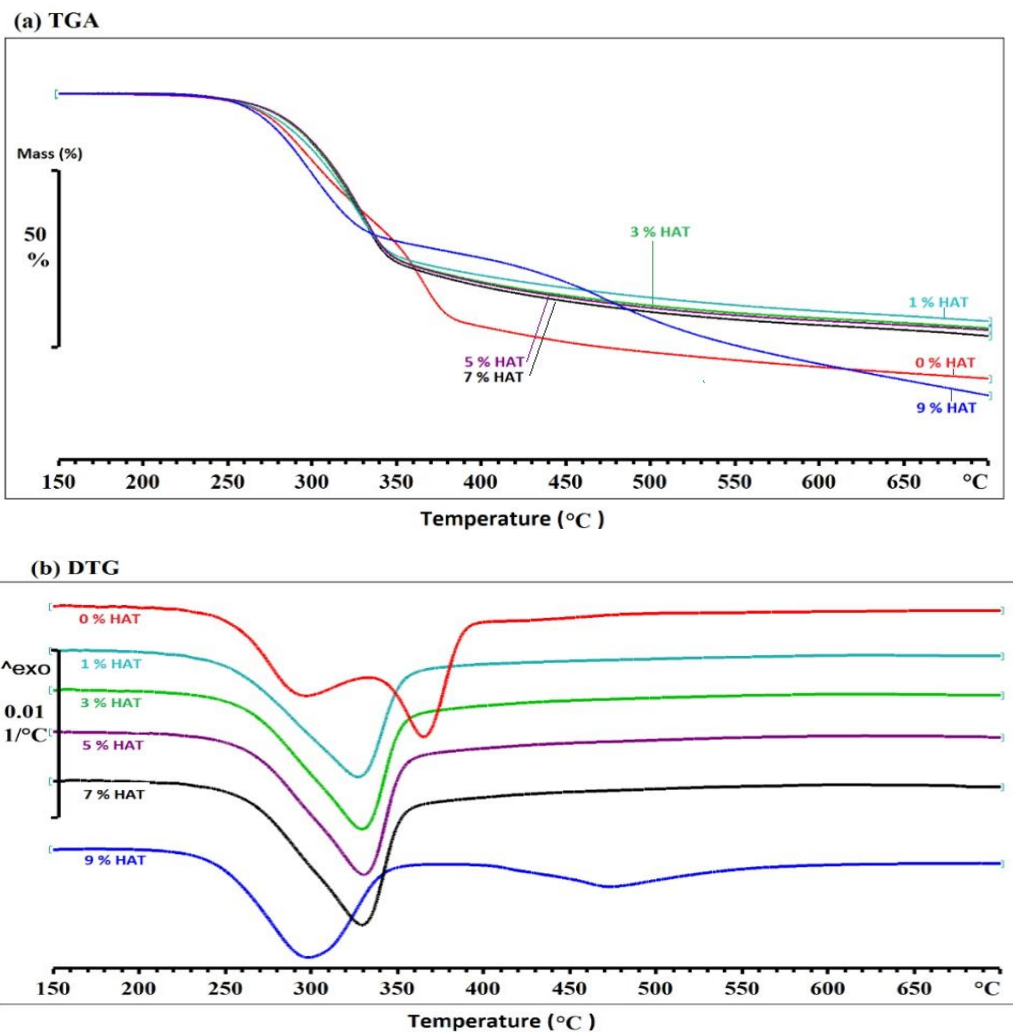


Figure 2-20. Effect of sodium hydroxide (NaOH) concentration on the thermal properties of hot alkali treated (HAT) oil palm shell (OPS) powder: (a) thermogravimetric analysis (TGA) and (b) derivative thermogravimetric (DTG) analysis

From the above discussion (Figure 2-13, Figure 2-17 and Figure 2-21), it can be concluded that the optimum concentration of hot alkali treatment required for maximum mechanical performance of natural filler reinforced polymer composites can be simply obtained from thermal analysis. In other words, the alkali concentration should be allowed to increase as far as possible whilst there is no significant change in TGA and DTG data. However, increasing the alkali concentration beyond the optimal value results in removal of some parts of the natural filler which results in a separation of phases between the lignin and cellulose components as reflected in Figure 2-20. Likewise, Figure 2-21 indicates that the lignin mass loss and the mass residue for natural filler started to dramatically change once the optimum alkali treatment conditions has been passed.

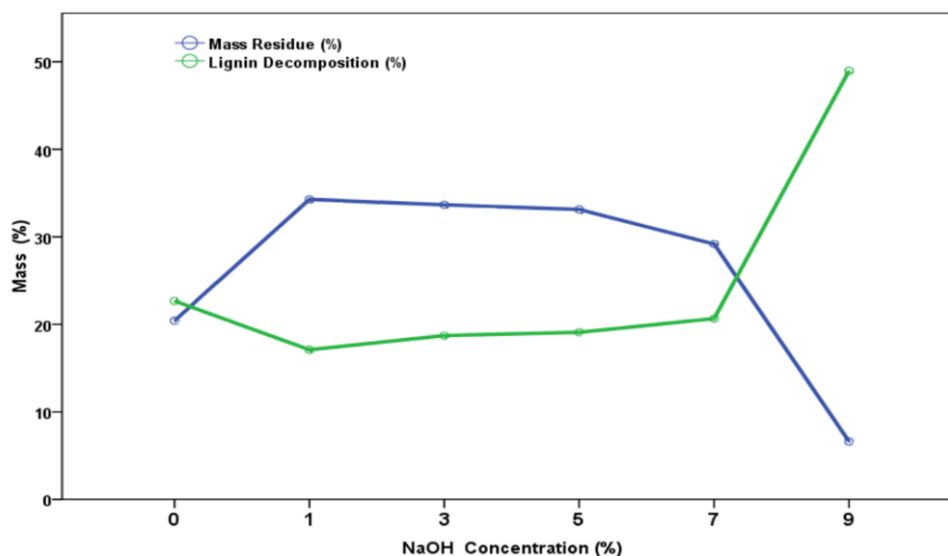


Figure 2-21. Effect of sodium hydroxide (NaOH) concentration on the lignin mass loss and mass residue of hot alkali treated oil palm shell (OPS) powder.

It is well known that, within natural fiber, lignin acts as a matrix phase whilst cellulose acts as the reinforcement phase whereas the role of hemicellulose is to bind the matrix and reinforcement together. However, should the treated fiber lose a portion of this binder (hemicellulose) due to the alkali concentration (9% in this case) being too high then phase separation occurs between the filler and matrix within the natural fiber as evident in Figure 2-21. This is in good agreement with FTIR the results which indicated that the tight linkage of polysaccharides in the cell wall by ether linkages can be removed by HAT. In

other words, further increases in alkali concentration beyond a certain point appears to deteriorate the structure of the natural filler which leads to poor mechanical performance of the natural filler and its resulting polymer composite. Previous research on the crystallinity of natural fibers ([Kalia et al., 2009](#)) has indicated that alkali treatment leads to the removal of hydrogen bonds in the network structure of natural fiber with a subsequent decrease in the amount of crystalline cellulose due to its conversion to amorphous cellulose. Other research work ([Ndazi et al., 2007](#)) which investigated the effect of alkali treatment of rice husk particles reported that the asperities of the filler surface had eroded with higher concentrations of alkali solution. This effect had resulted in the generation of cracks on the rice husk particles which led to a decrease in the mechanical performance of the resulting polymer composite due to ineffective stress transfer between the matrix and fibers. It should be noted that, whilst the present study utilized a constant time and varying concentration, a similar effect would presumably be noted for the situation of a constant concentration and varying treatment time.

2.2.5 Conclusions

The thermal analysis of treated oil palm shell powder from Palm Oil biomass and the mechanical performance of isophthalic unsaturated polyester composites reinforced with water and alkali treated OPS have been presented in this paper. The results of this study revealed that distilled water treatment significantly enhanced mechanical performance of the composites by improving the mechanical interlocking between the OPS powder and polymer matrix. The utilization of elevated temperature (90 °C) was effective for both water and alkali treatment in order to further enhance mechanical performance of the composites with sonication in hot distilled water achieving the highest mechanical performance through the optimal removal of impurities, wax and oily materials from the OPS powder surface.

Thermogravimetric analysis (TGA) of the OPS powder together with scanning electron microscopy indicated that the improvement in composite mechanical properties due to

washing treatment could be attributed to increased surface roughness of the OPS powder generated by the removal of surface impurities, waxes and lignin. Fourier transform infrared spectroscopy (FTIR) confirmed that Xylan, Quinine, Quinine methides elements and adsorbed water were removed as the parts of hemicellulose. Moreover, Syringyl and Guaiacyl elements, aldehydes and ketones and acetyl group in hydroxycinnamic acids associated with the alcoholic polysaccharides were also removed from lignin by hot water and hot alkali treatments. The optimum hot alkali concentration (7%) at 90 °C for 1 hr to enhance composite mechanical performance was found to be readily obtained from thermogravimetric analysis. For further increases in alkali concentration above this optimum amount, significant increases in lignin mass loss and decreases in mass residue were observed. It was concluded that, at excessively high alkali concentrations (and/or treatment times), hemicellulose, which acts as a binder for cellulose and lignin within natural fiber, is preferentially removed which causes a phase separation between the filler and matrix components of the natural fiber resulting in a deterioration of the fiber structure and subsequent poor composite mechanical performance.

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Chapter 3

Effect of Natural Filler Content

Chapter 3:

3 Optimize the Filler Content to Develop Thermoset Based WPC

Introduction:

In the previous chapter, the interfacial bonding between the fiber and the matrix in an OPS-UP composite has been investigated. Moreover, the effect of surface treatment on the quality of the bonding, the thermal stability of the filler and the mechanical properties of the composite has been investigated. It has been shown that the tensile and flexural properties were improved by optimizing the filler size and surface treatment. A hot alkali treatment with a 7% concentration showed the highest mechanical performance with some improvement in the thermal stability of the filler.

The effect of filler loading on the processing condition, mechanical performance, and the thermal stability of a thermoset based OPS composite was investigated in this chapter. How to increase the loading level of a lignocellulosic filler in thermoset based wood flour composites (WPC) was also analyzed. Moreover, the filler content was optimized and the curing reaction of thermoset resin in the presence of OPS was investigated in order to understand the role of filler load in the delaying of the curing reaction of thermoset resins. , The reason for this delay was considered and a potential mitigation response was developed to increase the level of filler load for these matrices.

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Effect of Filler Load on the Curing Behavior and Mechanical and Thermal Performance of Wood Flour Filled Thermoset Composites

Omid Nabinejad, D. Sujan, M. E. Rahman and Ian J Davies

Abstract:

The mechanical and thermal performance of wood flour composites (WFCs) containing thermoset resin is known to be strongly dependent on the curing reaction. In the present work, WFCs were prepared based on either unsaturated polyester, vinylester or epoxy reinforced by oil palm shell (OPS) flour with a major focus being the preferential reaction of the curing initiator with the natural fiber cells instead of the thermoset resin. Increasing the loading of OPS was found to delay the curing reaction of all thermoset resins by decreasing the peak exothermic temperature and increasing the time to peak. Selecting a suitable surface treatment for the OPS was observed to play a significant effect on the rate of curing reaction. Thermal degradation (in an inert atmosphere) and linear shrinkage of the WFCs was found to decrease with an increase in filler load. In terms of the mechanical performance, the flexural modulus increased steadily with filler load whereas the tensile modulus reached its maximum value of 2.74 GPa (30% improvement) at a filler content of 23 wt% for the hot alkali treated OPS reinforced polyester composite. Increasing the filler load was found to decrease the tensile strength whilst the flexural strength experienced an optimal value of 70.6 MPa (28% improvement) for a filler load of 9 wt%. Furthermore, the OPS filler exhibited improved interfacial bonding with the polyester matrix when compared to vinylester and epoxy.

Keywords: Wood Flour Composite, Curing Reaction, Oil Palm Shell, Thermal Degradation, Mechanical Property, Thermoset Resin.

3.1 Introduction

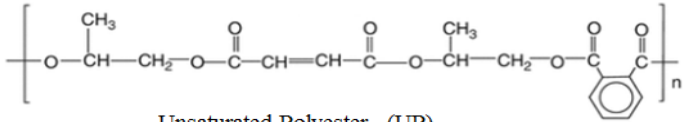
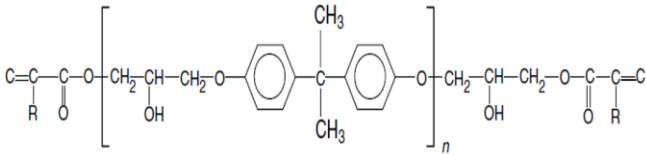
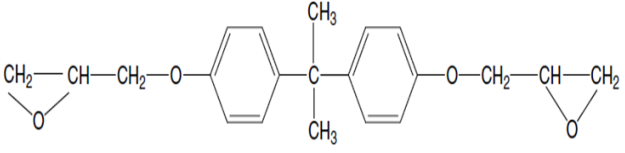
Natural fiber composites (NFCs) have become increasingly popular in the twenty-first century due to the growing environmental and accessibility concerns of petrochemical resources. Such materials, which are favored as a new generation of green materials, are inexpensive to synthesize compared to synthetic fiber-reinforced composites and possess high specific strength (O.Nabinejad and Sujana, 2016). Wood polymer composites (WPCs) are wood fibre/flour (WF) reinforced biocomposites frequently used in construction applications (decking, docks, landscaping timber, fencing), outdoor gardening and automotive products (Gurunathan et al., 2015). It is evident that the overall performance of WPCs improves through careful selection of materials and manufacturing processes (Olakanmi and Strydom, 2016) although the decision of selecting optimized materials can be a complicated process (Ali et al., 2015). An example of this complexity is the incompatibility between the natural fiber and polymer matrix which can lead to poor adhesion between the reinforcement and matrix, resulting in poor mechanical performance of the respective NFCs. Surface modification of the natural fiber by chemical and/or physical treatments, together with novel processing techniques, has been found to improve fiber-matrix interfacial bonding and subsequently lead to improved mechanical performance (Ku et al., 2011).

It is evident that the additional required processes increase the final cost of NFCs (Dicker et al., 2014). In order to decrease the overall manufacturing costs and owing to depleting wood resources, alternative low cost lignocellulosic sources have been investigated for use in NFCs (Bledzki et al., 2010). For instance, the shortage of wood resources can be alleviated by utilizing cereal residues as a filler or reinforcement in polymer composite materials (Quirino et al., 2012a). A comparison study between coconut shell, barley husk and soft wood reinforced PP stated that the tensile strength, elongation at break and Charpy impact of the coconut shell and barley husk composites was superior to that of the soft wood composite (Bledzki et al., 2010). Investigation on the effect of oil palm shell (OPS) powder size on the mechanical performance of polyester composites indicated that composites containing 75 to 150 μm sized OPS exhibited the highest mechanical performance with the removal of impurities during treatment playing a key role in the

presence of strong interfacial bonding between filler and matrix ([Nabinejad et al., 2015b](#)). In addition a study on the effect of different filler load of wood flour and wood fibers reinforced in soybean and linseed oil-based composites revealed that the maximum tensile strength was achieved for a relatively high filler load (80 wt%) of pine wood flour ([Quirino et al., 2012b](#)).

Surface treatment of cereal residues as a filler has a significant effect on the mechanical performance of NFCs. Alkali treatment of rice husk powder (with 5% NaOH concentration) was found to enhanced both flexural and tensile properties of the polyester composite ([Nabinejad et al., 2017](#)). Chemical treatment of OPS showed that both hot water and hot alkali treatment significantly improved the mechanical performance of the resulting composites with it being noted that some components of the hemicellulose, together with some elements of lignin, were removed by hot water and hot alkali treatments ([Nabinejad et al., 2016](#)). A study on the tensile and flexural modulus of polypropylene (PP) filled with grain byproducts such as olive stone flour (OSF) has indicated that the addition of maleated polypropylene (MAPP) as a coupling agent improved the flexural strength of the composites by enhancing interfacial bonding between the filler and PP matrix ([Naghmouchi et al., 2015](#)). It has also been reported that the flexural modulus of unsaturated polyester reinforced with olive nut flour (ONF) increased with ONF content whereas the flexural strength of untreated and γ -mercaptopropyl trimethoxysilane (MRPS) modified ONF reached its maximum for composites containing 30 and 40 wt% ONF, respectively ([Gharbi et al., 2014](#)).

Table 3-1. A comparative study of the curing system of thermosetting resins (Mohanty et al., 2005).

Type of resin with an idealized chemical Structure	Curing system	Advantages	Disadvantages
 <p data-bbox="380 505 659 529">Unsaturated Polyester (UP)</p>	<p data-bbox="968 375 1203 553">Room temperature curing catalyst with methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate as a promoter</p>	<p data-bbox="1297 435 1556 493">Easy to use, lowest cost resin (1-2 £/kg)</p>	<p data-bbox="1646 391 1938 537">Only moderate mechanical properties, high styrene emissions, limited range of working, high cure shrinkage</p>
 <p data-bbox="443 797 625 829">Vinylester (VER)</p>	<p data-bbox="968 643 1203 821">Room temperature curing catalyst with methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate as a promoter</p>	<p data-bbox="1289 670 1564 794">Very high chemical and environmental resistance, higher mechanical properties than polyester</p>	<p data-bbox="1646 656 1938 802">Postcure generally required for high properties, high styrene content, higher cost than polyester (1-2 £/kg), high cure shrinkage</p>
 <p data-bbox="541 1084 615 1117">Epoxy</p>	<p data-bbox="968 935 1203 1114">Room temperature curing catalyst with amine hardeners such as diethylene triamine, triethylene tetramine</p>	<p data-bbox="1289 902 1570 1143">High mechanical and thermal properties, high water resistance, long working times available, low curing shrinkage, temperature resistance can be up to 140 °C wet / 220 °C dry</p>	<p data-bbox="1646 964 1927 1084">More expensive than vinylester (3-15 £/kg), critical mixing, corrosive handling</p>

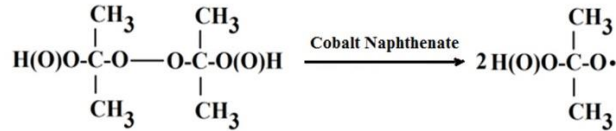
Curing of thermoset resins is an important aspect for the successful processing of composite materials. This should occur under controlled conditions in order to achieve a desired quality. Polyesters, vinylesters and epoxies account for approximately 90% of all thermosetting resin systems used in structural composites with a comparative study of the curing behavior and advantages and disadvantages of these resins being listed in

Table 3-1 (Mohanty et al., 2005). The curing process of polyester and vinyl ester with peroxide (*e.g.*, methyl ethyl ketone peroxide (MEKP)) is a free radical chain growth polymerization and exothermic reaction. These resins cure under free radical chain-growth cross-linking copolymerization between the resin double bonds and reactive diluents (*e.g.*, styrene monomer) (Beheshty et al., 2005).

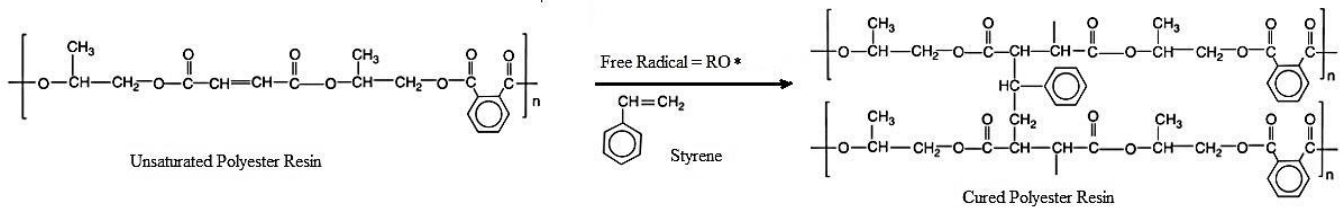
Table 3-1 illustrates the curing reactions for unsaturated polyester and vinyl ester resin.

It is clear that styrene and initiator contents are the principle components in the curing reaction of polyester and vinyl ester. It has been reported (Waigaonkar et al., 2011) that consideration of the interaction effects amongst different process variables provides important information for the manufacturing processes of fibre reinforced polymer (FRP) composites. Whilst gel time (t_{gel}) represents initiation of the crosslinking reaction, peak exothermic temperature (Θ_{peak}) controls the shrinkage and cracking of polymers. Increasing the loading of glass fiber and mineral fillers such as CaCO_3 is known to increase the gel time and decrease the peak exothermic temperature of the curing reaction. A significant delay in t_{gel} and slight increase in time to peak (t_{peak}) has also been reported by previous researchers (Osman E et al., 2012) for the curing reaction of kenaf reinforced unsaturated polyester with resin curing not occurring at 30 wt% of filler content and attributed to heat absorption by the excessive mass of natural fiber. A study on the degree of crosslinking of unsaturated polyester resin in curing reactions by (Kosar and Gomzi, 2010) revealed that the reduction in Θ_{peak} and enthalpy of reaction during the loading of inert fillers was as a consequence of the slower crosslinking reaction and amount of reactive components. However, it has been reported that the surface treatment of mineral filler (zirconia-silica) in urethane dimethacrylate composite improved the crosslink

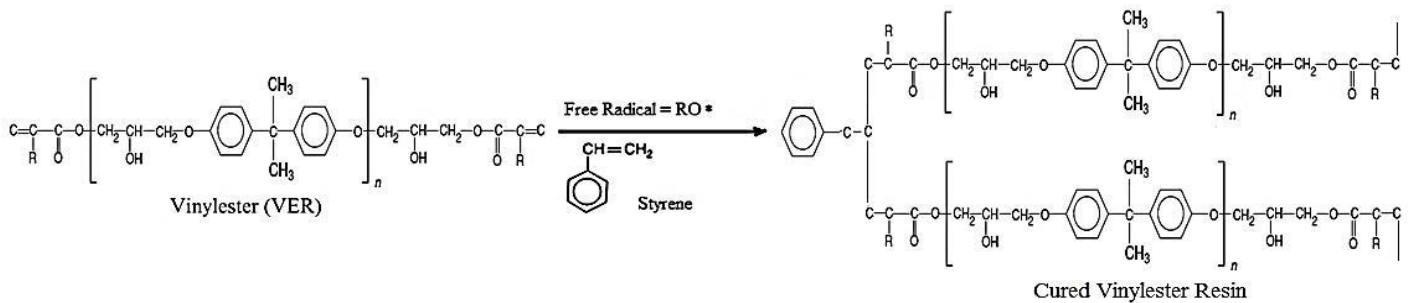
density of the composite by the increment of the rate of change of enthalpy (Mohsen et al., 1998).



