

**PREPARATION, CHARACTERIZATION AND
PROPERTIES OF POLYPROPYLENE/WASTE TYRE
DUST/KENAF POWDER COMPOSITES**

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UNIVERSITI SAINS MALAYSIA

2013

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DUST/KENAF POWDER COMPOSITES**

BY

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**Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science**

Nov 2013

ACKNOWLEDGEMENTS

First of all, I would like to extend my deepest gratitude to my supervisor, Prof. Dr. Hj. Hanafi Ismail for his assistance and guidance, constant support and endless encouragement throughout my study in USM.

I wish to thank the Dean of the School of Materials and Mineral Resources Engineering (SMMRE) and all staff for their helping hand. I would also like to take this opportunity to thank the technical staff of SMMRE, namely En Shahrizol, En Shahril, En Suharudin, En Mohamad Hassan, En Azam, En Rashid and En Hairi. My humble regards to other whose names are not mentioned here for their kind assistance.

I am also thankful to my seniors especially Mathialagan, Ooi Zhong Xian, Sam Sung Ting, Kahar, Nabil Hayeemasae and Norshahida. Thank for the guidance all the way in completing my study. Nice knowing all of you and thanks.

Last but not least, my special thanks to my parents and families for their endless care, love and support.

TABLE OF CONTENTS

TITLE PAGE	i
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xiv
LIST OF SYMBOLS	xv
ABSTRAK	xvi
ABSTRACT	xviii
CHAPTER 1 INTRODUCTION	
1.1. Overview	1
1.2. Problem Statement	2
1.3. Research Objectives	4
1.4. Thesis Outline	5
CHAPTER 2 LITERATURE REVIEW	
2.1. Natural Fiber Filled Polymer Composites	6

2.2. Polymer Composites	
2.2.1. Definition of Polymer Composites	7
2.2.2. Classification of Polymer Composites	7
2.2.2 (a) Thermoplastic Matrices	8
2.2.2 (b) Thermosetting Matrices	8
2.2.2 (c) Elastomer Matrices	8
2.2.2 (d) Thermoplastic Elastomers (TPEs) Matrices	9
2.3. Scrap Tyres/Waste Rubber	
2.3.1. Introduction	9
2.3.2. Composition and Characteristics of Tyres	10
2.3.3. Recycling of Tyres	12
2.4. Natural Fibers	
2.4.1. Classification and Composition of Natural Fibers	13
2.4.2. Advantages and Disadvantages of Natural Fibers	15
2.5. Basic Constituents in Natural Fiber Reinforced Composites	
2.5.1. Thermoplastic Elastomer (TPE) As A Matrix Material	17
2.5.1 (a) Polypropylene/Waste Tyre Dust Blend	17
2.5.2. Natural Fiber As A Filler	19
2.5.2 (a) Kenaf Fiber	19
2.5.3. Interfaces	20
2.5.3 (a) Coupling Agent	21

CHAPTER 3 MATERIALS AND METHODOLOGY

3.1. Materials	
3.1.1. Polypropylene (PP)	24

3.1.2. Waste Tyre Dust (WTD)	25
3.1.3. Kenaf Powder (KNFp)	25
3.1.4. Kenaf Short Fiber (KNFs)	26
3.1.5. 3-aminopropyltriethoxysilane (APTES)	26
3.1.6. Phthalic Anhydride (PA)	26
3.2. Composites Preparation	
3.2.1 (a) PP/WTD/KNFp Composites with Different KNFp loading	27
3.2.1 (b) PP/WTD/KNFs Composites with Different KNF loading	27
3.2.1 (c) PP/WTD/KNFp Composites with Addition of 3-aminopropyltriethoxysilane (APTES) as Coupling Agent	28
3.2.1 (d) PP/WTD/KNFp Composites with Addition of phthalic Anhydride (PA) as Coupling Agent	29
3.2.2 (a) Melt Blending of PP/WTD/KNFp, PP/WTD/KNFs, PP/WTD/KNFp/APTES and PP/WTD/KNFp/PA Composites	29
3.2.3. Compression Moulding	30
3.3. Testing and Characterization	
3.3.1. Processing Torque	30
3.3.2. Tensile Tests	30
3.3.3. Morphological Study	31
3.3.4. Water Uptake Test	31
3.3.5. Thermogravimetry Analysis (TGA)	32
3.3.6. Fourier-transform Infrared Spectroscopy (FT-IR)	32

CHAPTER 4 RESULTS AND DISCUSSION

4.1. Polypropylene/Waste Tyre Dust/Kenaf Powder (PP/WTD/KNFp)	
Composites with Variations of KNFp loading	
4.1.1. Processing Characteristic	33
4.1.2. Tensile Properties	35
4.1.3. Morphological Observation	38
4.1.4. Water Uptake	40
4.1.5. Thermogravimetric Analysis (TGA)	41
4.2. Polypropylene/Waste Tyre Dust/Kenaf Powder (PP/WTD/KNFp)	
Composites versus Polypropylene/Waste Tyre Dust/Kenaf Short Fiber (PP/WTD/KNFs)	
4.2.1. Processing Characteristic	43
4.2.2. Tensile Properties	45
4.2.3. Morphological Observation	48
4.2.4. Water Uptake	49
4.2.5. Thermogravimetric Analysis (TGA)	51
4.3. Polypropylene/Waste Tyre Dust/Kenaf Powder (PP/WTD/KNFp)	
Composites with Addition of 3-aminopropyltriethoxysilane (APTES) as A Coupling Agent	
4.3.1. Processing Characteristic	53
4.3.2. Tensile Properties	55
4.3.3. Morphological Observation	59
4.3.4. Water Uptake	60
4.3.5. Thermogravimetric Analysis (TGA)	62
4.3.6. Fourier Transform Infrared (FTIR) Analysis	64

4.4. Polypropylene/Waste Tyre Dust/Kenaf Powder (PP/WTD/KNFp)	
Composites with Addition of Phthalic Anhydride	
4.4.1. Processing Characteristic	68
4.4.2. Tensile Properties	70
4.4.3. Morphological Observation	73
4.4.4. Water Uptake	75
4.4.5. Thermogravimetric Analysis (TGA)	76
4.4.6. Fourier Transform Infrared (FTIR) Analysis	78

CHAPTER 5 CONCLUSIONS AND SUGGESTION FOR FUTURE

RESEARCH

5.1. Conclusions	81
5.2. Suggestion for future research	82

REFERENCES	83
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PUBLICATION LIST	91
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LIST OF TABLES