(a) Peroxide (MEKP) decomposition



(b) Curing reaction of unsaturated polyester with MEKP and styrene



(c) Curing reaction of vinylester with MEKP and styrene

Figure 3-1. Curing reactions for unsaturated polyester and vinylester resin.

Although green composites containing wood flour and wood fiber have been widely investigated by researchers, in most cases thermoplastic resins were used for the matrices (Quirino et al., 2012b). To the best of the authors' knowledge, no significant studies have been conducted on other possible effects of natural filler load on the curing reaction of thermoset resins. The aim of the present study was, therefore, to investigate the effect of oil palm shell (OPS) powder, as a natural filler load, on the curing reaction rate of thermoset resins such as polyester and vinylester cured with peroxide and that of epoxy

cured with amine hardener. Finally, the mechanical performance and thermal resistance of OPS-reinforced polymer composites will also be discussed in the present study.

3.2 Sample Preparation

Oil palm shell powder was prepared by grinding oil palm shell (OPS) in a ball mill and then sieving to a size range of 75~150 μm as this had previously produced optimal results ([Nabinejad et al., 2015b](#)). As a result of previous work by the authors ([Nabinejad et al., 2016](#)), the OPS powder was then treated for one hour under the following conditions: (i) soaked in distilled water (CDW) at 25 °C, (ii) soaked in hot distilled water (HDW) at 90 °C and (iii) hot alkali treatment (HAT) - 7 wt% NaOH concentration at 90 °C. Sodium hydroxide pellets (EMSURE[®] ISO) for analysis were purchased from Merck Millipore. The OPS was then added to the respective thermoset resin in concentrations of either 10, 20, 30, 40 and 50 parts by mass of filler to 100 parts per matrix which are equal to 9, 17, 23, 28 and 33 wt% respectively.

The unsaturated isophthalic polyester (UP) and vinylester (VE) resins were individually cured with 1.0 wt% of methyl ethyl ketone peroxide (MEKP) whereas the amine-cured epoxy resin (Miracast 1517A/B from Miracon) was cured with 33 wt% of hardener. Note that the detail of chemical structure of the resins and hardener can't be disclosed without permission from the manufacturer. In order to remove excess air bubbles, the mixtures were placed under 95% vacuum and then poured into a mold. The mixtures were finally cured at 80°C for either one hour (unsaturated polyester and vinylester) or five hours (epoxy).

3.3 Characterization Techniques

3.3.1 Temperature Measurement of the Curing Reaction

A continuous temperature recording device (Model GRAPHTEC midi LOGGER GL220) with an accuracy of ± 0.1 °C was used to record t_{peak} and Θ_{peak} at a controlled ambient temperature of 24 °C. Data recording was started immediately after mixing the resin with catalyst in an isolated paper cup using a thermocouple placed at the center of the mixture.

3.3.2 Thermal Analysis

Thermogravimetric analysis (TGA) (Model TGA/DSC1, Mettler Toledo) was used to investigate the thermal behavior of the OPS powder, polyester matrix and their resulting composites. The tests were conducted with 15 mg mass of sample under a flowing nitrogen atmosphere (80 ml·min⁻¹) with a heating rate of 10°C·min⁻¹ between 35°C and 700°C according to ASTM E1131-08.

3.3.3 Shrinkage Measurement

Linear shrinkage measurements were conducted according to ASTM D955-00.

3.3.4 Mechanical Characterization

A universal testing machine (Model LR10K Plus Digital Control Testing, Lloyds Instrument) was used to investigate the mechanical behavior of composite specimens under tensile and flexural loading. The tensile strength and modulus were measured according to ASTM D638-10 using a 10 kN load cell and crosshead speed of 2 mm·min⁻¹ whereas the flexural strength and modulus were measured using a 500 N load cell and crosshead speed of 2 mm·min⁻¹ using the three-point bend configuration according to ASTM D790-10.

3.3.5 Void Content Measurement

The void content of cured composites was determined according to ASTM D2734-16 through Equation (3-1) and (3-2):

$$\text{Void content (\%)} = \frac{\rho_{\text{theoretical}} - \rho_{\text{experimental}}}{\rho_{\text{theoretical}}} * 100 \quad (3-1)$$

$$\rho_{\text{theoretical}} = \frac{1}{\left(\frac{w_f}{\rho_f} + \frac{w_m}{\rho_m}\right)} \quad (3-2)$$

Where w_f and w_m are the weight fractions and ρ_f and ρ_m are the densities of the OPS powder and resin, respectively. In Equation (1) the densities of the specimens, $\rho_{experimental}$, were determined by pycnometer according to ASTM D792-08.

3.4 Result and Discussion

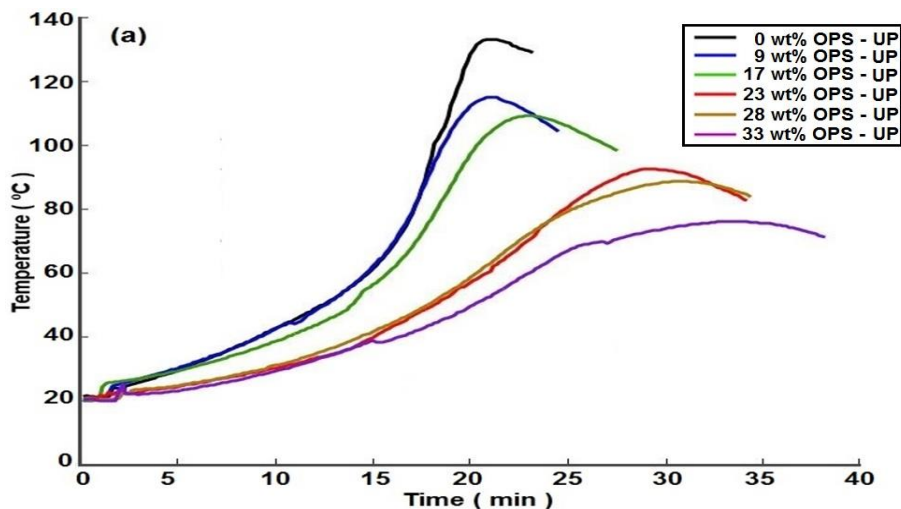
3.4.1 Effect of Filler Load on the Curing Reaction Rate of Thermoset Resins

The effect of untreated (*i.e.*, CDW) filler load on the curing reactions of polyester and vinylester resin and their respective composites after mixing with MEKP (as an initiator) have been presented in Figure 3-2 with it being clear that the curing process was exothermic in nature for all thermoset resins (including polyester, vinylester and epoxy) and resulting composites. Values of t_{peak} and Θ_{peak} for the curing reactions of the polyester, vinylester and epoxy resins and resulting composites have also been listed in Table 3-2. Figure 3-2(a) illustrates that the temperature of the neat polyester rose sharply during curing with a Θ_{peak} value of 133 °C and t_{peak} at 20.5 min. Figure 3-2 (a) also shows that the incorporation of untreated natural filler (CDW) powder into the polyester resin significantly reduced the rate of curing reaction with increased filler load tending to reduce the curing rate further. It can be observed that loading 9 wt% OPS into polyester reduced Θ_{peak} to 114.9 °C (a decrease of 13.6% compared to the neat resin) and increased t_{peak} to 20.8 sec (increase of 1.5%). Further additions of untreated filler to the polyester, in particular for amounts greater than 17 wt%, not only reduced Θ_{peak} but also significantly increased t_{peak} . For example, the recorded values of Θ_{peak} and t_{peak} for 28 and 33 wt% OPS in polyester were 88.6 °C at 30.2 min and 76.1°C at 33.3 min, respectively. Furthermore, it should be noted that the gelation process was not completed and that the mixture was not completely solidified even after 24 hrs for the case of 33 wt% OPS reinforced UP.

Similar trends in curing reaction rate were noted for the cases of adding untreated OPS powder to vinylester and epoxy mixtures as shown in Figure 3-2(b) & (c) with it being clear that vinylester and epoxy possessed longer reaction times in the curing stage when compared to unsaturated polyester. The neat vinylester was found to exhibit the highest curing reaction speed (compared with the vinylester composites) with reaction values of

Θ_{peak} at 129.2 °C and t_{peak} at 62.9 min. Figure 3-2(b) shows that filler load has a significant effect on the curing rate of vinylester when compared to polyester and epoxy. As the filler load increased the value of Θ_{peak} decreased whereas t_{peak} increased significantly with the lowest curing reaction rate being recorded for the 28 and 33 wt% filler load with a Θ_{peak} value of 51.7 °C at 260.3 min and 44.8 °C at 288.4 min respectively. In other word, 23 wt% filler load is the critical value for vinyl ester and should not be exceeded. It should be noted that, similar to the polyester case, the curing reaction of composites with 28 and 33 wt% of filler was not completed for the vinylester composites even after t_{peak} at 24 hours as shown in Figure 3-2(b).

The neat epoxy was found to exhibit a high Θ_{peak} with the value of Θ_{peak} at 131.2 °C and t_{peak} at 37.7 min (Figure 3-2(c)). It can be observed that loading 9 wt% OPS into epoxy only reduced Θ_{peak} to 114.3 °C and didn't change t_{peak} (37.8 min). In general, additions of untreated filler to the epoxy were found to exhibit the same range reduction in Θ_{peak} as for polyester with a longer delay in t_{peak} . It should also be noted that, in contrast to the results of polyester and vinylester, the gelation process was completed and that the mixture was solidified after 24 hrs for the case of 33 wt% OPS reinforced epoxy. It is therefore clear that the use of OPS as a natural filler slowed down the curing reaction rate for all thermoset resins including vinylester, polyester and epoxy.



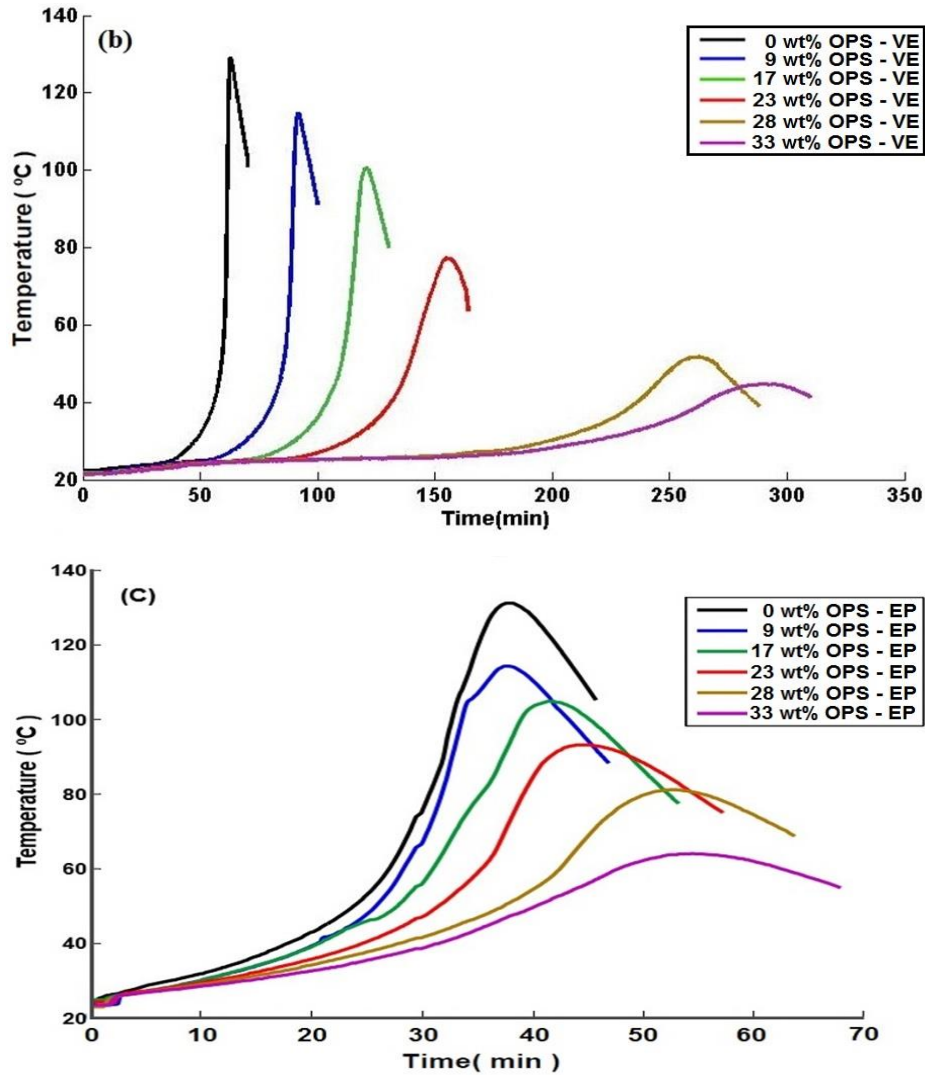
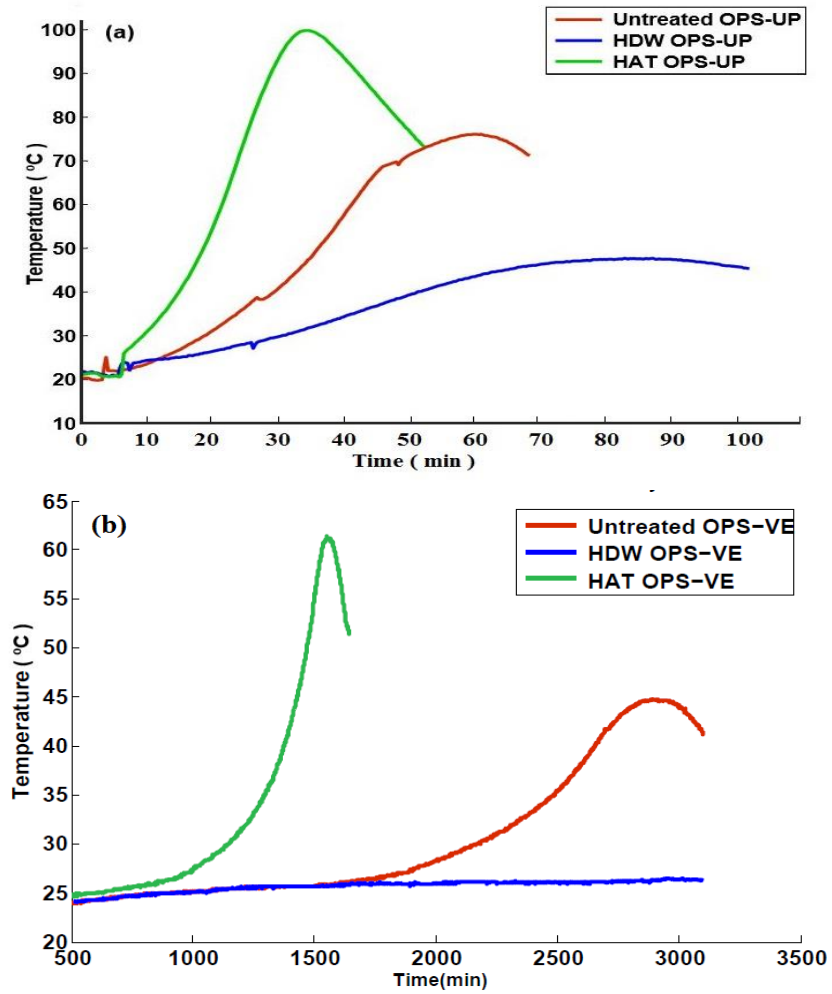


Figure 3-2. Effect of untreated (CDW) OPS natural filler load (wt%) on the curing reaction of: (a) polyester, (b) vinyl ester and (c) epoxy.

Time-temperature curves for treated (HDW and HAT) and untreated (CDW) 33 wt% OPS composites have been plotted in Figure 3-3 in order to investigate the influence of effective parameters on the delaying of the curing reaction from the point of view of chemical reactions. Figure 3-3 illustrates that the surface treatment of OPS has a significant effect on the curing rate of all thermoset resins. For example, θ_{peak} and t_{peak} values of 47.7 °C and 48 min value were obtained for the HDW OPS polyester composites (Figure 3-3(a)) which was 37.3% lower in θ_{peak} and 44.1% longer in t_{peak} when compared to the CDW (untreated) case. In contrast to this, θ_{peak} for the HAT treated polyester

composite was 99.8 °C whereas that of t_{peak} was 19.0 min, which indicates that the curing reaction rate could be significantly improved through use of a hot alkali treatment when compared to both the CDW and HDW cases. In other words, whereas the hot distilled water treatment delayed the reaction rate, the hot alkali treatment promoted the reaction rate of unsaturated polyester as shown in Figure 3-3(a) and in Table 3-2.

A similar trend was observed for the vinyl ester OPS composite (Figure 3-3(b)) with a θ_{peak} value of 61.4 °C and t_{peak} value of 155.2 min for the HAT treated OPS composite that were approximately 37.0% higher in θ_{peak} and 52% longer in t_{peak} when compared to the untreated CDW case. It is clear that no curing reaction was observed for the HDW treated OPS vinyl ester composite case.



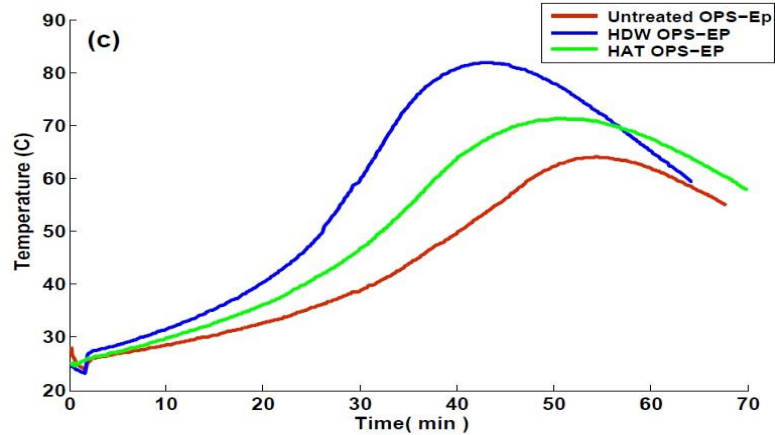


Figure 3-3. Effect of treatment for OPS powder (33 wt%) on the curing reaction of: (a) polyester, (b) vinylester and (c) epoxy composites.

It should also be noted that Θ_{peak} and t_{peak} values of 71.4 °C and 50.5 min, respectively, were obtained for the HAT OPS epoxy composites (Figure 3-3(c)) which was respectively 16.6% higher and 7.5% shorter when compared to the CDW (untreated) case. However, in contrast to the polyester and vinylester cases, epoxy resin exhibited a different behavior with the highest improvement being recorded for HDW as shown in Figure 3-3(c). Table 3-2 and Figure 3-3(c) show that Θ_{peak} and t_{peak} values of 82 °C and 43.7min were obtained for the HDW treated OPS epoxy composites, which were respectively 14.8% higher and 6.8% shorter compared to the HAT case.

Table 3-2. Time to peak temperature (t_{peak}) and peak exothermic temperature (Θ_{peak}) for the cure reactions.

Resin	Treatment Filler load (wt%)	Untreated (CDW)						Treated (HDW)	Treated (HAT)
		0	9	17	23	28	33	33	33
Polyester	Θ_{peak} (°C)	133.0	114.9	109.2	92.6	88.6	76.1	47.7	99.8
	t_{peak} (min)	20.5	20.8	22.7	29.2	30.2	33.3	48.0	19.0
Vinylester	Θ_{peak} (°C)	129.2	115	100.5	77.4	51.7	44.8	No Θ_{peak}	61.4
	t_{peak} (min)	62.9	91.7	120.8	155.2	260.3	288.4	No t_{peak}	155.2
Epoxy	Θ_{peak} (°C)	131.2	114.3	104.9	93.2	81.2	64.1	82.0	71.4
	t_{peak} (min)	37.7	37.8	41.7	44.3	52.7	54.3	43.7	50.5

As the filler content of 33 wt% produced different curing rate parameters for untreated and treated powder, it is thus clear that heat absorption via the addition of natural fiber mass is not the only effective parameter for delaying the curing rate as discussed previously. The noteworthy outcome of this result is that the type of chemical treatment, which changed the chemical composition and functional groups within the natural filler/fiber cell, was also an effective factor in influencing the curing reaction rate.

Cellulose as a natural polymer has a tendency to take part in radical reactions. It has been reported ([Johns et al., 2015](#)) that α -cellulose as a part of fiber cell derived plant resources, took part in free-radical copolymerization with Tung oil-based thermoset resins. A study on the peroxide treatment of sisal fiber by benzoyl peroxide has also shown that free radicals from the decomposition of the peroxide attacked the cellulose backbone which resulted in the formation of cellulose radicals ([Kaushik et al., 2013](#)). Therefore, peroxide treatment of natural fiber has also been used by researchers to improve the mechanical properties of polymer composites. This improvement in mechanical properties was attributed to the peroxide-induced grafting of polymer matrix onto cellulose surfaces in the fiber cell. For instance, direct grafting of polyethylene onto cellulose fibers by dicumyl peroxide was reported by ([Sapieha et al., 1990](#)). Moreover, the benzoyl peroxide-induced grafting was reported for oil palm fiber reinforced phenol formaldehyde composites ([Sreekala et al., 2000](#)) and sisal fiber reinforced polyethylene ([Joseph et al., 2000](#)).

It has also been reported that highly reactive radicals such hydroxyl radical ($\bullet\text{OH}$) are capable of attacking the polysaccharide back-bone. As a consequence it can cause polysaccharide chain scission in an aerobic environment ([Lindsay and Fry, 2006](#)). It is clear that hydroxyl radical abstracts a proton from a carbon-bond resulting a carbon centered radical ([Robert et al., 2014](#)) despite the chemical mechanism of the polysaccharide was not well established. A similar mechanism can be invoked for the reaction between radical from MEKP peroxide with OPS as a natural filler with the cellulose in the filler cell (either CDW or HDW treated) competing with styrene and polymer chains in the polyester and vinylester resins to react with the MEKP initiator. Based on these findings, a proposed reaction between MEKP and cellulose could be

represented by the schematic shown in Figure 3-4. As shown Figure 3-4 H is abstracted from either C₁, C₂, C₃, C₄ or C₆. Such a hypothesis supports the HDW and HAT treated cases. In the HDW case, hot distilled water effectively removes the impurities, guaiacyl, syringyl elements and primary alcohol molecules of lignin and water-soluble polysaccharides present on the surface of OPS (Nabinejad et al., 2016). This results in additional cellulose molecules being exposed on the surface of the natural filler cells to react with free radicals and consume the initiator. Thus, it caused a significant delay in curing (with the t_{peak} value of 48.0 min and θ_{peak} value of 47.7 °C) of polyester composite and prevented the polymerization reaction for the vinyl ester case.

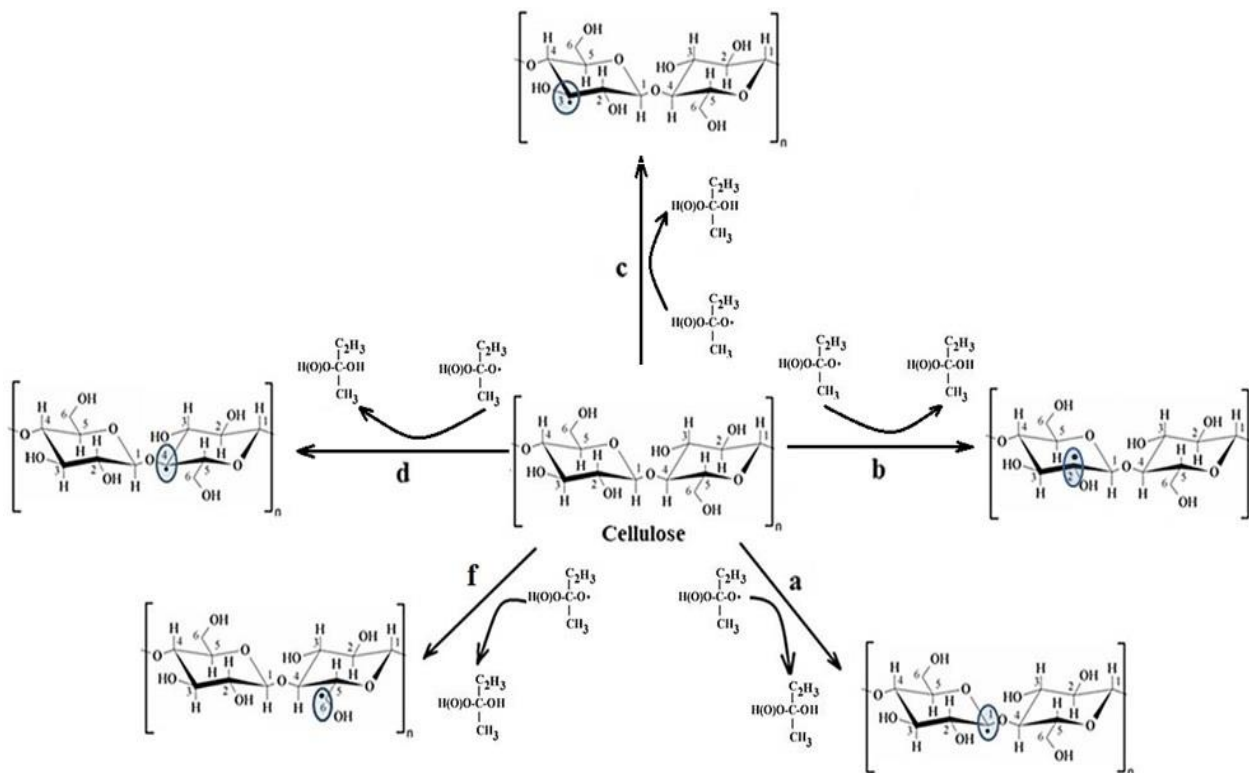


Figure 3-4. Suggested reaction between cellulose in natural filler and MEKP.
The dot (·) indicates a free-radical position

In contrast to this, the hot alkali treatment is known to change the chemical groups present on the surface of natural filler by two different mechanisms as discussed in our previous work (Nabinejad et al., 2016). In the first step, HAT removes some parts of lignin and hemicellulose. As HDW is also effective in removing of some portion of lignin and

hemicellulose, therefore, the removal in HAT of those elements may not be due to the direct reaction of hydroxyl groups with these components. This was a result of the combination of alkali concentration in hot water and subsequent washing process after treatment. It should be noted that the peak at wave number 1718 cm^{-1} in the FTIR test with the intensity of 0.223 was removed following the washing process after hot alkali treatment. The peak is referred to conjugated carbonyl groups of aldehydes and ketones and acetyl groups in hydroxycinnamic acids associated with alcoholic polysaccharides present within lignin. Moreover, the intensities of the peaks at 1239 and 1374 cm^{-1} , which are associated with xylan, quinine and quinine methide elements in hemicellulose, decreased significantly with hot alkali treatment by 92.2 and 52.2%, respectively. In the second step, these hydroxyl groups (OH) in cellulose are replaced by O^-Na^+ groups (Nabinejad et al., 2016). Therefore, the alkali treatment of natural filler results in mercerized cellulose as shown in Figure 3-5.

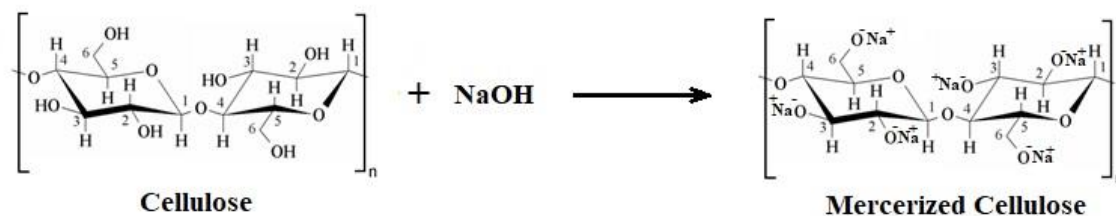


Figure 3-5. Mercerization (alkali treatment) of cellulose in natural fiber cell.

Consequently, mercerized cellulose has less tendency to compete with styrene and polymer chains and react with the free radicals decomposed from the initiator. As a result, the peroxide can only react with styrene and polymer chains and the curing reaction could thus be successfully completely. Accordingly, the t_{peak} value of 19.0 min for the HAT OPS polyester composite was comparable with that of the neat resin (20.5 min). This is in good agreement with the finding by (Sapieha et al., 1990) which claimed that the grafting reaction between peroxide and cellulose can be terminated in a critical concentration of peroxide when cellulose surfaces are no longer accessible. This hypothesis may be a good explanation for the results reported by other researchers (Osman E et al., 2012) where increasing the initiator (MEKP) level from 1 wt% to 3 wt% partially recovered the curing

reaction rate for 30 wt% kenaf reinforced polyester composites. In other words, some portion of the MEKP had been reacting with cellulose in the natural fiber cell with the remaining MEKP participating in the curing reaction of resin to complete the curing process.

The effect of treatment on the curing of epoxy resin, however, was found to follow a different mechanism. It has previously been reported that fibrillated cellulose can be treated by epoxide groups to create ether linkages (Moon Robert et al., 2011). Moreover, the reaction of the epoxide groups with cellulose can occur in alkaline conditions when the concentration of sodium hydroxide is sufficiently high (Hill, 2006). The reaction between the epoxide groups in epoxy resin and mercerized cellulose in natural filler to create ether linkages can be proposed according to Figure 3-6. Therefore, mercerized cellulose competes with the hardener to react with epoxide groups in epoxy resin which results in further delays in the curing reaction when compared with the HDW treated case.

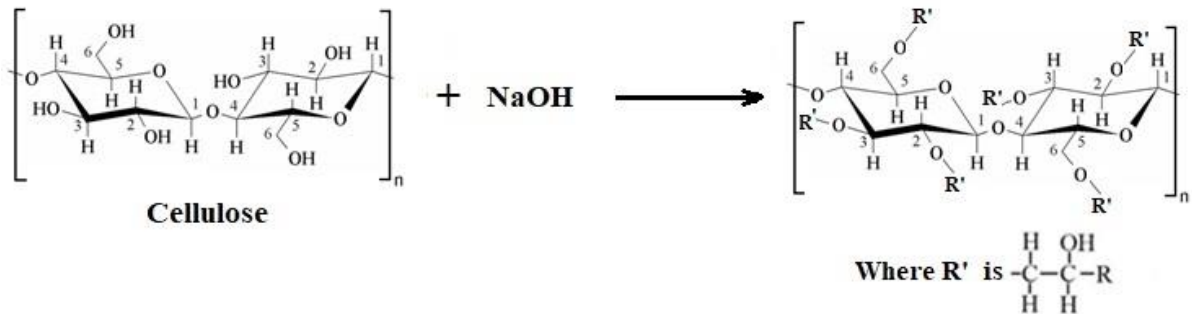


Figure 3-6. Suggested reaction between mercerized cellulose and epoxide groups in epoxy resin to create ether linkages.

From the above finding it can be concluded that the filler load was believed to delay the curing reaction in two steps depending on the filler type and matrix. The first mechanism was due to the absorption of heat generated by the exothermic reaction of the mixture, which could occur for both mineral and natural fillers with this phenomenon depending on the heat dissipation factor and heat conductivity between the filler and matrix within the mixture. The second step, which is the major reduction, is the delay in the curing reaction due to the initiator or resin consumption by cellulose. Therefore, despite the curing reactions of 33 wt% OPS composites being completed for all thermoset resins,

there was a minor reduction in θ_{peak} even after a suitable treatment of natural filler shown in Table 3-2. These reductions in θ_{peak} were attributed to the absorption of heat generated in the exothermic reaction by the natural filler.

The time-temperature profile in such curing reactions can be fitted by an exponential equation as presented in Equation (3-3).

$$T(t) = \sum_{i=0}^5 c_i t^i + \sum_{j=0}^2 A_j e^{-\frac{1}{2} \left(\frac{t-\mu_j}{\sigma_j} \right)^2} \quad (3-3)$$

Where $T(t)$ is the temperature ($^{\circ}\text{C}$), t is the time (min) and c_i , μ_j and σ_j are constants of the equation. The equation's constants for the above reactions are listed in Appendix. It is clear from the table that the constants are functions of the filler load and the type of treatment. Figure 3-7 shows the comparison between experimental and calculated results for the various neat resins.

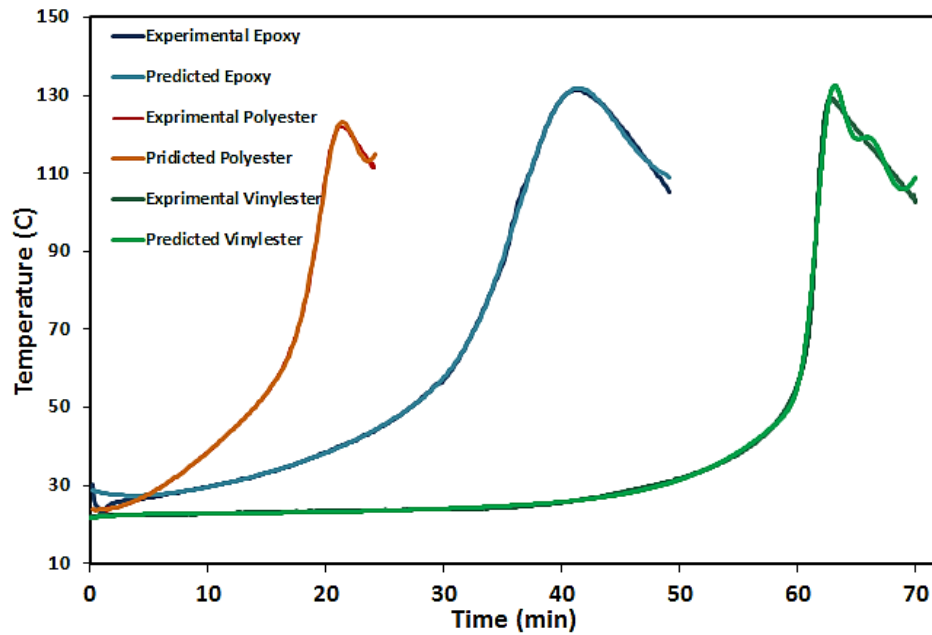


Figure 3-7. Comparison between calculated model from Equation 3-3 and the experimental data for neat polyester, vinylester and epoxy resins

3.4.2 Effect of Filler Load on Thermal Properties of Composite

The thermal properties of NFCs can be investigated by TGA where the specimen mass is monitored as a function of time or temperature upon exposure to a controlled temperature program in an inert or oxidizing atmosphere. Distinguishing the mass losses of ingredients within the composite may facilitate the interpretation of data from the TGA curves. However, it has previously been reported ([Nabinejad et al., 2015a](#)) that the filler content of NFCs can be obtained by a simple and generic equation derived from TGA curves, even in the presence of overlapping thermal degradation temperature ranges for the polymer matrix and natural filler.

Figure 3-8 presents TGA curves under nitrogen atmosphere for neat polyester resin, untreated OPS and their untreated composites with 9, 17, 23 and 28 wt% filler content (the sample for 33 wt% filler level was not prepared as the composite was not cured properly at that high level of untreated filler content). It is clear from the data that the onset of composite thermal degradation was found to decrease with increasing filler load with an onset value of 266 °C for the 28 wt% case, which was 66 °C lower than that for neat polyester resin. This result was attributed to the lower thermal stability of the lignocellulose filler (with onset value 254.6 °C) when compared with the polyester resin. Following this, the natural filler retarded the endset of thermal degradation at a higher temperature for contents of 9, 17 and 23 wt% and then shifted to a lower temperature for the sample with higher filler content (28 wt%) as shown in Figure 3-8. It is important to note that the range and degree of shift in thermal stability of the OPS-UP composite in an inert atmosphere depends on the filler load and thermal stability of the filler and matrix. For example, natural filler tends to reduce the thermal stability of the composite due to its lower thermal stability when compared to standard inorganic fillers such as silica. This is different from the previous result in an oxygen atmosphere where thermal degradation of the composite was shifted to higher temperatures when compared to the neat resin ([Nabinejad et al., 2015b](#)). A similar trend was previously reported for the thermal stability of silk reinforced poly(butylene succinate) biocomposites ([Lee et al., 2005](#)) and lignocellulosic filler-thermoplastic polymer bio-composites ([Yang et al., 2005](#)).

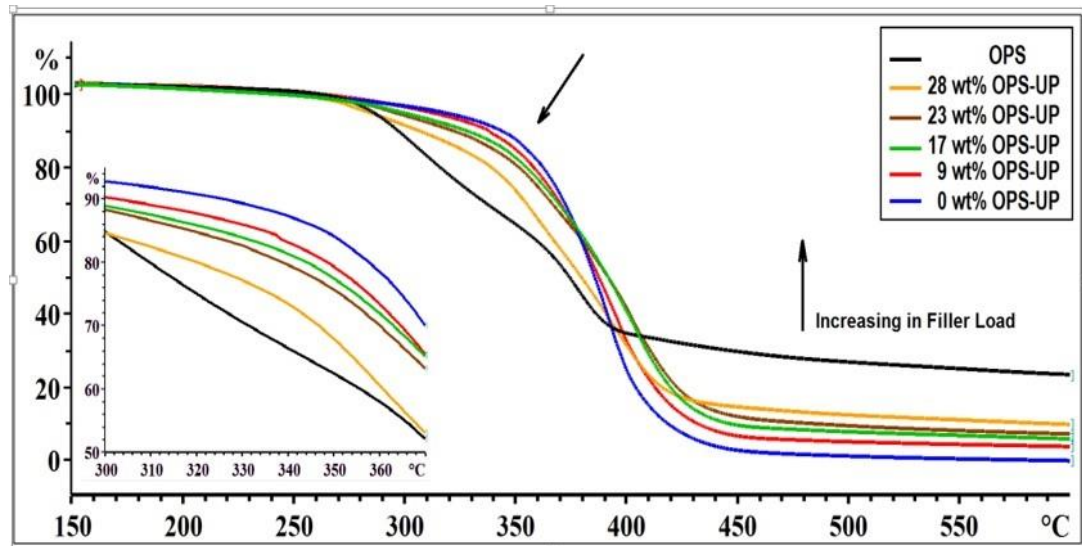


Figure 3-8. TGA curves for powdered untreated OPS, neat polyester matrix and their respective composites at different filler loads:

Figure 3-9 illustrates DTG curves for OPS-UP composites as a function of filler load with it being apparent that the peak positions did not exhibit a consistent trend. For example, the peak positions shifted to higher temperatures (393.10 and 396.30 °C for 9 and 17 wt% OPS loading, respectively) compared to the neat polyester resin (383.69 °C) at lower filler content but then shifted to lower temperatures (394.54 and 390.21 °C for 23 and 28 wt% OPS loads) at higher filler content. It has been previously reported (Nabinejad et al., 2015a) that the addition of OPS to polyester generates a new peak on the left shoulder of the main peak in the DTG curve. Therefore, Figure 3-9 also confirms that a phase separation existed for higher filler contents with this being attributed to the presence of OPS as natural filler in the matrix.

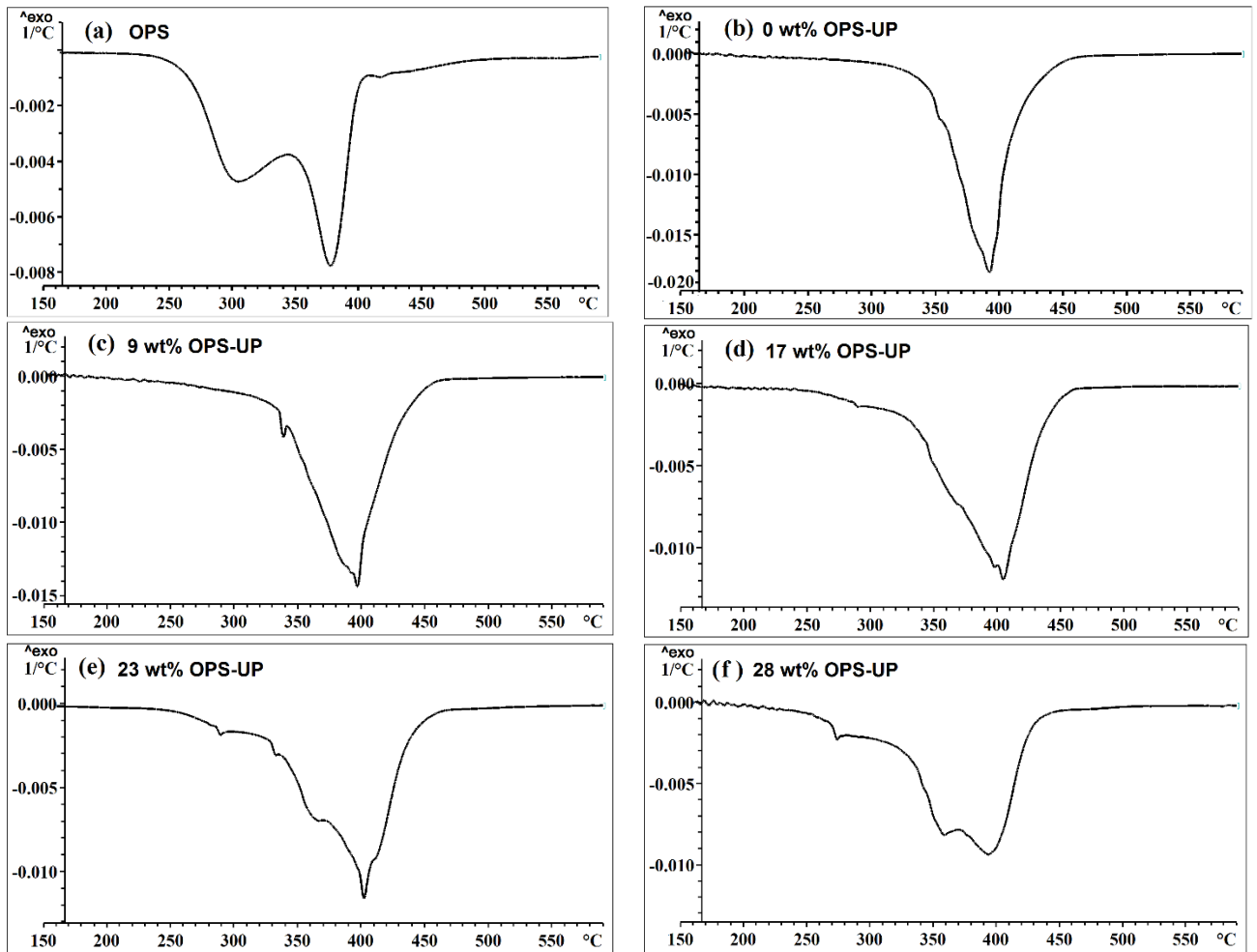


Figure 3-9. DTG curves for untreated powdered OPS, neat polyester matrix and their respective composites at different filler loads.