Table 2.1	Typical materials used in tyre manufacturing in Europe and USA	11
Table 2.2	Typical elemental analysis of waste tyres	11
Table 2.3	Typical chemical composition of natural fibers	14
Table 2.4	Properties of selected natural and synthetic fibers	15
Table 3.1	List of the materials used	24
Table 3.2	Technical specifications of PP	25
Table 3.3	Physical properties of APTES	26
Table 3.4	Properties of PA	27
Table 3.5	Composition and mixing sequence of PP/WTD/KNFp composites with different KNFp loading	27
Table 3.6	Composition and mixing sequence of PP/WTD/KNF composites with different KNF form	28
Table 3.7	Composition and mixing sequence of PP/WTD/KNFp composites with addition of 3-aminopropyltriethoxysilane (APTES)	28
Table 3.8	Composition and mixing sequence of PP/WTD/KNFp composites with addition of phthalic anhydride (PA)	29
Table 4.1	Thermal degradation parameters of KNFp, PP/WTD matrix and PP/WTD/KNFp composites at 10 phr and 20 phr KNFp loading	43
Table 4.2	Thermal degradation parameters of PP/WTD/KNFp and PP/WTD/KNFs composites at 10 phr and 20 phr KNF loading	52
Table 4.3	Thermal degradation parameters of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/APTES composites at 10 phr and 20 phr KNFp loading	63
Table 4.4	Thermal degradation parameters of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/PA composites at 10 phr	

LIST OF FIGURES

Figure 2.1	Classification of natural fibers	13
Figure 2.2	Kenaf plants	20
Figure 4.1	Torque-time curves of PP/WTD matrix and PP/WTD/KNFp composites as a function of KNF loading	33
Figure 4.2	Effect of KNFp loading on the stabilization torque of PP/WTD/KNFp composites	34
Figure 4.3	Effect of KNFp loadings on the tensile strength of PP/WTD/KNFp composites	36
Figure 4.4	Effect of KNFp loadings on the tensile modulus of PP/WTD/KNFp composites	37
Figure 4.5	Effect of KNFp loadings on the elongation at break of PP/WTD/KNFp composites	37
Figure 4.6	SEM micrographs of the tensile fractured surfaces at magnification (a) – (c) of 100x of the (a) PP/WTD matrix (b) PP/WTD/KNFp composites at 10 phr KNF loading and (c) PP/WTD/KNFp composites at 20 phr KNFp loading	39
Figure 4.7	Water uptake of PP/WTD matrix, and PP/WTD/KNFp composites at different KNFp loadings	41
Figure 4.8	Typical thermal degradation curves of the KNFp, PP/WTD matrix and PP/WTD/KNFp composites at 10 phr and 20 phr KNF loadings	42
Figure 4.9	Torque-time curves of PP/WTD matrix and PP/WTD/KNFs composites at different KNFs loadings	44
Figure 4.10	Stabilization torque of PP/WTD/KNFp and PP/WTD/KNFs composites as a function of KNF loading	45

Figure 4.11	Tensile strength of PP/WTD/KNFp and PP/WTD/KNFs composites as a function of KNF loading	47
Figure 4.12	Tensile modulus of PP/WTD/KNFp and PP/WTD/KNFs composites as a function of KNF loading	47
Figure 4.13	Elongation at break of PP/WTD/KNFp and PP/WTD/KNFs composites as a function of KNF loading	48
Figure 4.14	SEM micrographs of the tensile fractured surfaces of the (a) (a) – (b) PP/WTD/KNFp composites (b) PP/WTD/KNFs composites, at 10 phr KNF loading; (c) PP/WTD/KNFp composites (d) PP/WTD/KNFs composites, at 20 phr KNF loading with a magnification of 100x	49
Figure 4.15	Water uptake of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFs composites at 10 phr and 20 phr KNF loading	50
Figure 4.16	Equilibrium water uptake of PP/WTD/KNFp and PP/WTD/KNFs composites at 10 phr and 20 phr KNF loading	51
Figure 4.17	Typical thermal degradation curves of PP/WTD/KNFp and PP/WTD/KNFs composites at 10 phr and 20 phr KNF loading	52
Figure 4.18	Torque-time curves of PP/WTD matrix and PP/WTD/KNFp/APTES composites at different KNFp loadings	53
Figure 4.19	Stabilization torque of PP/WTD/KNFp and PP/WTD/KNFp/APTES composites at different KNFp loading	54
Figure 4.20	Tensile strength of PP/WTD/KNFp and PP/WTD/KNFp/APTES composites as a function of KNFp loading	57
Figure 4.21	Proposed possible interaction scheme between KNFp and 3-aminopropyltriethoxysilane (APTES)	57
Figure 4.22	Tensile modulus of PP/WTD/KNFp and PP/WTD/KNFp/APTES composites as a function of KNFp loading	58

Figure 4.23	Elongation at break of PP/WTD/KNFp and PP/WTD/KNFp/APTES composites as a function of KNFp loading	58
Figure 4.24	SEM micrographs of the tensile fractured surfaces of the (a) (a) – (d) PP/WTD/KNFp composites (b) PP/WTD/KNFp/APTES composites, at 10 phr KNF loading; (c) PP/WTD/KNFp composites (d) PP/WTD/KNFp/APTES composites, at 20 phr KNF loading with magnification of 100x	59
Figure 4.25	Water uptake of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/APTES composites as a function of KNFp loadings	60
Figure 4.26	Equilibrium water uptake of PP/WTD/KNFp and PP/WTD/KNFp/APTES composites as a function of KNFp loadings	61
Figure 4.27	Typical thermal degradation curves of PP/WTD matrix, PP/WTD/KNF composites and PP/WTD/KNF/APTES composites, at 10 phr and 20 phr of KNFp loading	63
Figure 4.28	Typical FTIR spectra of PP, PP/WTD matrix, APTES and KNFp	65
Figure 4.29	Comparison of the FTIR spectra of PP/WTD, PP/WTD/KNFp, and PP/WTD/KNFp/APTES composites	67
Figure 4.30	Torque-time curves of PP/WTD matrix and PP/WTD/KNFp/PA composites at different KNFp loadings	68
Figure 4.31	Stabilization torque of PP/WTD/KNFp and PP/WTD/KNFp/PA composites at different KNFp loading	69
Figure 4.32	Tensile strength of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/PA composites as a function of KNFp loading	71
Figure 4.33	Proposed possible reaction between KNFp and phthalic anhydride	71
Figure 4.34	Tensile modulus of PP/WTD matrix, PP/WTD/KNFp and	

	PP/WTD/KNFp/PA composites as a function of KNFp loading	72
Figure 4.35	Elongation at break of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/PA composites as a function of KNFp loading	73
Figure 4.36	SEM micrographs of the tensile fractured surfaces of the (a) (a) – (d) PP/WTD/KNFp composites, (b) PP/WTD/KNFp/PA composites, at 10 phr KNF loading; (c) PP/WTD/KNFp composites, (d) PP/WTD/KNFp/PA composites, at 20 phr KNF loading with magnification of 100x	74
Figure 4.37	Water uptake of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/PA composites at different KNF loadings, as a function of time	75
Figure 4.38	Equilibrium water uptake of PP/WTD/KNFp and PP/WTD/KNFp/PA composites as a function of KNFp loading	76
Figure 4.39	Typical TGA curves of PP/WTD matrix, PP/WTD/KNFp and PP/WTD/KNFp/PA composites at 10 phr and 20 phr KNFp loading	77
Figure 4.40	FTIR spectra of PP/WTD/KNFp and PP/WTD/KNFp/PA composites at 10 phr KNFp loading	79