The presence of a phase separation could be attributed to the weaker interfacial bonding between the natural filler and matrix at higher filler contents above 17%. For example, the weaker interaction between filler and matrix at higher filler load might be due to the lack of sufficient polymer phase to wet the high surface area natural filler powder. This phase separation (as shown in Figure 3-10) was affected to some extent by the surface treatment of the natural filler with the two main peaks in the DTG curve becoming narrower, together with the small peak on the left shoulder of the small main peak being eliminated, due to the hot alkali treatment. In addition, the main peak positions (at 349.25 and 403.43 °C) were shifted to lower values (336.97 and 362.17 °C) as a result of the treatment. Moreover, the alkali treated composite recorded a lower mass residue (8.37 %) when

compared to the untreated OPS-UP (10.44 %) case as shown in Figure 3-10(a). These results might be due to the fact that alkali treatment can remove selected phases from the natural fiber cell (such as impurities, waxes, some components of hemicellulose and lignin) which possess a higher mass residue and degradation at elevated temperature (Nabinejad et al., 2016). Subsequently, the treated composite experienced a lower mass residue with the degradation both starting and finishing at lower temperatures when compared to the untreated OPS composite.

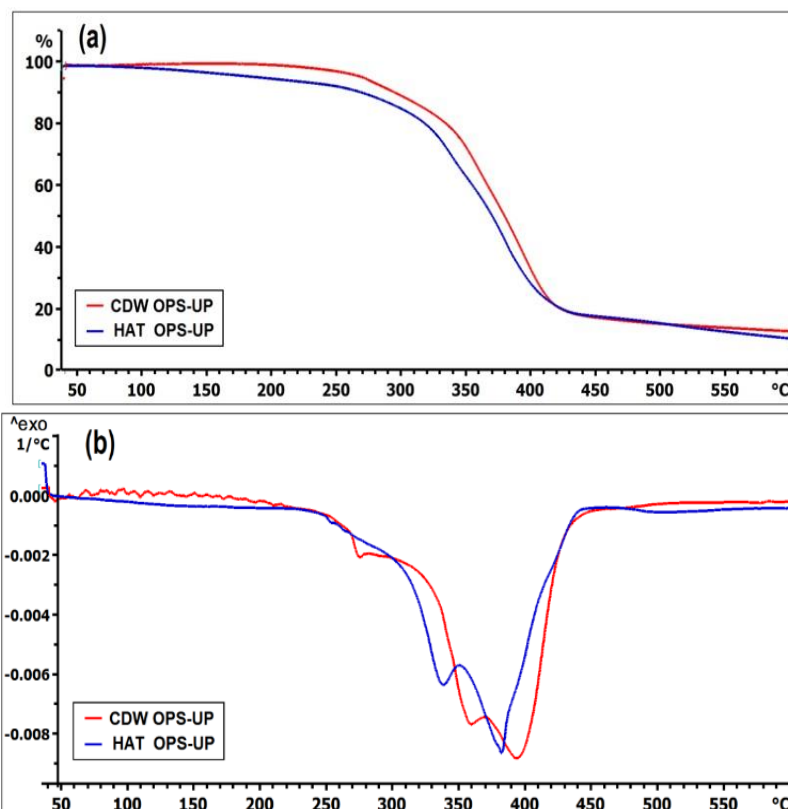


Figure 3-10. Influence of untreated (CDW) and treated (HAT) OPS powder (28 wt%) on the thermal analysis of polyester composites: (a) TGA and (b) DTG.

Mass residues of the OPS-UP composites obtained from the TGA curves in Figure 3-8 were plotted in Figure 3-11 as a function of filler load. The mass residue was found to increase linearly with increasing filler load with this being attributed to the fact that OPS as a natural fiber possessed higher mass residue in the inert atmosphere as compared to the polyester resin.

Linear shrinkage of NFCs is an important consideration for composite designers and manufacturers. The effect of filler load on linear shrinkage of OPS-UP composites have been plotted in Figure 3-11 with an approximate linear decrease in shrinkage being noted as filler content increased. It has previously been reported that resin shrinkage, which is due to the rearrangement and reorientation of the resin molecules in the liquid and semi-gelled phase during and following the curing period (Mohanty et al., 2005), can be controlled by peak exothermic temperature (θ_{peak}) (Osman E et al., 2012). Polymer chain pinning between the matrix and reinforcement can be another factor, which prevents the rearrangement and reorientation of resin molecules in the polymer matrix by limiting movement of the resin molecules which leads to a reduction in θ_{peak} . In other words, the more that θ_{peak} reduces (at higher filler content as shown in Figure 3-2 and Table 3-2) the less able that the resin molecule can move, which results in reduced rearranging and reorienting of the resin molecules in the liquid and semi-gelled phases. Therefore, the composite with the highest (28 wt%) filler load would be expected to exhibit the lowest linear shrinkage as shown in Figure 3-11.

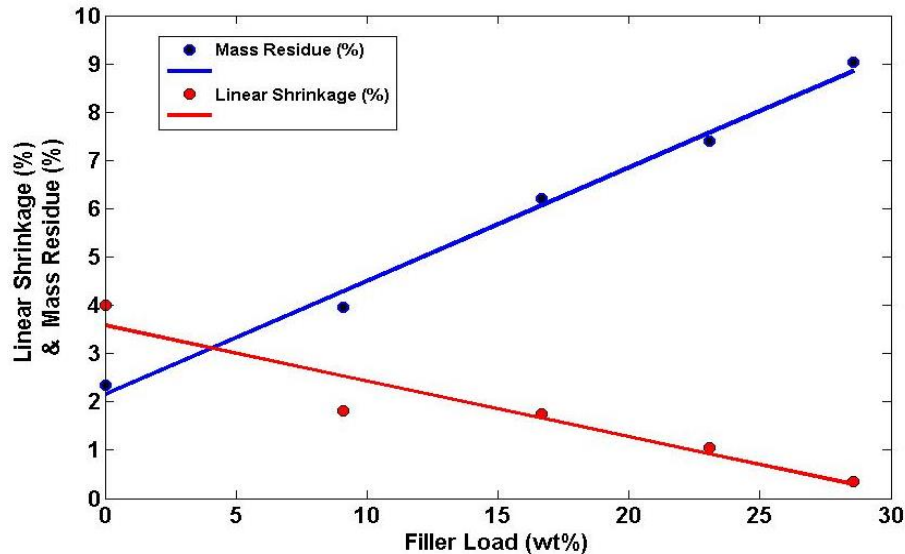


Figure 3-11. Effect of untreated OPS filler content on the mass residue and linear shrinkage of polyester composites.

3.4.3 Mechanical Properties

3.4.3.1 Effect of Filler Load on Composite Mechanical Properties

Figure 3-12(a) and (b) illustrate the influence of 7 wt% treated (HAT) OPS loading on the tensile and flexural strength of unsaturated polyester (OPS-UP) composites, respectively. It can be observed from Figure 3-12(a) that the tensile strength of the OPS-UP composite with 9 wt% of OPS decreased to 39.8 MPa compared to 43.6 MPa for the neat polyester resin – a decrease of 8.6%. The tensile strength then remained steady from 9 to 23 wt% OPS with a further increase in filler load from 23 to 33 wt% producing a 24.4% drop in tensile strength to 31.1 MPa.

In contrast to this results, the flexural strength of the 9 wt% OPS-UP composite was approximately 16% higher (62.2 MPa) when compared to that of the neat polyester (55.19 MPa) as shown in Figure 3-12(b). The flexural strength of the OPS-UP composite increased to 64.1 MPa for the 17 wt% filler content before decreasing for the 33 wt% case at 52.4 MPa, where this was lower than that of the neat resin sample. The results were in good agreement with those of a previous study ([Olakanmi and Strydom, 2016](#)) where the flexural strength of WPCs manufactured from compounded low and medium melt flow index high density polyethylene experienced a maximum value for a set amount of wood flake content. Low wettability of filler by the matrix and phase separation between them at high filler content, as discussed in Section 3.2, were considered to be the main reasons for the decreasing flexural strength at high filler content. However, some researchers ([Naghmouchi et al., 2015](#)) attributed reductions in the ultimate tensile stress of OWF filler in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer to a reduction in the overall degree of crystallinity of the matrix (PHBV) phase, together with induced embrittlement in the NFC due to the loading of OWF in the polymer.

Figure 3-12 (c) illustrates the influence hot alkali treated OPS powder on the tensile moduli of OPS-UP composites. The treated (HAT) OPS-UP composites showed a different trend with respect to tensile modulus with it remaining almost constant until a loading of 9 wt% OPS (2.19 GPa) and then increasing significantly to a maximum value

of 2.74 GPa for the case of 23 wt% OPS and then declining to a value of 2.12 GPa (similar to that of the neat resin) for the case of 33 wt% OPS. In contrast to the trend for tensile modulus, the composite flexural modulus rose sharply following the addition of OPS powder as shown in Figure 3-12(d). It was observed that the use of OPS filler increased the flexural modulus from 2.95 GPa for the neat resin to 4.86 GPa for HAT OPS-UP composite – an increase of 64.7% compared to the neat resin.

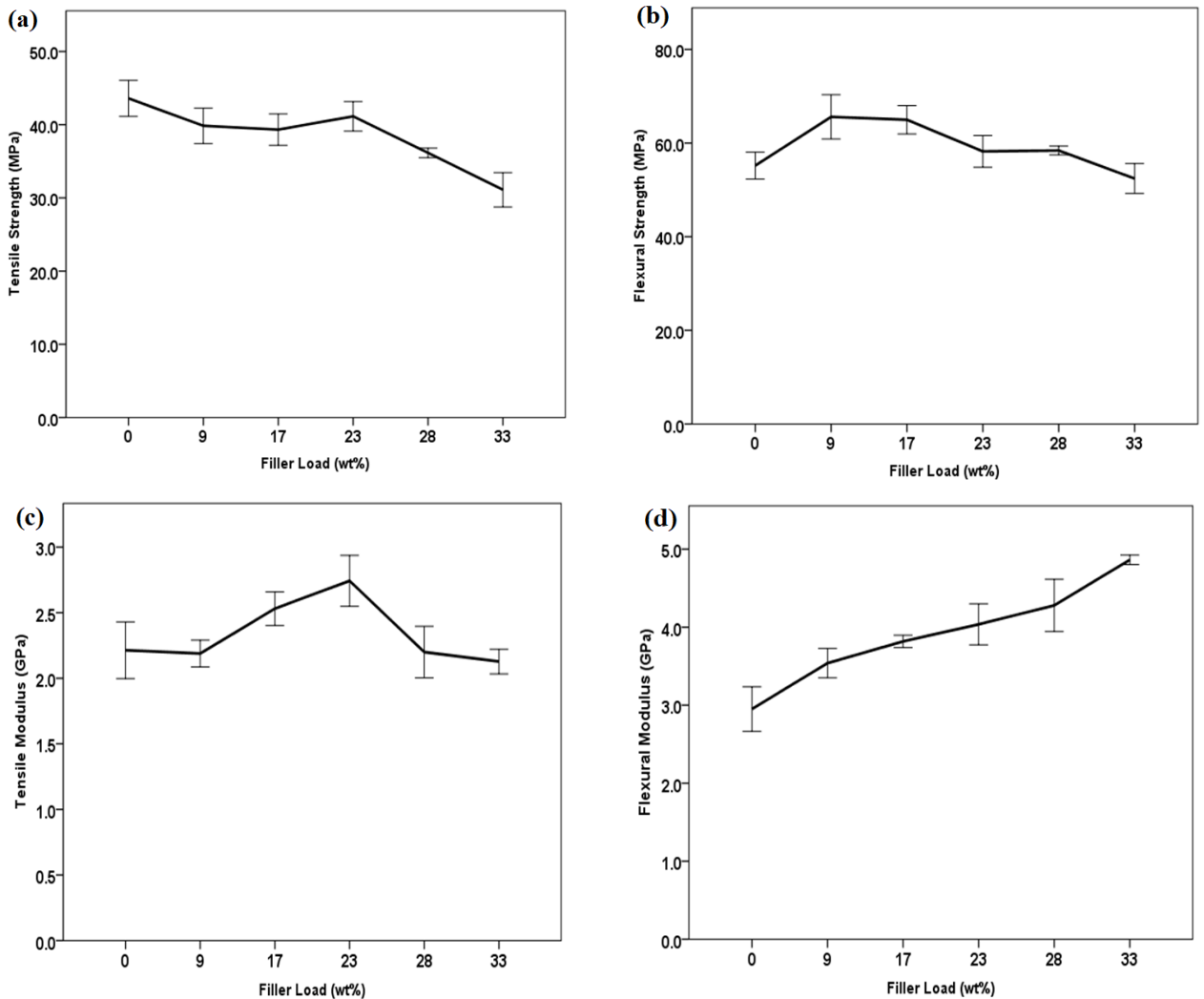


Figure 3-12. Influence of filler content on the mechanical properties of HAT treated OPS filler reinforced unsaturated polyester (OPS-UP) composites: (a) tensile strength, (b) flexural strength, (c) tensile modulus and (d) flexural modulus.

This result was in good agreement with that of another study ([Arrakhiz et al., 2013](#)) where the tensile and flexural modulus of low density polyethylene (LDPE) reinforced by doum palm fiber exhibited improvements of 145% (at 30 wt% fiber load) and 135% (20 wt% fiber load), respectively. The outcome is in contrast with the result of coconut shell reinforced UP where the flexural modulus of the composite increased with increases in filler content to 10 and 20 vol. % and then remained stable with a minor fluctuation before a significant decline at 50% ([Adeosun et al., 2015](#)). In another study, the flexural modulus of coconut shell reinforced epoxy reached its maximum at 30 wt.% of filler before declining on further addition ([Singh et al., 2013](#)).

The effect of filler load on the density and void content of polyester composites has been presented in Table 3-3 with the results showing that the density and void content of the composites increased gradually as the filler content increased. The increase in composite density was due to the fact that the value for the density of OPS is 1.47 g/cm³ compared to 1.22 g/cm³ for neat polyester (cured) resin. Table 3-3 shows that the void content increased significantly (more than sevenfold) from 0.025% for the 0.0 wt% OPS (neat polyester) case to 0.212% for the 28 wt% OPS case. This level of void content might be due to the high viscosity of the resin mixture during sample fabrication and insufficient resin matrix to wet the OPS powder at high filler load. Although only a minor increment in the void content was observed at high filler load, it is evident that even this level of void content contributed to the reduction in tensile and flexural strength of the composites as shown in Figure 3-12.

Table 3-3. Influence of filler content on the density and void contents of OPS filler reinforced unsaturated polyester (OPS-UP) composites.

No	OPS wt%	$\rho_{theoretical}$	$\rho_{experimental}$	Void%
1	0	1.221	1.220	0.025
2	9	1.240	1.239	0.026
3	17	1.256	1.255	0.077
4	23	1.270	1.268	0.178
5	28	1.283	1.280	0.212

3.4.3.2 Effect of Matrix Type on Composite Mechanical Properties

The effect of different thermoset matrices on the tensile and flexural properties of OPS filled polyester and vinylester composites has been presented in Figure 3-13 together with values for similar epoxy matrix composites as a comparison (which would be expected to exhibit superior mechanical performance compared to polyester or vinylester). It has been reported that the non-homogeneous dispersion of filler or short fiber within a polymer matrix can be due to the poor ability of the polymer to wet filler/fiber in the composite (Mirza et. al., 2015). Therefore, it is evident that the lack of sufficient polymer phase to wet the high surface area of natural filler powder at high filler content results in low interfacial bonding which limits the mechanical performance. Therefore, the filler content was kept constant at 13 wt% in this section to study the effect of matrix type on the mechanical properties of the composites. Whilst the addition of treated OPS was found to improve the tensile strength of the polyester composites by approximately 15%, that of the vinylester composite remained unchanged whereas the value of the epoxy composite decreased significantly by 22.5% – all compared to the respective neat polymer cases. Moreover, the use of OPS decreased the flexural strength for all three composites with the lowest and highest reductions being 5.2% and 23.3% for the polyester and epoxy composites, respectively.

Although the addition of OPS powder generally decreased the thermoset composite strength (except for the tensile strength of the OPS-UP composite), it improved the tensile and flexural moduli for all matrices. For example, the largest improvements were recorded for the tensile and flexural moduli of the treated OPS polyester composites (13.7% and 21.2%, respectively) with the smallest improvements being for the epoxy composites (3.7% and 5.7%, respectively). It should be noted that vinylester as shown in

Table 3-1, which is a resin produced by the esterification of an epoxy resin, has a molecular structure and consequently the chemical and physical characteristics intermediate between those of polyester and epoxy (Kazim, 2017). In other word, the

degree of wettability of the natural filler by vinyl ester is expected to be between that of polyester and epoxy. Therefore, the mechanical performance of the vinyl ester composites would be anticipated to be between those of the polyester and epoxy composites.

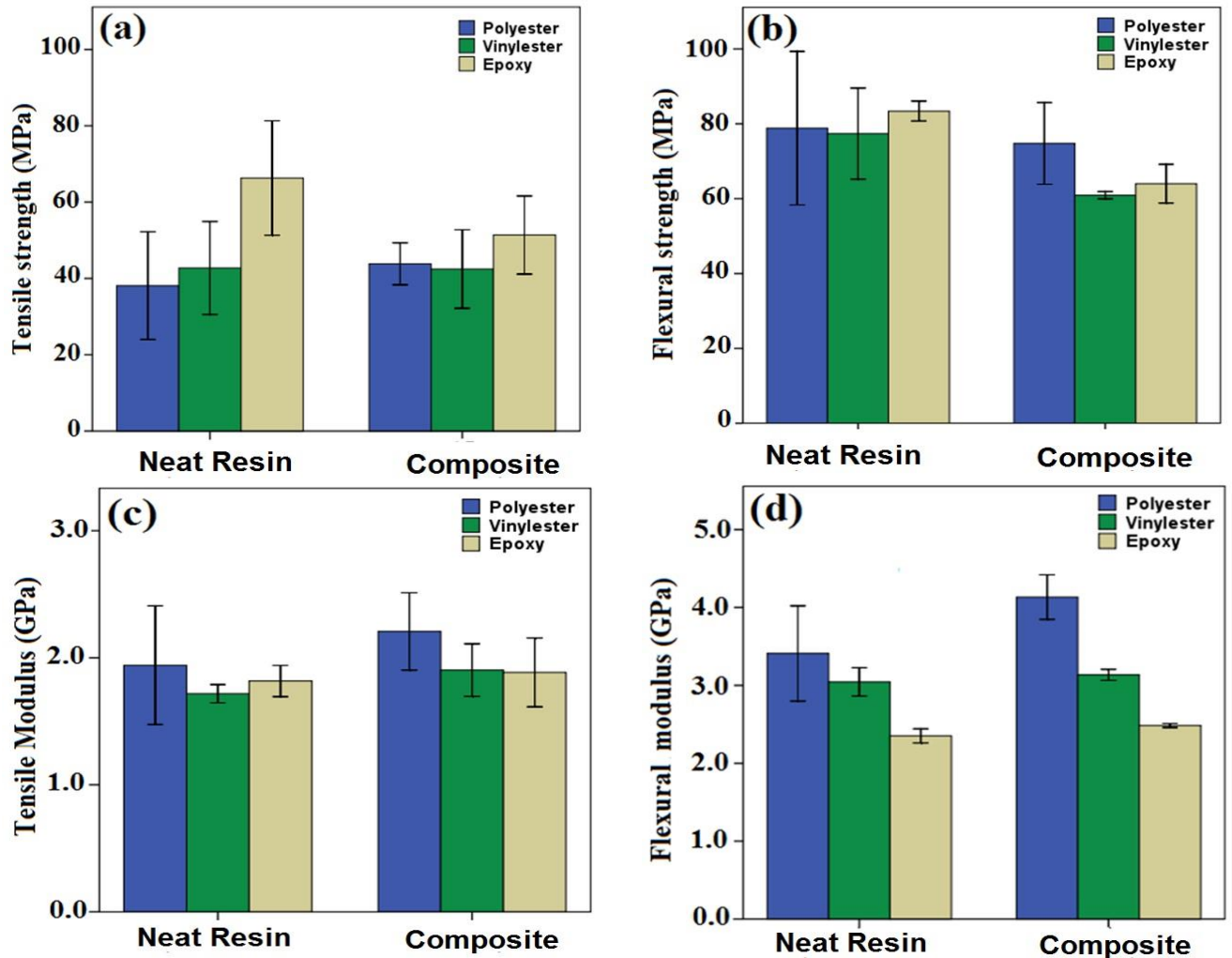


Figure 3-13. Effect of matrix type on the mechanical properties of 13 wt% OPS filler reinforced unsaturated polyester (OPS-UP) composites: (a) tensile strength, (b) flexural strength, (c) tensile modulus and (d) flexural modulus.

3.5 Conclusions

Wood flour reinforced biocomposites comprising of oil palm shell (OPS) powder and thermoset resins were fabricated and the effect of filler load investigated in this research.

The results showed that;

- Filler loading delayed the curing reaction of the thermoset resins by decreasing the peak exothermic temperature and increasing the time to peak of the reaction. Heat absorption by the natural filler together with initiator/resin consumption (peroxide (MEKP) for polyester, vinylester and resin for epoxy) due to a reaction with the cellulose present on the natural filler surface were found to be effective factors in delaying the curing reaction.
- Depending on the resin type, a suitable surface treatment for the natural filler (HDW for epoxy composite and HAT for polyester and vinylester composites) was found to mitigate the side effects of filler load on the curing rate.
- Loading of natural filler was found to shift the peak position for thermal degradation of OPS-UP composites to a higher temperature whereas the onset of thermal degradation shifted to a lower temperature (66 °C reduction for 28 wt% filler load).
- Linear shrinkage of the OPS-UP composites was found to decrease from 4% for the neat resin to 0.35% shrinkage for 28 wt% filler load.
- While the tensile strength of the composites decreased with increasing filler load, the flexural strength experienced a maximum value at 17 wt% OPS. The trend for flexural modulus showed a steady increase with filler load, however, the tensile modulus reached a maximum at 23 wt% OPS. Reductions in the mechanical properties were attributed to increasing amounts of voids being trapped in the matrix (from 0.025 vol% voids for the neat resin to 0.212 vol% voids for 28 wt% OPS-UP).
- Natural filler was found to be more compatible with unsaturated polyester than with vinylester and epoxy, with epoxy having the lowest compatibility.