LIST OF ABBREVIATIONS

APTES	3-aminopropyltriethoxysilane
ASTM	American Society for Testing and Materials
EPDM	ethylene propylene diene monomer
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared
HDPE	high density polyethylene
KNFp	kenaf (powder)
KNFs	kenaf (short fiber)
LCD	liquid crystal display
LDPE	low density polyethylene
MAPE	maleic anhydride polyethylene
MAPP	maleic anhydride polypropylene
NBR	acrylonitrile butadiene rubber
NBRr	recycled acrylonitrile butadiene rubber
NFRPCs	natural fibers reinforced polymer composites
NKTB	National Kenaf and Tobacco Board
NR	natural rubber
PA	phthalic anhydride
PE	Polyethylene
phr	parts per hundred parts of resin
POFA	palm oil fatty acid
PP	Polypropylene
PPMAH	polypropylene grafted-maleic anhydride
PMCs	polymer matrix composites
PU	Polyurethane

LIST OF SYMBOLS

C	Carbon
E_b	elongation at break
Kg	Kilogram
cm^3	centimetre cube
O_2	Oxygen
%	Percentage
wt.%	weight percent
G	Gram
MPa	MegaPascal
GPa	GigaPascal
J/m	joule per metre
$^{\circ}\text{C}$	degree celcius
Mm	Millimetre
μm	Micrometer
g/l	gram per litre
$T_{50\%}$	temperature at 50% weight loss
W_t	total water uptake (in weight)
W_1	weight of specimen before immersion
W_2	weight of specimen after immersion

**PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT
POLIPROPILENA/ SERBUK BUANGAN TAYAR/ SERBUK KENAF**

ABSTRAK

Komposit elastomer termoplastik polipropilena (PP)/serbuk buangan tayar (WTD)/serbuk kenaf (KNFp) telah disediakan dengan satu komposisi tetap adunan elastomer termoplastik PP/WTD pada 70/30 (bt./bt.%). Jumlah KNFp yang digunakan dalam kajian ini adalah 0, 5, 10, 15 dan 20 phr. Semua komposit telah disediakan dengan menggunakan pencampur dalaman Thermo Haake Rheomix Polydrive R600/610 pada suhu 180 °C dan kelajuan rotor 50 rpm untuk masa adunan 10 minit. Hasil kajian menunjukkan bahawa kestabilan tork, modulus tensil, penyerapan air dan kestabilan terma komposit meningkat dengan peningkatan kandungan KNFp. Walau bagaimanapun, kekuatan tensil dan pemanjangan pada takat putus berkurang. Penggantian KNFp dengan gentian pendek kenaf (KNFs), telah meningkatkan kekuatan tensil dan modulus tensil komposit. Walau bagaimanapun, peningkatan dalam tork pemprosesan menyebabkan kesukaran semasa penyediaan komposit PP/WTD/KNFs. Penambahan 3-aminopropiltriethoxysilana (APTES) kepada komposit telah menyebabkan kestabilan tork, kekuatan tensil dan modulus tensil yang lebih tinggi, manakala pemanjangan pada takat putus dan penyerapan air berkurang. APTES didapati berkesan untuk bertindak sebagai agen pengkupel disebabkan peningkatan dalam lekatan antara muka komposit seperti yang ditunjukkan oleh mikrograf SEM. Bagi komposit PP/WTD/KNFp dengan penambahan fetalik anhidrida (PA), kekuatan tensil, modulus tensil dan penyerapan air telah meningkat, tetapi pemanjangan pada takat putus dan tork pemprosesan telah

menurun. Penambahan PA didapati membantu pemrosesan komposit. Kestabilan terma komposit sama ada dengan penambahan APTES atau PA telah meningkat sedikit, tetapi tidak begitu ketara.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/WASTE TYRE DUST/KENAF POWDER COMPOSITES

ABSTRACT

Thermoplastic elastomer composites of polypropylene (PP)/waste tyre dust (WTD)/kenaf powder (KNFp) were prepared with a fix thermoplastic elastomer blend composition of PP/WTD at 70/30 (wt./wt.%). The amount of KNFp used in this research was 0, 5, 10, 15 and 20 phr. All composites were prepared using a Thermo Haake Rheomix Polydrive R600/610 internal mixer at temperature of 180 °C and rotor speed of 50 rpm for a mixing time of 10 minutes. The results showed that the stabilization torque, tensile modulus, water uptake and thermal stability of composites increased with increasing KNFp loading. However, the tensile strength and elongation at break was decreased. By substituting KNFp with kenaf short fiber (KNFs), the tensile strength and tensile modulus of the composites were higher. However, the increasing in processing torque causes a difficulty during preparation of the PP/WTD/KNFs composites. Addition of 3-aminopropyltriethoxysilane (APTES) to the composites has resulted in higher stabilization torque, tensile strength and tensile modulus, whereas the elongation at break and water uptake were lower. APTES was found to be effective to act as coupling agent due to the enhancement in interfacial adhesion of the composites, as shown by the SEM micrographs. For PP/WTD/KNFp composites with the addition of phthalic anhydride (PA), tensile strength, tensile modulus and water uptake were increased, but the elongation at break and processing torque were decreased. Addition of PA was found

to aid the processing of composites preparation. Thermal stability of the composites with either APTES or PA was slightly increased, but not that significant.

CHAPTER 1

INTRODUCTION

1.1 Overview

The incorporation of natural fibers into polymer composites has been accepted and widely studied for the past few years. As the world moving towards making the world go 'green', utilization of natural fibers composites have gaining attention which can result in production of environmental friendly products with low production cost (Aji et al., 2009; Xie et al., 2010; Abdul Khalil et al., 2010). The advantages contributing to the growing demand of natural fibers in polymer composites are low cost, light weight, less harmful to human and environments, less abrasive to machine, abundance and biodegradability (Liu et al., 2007; Jonoobi et al., 2009; Malkapuram et al., 2009; Ismail et al., 2010b; Akil et al., 2011; Bernard et al., 2011).

Kenaf (*Hisbiscus cannabinus L.*) is a fiber crop that grows annually under warm season in tropical and subtropical areas. Kenaf belongs to non-wood lignocellulosic plant that can grow under a wide range of climatic conditions with relatively little care (Ashori et al., 2006; Jonoobi et al., 2009; Ibrahim et al., 2011). Among the reason that kenaf fibers have been widely explored is they possesses attractive mechanical properties and can be used as reinforcement in polymer composites (Liu et al., 2007; Ismail et al., 2010b; Anuar and Zuraida, 2011; Akil et al., 2011; Bernard et al., 2011). Anuar and Zuraida (2011) reported that the incorporation of kenaf fiber has increased the tensile modulus of the thermoplastic natural rubber (TPNR) and polypropylene-ethylene polypropylene diene monomer (PP/EPDM) composites as compared to the unreinforced one.