For the future work, determination of activation energy of curing reactions to correspond it to the constants of reaction in the Equation (3-3), and investigation on the grafting reaction of cellulose radical with polyester/vinylester resins are recommended.

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Chapter 4

Develop an Empirical Model to Estimate the Filler Content of the Composite

Chapter 4:

4 Develop an Empirical Model to Estimate the Filler Content of the Composite.

Introduction:

The effect of processing parameters (filler size, surface treatment, and filler percentage) on the mechanical performance and thermal stability of thermoset based OPS composite has been investigated in the previous chapters. The limitations in the loading of natural filler in thermoset resin at high filler percentages has also been addressed in chapter 3. The measurement of filler percentage can indicate the effectiveness of a given processing method and quantify the dispersion of filler within the matrix. Thermogravimetric Analysis (TGA) is a common method to determine the percentage of the composite, but fails to measure the level filler content in NFC/WPC. This chapter addresses the inability of TGA to predict accurately the filler content for composites, as the thermal degradation of the filler and matrix occurs within similar temperature ranges. Therefore, a different methodology, based on the TGA method, with a semi-empirical model was developed in this chapter for determining filler percentage of NFC/WPC.

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Determination of Filler Content for Natural Filler Polymer Matrix Composite by Thermogravimetric Analysis

Omid Nabinejad, D. Sujan, M. E. Rahman and Ian J. Davies

Abstract:

Determination of filler content by thermogravimetric (TG) analysis is commonly utilized to investigate the effectiveness of processing methods for composite materials and to quantify the dispersion of filler within the matrix. However, the existing analysis method is not capable of accurately predicting the filler content for natural fiber composites for the case where thermal degradation of the filler and matrix occur within similar temperature ranges. In the present study, the authors have proposed a generic equation for the determination of filler content which can be utilized for any given range of thermal degradation temperatures in natural filler polymer composites. Oil palm shell (OPS) unsaturated polyester (UP) composites were selected to verify the proposed equation using the thermogravimetric (TG) test with the results indicating good agreement between the estimated and experimental filler contents with a maximum error on the order of 10%. The suggested technique provides a simple, yet generic, approach to determining the filler content of green or lignocellulose based polymer composites by TG analysis.

Keyword: Filler content prediction, natural fiber, wood-based composites, thermogravimetric analysis, TG

4.1 Introduction

Fillers and reinforcements based on cellulose have been widely used in the modern composite industry with the demand for natural fiber composites being predicted to increase rapidly (Dai and Fan, 2014). For example, it has been suggested (Biocomposites, 2013) that the production capacity of bioplastic and biocomposites will increase from approximately 1.4 Mt in 2012 to 6 Mt by 2017 with the main advantages of these materials

being their ease of recycling and biodegradability (Mohanty et al., 2002). The future growth of biocomposites requires extensive research in order to understand their characteristics and behavior to utilize them in advanced composite materials with different experimental methods having been developed to determine the optimum parameters required to enhance composite performance.

For instance, the measurement of filler content by thermal analysis is one method that can indicate the effectiveness of a given processing method and quantify the dispersion of filler within the matrix. Thermogravimetric (TG) analysis is a well-known technique that can be utilized to characterize organic and inorganic materials through measuring changes in mass as a sample is subjected to a change in temperature and/or environment. In this case, TG can be used to quantify the thermal stability of polymer composites which is known to be influenced by a number of parameters including the individual thermal stability of the matrix and reinforcement phases, the degree and type of dispersion of the reinforcement and interfacial bonding (Yang et al., 2011).

Previous researchers have already investigated the influence of chemical interactions between matrix and natural fiber on mass residue following the TG test (Nabinejad et al., 2015, Fukatsu, 2002) with the chemical interaction between polymer matrix and cotton fiber and oil palm shell (OPS) being noted to influence thermal degradation of the resulting composite. In contrast to this, other studies have struggled to analyze thermal degradation mechanisms in natural filler composites using TG due to the inability to analyze evolved gases during heating although this has been mitigated through combining TG with other gas measurement techniques such as mass spectroscopy (MS) and/or Fourier transform infrared spectroscopy (FTIR) (Wilkie, 1999, Nistor and Vasile, 2012, Jang and Wilkie, 2005).

With regards to polymer matrix composites, some filler materials do not decompose in the range of thermal degradation temperatures associated with typical engineering polymers. For example, calcium carbonate, mica, silica, talc, glass fiber, carbon fiber and aramid fiber have significantly higher thermal degradation temperatures compared to most polymers. Thus, in these composites the yield of filler content can be determined by direct

step analysis from TG experiments. However, the thermal degradation temperature range of filler and polymer are often comparable in natural fiber composites with the filler likely degrading prior to that of the polymer such that the resulting TG curve may not provide sufficient information for the determination of filler content. In order to overcome this problem, previous researchers ([Fuad et al., 1994a](#), [Fuad et al., 1994b](#)) suggested an alternative method to determine the filler content of wood-based composites using the TG method with the mass percentage of oil-palm wood flour (OPWF) filler in a polypropylene matrix being determined according to:

$$P_f = \psi \frac{m_d}{m_c} \quad (4-1)$$

Where ψ is a constant related to the mass losses of the filler and matrix components when subjected to a specified range of temperature, m_c is the initial composite mass and m_d is the mass loss of the composite at a temperature where maximum degradation of the filler occurs from thermogravimetric analysis.

Although the above formula has been shown to work for OPWF-polypropylene composites, it has proven less successful when addressing other wood-based composites, in particular for the case of overlapping filler and matrix decomposition temperatures. In the present study, different amounts of oil palm shell in the form of wood-based flour were added to unsaturated polyester (UP) resin to form OPS-UP composite specimens ([Nabinejad et al., 2014](#), [Nabinejad et al., 2015](#)). Due to the overlapping thermal degradation temperatures for OPS (270 to 470°C) and polyester (300 to 450°C), the formula proposed by previous researchers ([Fuad et al., 1994a](#), [Fuad et al., 1994b](#)) cannot be utilized to determine the quantity of filler in these composites. Therefore, in the present study the authors have derived a generic formula to determine the filler content of wood or lignocellulosic based natural filler polymer composites.

4.2 Sample Preparation

4.2.1 Materials

Raw OPS material (Lambir Oil Palm Company, Sarawak, Malaysia) was ground in a ball mill with the resulting powder being sieved to a size range of 75~150 μm . Following this, the OPS powder was soaked in methanol for 1 hour at room temperature and then washed with distilled water in order to remove impurities and subsequently dried in an oven at 100°C for 2 hours. The OPS powder was added to isophthalic unsaturated polyester (UP) and 1.5 wt.% of methyl ethyl ketone peroxide (MEKP) in either 10, 20, 30 and 40 parts by mass of filler to 100 parts (phr) polyester resin, resulting in experimental filler content of 9.09, 16.67, 23.08 and 28.57 mass%, respectively. The compounds were then placed under weak vacuum to remove excess air bubbles and finally poured into a mold and cured at 80°C for one hour before demolding.

4.2.2 Thermogravimetric Analysis

The thermal behavior of the OPS powder, polyester matrix and their resulting composites was investigated using TG and derivative thermogravimetric (DTG) analysis (Mettler Toledo TGA, Model; TGA/DSC1) between 35°C and 700°C under a flowing nitrogen atmosphere (80 ml·min⁻¹) with a heating rate of 10°C min⁻¹ according to ASTM E1131-08. The original mass of OPS was approximately 9.4 gr and the other samples (UP and OPS-UP) were in the range of 15 to 20 gr, where Table 4-1 shows the dried based condition of all the samples.

It has previously been reported that natural fibers exhibit similar trends in their TG and DTG curves as a result of the lignocellulose based fibers. It has been stated that natural fibers usually degrade in three main stages with most of the thermal decomposition occurring in the range of 215 to 470°C ([Nabinejad et al., 2015](#), [Fukatsu, 2002](#), [Nistor and Vasile, 2012](#), [Jang and Wilkie, 2005](#)) as shown in Table 4-1. Figure 4-1 shows the TG and DTG curves of powdered OPS in the range of 35 to 700°C with the step records based on Figure 4-1 being listed in Table 4-2.

From Table 4-2 it can be observed that the main decomposition of OPS occurred between 150 to 387°C with a 63.26% decrease in mass attributed to the degradation of hemicellulose and cellulose (Nabinejad et al., 2015). Furthermore, if the evaporation of moisture were to be neglected then the dry OPS powder decomposed in three main stages. In contrast to this, the TG and DTG curves for pure polyester (Figure 4-2) indicated the presence of a single decomposition stage comprising of a broad peak between 270 and 470°C with a maximum at 376°C. Through comparison of Figure 4-1 and Figure 4-2 it was clear that the OPS filler and polymer possessed overlapping ranges of thermal degradation temperature. Therefore, the thermal degradation temperature range of OPS-UP composites would be expected to overlap due to the constituent ranges of the matrix and filler.

This was indeed noted to be the case in Figure 4-3 with the TG and DTG curves for an OPS-UP composite containing 20 phr (16.67 mass%) of OPS powder, suggesting thermal degradation for this composite to have occurred in the range of 250 to 460°C and thereby confirming that the thermal degradation temperature range of the OPS-UP composite overlapped with those of the OPS and pure polyester components.

Table 4-1. Thermal decomposition trends of common natural fiber or filler (Monteiro et al., 2012, Nabinejad et al., 2015, De Rosa et al., 2010, Satyanarayana et al., 2007)

Natural fiber or filler	Moisture evaporation		Lignocellulose decomposition					Mass residue 3rd stage mass loss/%
	1st stage mass loss/%	1st stage DTG T_{peak} /°C	2nd stage T_{onset} /°C	2nd stage mass loss/%	Hemicellulose T_{peak} /°C	Cellulose T_{peak} /°C	2nd stage DTG T_{endset} /°C	
OPS	7.3	52	248	63.2	293	376	387	29.5
Okra fiber	8.4	55	220	76.7	303	359	390	15
Wood	2	107	290	85	270	367	400	13
Jute	8	60	260	89	290	340	470	3
Sisal	9	52	250	76	275	367	465	15
Cotton	4	55	265	91	280	330	410	5

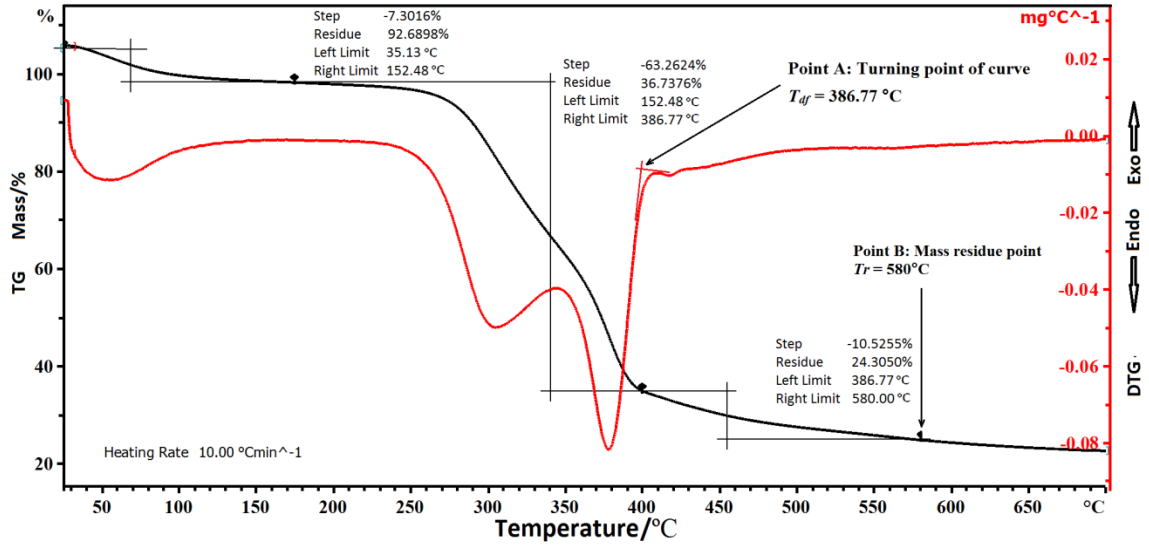


Figure 4-1. TG and DTG curves for powdered OPS.

Table 4-2. Temperature and constituent chemical composition data obtained from the thermal decomposition of powdered OPS using TG and DTG.

Stage 1: Moisture Evaporation		Stage 2: Hemicellulose Decomposition		Stage 3: Cellulose Decomposition		Stage 4: Lignin Decomposition		Char
Temperature Range/°C	Mass loss/%	Temperature Range /°C	Mass loss/%	Temperature Range /°C	Mass loss/%	Temperature Range /°C	Mass loss/%	Mass Residue/%
30-155	7.3	155-345 Peak at 293	32.0	345-387 Peak at 376	31.25	387-700	10.53	18.92

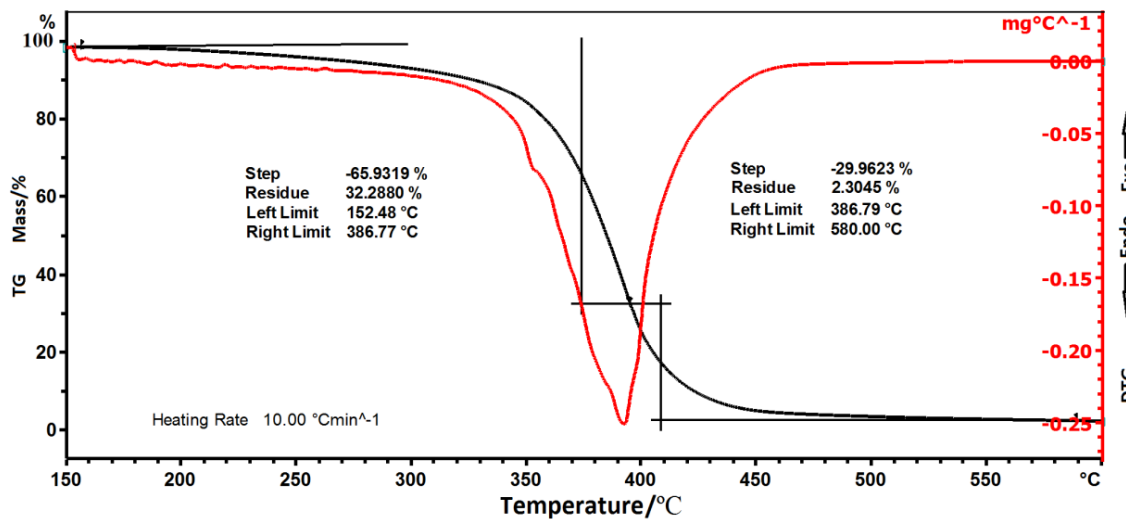


Figure 4-2. TG and DTG curves polyester matrix

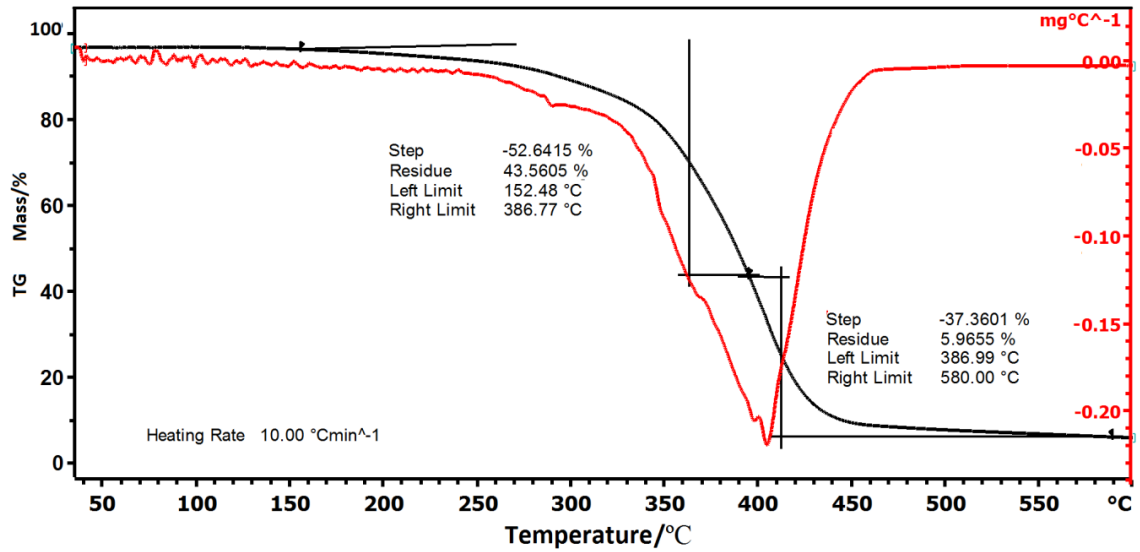


Figure 4-3. TG and DTG curves for a 20 phr OPS-UP composite

4.3 A Generic Approach to Determine the Filler Content

In order to overcome the difficulty in evaluating the filler content within natural reinforced polymer composites, the present authors propose two key temperatures from the TG curve (instead of one point as was the case previously (Fuad et al., 1994a)). It is known that all natural fibers exhibit similar trends in their TG and DTG curves with point A (as presented in Figure 4-1) representing the temperature at which the majority of thermal degradation occurred and is denoted as T_{df} . In other words, T_{df} indicates the point at which the trend of the DTG curve suddenly plateaus due to the cellulose and hemicellulose having decomposed following completion of Stage 3 as referred to in Table 4-2.

Furthermore, point B (as presented in Figure 4-1) represents the temperature utilized to record the mass residue and referred to as T_r , *i.e.*, the temperature above which no significant mass loss occurs. A detailed explanation of the analysis proposed in this work is given as follows:

In order to maintain consistency, the term “dried” indicates the state of the component or composite following Stage 1 heating and following the evaporation of moisture as

mentioned in Table 4-2. Therefore, in the present work the TG test was started from 150°C whereupon all moisture should have been removed. It is also important to note that the TG test should be continued until the majority of the sample had decomposed which was considered to be 580°C in the present case.

For any composite, according to the rule of mixtures:

$$P_f = 100 \frac{m_f}{m_c} \quad (4-2)$$

where P_f is the filler mass percentage, m_f is the dried filler mass and m_c is the dried mass of the composite. The dried mass of the composite, m_c , can also be expressed as:

$$m_c = P_f * m_f + (1 - P_f)m_p \quad (4-3)$$

where m_p is the dried polymer mass.

It is also possible to express the mass loss at T_{df} , i.e., where the maximum mass loss for natural filler occurs in the composite TG curve, using the following equation:

$$m_{dc} = M_{df} * m_f + M_{dp} * m_p \quad (4-4)$$

where m_{dc} is the total mass loss for the composite and M_{df} and M_{dp} are the percentage decreases in filler and polymer masses, respectively, at temperature T_{df} .

Whilst the degradation mechanisms for the filler and polymer may not be the same (Fukatsu, 2002), in this analysis it is assumed that the percentage mass residue of the composite is constant for each filler content at a temperature while the majority of the sample had decomposed and is equal to the sum of the mass residues for the filler and polymer at the final temperature of the TG test. In this analysis, the mass residue at the

final temperature can be calculated similarly to that of Equation (4-4) and expressed as follows:

$$m_{rc} = M_{rf} * m_f + M_{rp} * m_p \quad (4-5)$$

where m_{rc} is the total mass residue of the composite at T_r , M_{rf} is the filler residue percentage and M_{rp} is the polymer residue percentage. Using Equations (4-2) to (4-5) the expression for P_f can be given by:

$$P_f = \frac{100}{m_c} [\alpha * m_{dc} + \beta * m_{rc}] \quad (4-6)$$

where α is a mass drop coefficient:

$$\alpha = \frac{M_{rp}}{(M_{rp} * M_{df} - M_{rf} * M_{dp})} * 100 \quad (4-6(a))$$

and β is a mass residue coefficient:

$$\beta = \frac{-M_{dp}}{(M_{rp} * M_{df} - M_{rf} * M_{dp})} * 100 \quad (4-6(b))$$

The first step for the analysis would be to determine T_{df} from the TG and DTG curves, *i.e.*, the temperature at which the majority of thermal degradation occurred. For the present example in Figure 4-1, T_{df} was found to be 386.77°C. The second step in the procedure was to determine the mass loss from the TG and DTG scans for the pure OPS filler, pure polymer and total mass loss of the composite, m_{dc} , all measured at a temperature T_{df} . Finally, the mass residue values for the pure filler, pure polymer and composite specimens should be determined at the same arbitrarily high temperature for each specimen with a temperature of 580°C (and denoted as T_r) being used for the present case.

4.4 Results and Discussion

Figure 4-4 shows TG curves for the powdered OPS filler, pure polyester matrix and composites containing nominally 10, 20, 30 and 40 phr OPS (referred to as “C10”, “C20”,

“C30” and “C40”, respectively) from 150 to 580°C. It is clear from the figure that OPS has the highest mass residue whereas the polyester matrix possessed the lowest mass residue. As a result of this, the addition of greater amounts of OPS filler to the polymer tended to increase the mass residue of the composite and move closer to the mass residue of the pure OPS filler. Furthermore, the starting point for thermal degradation of the composites shifted to lower temperatures (compared to the pure polyester matrix) as the amount of OPS filler increased. The step analysis of the OPS filler, polyester matrix and their respective composites for four different filler contents have been presented in Table 4-3 with the values of T_{df} and T_r being 386.8°C and 580°C, respectively.