There are numerous researches on the synthetic or natural filler filled thermoplastic elastomers (TPEs) composites has been reported (Salmah et al., 2006; Zainal and Ismail, 2011a; Santiagoo et al., 2011). Generally, the incorporation of inorganic filler into TPEs composites was to improve the final properties of the composites. Previous studies on short glass fiber (SGF) filled polypropylene (PP)/waste tyre dust (WTD) shows an increasing modulus and thermal stability of the composites (Zainal and Ismail, 2011a). However, the drawbacks of using glass fibers are their relatively high cost, non-biodegradable, abrasive (may damage mixing chamber of the equipment) and health concerns (respiratory problems upon inhalation) (Akil et al., 2011). As a solution, the trend has shifted to replace the synthetic to natural fibers filled polymer composites for the economic and ecological reasons.

The main disadvantages of using natural fibers as filler in polymer composites is their incompatibility with the polymer (Suryadiansyah et al., 2007; Malkapuram et al., 2009; Santiagoo et al., 2011; La Mantia and Morreale, 2011). Natural fibers are well known for their hydrophilic, while polymer is generally hydrophobic. The weak interfacial adhesion between fiber and matrix which may result the stress applied not efficiently transferred from matrix to fiber upon stress application (Rezaur Rahman et al., 2010; Zainal and Ismail, 2011b). Hence, the introduction of a third material is required to improve the fiber/matrix interfacial adhesion, subsequently improving the composite's properties (Osman et al., 2010).

1.2 Problem Statement

Globally, great focus has been given to the increasing accumulation of waste rubber by the environmentalists about its proper way of utilization (Jose et al., 2007;

Supri et al., 2012a). The tyre industries are the major contributors to the increasing amount of waste rubber. In the effort to conserve the natural resources and also to minimize the environmental pollutions, the waste rubber have been used as ground scrap rubber or rubber powder and blended with different polymers (thermoplastic and elastomeric materials) which is cheaper with better processability (Phinyocheep et al., 2002; Jose el al., 2007; Awang et al., 2008; Xin et al., 2009a; Ismail et al., 2011a). Despite numerous studies on the thermoplastic elastomers (TPEs) blends based on virgin rubber (Salmah et al., 2006; Anuar and Zuraida, 2011), the use of waste rubber in TPEs blends also gained attention. In this study, waste tyre dust (WTD) was melt-mixed with polypropylene (PP) and served as thermoplastic elastomer (TPE) matrices.

Kenaf (KNF), also known as *Hisbiscus cannabinus* L. has recently gaining great attention worldwide and is well known for its low density, high specific mechanical properties, biodegradability and less abrasive to equipment (Liu et al., 2007; Aji et al., 2009; Abdul Khalil et al., 2010; Akil et al., 2011). In Malaysia, KNF is now a fiber crop grown commercially and government are highly supporting the research and development related to KNF crop (Jonoobi et al., 2009; Ibrahim et al., 2011). For instance, the National Kenaf and Tobacco Board of Malaysia encourage KNF planting instead of tobacco by offering incentives and funding to the tobacco farmers (Ibrahim et al., 2011; Mohd Shahwahid et al., 2012). Thus, the exploration on the potential of KNF as filler in PP/WTD blend has become the point of interest in this study.

Regardless of the fact that there are numerous researches all over the world regarding KNF (Ashori et al., 2006; Aji et al., 2009; Ismail et al., 2010; Anuar and Zuraida, 2011; Ismail et al., 2011a; El-Shekeil et al., 2012), the utilization of KNF as

filler in thermoplastic elastomer (TPE) or more particular in PP/WTD blend has not been widely explored. The main challenge regarding the incorporation of KNF into polymer system is the incompatibility between the hydrophilic natural fibers and the hydrophobic polymers that resulted in undesired properties of final composites. The poor interfacial adhesion as a consequence of the incompatibility between the two components tended to reduce the stress transfer ability from matrix to fibers. As a result, composites with unsatisfied properties were produced.

In order to solve the weak fiber/matrix interfacial adhesion, the addition of a third material such as coupling agent can be useful. Coupling agent is a chemical that contain bifunctional groups that playing the role at the interface to form a linkage between the hydrophilic fibers and the hydrophobic polymer matrix (Xie et al., 2010; Gao et al., 2012). Silanes have successfully functioned as a coupling agent in glass fiber (inorganic filler) reinforced polymer composites (Zainal and Ismail, 2011b) and feldspar (mineral filler) filled polymer composites (Ansari and Ismail, 2009). It is also reported that silane treatment on natural filler (rice husk powder) has promised enhancement in tensile strength and modulus of TPEs composites (Santiagoo et al., 2011).

1.3 Research Objectives

The ultimate aim of this research is to assess the potential of KNF powder (KNFp) as filler in PP/WTD blend. The other objectives of this research are as below:

- i. To investigate the effect of KNFp loading on the processing torque, tensile properties, morphological properties, water uptake and thermal properties of PP/WTD/KNF powder composites.
- ii. To study and compare between PP/WTD/KNF powder and PP/WTD/KNF short fiber composites in terms of their processing torque,

tensile properties, morphological properties, water uptake and thermal properties.

- iii. To examine the effect of 3-aminopropyltriethoxysilane (APTES) as coupling agent on the properties of PP/WTD/KNFp composites. The properties were processing torque, tensile properties, morphological, water uptake and thermal properties.
- iv. To examine the effect of phthalic anhydride (PA) as coupling agent on the properties of PP/WTD/KNFp composites. The properties were processing torque, tensile properties, morphological properties, water uptake and thermal properties.

1.4 Theses Outline

This thesis is divided into five chapters as the following:

Chapter 1 covers the introduction of the research. It contains brief introduction about research background, problem statements, research objectives and organization of thesis.

Chapter 2 provides related literature on this work along with some review of significant works and findings of previous researches.

Chapter 3 provides the details of the materials used and the methodology to prepare PP/WTD/KNF composites.

Chapter 4 contains results and discussion of this research. It covers the composites' processing, mechanical properties, morphological, water uptake and thermal properties.

Chapter 5 covers the conclusions of findings in previous chapter with recommendation for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Fiber Filled Polymer Composites

Composite materials consist of two or more distinct materials bonded together with each of the materials having its unique characteristics. A composite is a heterogeneous material that comprise of a reinforcing agent and a matrix, in order to achieve desired characteristics and properties (Pickering, 2008). According to Spoljaric et al. (2009), composite is a material that consists of two or more materials of different properties which is matrix (continuous phase) phase and a filler or reinforcement (dispersed phase). The filler or reinforcement can be of fibrous, powdered, spherical, crystalline, platelet or particulate form. These reinforcements can be natural, synthetic, metallic or ceramic material, and exhibit flexible or rigid properties (Pickering, 2008; Spoljaric et al., 2009).

As the world moving forward to fully become environmental friendly and more affordable to live in, the need for global concern about preservation of natural sources and recycling has become vital (Pickering, 2008; Aji et al., 2009). The scenario has led to the growing demand of natural fibers as the filler in composite materials. In addition, the availability of natural fibers in worldwide also contribute to the growing demand of producing natural fiber filled polymer composites (Akil et al., 2011). Polyethylene and polypropylene are the conventional petroleum based plastics that are used extensively with natural fibers (Malkapuram et al., 2009; Ismail et al., 2010a; Santiagoo et al., 2011; Salmah et al., 2012).