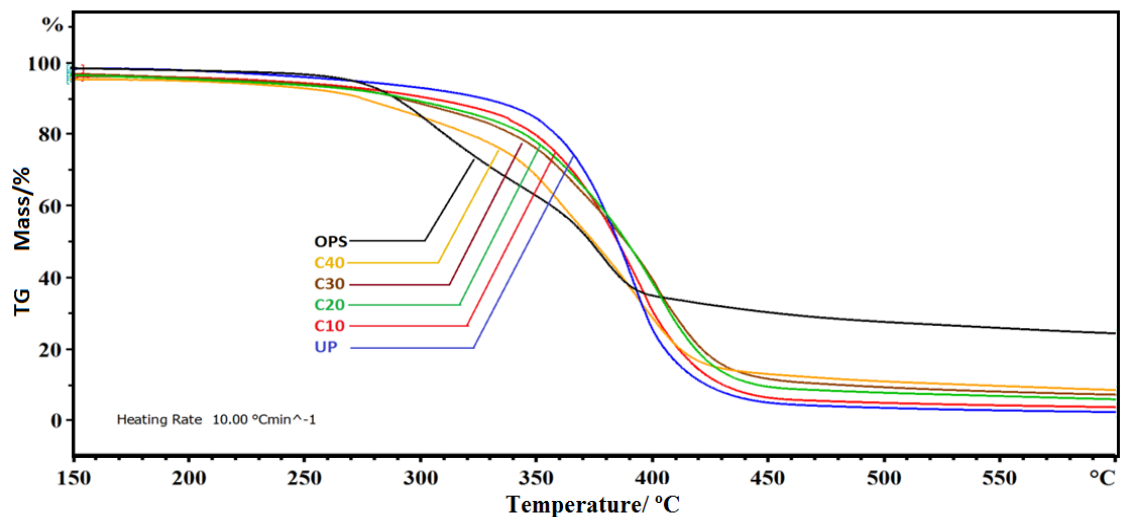


Figure 4-4. TG curves for the powdered OPS, pure polyester matrix and OPS-UP composites containing 10, 20, 30 and 40 phr of OPS (referred to as “C10”, “C20”, “C30” and “C40”, respectively)

In order to compare the filler contents obtained using the previous (Fuad et al., 1994a) and current techniques, the filler content for the OPS-UP composites mentioned in Table 4-3 were first analyzed using the previous method with the value for ψ in Equation (4-1) of 0.4065 being calculated. Using this value for ψ , together with the TG data in Table 4-3, a comparison of the filler percentages obtained from Equation (4-1) with those of the experimental values has been presented in Table 4-4. It can be clearly seen that the estimated value for the filler content remained relatively constant whereas the experimental filler content value increased from 9.09 to 28.57 mass%. Although the

prediction values from Equation (4-1) were close to the experimental values for the C30 and C40 composite specimens, this may well simply have been coincidence due to the estimated values all being within a narrow range of 24 – 28 mass% irrespective of the actual experimental values. Therefore, it was concluded that overall the previous method did not provide satisfactory agreement between the estimated and experimental values.

It is suggested that the discrepancy between estimated and experimental values in Table 4-4 may be attributed to ψ not being a constant value for the case of overlapping TG curves for the filler and polymer components although other parameters having an influence on the filler determination formula cannot be ruled out.

Table 4-3. Step analysis of the OPS filler, polyester matrix (UP) and OPS-UP composites containing different filler contents (data obtained from the average of three specimens).

Sample name	OPS	UP	C10	C20	C30	C40
Total mass of sample	8.73	13.85	14.19	18.37	15.86	10.65
Mass drop/gr at $T_{df}=386.8^{\circ}\text{C}$	5.68	10.19	9.32	11.65	9.52	7.34
Mass residue/gr at T_{df}	3.05	3.66	4.87	6.73	6.33	3.32
Mass drop percentage/%	$M_{df}=65.07$	$M_{dp}=73.55$	65.69	63.38	60.06	68.88
Mass residue/gr at $T_r=580^{\circ}\text{C}$	2.16	0.32	0.56	1.14	1.17	0.96
Mass residue percentage	$M_{rf}=24.77$	$M_{rp}=2.35$	3.97	6.20	7.39	9.03

With respect to the current analysis, through using Equations (4-6a) and (4-6b) and Table 4-3 or Equation (4-6) and the boundary conditions of filler $P_f = 100$ mass% and resin $P_f = 0$ mass%, the values for coefficients α and β in Equation (4-6) could be determined with the resulting filler mass percentage for OPS-UP composite being represented as follows:

$$P_f = \frac{100}{m_c} [-0.1406m_{dc} + 4.4065m_{rc}] \quad (4-7)$$

Comparison of the estimated P_f values from Equation (4-7) and experimental values have been presented in Table 4-5. As opposed to the previous comparison in Table 4-4, the new analysis provided much better agreement between the estimated and experimental values with a maximum error of 10.43% in the case of the nominally 20 phr OPS-UP composite.

Table 4-4. Comparison of experimental and estimated filler mass percentages (P_f) obtained from Equation (4-1)

Composite Sample	OPS Mass/phr	Experimental Filler Content mass/%	Equation (4-1) (Fuad et al., 1994a) Filler Content mass/%	Deviation Error/%
C10	10	9.09	26.69	193.6
C20	20	16.67	25.76	54.52
C30	30	23.08	24.41	5.76
C40	40	28.57	27.99	2.03

It is worth mentioning that Equation (4-6) is a generic equation that can be utilized to determine filler content for any cellulose-based polymer composite under any given range of thermal degradation temperatures. It should also be noted that, due to the non-homogeneous nature of natural filler polymer composites, sample preparation and selection are vital in order to obtain consistent results from the above formula. According to ASTM E1131-08 (“Standard test method for compositional analysis by thermogravimetry”), determination of the filler content requires the use of several specimens from different locations of the composite sample. Moreover, obtaining accurate values for the mass losses of the fiber, matrix and composite at T_{df} are also crucial for the calculation of P_f from Equation (4-6).

Table 4-5. Comparison of experimental and estimated filler mass percentages (P_f) obtained from Equation (4-7)

Composite Sample	Experimental Filler Content mass/%	Equation (7) Filler Content mass/%	Deviation Error/%
C10	9.09	8.24	-8.57
C20	16.67	18.41	10.43
C30	23.08	24.13	4.57
C40	28.57	30.10	5.36

4.5 Conclusions

Thermogravimetric (TG) analysis is a common method to measure the filler content of composite materials, especially for mineral based fillers, which have a notable mass loss in their TG curve. However, the presence of overlapping thermal degradation temperature ranges for the natural filler and some matrix is of major concern when attempting to determine the filler content by the current analysis method.

In light of this, the authors proposed a new, more general, analysis method based on two key points in the TG curve of the composite specimens which can be utilized for any range of thermal degradation temperatures. The result showed that there to be good agreement between the estimated and experimental filler content for OPS-UP composites with the maximum error being on the order of 10%, which provides a simple, yet generic, approach to determining the filler content for natural or lignocellulose based polymer composites by TG analysis.

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Chapter 5

Hybrid Composite (Effect of Using Nanoparticles)

Chapter 5:

5 Hybrid Composite (Effect of Using Nanoparticles)

Introduction:

As stated in chapter 2, improvements in the mechanical properties of the composites were attributed to factors such as the high surface area, and the polymer chain pinning between the OPS powder and the polymer matrix. As has also been shown in chapter 1, nanoparticles have been used by researchers in composite materials due to their considerable high surface area. Therefore, nanoparticles can improve the wettability of OPS powder and matrix by “building a bridge” between the natural filler and polymer matrix, which results in improved mechanical properties.

This chapter presents a methodology to improve the mechanical performance of WPC via developing of a hybrid composite comprising of pristine Multi-Walled Carbon Nanotube (MWCNTs), and OPS reinforced unsaturated polyester composite. The dispersion and the optimum level of pristine MWCNTs for better mechanical properties of the hybrid composite are determined. Moreover, the consequence of higher concentration on the processing parameters. Eventually, the effect of MWCNTs on the thermal stability of hybrid composite is also investigated.

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Hybrid Composite Using Natural Fiber and Multi Walled Carbon Nano Tube (MWCNTs)

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Abstract:

This paper presents an experimental study on the development of hybrid composites comprising of multi-walled carbon nanotubes (MWCNTs) and natural filler (oil palm shell (OPS) powder) within unsaturated polyester (UP) matrix. The results revealed that the dispersion of pristine MWCNTs in the polymer matrix was strongly enhanced through use of the solvent mixing method assisted by ultrasonication. Four different solvents were investigated, namely, ethanol, methanol, styrene and acetone – the best compatibility with minimum side effects on the curing of the polyester resin was exhibited by the styrene solvent and this produced the maximum tensile and flexural properties of the resulting nanocomposites. A relatively small amount of pristine MWCNTs well dispersed within the natural filler polyester composite was found to be capable of improving mechanical properties of hybrid composite. However, increasing the MWCNT amount resulted in increased void content within the matrix due to an associated rapid increase in viscosity of the mixture during processing. Due to this phenomenon, the maximum tensile and flexural strengths of the hybrid composites were achieved at MWCNT contents of 0.2 to 0.4 phr and then declined for higher MWCNT amounts. The flexural modulus also experienced its peak at 0.4 phr MWCNT content whereas the tensile modulus exhibited a general decrease with increasing MWCNT content. Thermal stability analysis using TGA under an oxidative atmosphere showed that adding MWCNTs shifted the endset degradation temperature of the hybrid composite to a higher temperature.

Keywords:

MWCNTs (multi-walled carbon nanotube), OPS (oil palm shell), unsaturated polyester resin, hybrid composite, voids content, mechanical properties, thermal properties.

5.1 Introduction:

Nanocomposites containing carbon nanotubes (CNTs) have been an area of intensive research in recent years due to the superior mechanical, physical and electrical characteristics of CNTs ([Bensadoun et al., 2011](#)) which results in a low weight composite with excellent strength properties ([Kim et al., 2011](#)). However, practical use of these materials has been limited by factors such as poor dispersion of the nanoparticles together with poor interfacial bonding with the host polymer matrix ([White et al., 2016](#)). CNTs by their nature possess a strong tendency for agglomeration due to their large aspect ratio and inter-particle interactions. Such a phenomenon produces a non-homogeneous and random distribution of nanoparticles within the polymer matrix ([Seyhan et al., 2007](#)) which can limit the mechanical, thermal and electrical performance of the resulting nanocomposites.

Therefore, four particular areas of research related to CNTs and their polymer composites have been identified as follows: (i) production of dimension controllable and high purity nanotubes, (ii) improvement in interfacial bonding strength between the matrix and CNTs, (iii) enhancement in the dispersion and alignment of the CNTs within the matrix and (iv) real life applications of carbon nanotubes ([Lau et al., 2006](#)). The formation of networks of well dispersed carbon nanotubes in the polymer matrix, achieved by covalent or noncovalent functionalization of CNTs, has been identified as a key feature for the reinforcing ability of CNTs in polymer nanocomposites ([Gupta et al., 2013](#)). Apart from strong van der Waals forces and interactions between relatively small diameter CNTs, the viscosity of the polymer matrix, length and volume fraction of the CNTs, together with the degree of entanglement, are other critical factors which need to be considered for the dispersion of CNTs within polymer matrices ([Seyhan et al., 2009](#)).

A number of different techniques including shear mixing, solution mixing, ultrasonication, chemical treatment, and their various combinations, are commonly used by researchers to achieve a sufficient distribution of nanoparticles in the matrix ([Rahmanian et al., 2015](#)). Direct mixing with high speed mechanical stirring and sonication have been reported to be the most common techniques utilized to disperse CNTs within thermoset resins such as epoxy and vinylester ([Seyhan et al., 2009](#)). High

shear forces with a three roll mill have also been claimed to break up CNT agglomerations and enhance dispersion in an epoxy matrix ([Gojny et al., 2005](#)). In the solvent mixing method, CNTs are mixed in a solvent prior to being added into the polymer or a solvent-diluted polymer. Appropriate selection of the solvent can reduce the high cohesive strength of the CNTs, which has been reported to be the main reason for the poor dispersion of CNTs within the polymer matrix ([Gupta et al., 2013](#)). However, despite this, re-agglomeration remains as a natural phenomenon during the subsequent curing process ([Zhang et al., 2016](#)).

Hybrid polymer composites using natural filler and CNTs could prove to be a fruitful area of research due to the opportunities to improve the properties of natural filler composites through incorporation of carbon nanotubes. Previous studies on the influence of carbon nanotube loading showed that it can improve the mechanical performance of natural fiber composites such as; ramie fiber-reinforced epoxy ([Shen et al., 2014](#)), jute fiber natural rubber ([Tzounis et al., 2014](#)), bagasse stalk/poplar polypropylene ([Nourbakhsh et al., 2016](#)) and wood flour (WF) and high-density polyethylene (HDPE) ([Farsi et al., 2013](#)) hybrid composites. In the present work, the authors have therefore investigated the influence of solvent selection in the solvent mixing method assisted with ultrasonication on the mechanical properties of nano composites comprising of unsaturated polyester reinforced by MWCNTs. In addition to this, the effect of MWCNT content on the critical processing parameters and resulting mechanical and thermal properties of hybrid composites containing oil palm shell (OPS) filler was studied.

5.2 Materials and Test Method:

Unsaturated isophthalic polyester was selected for this study as a typical low cost and important thermoset resin. Raw OPS prepared from palm oil biomass was first ground in a ball mill and then mechanically sieved using a mesh size of 75 to 150 μm . Following this, the powdered OPS was treated in an alkali solution (7% NaOH concentration) for 1

hour at 90 °C (Nabinejad et al., 2016)) and then washed with distilled water in order to remove impurities and finally dried in an oven at 100 °C for 12 hours.

As the cost of MWCNTs is considerably lower than that of single-walled carbon nanotubes (SWCNTs) (Bokobza, 2007), pristine MWCNTs produced by carbon vapor deposition (CVD) were chosen for this study. The estimated Young’s modulus of the MWCNTs was reported to be between 270 and 950 GPa with a predicted tensile strength in the range of 11 to 63 GPa (Yakobson and Avouris et al., 2001). Table 5-1 and Figure 5-1 present the physical specifications and TEM image of MWCNTs used in this study.

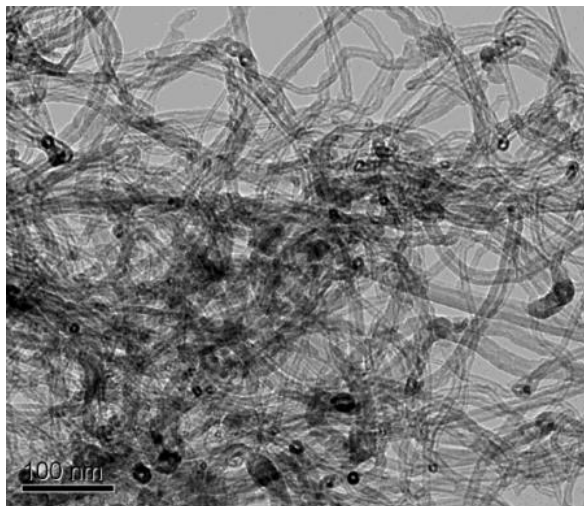


Figure 5-1. TEM micro image of 12-15nm MWCNTs

Table 5-1. Specification MWCNTs

Available Diameters	Available Lengths	Purity	Amorphous Carbon	Ash	Specific Surface Area	Density	PH	Layer
12 – 15nm	3 ~ 15µm	>97%	<2%	<0.2 phr	230 -300m ² /g	2.6 g/m ³	7-8	8-15

5.2.1 Fabrication Technique

In order to achieve effective mixing with suitable dispersion, the pristine MWCNTs were mixed in a solvent (ethanol, methanol, acetone or styrene) and ultrasonicated for 10 min (Hielscher Ultrasonic Processor UP100H; 100 watts, 30 kHz). Following this, the ultrasonicated mixture was added to isophthalic unsaturated polyester (UP) resin under

shear mixing (10 min at 600 rpm) and then ultrasonicated for an additional 5 min in order to ensure a sufficiently uniform dispersion of MWCNTs in the solvent-resin mixture. The mixture was then heated at a temperature just above the boiling temperature of the solvent whilst being subjected to shear mixing in order to evaporate the solvent such that a homogeneous mixture of polyester resin and MWCNTs remained.

In the first stage of testing, nanocomposite specimens were manufactured containing 0.8 phr (parts by mass of filler to 100 parts of the matrix) of pristine MWCNTs in polyester resin and 1.0 phr of methyl ethyl ketone peroxide (MEKP) as an initiator. The mixture was gently mixed and then placed under high vacuum in order to remove excess air bubbles prior to pouring into the moulds to produce bar and dumbbell specimens according to ASTM D760-10 and ASTM D638-10 for flexural and tensile testing, respectively. The cured specimens were then post cured at 80 °C for 1 hour prior to being removed from the moulds. In addition to this, nanocomposite reference specimens were also prepared without the use of any solvent, *i.e.*, using sonication and shear mixing only. These specimens were referred to as MWCNT-UP composites.

In the second stage of testing, hybrid composites were prepared by manufacturing UP composites containing 15 phr of treated OPS powder together either 0.2, 0.4, 0.6 and 0.8 phr MWCNTs. Figure 5-2 presents the processing steps used before curing stage to fabricate MWCNT-UP composites and hybrid composite.

It should be noted that the preparation of samples containing 15 phr OPS and 0.8 phr MWCNTs was found to be extremely difficult due to the high viscosity of the mixture at the moulding stage. These specimens, referred to OPS-MWCNT-UP hybrid composites, contained 4 mg/ml of MWCNTs within the solvent. Whilst this value may be higher than the dispersability of CNTs within the solvent, it is known that the use of excessive solvent may have an effect on the glass transition and consequently the performance of nanocomposites (Gupta et al., 2013, Erikson et al., 2015). Moreover, a similar quality of carbon nanotube dispersion was found to exist for all cases (0.2, 0.4 and 0.6 and 0.8 phr MWCNTs) prior to mixing with resin. Finally, it was deemed essential to achieve a reasonable weight of nanoparticles in the final composite in order to be applicable.

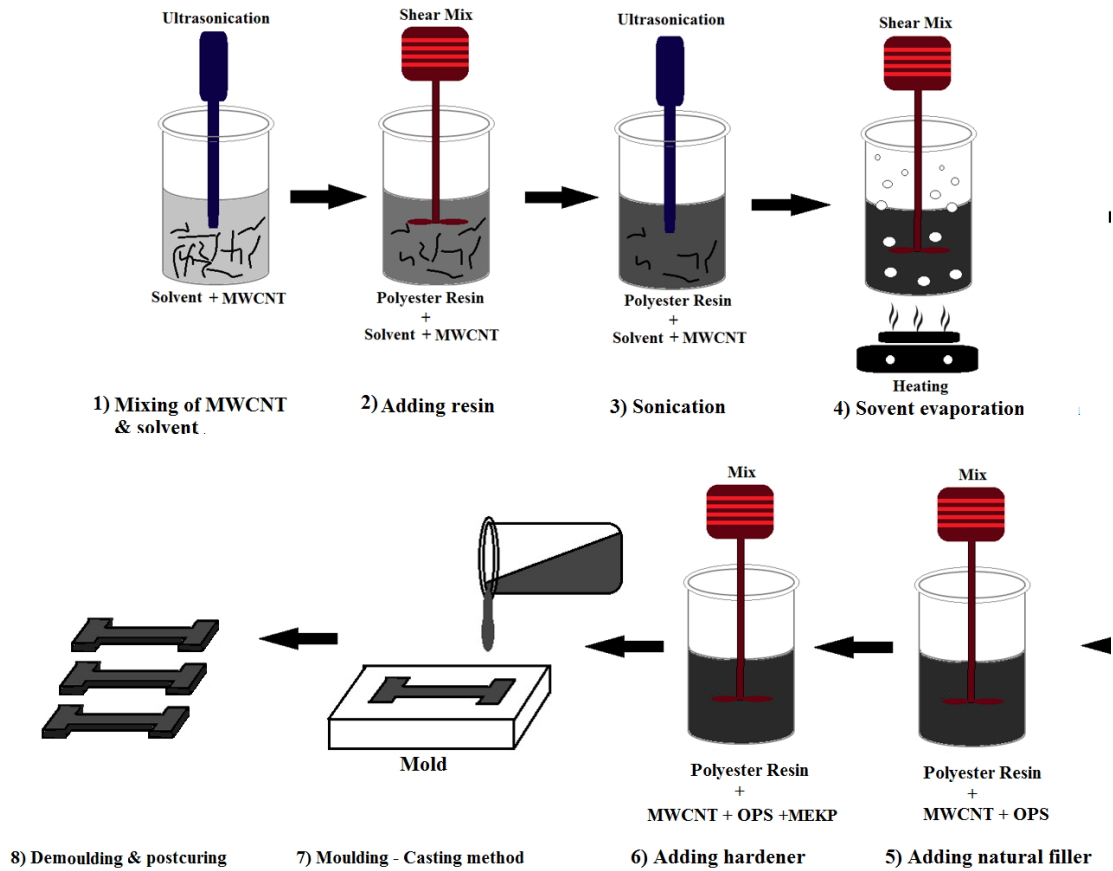


Figure 5-2. Schematic of preparation of OPS-MWCNT-UP hybrid composite

Dumbbell and bar shape specimens were prepared for the hybrid (OPS-MWCNT-UP) composites with Table 5-2 summarizing the specimens and preparation conditions used in this study.