As compared to the commercially available synthetic fibers (for example, glass fiber, carbon fiber and aramids), numerous economic and ecological advantages can

be obtained from natural fibers (wood, kenaf, jute and others) (Holbery and Houston, 2006). These advantages render them to be use in producing composites with desired end properties. Automotive parts from natural fibers filled polymer composites gained tremendous interest due to their light weight and mechanical properties. Such automotive parts produced are lighter, ensures fuel efficiency and lower production cost (Pickering, 2008)

2.2 Polymer Composites

2.2.1 Definition of Polymer Composites

Generally, there is no specific definition to describe polymer composites, or also known as polymer matrix composites (PMCs). Ansari and Ismail (2009) have stated that a polymer composite is comprised of a polymeric matrix with a thoroughly dispersed fibers and/or filler. According to Hakimah (2010), polymer composites can be defined as a mixture of two or more materials with at least one of the constituent is a polymer. Last but not least, Supri et al. (2012b) has defined the polymer composites as the materials that formed by combining fibers and polymers resin, which also recognized as fiber-reinforced plastic.

2.2.2 Classification of Polymer Composites

Polymer composites can be classified into four different classes based on polymer matrices, such as thermoplastics, thermosets, elastomers and thermoplastic elastomers (TPEs).

2.2.2 (a) Thermoplastic Matrices

Thermoplastics are polymers that soften when heated and harden when cooled whereby the processes are reversible. These polymers can be reshaped and reformed by application of heat and pressure, often without significant changes to their properties. Many thermoplastics contain of long linear or branched chains of covalently bonded carbon atoms. Hence, these polymers possess strong intramolecular bonds but weak intermolecular bonds, and they can be either semicrystalline or amorphous in structure. Polyethylene (PE) and polypropylene (PP) are the most widely used conventional thermoplastic for packaging, containers, bottles, household goods and composites (Stuart, 2002; Timings, 1998; Pickering 2008).

2.2.2 (b) Thermosetting Matrices

Thermosets are polymers that do not soften when heated but decompose upon continuous heating. They have cross-linked or network structures with covalent bonds between all molecules. Once they have been solidified by cross-links, they cannot be remelted or reshaped and the processes are totally irreversible. Thermosets are stronger, more rigid and brittle compared to thermoplastics. The common examples of thermosetting polymers used are epoxies, phenol-formaldehyde (phenolic) and polyesters (Stuart, 2002; Timings, 1998; Pickering, 2008).

2.2.2 (c) Elastomer Matrices

Elastomers or rubbers are polymers that may be reformed or change in dimensions when stressed but returned to their original dimensions when the stress is removed. Elastomers have relatively few cross-links compare to true thermosets

which have many crosslinks. Natural rubber (NR) and synthetic rubbers (styrene butadiene rubber (SBR), ethylene propylene diene rubber (EPDM), nitrile rubber (NBR), polyurethane (PU) rubber, silicon rubbers) are commonly used in the preparation of polymer composites (Stuart, 2002; Timings, 1998; Pickering, 2008).

2.2.2 (d) Thermoplastic Elastomers (TPEs) Matrices

The development of TPEs has narrowed the gap between thermoplastic and conventional elastomer by which it can be classified as a material that combined the properties of semicrystalline thermoplastic and rubbery elastomers (Xin et al., 2009a; Ismail et al., 2010a; Zainal and Ismail, 2011a). The unique characteristic of TPEs are they possess the properties of elastomer at lower temperatures but can be processed as that of thermoplastic at elevated temperatures (Anuar and Zuraida, 2011; Zainal and Ismail, 2011a). TPEs composites are easily processed using extruders or internal mixers since no vulcanization or compounding is needed. Polypropylene (PP) is one of the most popular thermoplastic used together with elastomers to produce TPEs blends or TPEs composites (Salmah et al., 2006; Xin et al., 2009a; Anuar and Zuraida, 2011; Santiago et al., 2011; Zainal and Ismail, 2011b).

2.3 Scrap Tyres/Waste Rubber

2.3.1 Introduction

According to Rubber Manufacturers Association (RMA, 2009), in the year of 2007, about 4,596 thousand tonnes of tyres were generated in the United States. There are about 54% of the scrap tyres were recycled into tyre-derived fuel (TDF) and the remaining are used in other applications such as civil engineering, ground

rubber, being exported, and other applications (Lin et al., 2008). With the development in rubber industry, the world's annual amount of used rubber products is increasing; with most of them are used automobile tyres (Sienkiewicz et al., 2012). The used automobile tyres included the tyres for aeroplanes, passenger cars, trucks, buses and two-wheelers (Adhikari et al., 2000). The other sources of the waste rubber are used rubber pipes, rubber belts, rubber shoes, waste produced in rubber processes and other (Fang et al., 2001). Worldwide, the increasing accumulation of waste rubber have caused serious environmental problem since rubbers are non-biodegradable and do not decompose easily as they having three dimensional network structure (Jose et al., 2007; Lin et al., 2008). Innovative and proper methods of recycling tyre rubber are in great demand since landfilling scrap tyres lead to the wastage of valuable rubber and environmental pollution.

2.3.2 Composition and Characteristics of Tyres

Tyre is a product that having complex structure and composition. The composition of the tyres varies according to the manufacturing companies and formulations used. A tyre not only composed of rubber, but also present with other constituents such as additives (fillers, activator, accelerator, antioxidants, extender oil and etc), fabric belts, beads and textile overlays. Natural rubber (NR) and synthetic rubbers (namely styrene butadiene rubber (SBR) or butyl rubber (IIR)) were used in the production of tyres. A typical composition on the raw materials used in tyre manufacturing is presented in Table 2.1 (Sienkiewicz et al., 2012). Meanwhile, Table 2.2 shows the elemental analysis carried out on scrap tyres (Galvagno et al., 2002; Ko et al., 2004).

Table 2.1: Typical materials used in tyre manufacturing in Europe and USA (Sienkiewicz et al., 2012)

Materials	In USA		In European Union	
	Passenger tyre	Truck tyre	Passenger tyre	Truck tyre
Natural rubber (%)	14	27	22	30
Synthetic rubber (%)	27	14	23	15
Carbon black (%)	28	28	28	20
Steel (%)	14-15	14-15	13	25
Fabric, fillers, accelerators, etc. (%)	16-17	16-17	14	10

Table 2.2: Typical elemental analysis of waste tyres (Galvagno et al., 2002)

Element	Percentage (%)
Carbon	85.16
Hydrogen	7.27
Nitrogen	0.38
Sulfur	2.30
Oxygen	0.54
Ashes	4.36

It should be noted that the widely variations on the chemical compositions and the cross-linked structures of rubber in tyres, are the main reason that made their disposal and reprocessing to be more difficult. Again for the similar reason, the tyres produced are highly resisted to biological degradation, chemical reagents, photochemical decomposition and high temperatures. Therefore, the proper way of managing the used tyres has become the main challenge to the mankind worldwide. (Sienkiewicz et al., 2012; Ko et al., 2004)

2.3.3 Recycling of Scrap Tyres

From the processing and economic point of view, the process of recycling scrap tyres would be of much as it avoids the problem of landfilling and incineration by diverting the waste rubber into a useful product (Jose et al., 2007). Numerous researches have been done regarding the recycling of waste rubber into a useful product (Pierce and Blackwell, 2003; Lin et al., 2008; Xin et al., 2009a). Waste tyre powder is capable of absorbing oil as reported by Lin et al. (2008). The sorption efficiency of waste tyre powder depends on the particle size and environmental temperature. Xin et al. (2009a) has introduced the waste ground rubber tyre (WGRT) in polypropylene (PP) in the production of foam with carbon dioxide as foaming agent.

Several studies to investigate the properties of waste rubber related polymer blend or polymer composites have been reported (Phinyocheep et al., 2002; Jose et al., 2007; Awang et al., 2008; Ismail et al., 2010c; Santiagoo et al., 2011; Zainal and Ismail, 2011b; Supri and Ismail, 2012a). Supri and Ismail (2012b) reported that the addition of vinyl alcohol-phthalic anhydride into low density polyethylene/tyre dust (LDPE/TD) blend has enhanced the tensile strength, modulus as well as the thermal stability of the blend. According to Ismail et al. (2010c), similar findings on the enhancement of properties of rice husk powder (RHP) filled polypropylene/recycled acrylonitrile butadiene rubber (PP/NBRr) composites with the incorporation of maleic anhydride grafted polypropylene (PPMAH) has been reported.

2.4 Natural Fibers

2.4.1 Classification and Composition of Natural Fibers

The classification of natural fibers based on their origins, i.e. plants, animals or minerals are shown in Figure 2.1 (John and Thomas, 2008; Akil et al., 2011). Fibers produced from vegetable or plants are among the three groups of natural fibers widely used as reinforcing material or filler in polymer composites (Pickering, 2008; John and Thomas, 2008; Sgriccia et al., 2008; Aji et al., 2009; Akil et al., 2011).

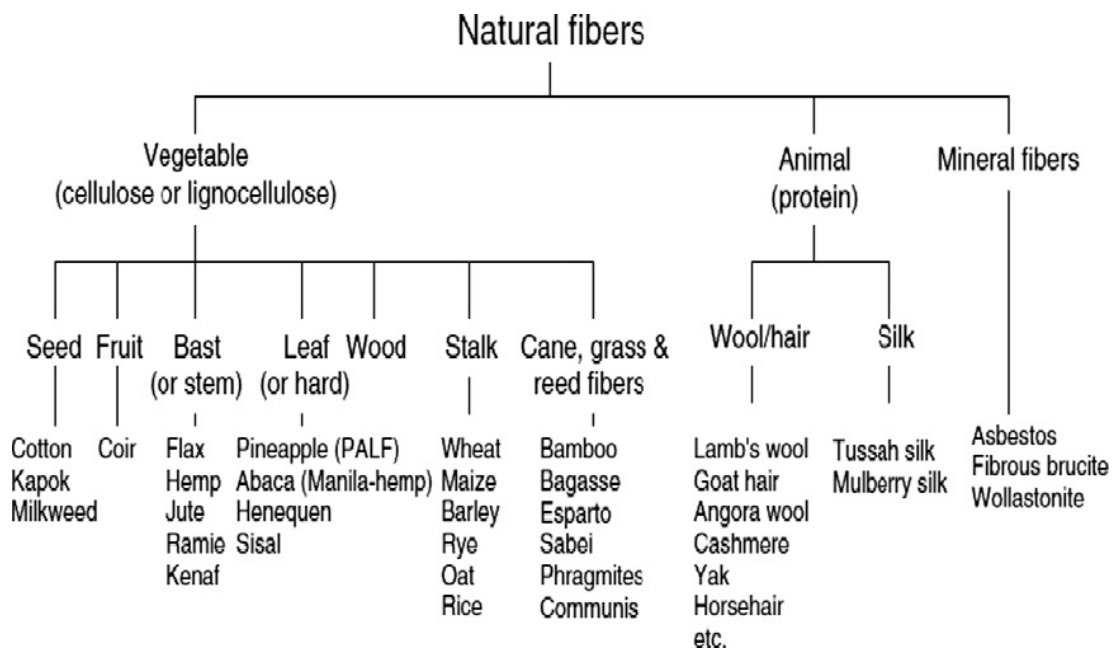


Figure 2.1. Classification of natural fibers (John and Thomas, 2008; Akil et al., 2011)

Natural fibers are regarded as naturally occurring composite materials with the main constituents of cellulosic material, as well as other components such as lignin, pectins and waxes (Akil et al., 2011). Table 2.3 represent the typical chemical composition of natural fibers (Malkapuram et al., 2009; Akil et al., 2011). Meanwhile, the properties of selected natural and synthetic fibers are shown in Table 2.4 (Ku et al., 2011).

Table 2.3: Typical chemical composition of natural fibers (Malkapuram et al., 2009; Akil et al., 2011)

Fibers	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Pectin (wt.%)
Flax	71	18.6-20.6	2.2	2.3
Hemp	70-74	17.9-22.4	3.7-5.7	0.9
Jute	61-71.5	13.6-20.4	12-13	0.2
Kenaf	45-57	21.5	8-13	3-5
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	1.9
Nettle	86			
Sisal	66-78	10-14	10-14	10
Agave	77.6	4-8	13.1	
Banana	63-64	10	5	
Abaca	56-63		12-13.1	1
Oil palm EFB	65		19	
Cotton	85-90	5.7		0-1
Coir	32-43	0.15-0.25	40-45	3-4
Cereal straw	38-45	15-31	12-20	8

*wt.% = weight percentage

Cellulose is a natural polymer containing D-anhydro-glucose ($C_6H_{11}O_5$) as the repeating units, with each contains three hydroxyl groups. The ability of these hydroxyl groups to form hydrogen bonds intramolecularly or intermolecularly, is the reason that all natural fibers being hydrophilic in nature. Cellulose is the component that defined the high modulus of natural fibers (Akil et al., 2011). The reinforcing efficiency of natural fiber filled composites depends on the nature of cellulose and their degree of crystallinity. Generally, the cellulose content determines the tensile strength and modulus of the natural fibers. Fiber with higher strength and rigidity can

be attained by aligning the cellulosic fiber along the fiber length (John and Thomas, 2008; Aji et al., 2009; Jonoobi et al., 2009; Akil et al., 2011).