Table 5-2. Samples formulation and preparation conditions

Sample ID	First Sonication	Solvent	Heating Temperature	Second Sonication	MWCNT phr	OPS phr
Without solvent	15 min	--	--	--	0.8	0
With Methanol	10 min	Methanol	70 °C	5 min	0.8	0
With Ethanol	10 min	Ethanol	90 °C	5 min	0.8	0
With Acetone	10 min	Acetone	70 °C	5 min	0.8	0
With Styrene	10 min	Styrene	145 °C	5 min	0.8	0

0.2 MWCNT	10 min	Styrene	145 °C	5 min	0.2	15
0.4 MWCNT	10 min	Styrene	145 °C	5 min	0.4	15
0.6 MWCNT	10 min	Styrene	145 °C	5 min	0.6	15

5.2.2 Characterization Techniques

The tensile and flexural properties of the hybrid composite specimens were investigated using a universal tensile testing machine (Lloyds instrument model LR10K Plus Digital Control Testing) with the flexural strength and modulus being evaluated according to ASTM D790-10 with a 500 N load cell and crosshead speed of 2 mm·min⁻¹. Similarly, the tensile strength and modulus of specimens were evaluated according to ASTM D638-10 using a 10 KN load cell and crosshead speed of 2 mm·min⁻¹. Investigation of the fracture surfaces of composite tensile specimens was carried out using scanning electron microscopy (SEM; HITACHI S-3400N). The thermal behaviour of the composites was studied using thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis (Mettler Toledo TGA, Model; TGA/DSC1) with a temperature range of 25-700 °C and a heating rate of 10 °C·min⁻¹. The TGA test was performed according to ASTM E 1131-03 in a flowing oxygen atmosphere with the flow rate being 80 ml·min⁻¹.

Viscosity measurements of the resin mixtures were evaluated by Brookfield Dial Viscosity measurements of the resin mixtures were evaluated using a Brookfield Dial Viscometer LVT prior to adding the initiator and after allowing the mixture to cool to ambient temperature. Densities of specimens and their components were determined by pycnometer according to ASTM D792-08 with the void content of hybrid composites ($\rho_{experimental}$) being determined through Equation (1) and (2) according to ASTM D2734-16:

$$Void\ content\ (\%) = \frac{\rho_{theoretical} - \rho_{experimental}}{\rho_{theoretical}} * 100 \quad (4-1)$$

$$\rho_{theoretical} = \frac{1}{\left(\frac{w_f}{\rho_f} + \frac{w_m}{\rho_m} + \frac{w_{cnt}}{\rho_{cnt}}\right)} \quad (4-2)$$

Where w_f , w_m , and w_{cnt} are the weight fractions and ρ_f , ρ_m and ρ_{cnt} are the densities of the OPS powder, resin and MWCNT, respectively.

5.3 Result and Discussion

5.3.1 Solvent Selection for MWCNT –UP Nanocomposite

5.3.1.1 Mechanical Properties

The effect of solvent type on the tensile and flexural properties of 0.8 phr MWCNT-UP nanocomposites has been presented in Figure 5-3 with it being clear that the solvent selection has a significant effect on the mechanical performance of nanocomposites. The strength, modulus and strain values for both tensile and flexural properties have also been listed in Table 5-3. Figure 5-3(a) and Table 5-3 indicated that the nanocomposite prepared without solvent mixing exhibited values of 19 MPa, 743 MPa and 3.4% for the tensile strength, modulus and strain to failure, respectively. It can also be observed that the sample prepared by styrene mixing showed a significant improvement in tensile strength and modulus (by 45% and 115%, respectively) but a considerable reduction in tensile strain to failure (22%) when compared to the case without solvent mixing.

Figure 5-3(a) also illustrates that the incorporation of other solvents including Methanol, Ethanol and Acetone into the polyester resin led to significant reductions in the tensile properties of the nanocomposites. In other words, the tensile strength declined by 13.5%, 50% and 74.7% for the cases with Ethanol, Methanol and Acetone solvent cases respectively. Moreover, Ethanol, Methanol and Acetone solvents reduced the tensile modulus by 55%, 26.7% and 63.79% respectively. The values for tensile strain (Table 5-3) and the significant changes in tensile behaviour (Figure 5-3(a)) it was clearly concluded

that the use of methanol, ethanol and acetone solvents adversely affected the MWCNT-UP nanocomposite tensile properties.

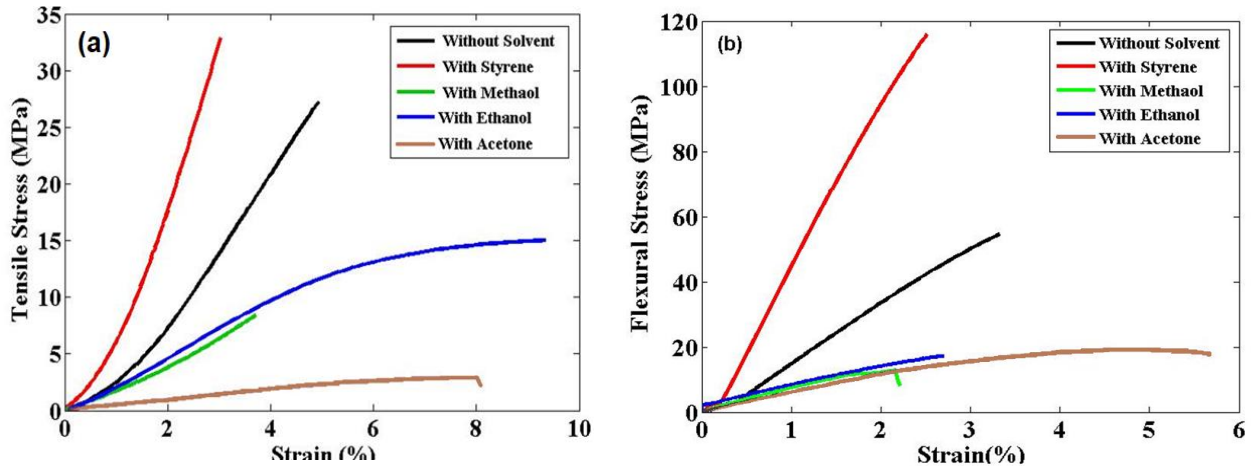


Figure 5-3. Effect of different solvents (in solvent mixing method) on the mechanical performance of 0.8 phr MWCNTs nanocomposite (a) Tensile Strength (b) Flexural Strength

A similar trend in the effect of solvent type was noted for the flexural properties of the MWCNT-UP nanocomposites as shown in Figure 5-3(b). It was clear that the sample prepared without solvent possessed a higher flexural strength and modulus when compared to ethanol, methanol and acetone with values of 58 MPa, 2106 MPa and 3.3% for the flexural strength, modulus and strain to failure, respectively. Similar to the tensile behaviour, the composite prepared using styrene solvent possessed the highest flexural properties with the flexural strength and modulus being increased by 38 and 77%, respectively, while the flexural strain decreased by 24%, when compared to the case without solvent. It should be noted that similar to the tensile strength case, the use of ethanol, methanol and acetone decreased the nanocomposite flexural properties with the worst case being recorded for acetone as shown in Figure 5-3(b) and Table 5-3.

Table 5-3. Value of tensile and flexural properties of 0.8 phr MWCNT-UP nanocomposite

Method of mixing	Tensile strength (MPa)	Tensile Modulus (MPa)	Tensile Strain (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Flexural Strain (%)
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Without Solvent	19.02 (5.82)	743 (96.22)	3.36 (0.53)	57.60 (4.85)	2106 (171.44)	3.31 (0.07)
With Styrene	27.56 (4.25)	1597 (45.87)	2.64 (0.34)	79.57 (8.37)	3728 (424.72)	2.52 (0.03)
With Ethanol	16.29 (3.17)	334 (43.61)	6.82 (1.69)	18.89 (0.95)	738 (84.99)	3.57 (0.18)
With Methanol	9.51 (0.57)	544 (39.73)	2.57 (0.05)	13.94 (1.63)	985 (80.4)	1.99 (0.04)
With Acetone	8.92 (3.73)	317 (53.34)	4.81 (1.7543)	18.43 (0.45)	853 (37.88)	4.06 (1.01)

It is clear from Figure 5-3 that the type of solvent not only possesses a significant effect on the tensile and flexural property values but can also change the composite behaviour from elastic to plastic. The considerable reduction in strength properties for the MWCNT-UP nanocomposites prepared using ethanol, methanol and acetone may be attributed to the negative effect of the solvent in the curing stage by hindering the polymerization reaction of the unsaturated polyester. Indeed, some researchers ([Gupta et al., 2013](#)) have claimed that this negative effect on the thermal and mechanical performance of nanocomposites due to the presence of trace amounts of residual solvent and/or entrapped bubbles is the main drawback of the solvent mixing method. This finding is in good agreement with previous research ([Galtieri et al., 2017](#)) which indicated some solvent such as acetone has a negative effect on the cross-linking cure reaction of unsaturated polyester resin and change the network structure of the thermoset polymer. In addition, these solvents can hinder the reaction of unsaturated groups of the polyester chains with styrene monomer by the formation of oligomer units. Consequently, the nanocomposites prepared with these solvents exhibited lower mechanical properties when compared to the nanocomposite without solvent. Such a phenomenon may indeed be true for some solvents, in particular those possessing a low boiling point and low compatibility with the host matrix.

However, amongst the solvents investigated, styrene has the highest boiling point and is known to be highly compatible with unsaturated polyester resin. It should be noted that unsaturated polyester resin normally contains 35% styrene monomer which participates

in the polymerization reaction as the principle component in the curing reaction of polyester. Although an excess amount of styrene may change the curing rate and reduce the mechanical properties of the cured unsaturated polyester, this solvent doesn't possess any critical side effects for the mechanical performance of the resulting composites. Thus, it is suggested that styrene can be used as a solvent in order to improve the dispersion of nanoparticles within matrices which contain styrene as a monomer such as polyester and vinyl ester. Therefore, the suitable selection of solvent together with the effective removal of solvent from the polymer matrix should be considered as the most important factors in the solvent mixing method to disperse CNTs within a polymer matrix.

5.3.1.2 Morphological Study by SEM

Figure 5-4 illustrates the fracture surfaces of 0.8 phr MWCNT-UP nanocomposites using SEM. In the specimen produced without the aid of a solvent (Figure 5-4(a)) the appearance of nanoparticle agglomeration was clearly noted even though the specimen had been subjected to 15 min of continuous sonication followed by 10 min of high shear mixing. In other words, this non-solvent procedure was not capable of dispersing the MWCNTs within the polyester matrix. On the other hand, the specimen prepared with the use of styrene solvent Figure 5-4(b) indicated a well-dispersed nanocomposite with almost no agglomeration being observed. The lower tensile and flexural properties of the nanocomposites prepared without solvent mixing, when compared to those of the composites prepared using styrene solvent (Table 5-2), were therefore attributed to the presence of nanoparticle agglomeration in the former case.

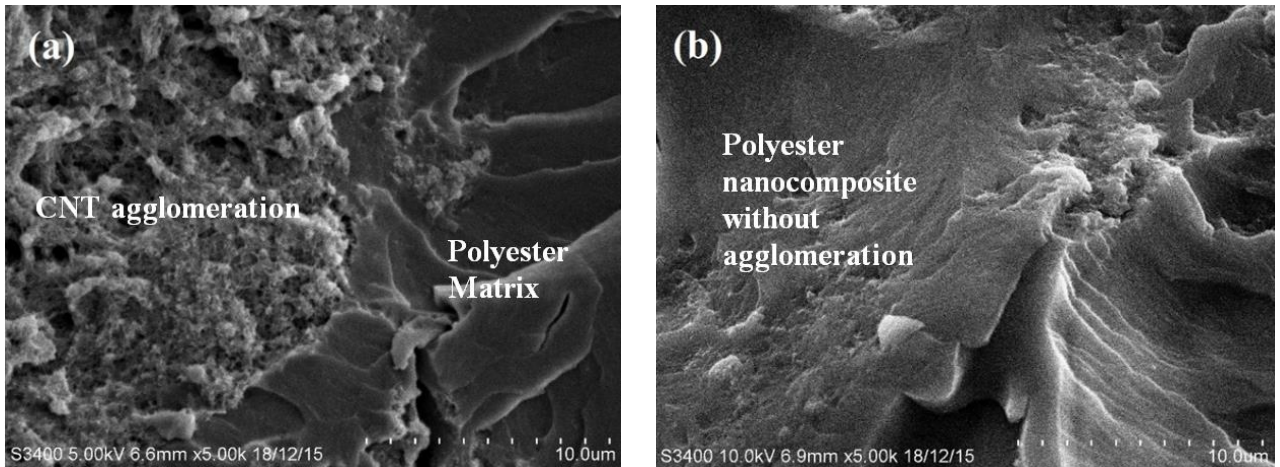


Figure 5-4. SEM image of 0.8 phr MWCNT-UP nanocomposite (a) Without styrene (agglomeration), (b) With styrene no agglomeration but void generated

5.3.2 Performance of Oil Palm Shell MWCNT Polyester Hybrid Composite

Figure 5-5 presents the effect of MWCNT concentration (0 - 0.6 phr) on the tensile and flexural properties of polyester composites reinforced with 15 phr of alkali treated OPS powder. It can be seen from the results that the tensile strength (Figure 5-5(a)) reached its maximum value for the case of 0.2 phr MWCNT concentration with a slight increase from 34.3 MPa for the 0 phr MWCNT case to 38 MPa for 0.2 phr MWCNT case but then decreasing to 30.1 MPa for the 0.6 phr MWCNT case. The flexural strength exhibited a similar trend (Figure 5-5(b)) with a significant increase from 54.2 MPa for the 0.0 phr MWCNT case to 67.1 MPa for the 0.4 phr MWCNT case and then followed by a significant decline to 46.6 MPa for the 0.6 MWCNT case. These results are in contrast to that of a previous study which investigated the effect of adding low contents (0.05, 0.1 and 0.3 wt.%) of CNTs to a specially synthesized styrene-free polyester resin using the three roll milling technique, where the addition of CNT was found to have no significant effect on the tensile strength of the resulting nanocomposites (Seyhan et al., 2009).

In contrast to the trend for tensile strength, the tensile modulus (Figure 5-5(b)) indicated a general decline from 1905 MPa to 1461 MPa upon increasing the MWCNT concentration from 0 to 0.6 phr. In contrast to this, the flexural modulus exhibited an increase of 22.3% from 3222 to 4148 MPa upon increasing the MWCNT concentration from 0 to 0.2 phr. The flexural modulus remained stable for the 0.4 phr case and then

decreased to 2951 MPa for the 0.6 phr MWCNT case. It should also be noted that the strength and modulus values for the 0.6 phr MWCNT case were all lower compared to the case of no MWCNT addition Figure 5-5.

This result is consistent with a previous study (Yang et al., 2012) on the effect of MWCNT addition (0.1 and 0.2 phr) on vinylester composites using different amounts of dispersing agent which reported a slight improvement in tensile strength and modulus of the resulting nanocomposite. It has been previously reported that the presence of CNTs in polymer matrix hinders the motion of polymer chain segments which leads to better flexural properties of the nanocomposite. On the other hand, the enhancement mechanisms in natural fiber/CNT hybrid composite attributed to the three aspects; (1) CNTs enhances the interlaminar shear strength between natural filler and matrix; (2) the entanglement of natural fibrils and CNTs leads to an increase in the quasi-static fracture toughness; and (3) CNTs improves the load transfer between fibers and matrix, which yields better modulus of hybrid composite (Shen et al., 2014).

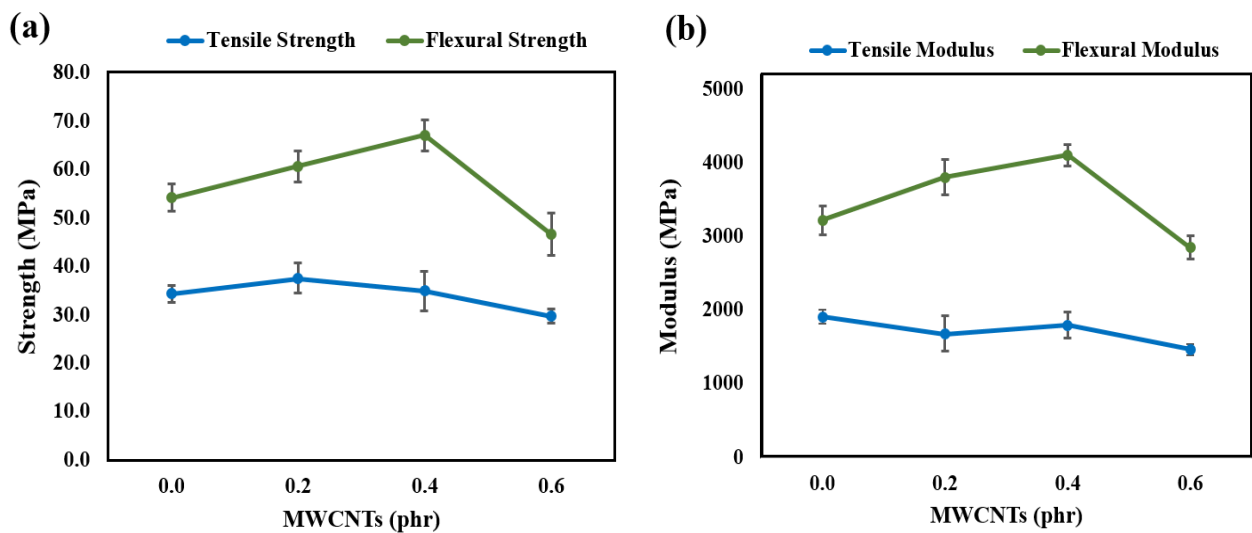


Figure 5-5. Effect of MWCNTs concentration on (a) Tensile and flexural strength (b) Tensile and flexural modulus

5.3.2.1 Morphological Study by SEM

Fracture surfaces of the composites were analyzed using SEM in order to investigate the influence of MWCNT addition on the void generation in the UP resin matrix with the result being presented in Figure 5-6. It would appear that the hybrid composite with 0.8 phr MWCNT (Figure 5-6(b)) possesses a significant amount of void content when compared with OPS-UP composite with no MWCNT (Figure 5-6(a)). The presence of voids in the nanocomposites was also observed in Figure 5-4(b). In other words, the sample without solvent, which possessed poor dispersion and noticeable agglomeration (Figure 5-4(a)), also resulted in a low void content when compared with the sample prepared using the solvent mixing method. Indeed, the microstructural investigation showed that the specimens with better nanoparticles dispersion within the polyester matrix and higher percentage of MWCNT tended to possess a higher microvoids content.

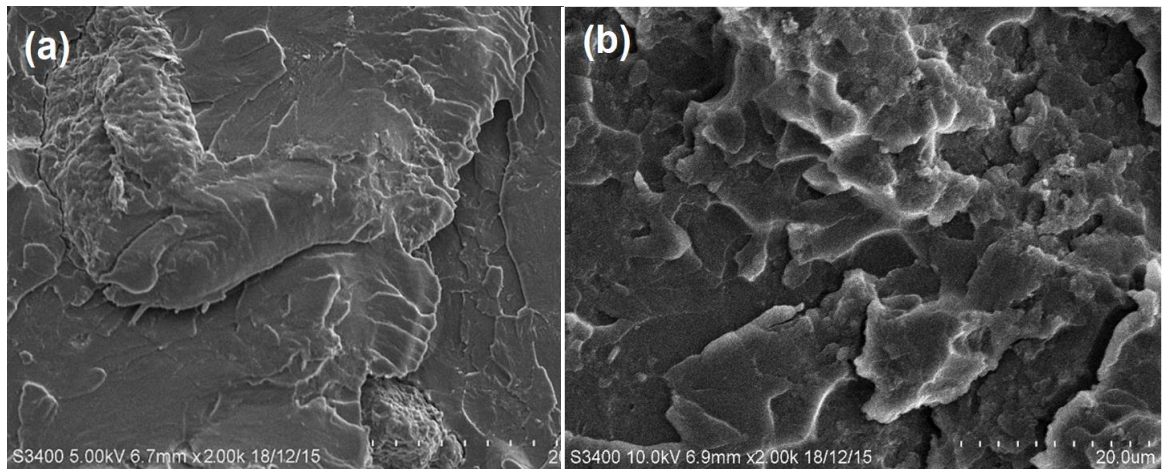


Figure 5-6. SEM images (a) OPS-UP composite with no MWCNT and (b) hybrid composite with 0.8 phr MWCNT (with microvoids)

5.3.2.2 Void Content of the Hybrid Composites

The effect of MWCNT concentration on the voids content of polyester composites reinforced with 15 phr of alkali treated OPS powder has been presented in Figure 5-7 with the results showing that the void content of the hybrid composites increased exponentially as the MWCNT content increased. For example, the void content increased only slightly

from 0.47% for the 0 phr MWCNT case to 0.51% for the 0.2 phr MWCNT case. On the other hand, it is evident that a high level of void content contributed to a significant reduction in mechanical properties. Although, the void content of the 0.2 phr MWCNT increased by 8.7%, it did not result in lower mechanical properties as shown in Figure 5-5.

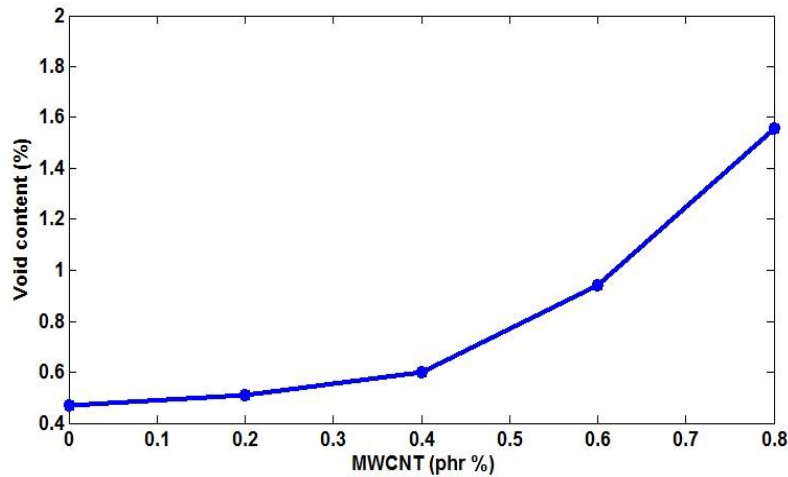


Figure 5-7. Influence of MWCNT addition on the voids content of OPS-MWCNT-UP composites.