Table 2.4: Properties of selected natural and synthetic fibers (Ku et al., 2011)

Fibers	Density (g/cm ³)	Elongation (%)	Tensile strength (MPa)	Elastic modulus (GPa)
Cotton	1.5-1.6	7.0-8.0	400	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	500-1500	27.6
Hemp	1.47	2-4	690	70
Kenaf	1.45	1.6	930	53
Ramie	N/A	3.6-3.8	400-938	61.4-128
Sisal	1.5	2.0-2.5	511-635	9.4-22
Coir	1.2	30	593	4.0-6.0
Softwood kraft pulp	1.5	4.4	1000	40
E-glass	2.5	0.5	2000-3500	70
S-glass	2.5	2.8	4570	86
Aramid	1.4	3.3-3.7	3000-3150	63.0-67.0
Carbon	1.4	1.4-1.8	4000	230-240

2.4.2 Advantages and Disadvantages of Natural Fibers

The great focus on the development of natural fibers in the production of polymer composites are due to their advantages such as productivity (cheaper, renewable resources), properties (comparable mechanical properties with synthetic fibers) and biodegradability (Alemdar and Sain, 2008; Sgriecchia et al., 2008; Malkapuram et al., 2009; Ismail et al., 2011a; Ku et al., 2011). In addition, natural

fibers are less abrasive to molding equipment, which can significantly reduce the cost for equipment maintenance. Besides, the environmental friendly and safer processing of natural fibers filled polymer composites tend to reduce the risk of health problems (Akil et al., 2011). Natural fibers present positive impact to the environment as they are renewable resources, biodegradable and energy saving. Moreover, the combustion of natural fibers does not produce excessive carbon dioxide into the atmosphere (John and Thomas, 2008; Akil et al., 2011).

As we know, most of the polymers are hydrophobic in nature. Meanwhile the high content of hydroxyl group in natural fibers contributes to their hydrophilicity or polar nature (Akil et al., 2011). The major disadvantages of using natural fibers as filler in polymer composites are their incompatibility because of different polarity (hydrophilic natural fibers are incompatible with hydrophobic polymer), which yields composites with inferior mechanical properties and poor fiber-matrix interphase (Li et al., 2007; Ismail et al., 2010b; Akil et al., 2011). In addition, the low swelling resistance in moisture or water and low processing temperatures limits the usage of natural fibers (Sanadi et al., 1995; Zabihzadeh, 2010; Xie et al., 2010). The absorbed moisture may disturb the interaction between fiber and matrix that results in weaker interfacial adhesion. Besides that, changes in composite's dimension or shape may occur with the high moisture absorption by the natural fibers. The next disadvantage is natural fibers possess low thermal stability where they can be thermally degraded during composite processing (at about 200 °C) (Xie et al., 2010). This phenomenon restricts their application only at low temperature applications (Sgriccia et al., 2008; Spoljaric et al., 2009; Xie et al., 2010).

2.5 Basic Constituents in Natural Fiber Filled Composites

2.5.1 Thermoplastic Elastomer (TPE) As A Matrix Material

Thermoplastic elastomer (TPE) can be produced in the form of blend by melt-mixing a thermoplastic (e.g., PP, PE) and elastomer (e.g., NR, EPDM, SBR, etc). Polypropylene (PP) based TPEs blend are widely produced and studied by blending with either natural rubber (NR) or ethylene propylene diene monomer (EPDM) (Ismail and Suryadiansyah, 2002; Salmah et al., 2008). However, the increasing amount of waste rubber may cause a threat to the environment and human health if not properly managed. Blending the waste rubber with plastics has become a new route for recycling purposes as well as forming new usable materials.

2.5.1 (a) Polypropylene/Waste Tyre Dust Blend

Polyolefin such as polypropylene (PP) are among the extensively used polymer in the manufacturing of natural fibers filled polymer composites (Rezaur Rahman et al., 2010). Low cost and density are the reasons for the popularity of PP as matrix material. Besides, PP is chosen as a matrix material for its good balance of properties and can be processed at relatively low processing temperature. These advantages are essential especially in producing natural fiber filled polymer composites due to the low thermal resistivity of natural fibers. (Awang et al., 2007; Ruksakulpiwat et al., 2007; Spoljaric et al., 2009)

There are a lot of researches on the polypropylene (PP)-based blends or composites been reported for the past few years (Othman et al., 2006; Salmah et al., 2008; Ansari and Ismail, 2009; Zainal and Ismail, 2011b). One of them is PP-based thermoplastic elastomers (TPEs) composites. Earlier, PP-based TPEs blends are formed by blending PP with natural or synthetic rubbers. Study by Salmah et al.

(2008) reveals the improvement in tensile properties and water absorption resistance of paper sludge filled PP/EPDM composites as a function of dynamic vulcanization and in the presence of compatibilizer.

Continuous accumulation of the waste rubber especially from used automobile tyres has raised the effort of recycling the waste rubber. A few approaches have been made to avoid the waste rubber from going to landfill or incineration. One of them is by reuse the scrap/waste rubber by blending them into plastic to formulate new usable materials (Adhikari et al., 2000; Fang et al., 2001; Xin et al., 2009a). Blending the waste rubber with plastics plays significant role on the invention of new materials, as well as an alternative way of recycling (Ismail et al., 2002; Xin et al., 2009b). Instead of disposing the waste rubber into landfill, waste rubber tyre powder can be incorporated as filler in producing TPEs blends or TPEs composites. Study by Xin et al. (2009a) is an example of utilizing waste ground rubber tyre (WGRT) as filler to produce PP/WGRT foam. Many other studies have been carried out to improve the properties of polymer/waste rubber composites (Awang et al., 2008; Anis Sakinah et al., 2009; Xin et al., 2009a; Santiagoo et al., 2011; Zainal and Ismail, 2011b; Supri et al., 2012a). For instance, Awang et al. (2008) reported that the tensile properties and swelling resistance are improved for latex modified waste tyre dust (WTD_{ML}) compared to the unmodified waste tyre dust in PP/ WTD_{ML} blend.

Although many works have been reported on PP/WTD blend, but the hydrophobic characteristic of this blend have leads to the incompatibility issue especially being utilized with hydrophilic materials such as natural fibers. Therefore, the modification of matrix or fiber is essential to tackle the incompatibility between

the hydrophobic PP/WTD blend with hydrophilic natural fiber (Malkapuram et al., 2009).

2.5.2 Natural Fiber As A Filler

2.5.2 (a) Kenaf Fiber

Kenaf (*Hibiscus Cannabinus L.*) is a type of fiber crop grown rapidly in temperate and tropical climate. Figure 2.2 shows the kenaf plant. Kenaf is fibrous plants that are made up of 60 to 75% inner core fiber and 25 to 40% outer bast fiber, in the stem. Traditionally, kenaf has been used to make ropes, canvas and textiles. However, with the rising global demand for paper based products, kenaf has been introduced to make paper products to avoid deforestation of wood (Ibrahim et al., 2011). Kenaf is able to replace wood which only harvested once over 20 to 25 years, due to its shorter harvesting period (2 to 3 times in a year). Kenaf is harvested early to produce high protein animal feed or at maturity for their fibers (Ashori et al., 2006; Aji et al., 2009; Villar et al., 2009; Abdul Khalil et al., 2010; Akil et al., 2011; Ibrahim et al., 2011; El-Shekeil et al., 2012; Mohd Shahwahid et al., 2012).

Malaysia is a strategic location for the growing of kenaf because of its tropical climate. Recently, attention has been given by the Malaysia government on promoting and encouraging the development of kenaf plantation. Kenaf shows a great economic potential which urges the National Kenaf and Tobacco Board (NKTB) of Malaysia to allocate incentives for the plantation of kenaf instead of tobacco. Besides, the NKTB is also streaming various fundings for universities and research centers to encourage their research on kenaf cultivation and utilisation (Ibrahim et al., 2011; Mohd Shahwahid et al., 2012).