Thus, it can be concluded that the strong bond created between the OPS powder and host matrix through use of MWCNTs, not only neutralized the negative effect of an increased void content but also improved the mechanical properties of the hybrid composite. However, in contrast to this, the void content reached values of 0.60% and 0.92% for 0.4 phr and 0.6 phr MWCNTs cases, respectively, with these levels of void content being sufficiently high as to neutralize any positive effect of the MWCNTs with regards to mechanical properties. This was consistent with the mechanical property results (Figure 5-5) and microscopic observation (Figure 5-6) where the 0.2 and 0.4 phr MWCNT hybrid composites exhibited better mechanical performance when compared to the 0.6 phr case.

5.3.2.3 Viscosity Behaviour of the Resin Mixtures

As mentioned previously, the hybrid composite containing 0.8 phr MWCNT content was comparatively difficult to fabricate with reasonable quality due to the high viscosity of the mixture as the degassing process became ineffective at such high levels of viscosity. The difficult handling in the fabrication process of CNT nanocomposite has previously ([Rahmanian et al., 2015](#)) been attributed to the large aspect ratios of CNTs which shows greater viscoelastic behaviour and consequently creates a greater aggregation of nanotubes. Figure 5-8 shows the effect of MWCNT concentration on the viscosity of both the neat resin and OPS-UP composites prior to cure. It is clear that as the content of MWCNTs increased, the viscosity of both the resin and OPS-UP mixtures increased dramatically upon reaching a critical nanoparticle content. Whereas this critical MWCNT content was found to be 0.4 phr for polyester without OPS powder, it was reduced to 0.2 phr for the 15 phr OPS-UP case. This was consistent with the influence of MWCNTs on the void generation of composite (Figure 5-7) where increasing the MWCNTs amount causes air bubbles trapped within the matrix due to an associated rapid increase in viscosity of the mixture during high shear mixing process (Figure 5-2).

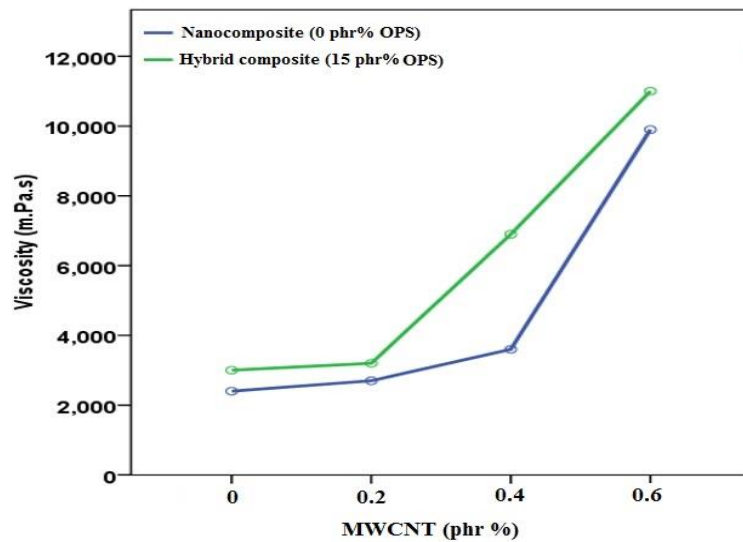


Figure 5-8. Effect of MWCNT content on the Viscosity of 15% OPS-UP mixture and OPS-UP MWCNT mixture

It is evident that the heat applied during the evaporation process of processing reduced the resin viscosity which resulted in improved dispersion of nanoparticles within the polymer matrix. However, as the temperature of the mixture (during styrene solvent evaporation) was set to be 145 °C, the risk of an unexpected reaction before the curing stage should be considered. This is due to the fact that high temperature may result in gelation during the heating process and excess removal of styrene (from its minimum level in polyester), leading to a reduction in styrene monomer which would prevent a successful curing process. It is expected that solvent evaporation under a system equipped with continuous weight monitoring, together with heating under vacuum, could mitigate the side effects and any measurement errors. With this system, the solvent evaporation process could be stopped when the weight of the mixture had reached a set point. Moreover, use of a vacuum system would also reduce the styrene vapor pressure and consequently the degassing process could be operated at a lower temperature which would reduce the risk of gelation during the evaporation stage and the level of void content.

5.3.2.4 Thermal behaviour of hybrid composite

Figure 5-9 displays the influence of MWCNTs on thermal degradation of the hybrid composites. In previous work ([Nabinejad et al., 2015](#)) the authors noted that the DTG curve of the OPS-UP composite exhibited two main peaks with the first main peak, which is a broad peak comprising of two overlapping smaller peaks, being associated with the polyester and OPS components. In contrast to this, the second peak, which was sharp in nature, was attributed to the styrene component.

The DTG curves in Figure 5-9 indicated the onset temperature for the broad peak to be 294 °C irrespective of whether or not MWCNTs were present. In contrast to this, the endset of this broad peak increased from 407 to 424 °C upon the addition of 0.6 phr MWCNT content. Moreover, the broad peak for the 0 phr MWCNT case was found to comprise of two distinct smaller peaks with maxima of 364 and 376 °C. In contrast to this, the peaks for the 0.6 phr MWCNT case were found to combine to form a single peak with a maximum at 367 °C. In previous work by the present authors, the level of separation

between these two small peaks was found to indicate the degree of phase separation between the polymer matrix and natural filler. Therefore, applying the same rationale to Figure 5-9 would suggest that the addition of MWCNTs improves the homogeneity of the composite by providing an enhanced bond between the natural OPS filler and matrix. Finally, the DTG curves also indicated that the thermal decomposition which occurred between 418 and 458 °C (maximum at 438 °C) for the composite without MWCNTs shifted to between 424 and 474 °C (maximum at 457 °C) for the case with MWCNTs.

With respect to the TGA curves, both composite specimens (with and without MWCNTs) exhibited the same degree of mass loss (76%) during the first stage. However, the mass loss of the composites in the second stage, which is attributed to the styrene component, increased from 13% for 0 phr MWCNT content to 15% for 0.6 phr MWCNT content. This increase in mass loss associated with styrene for the 0.6 phr MWCNT hybrid composite might be attributed to the presence of excess styrene that was not completely extracted from the matrix during the solvent evaporation stage. In other words, this additional 1.8% of mass loss (which is equivalent to 2.1 phr), remained in the matrix due to the evaporation process. As a result of this, the nanocomposite with MWCNTs exhibited a lower char yield (9.5%) compared to that of the composite without MWCNTs (11%).

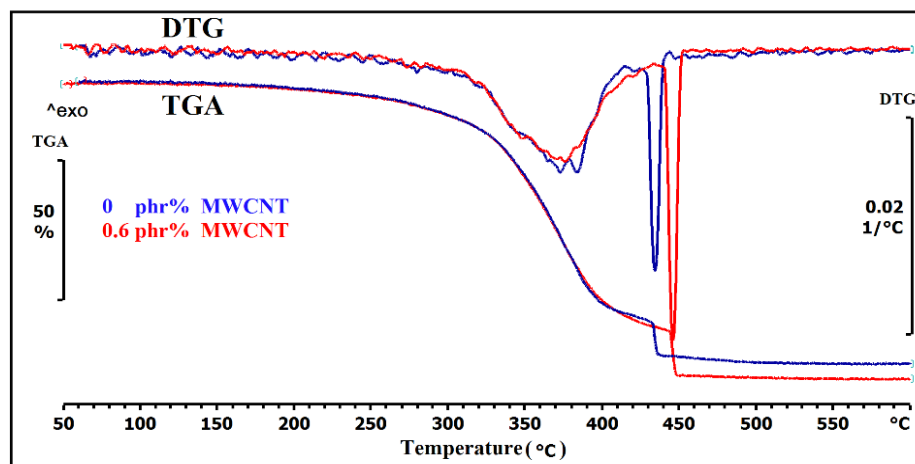


Figure 5-9. TGA and DTG curves of hybrid composite with 0 and 0.6 phr MWCNTs under oxygen purge

From the above discussion, it can be summarized that the decomposition temperature under oxygen atmosphere started at the same temperature for both composites. However,

the presence of MWCNTs shifted the endset degradation temperature of the hybrid composite to a higher temperature. A previous study on the TGA measurements of poly(p-phenylenediamine)-MWCNT nanocomposites under nitrogen atmosphere showed that the thermal stability of the polymer improved through the addition of MWCNTs at the expense of increased mass residue (Pham et al., 2011). Investigations on the effect of MWCNT addition in polyester or vinylester nanocomposites by TGA measurement under nitrogen atmosphere has also shown that carbon nanotubes increased the thermal stability of the nanocomposite by restricting the mobility of polymer chains without disrupting the main steps of the curing reaction (Seyhan, 2008).

5.4 Conclusion

Hybrid composites comprising of pristine multi-walled carbon nanotubes (MWCNTs), oil palm shell (OPS) powder and unsaturated polyester resin (UP) were fabricated in this study. The solvent mixing method assisted by ultrasonication was used to investigate the effect of different solvents on the dispersion of nanoparticles in the UP matrix. The results of this study revealed that:

- The solvent mixing method resulted in improved dispersion and lower agglomeration. The use of styrene monomer as a solvent resulted in the best compatibility with the polyester matrix when compared to ethanol, methanol and acetone. This improved compatibility resulted in the highest tensile and flexural properties with minimum side effects for the resulted nanocomposites produced using styrene solvent.
- Voids trapped in the matrix due to the high viscosity of the mixture, which caused manufacturing issues in the casting process of hybrid composites containing greater than 0.4 phr MWCNT concentration, limited the level of MWCNTs used to fabricate the hybrid composites.
- The tensile and flexural strength of the hybrid composites experienced a maximum at 0.2 phr and 0.4 phr MWCNT content and then declined at 0.6 phr MWCNT content.

The flexural modulus also reached a peak at 0.4 phr MWCNT content whereas the tensile modulus showed an overall general decline with increasing MWCNT content.

- Thermogravimetric measurements under oxygen atmosphere showed that using MWCNTs reduced the mass residue and shifted the endset degradation temperature of the hybrid composite to a higher temperature when compared to the sample without MWCNTs.
- As both unsaturated polyester and vinylester resins contain styrene monomers and possess a similar polymerization mechanism, it can be hypothesized that the aforementioned mixing technique would also be suitable for vinylester resin in order to produce nano or hybrid composites containing MWCNTs.

Investigation on the rheological and mechanical behaviour of hybrid composites using a silane treatment for both MWCNTs and natural fiber is recommended for future study. Solvent evaporation under a system equipped with continuous weight monitoring and vacuum system is suggested to fabricate hybrid composites with reduced void content that would also minimize the risk of overheating the system.

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Chapter 6
Thesis Conclusion

Chapter 6:

6 Thesis Conclusion

6.1 Conclusion

This thesis presented an experimental study on the development of eco-friendly composite materials from palm oil biomass. To optimize the mechanical performance and quantify the thermal stability of composites, a wood flour composite comprising of oil palm kernel shell (OPS) powder reinforced in thermoset resins was analyzed in this study. The following observations and conclusions can be made based on the study results:

In general, the tensile and flexural modulus of unsaturated polyester composite was found to be essentially independent of the size of OPS powder, in the range of 50 to 600 μm . However, the tensile and flexural strength experienced maximum value between 75 and 150 μm . Any further reduction in filler size acted as defects within the composite due to the inability of the polymer matrix to wet the fillers. Increasing the loading of OPS powder decreased the tensile strength of the OPS-UP composite, while resulting in the flexural strength experiencing a maximum value at low filler content. Filler loading improved the flexural modulus; however, it caused the tensile modulus to reach a maximum value at higher filler content. In terms of resin selection, unsaturated polyester was more compatible with the natural filler when compared with vinylester and epoxy, where the lowest compatibility was recorded for epoxy resin.

Any chemical treatment methods -such as methanol washing- which were able to remove the impurities and waxes from the surfaces of the OPS resulted in a better interfacial bond between filler and matrix. It was due to increasing the surface roughness of OPS powder, improving the mechanical interlocking and polymer chain entanglement between the natural filler and polymer molecules. Alkali treatment led to a better interaction between filler and matrix when compared to the methanol wash treatment. However, chemical treatment at elevated temperatures (above 90 °C) especially with the assist of sonication resulted in the highest tensile and flexural properties for both hot water and hot alkali

treatment. Characterization by FTIR and TGA confirmed that hot water and hot alkali treatment remove some parts of hemicellulose (Xylan, Quinine, Quinine methides elements and adsorbed water) and lignin (Syringyl and Guaiacyl elements, aldehydes and ketones and acetyl group in hydroxycinnamic acids associated with the alcoholic polysaccharides) from the surface of OPS powder. The optimum mechanical performance of the composite recorded for 7% hot alkali concentration at 90 °C for 1 hr. Beyond this concentration, the majority of hemicellulose, which acts as a binder for cellulose and lignin, was removed. Therefore, the structure of the natural filler was became brittle and subsequently a composite with poor mechanical performance was experienced.

Natural fiber composites with high filler load, reinforced in thermoset resins were also fabricated in this study. It has been shown that heat absorption by filler is not the only parameter, which delays the curing reaction of thermoset resins. Initiator/resin consumption as a result of reacting with cellulose was found to be the main reason for the delay in the curing reaction. This reaction depends on the level of loading of this lignocellulosic material and the type of thermoset resins. A suitable surface treatment on the natural filler was able to deactivate the cellulose in the natural filler cell. Therefore, the polymerization process in the curing reaction of thermoset resins was not disturbed by cellulose molecules and consequently, the curing rate was recovered and improved.

In order to develop a hybrid composite with nanoparticles to improve the mechanical performance, pristine MWCNTs (multi-walled carbon nanotube) were well dispersed in an unsaturated polyester matrix using the solvent mixing method and with the addition of sonication. Using Styrene monomer as the solvent in this method showed the greatest efficiency and the fewest side effects on the performance of polyester nanocomposites compared to Ethanol, Methanol, and Acetone. The effect of a pristine MWCNT concentration on the mechanical properties of MWCNT-OPS UP hybrid composite revealed that 0.4 phr is the optimum concentrations. The dramatic rise in the viscosity of resin mixture prior to curing at a high concentration of nanoparticle (more than 0.4 phr) caused some difficulty in handling, which led to significant voids trapped in the matrix and limited the level of MWCNTs used in the fabrication of the nano or hybrid composite.

An investigation of the thermal stability of the OPS showed that untreated OPS start to degrade slowly at 144 °C due to the lignin characteristic. Major degradation occurs at 244 °C due to the hemicellulose and subsequently cellulose characteristics in the natural filler. Therefore, any polymer with a processing temperature (including melting and post curing) near this temperature is not recommended to prepare for NFC or WPC. Alkali treatment however increased the processing temperature of the natural filler to a higher temperature and consequently polymers with higher processing temperature can be used to prepare NFC or WPC.

In terms of the thermal behavior of polyester composites, increasing the filler loading decreased the linear shrinkage of the natural filler composite. The loading of the natural filler shifted the thermal degradation of the composite to higher temperatures in an inert atmosphere when compared with neat polyester resin. However at high filler content (23 & 28 wt%) phase separation was observed in the DTG curve. This change might be attributed to the insufficient matrix for the wet filler which resulted in phase separation between filler and matrix at higher filler loading. In addition, alkali treatment of natural filler shifted the thermal degradation of the composite to a lower temperature in the inert atmosphere. Loading pristine MWCNTs to the composite, shifted the endset of degradation to the higher temperature without any significant change of the onset.

Although TGA is a reliable method in material characterization to measure the filler content, it fails to determine the filler content for natural fiber composites due to the overlapping of thermal degradation temperature ranges for the natural filler and some polymer matrixes. A simple but generic analysis method has been developed in this research, based on two key points in the TGA curve of the natural filler composite specimens to determine filler content NFC or WPC.

Therefore, the results have satisfied the objectives of this study by developing a hybrid composite comprising of thermoset resin reinforced with palm oil biomass and carbon nanotube.

6.2 Recommendations for Future Work

Further research is recommended to be undertaken in the following areas:

- Determine the levels of heat dissipation and initiator/resin consumption during the loading of lignocellulose fiber/filler in the thermoset resins.
- Investigate the mechanism of the grafting reaction of cellulose radical and polyester/vinylester resins.
- Determine the activation energy of curing reactions of lignocellulose fiber/filler and thermoset resins.
- Determine a reference table of coefficients α and β in Equation (4-6) for different natural filler and polymer matrix combinations should be assembled, in addition to focusing on the evaluation or development of existing equation for non lignocellulosic-based natural filler.
- Investigate the effect of in situ silane treatment of natural filler and carbon nano tube on the final mechanical performance of the hybrid composite.

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Appendix I: Equation Constants for Equation 3-3

Sample			C0	C1	C2	C3	C4	C5	A1	A2	$\mu 1$	$\mu 2$	$\sigma 1$	$\sigma 2$
Poly ester	Untreated	0 %	23.82042839	-0.284863687	0.265178574	-1.005E-02	4.027E-05	8.20E-06	19.632559	9.440061	1.68085	21.156969	32.225294	1.425115
		9 %	24.49792576	-0.147572651	0.37441268	-3.087E-02	1.488E-03	-2.53E-05	18.3441	13.332617	1.835902	20.79179	24.235948	1.826287
		17 %	25.08715481	0.016492212	0.237272694	-1.891E-02	1.038E-03	-1.97E-05	17.790067	22.373559	2.815778	21.358931	21.796848	2.529743
		23 %	21.45353497	0.237852801	9.15E-02	3.010E-04	-1.321E-04	2.47E-06	23.675989	12.257049	3.358811	28.959851	21.618617	2.96605
		28 %	17.53443998	2.564953587	-0.36042057	3.300E-02	-1.049E-03	1.10E-05	23.535388	6.351038	2.415632	29.135646	9.727905	3.088692
	33 %	22.97262998	-0.905555416	0.215090089	-6.675E-03	4.907E-05	4.45E-07	25.21627	11.189506	2.917391	32.154797	13.126952	3.492266	
	HDW	33 %	24.94738107	-0.589367786	0.103586906	-4.302E-03	7.960E-05	-5.42E-07	27.170897	1.771322	4.787815	38.553226	6.630731	8.067817
	HAT	33 %	17.33698747	2.544593677	-0.121576115	2.288E-02	-1.051E-03	1.32E-05	17.426998	25.266395	3.678003	21.839594	3.501185	2.755628
Vinylester	Untreated	0 %	21.69199228	0.336725005	-3.62E-02	1.83E-03	-4.09E-05	3.53E-07	62.764326	58.635996	1.171633	65.732025	39.959677	1.745296
		9 %	21.71902053	3.28E-02	2.33E-05	1.02E-04	-3.24E-06	2.90E-08	91.269037	49.613324	1.943515	95.432711	26.024649	2.033977
		17 %	21.93883365	-7.37E-02	7.82E-03	-1.64E-04	1.17E-06	-1.03E-09	120.002487	40.482467	4.459394	126.122753	3.701116	1.43616
		23 %	21.736289	-6.81E-02	7.17E-03	-1.43E-04	1.07E-06	-2.37E-09	147.29621	13.760718	7.118236	155.829187	14.053716	4.765473
		28 %	253.3831099	-7.063757774	8.63E-02	-5.19E-04	1.53E-06	-1.76E-09	243.635593	2.205498	8.988349	260.562854	8.187624	10.221534
		33 %	14.8542683	0.164385565	6.12E-05	-1.31E-05	7.52E-08	-1.16E-10	268.477801	2.465383	12.709614	288.34514	4.044871	12.336001
	HDW	33 % *	-	-	-	-	-	-	-	-	-	-	-	-
	HAT	33 %	0.677733328	1.07834133	-1.62E-02	9.77E-05	-1.43E-07	-1.42E-10	149.406163	7.37446	7.402714	155.449158	9.649705	3.912931
Epoxy	Untreated	0 %	28.86440061	-0.851426069	0.150561204	-7.79E-03	2.22E-04	-2.14E-06	39.450145	24.848147	3.963744	41.234097	19.972124	3.796232
		9 %	18.91767633	2.50479395	-0.223899427	1.16E-02	-2.19E-04	1.31E-06	34.459933	36.059912	3.72904	40.752924	18.945434	4.268533
		17 %	25.06167566	0.361494666	0.016835149	-2.95E-04	2.28E-05	-3.64E-07	40.690169	15.249647	5.016034	41.142748	18.816695	5.692739
		23 %	25.47992111	0.354849836	1.74E-03	3.76E-04	-1.00E-06	-6.44E-08	41.084868	19.197813	4.192894	47.435084	19.935346	5.476209
		28 %	24.93929275	0.449145527	-9.47E-03	6.94E-04	-9.09E-06	2.31E-08	49.195303	18.060186	4.926236	56.646003	7.21336	3.490461
	33 %	25.35229147	0.299517525	1.08E-03	9.84E-05	1.74E-06	-4.40E-08	47.597818	6.681187	8.168277	54.578262	4.563383	5.638766	
	HDW	33 %	26.07958511	0.520026982	-9.68E-03	1.63E-03	-3.97E-05	2.56E-07	39.773621	20.192378	7.62293	54.99481	7.286847	7.343174
	HAT	33 %	25.3881767	0.287350635	2.24E-02	-8.17E-04	1.46E-05	-9.97E-08	43.83207	17.218955	8.870587	56.738199	6.915924	6.599228

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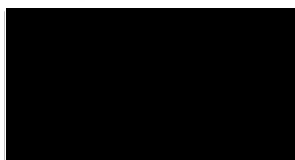
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Omid Nabinejad



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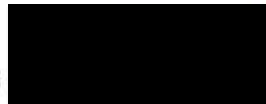
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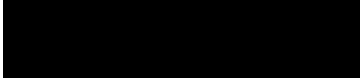
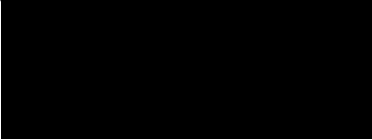
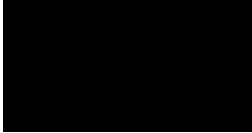
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