Figure 2.2. Kenaf plants (Akil et al., 2011)

There are quite a number of studies reported on kenaf filled polymer composites (Sanadi et al., 1995; Feng et al., 2001; Ismail et al., 2010a; Ismail et al., 2010b; Tajeddin et al., 2010; Bernard et al., 2011; El-Shekeil et al., 2012). According to El-Shekeil et al. (2012), a 30% kenaf fiber loading gives the best tensile strength to kenaf fiber reinforced thermoplastic polyurethane composites. They also found that the modulus increased while strain and abrasion resistance of the composites decreased with increasing kenaf fiber content. Ismail et al. (2010b) reported the deterioration of the tensile strength and elongation at break of kenaf fiber filled high density polyethylene/soya powder composites with increasing fiber loading.

2.5.3 Interfaces

A major drawback in natural fibers based polymer composite is the difference on the surface properties between fiber and matrix. Natural fibers are well known for their hydrophilic/polar character while polymer is generally hydrophobic/non-polar.

The weak interfacial adhesion between the fiber and matrix resulted in composites with unsatisfied final properties. In order to enhance the compatibility between fiber and matrix, the surface modifications on either fiber or matrix have been carried out (Demir et al., 2006; Malkapuram et al., 2009; Xie et al., 2010).

A reliable natural fiber filled polymer composites with good mechanical properties can be manufactured if there is a strong interfacial bonding formed between fiber and polymer matrix. Stronger interfacial bonding is essential on allowing an efficient stress transfer from matrix to fiber upon stress application (Malkapuram et al., 2009). Without such treatment/modification, optimum stress transfer from matrix to fiber cannot be achieved due to the unstable fiber/matrix interface and hence, the reinforcement effect of the fiber remains not exploited (Abdelmouleh et al., 2007; Osman et al., 2010).

2.5.3 (a) Coupling Agent

Coupling agents are chemical that contains bifunctional groups, where one functional group react with natural fiber and the other group react with polymer matrix, hence forming a linkage between them (Xie et al., 2010; Ismail et al., 2012). Coupling agent also recognized as the chemical agent that altering the interface of both filler and polymer, thus bridging the filler and polymer together (Supri et al., 2012b). Therefore, the basic concept of the coupling agent is to link or bridge two incompatible components and subsequently improve the interfacial adhesion between them. According to Malkapuram et al. (2009), there are a few functions of coupling in materials, such as to eliminate weak boundary layers, form a flexible layer, produce a cross-linked interphase region, improve the wettability, form covalent bonds and alter the acidity of material surface.

Coupling agent and compatibilizer can be used interchangeably, where both of them are responsible in improving the interfacial adhesion of two incompatible materials. Melt grafting polypropylene or polyethylene with anhydride (MAPP or MAPE) is the example of compatibilizer/coupling agent that has been extensively used for natural fibers filled polymer composites (Feng et al., 2001; Demir et al., 2006; Suryadiansyah et al., 2007; Ismail et al., 2010; Santiagoo et al., 2011; Gao et al., 2012). An ester bond is formed from the reaction of anhydride groups of the copolymers with surface hydroxyl group of natural fibers. Meanwhile the other end of the coupling agent reacts with the polymer matrix due to their similar polarities (Feng et al., 2001; Xie et al., 2010).

Previous studies show that MAPP is an effective compatibilizer in improving the fiber/matrix interface of natural fiber filled polymer composites. As a result, higher properties of the resulting composites were attained. Feng et al. (2001) studied on the enhancement of interfacial adhesion of polypropylene (PP) matrix and kenaf fibers using MAPP as coupling agent. The results reveal that higher tensile and impact strengths was obtained for composites with MAPP. Ismail et al. (2010b) studied the effect of MAPE compatibilizer in kenaf core reinforced high density polyethylene (HDPE)/soya powder composites. Their finding shows an improvement in mechanical properties and water resistance due to the better matrix-fiber adhesion at the interface (Ismail et al., 2010b).

Phthalic anhydride is an important industrial chemical, where they have find their usage for the large scale production of plasticizers for plastics. Phthalic anhydrides are recognized as cyclic anhydrides and can be obtained through the catalytic oxidation of ortho-xylene and naphthalene (Xiao et al., 2001; Uzun et al., 2013). Phthalic anhydride has been used to chemically modify the cellulose materials

for instance, wood, sugarcane bagasse and agro-based fibers (Liu et al., 2007; Bodirlau and Teaca, 2009; Julio et al., 2010). In addition, Supri et al. (2012a) found that the addition of the phthalic anhydride can give higher tensile strength, modulus of elasticity, thermal stability and swelling resistance to the low density polyethylene/tyre dust (LDPE/TD) composites. They reported that phthalic anhydride is capable of acting as coupling agent, which improving the interfacial adhesion between LDPE matrix and tyre dust.

Silane is another type of coupling agent that have been successfully applied in inorganic filler and mineral filler based polymer composites (Ansari and Ismail, 2009; Zainal and Ismail, 2011a; Mathialagan et al., 2012). Silanes possess three advantages such as (1) abundantly available; (2) capable of reacting with hydroxyl groups of fillers via the alkoxy group of silane; and (3) possess multi-functional groups at the other end that are interchangeable as that of matrix to be used (Shokoohi et al. 2008). According to Zainal and Ismail (2011b), the tensile strength, tensile modulus and thermal stability of polypropylene/waste tyre dust (PP/WTD) filled with short glass fiber (SGF) composites were improved as a function of silane coupling agent and dynamic vulcanization.

Silanes comprised of bifunctional structures which allow them to function as a coupling agent in natural fibers filled polymer composites. There are a lots of researches investigating on the possibility of using silanes as coupling agent in natural fibers filled polymer composites (Ismail et al., 2002; Xie et al., 2010; Santiagoo et al., 2011; Ismail et al., 2012). Santiagoo et al. (2011) reported that the addition of rice husk powder (RHP) treated with silane coupling agent into polypropylene/recycled acrylonitrile butadiene rubber (PP/NBRr) have resulted in higher processing torque and tensile properties of the biocomposites.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

The materials used in this research are shown in Table 3.1. All the materials were used as received except for KNF fiber which was further processed

Table 3.1: List of the materials used.

Material	Function	Grade/Trade name	Supplier
Polypropylene (PP)	Matrix	TitanPro 6331	Titan PP Polymers (M) Sdn. Bhd.
Waste Tyre Dust (WTD)	Matrix	-	Mega Makmur Saintifik Sdn. Bhd.
Kenaf (KNF)	Filler	-	National Kenaf and Tobacco Board (NKTB)
3-aminopropyltriethoxysilane (APTES)	Coupling Agent	A3648	Sigma Aldrich Corporation
Phthalic Anhydride (PA)	Coupling Agent	320064	Sigma Aldrich Corporation

3.1.1 Polypropylene (PP)

PP homopolymer resin pellets (Grade 6331) used in this study was obtained from Titan PP Polymers (M) Sdn. Bhd.. The typical properties of PP are tabulated in Table

3.2