Characterization and Properties of Low Linear Density Polyethylene/*Typha Latifolia* (LLDPE/*Typha Latifolia*) Composites

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
Br	Bromine
Ca	Calcium
Cu	Copper
DFs	Bamboo-fibers
DTG	Derivative Thermogravimetric
DSC	Differential scanning calorimetry
CMT	Compression Molding Technique
Fe	Iron
FTIR	Fourier Transform Infrared Spectroscopy
FRP	Fiber reinforced polymer
Hf	Hafnium
K	Carbon
LLDPE	Linear Low Density Polyethylene
Mn	Magnesium
NAOH	Sodium Hydroxide
NF	Natural fiber
PP	Polypropylene
RMT	Roller mill Technique
Re	Rhenium
SiC	Silicone carbide
SEM	Scanning Electron Microscopy
Sr	Strontium
Tg	Glass transition temperature
TGA	Thermogravimetric analyzer
TPS	Thermoplastic starch
Tm	Melting temperature
Zn	Zinc

LIST OF SYMBOLS

cm	centimeter
g	gram
mm	Millimeter
μm	Micron
%	percentage
Psi	pound per square inch
g/min	gram per minute
g/cm^3	Gram per cubic centimetre
Kj/m^2	Kilojoule/square meter

Pencirian Dan Sifat-Sifat Komposit Polietilena Linear Berketumpatan Rendah/*Typha Latifolia* (LLDPE/*Typha Latifolia*)

ABSTRAK

Fabrikasi terhadap polimer (polietilena linear berketumpatan rendah) dengan gentian asli seperti *Typha Latifolia*, boleh menghasilkan peluang baru dalam penghasilan produk plastik berasaskan hijau. Dalam kajian ini, tiga objektif telah dijalankan seperti pencirian terhadap gentian *Typha Latifolia*, kesan terhadap perbezaan saiz dan juga penambahan serta kesan modifikasi NaOH terhadap gentian pada komposit LLDPE/*Typha Latifolia*. Eksperimen ini telah dijalankan menggunakan mesin ekstruder dengan parameter suhu $150^{o}C$ – $160^{0}C$ dan kelajuan 70rpm. Pencirian seperti sifat-sifat tensil (kekuatan tensil, pemanjangan takat putus dan modulus), *X-ray fluoresen* spektrometri (XRF), Fourier transform infrared spectroscopy (FTIR), analisa thermogravimetrik (TGA) dan pengimbasan mikroskop elektron (SEM) telah dijalankan ke atas komposit. Keputusan menunjukkan bahawa taburan saiz halus bagi *Typha Latifolia* adalah antara 99.19μm dan 447.37μm pada analisis saiz partikel manakala bagi saiz kasar adalah dalam lingkungan saiz antara 1- 4mm. Keputusan XRF telah mengesan kehadiran kalsium oxalate monohidrat dan potassium yang mana berada pada taburan *Typha Latifolia* yang tinggi. Pencampuran *Typha Latifolia* dalam LLDPE telah menunjukkan bahawa penurunan kekuatan tensil dan pemanjangan takat putus kecuali pada modulus. Walaubagaimanapun, *Typha Latifolia* bersaiz halus telah menunjukkan nilai tinggi pada sifat-sifat tensil berbanding saiz kasar pada semua nisbah penambahan komposit LLDPE/*Typha Latifolia*. Penambahan sebanyak 15% *Typha Latifolia* yang bersaiz halus dengan rawatan sebanyak 3% NaOH telah menunjukkan nilai yang optimum pada kekuatan tensil dan pemanjangan takat putus komposit LLDPE/*Typha Latifolia* kecuali modulus. Keadaan ini dipercayai bahawa modifikasi NaOH telah menyebabkan pemanjangan pada gentian seterusnya meningkatkan sifat-sifat tensil komposit. Pemerhatian terhadap morfologi komposit pula telah membuktikan bahawa modifikasi telah meningkatkan kesan lekatan antara gentian dan matrik.

Characterization and Properties of Low Linear Density Polyethylene/*Typha Latifolia* (LLDPE/*Typha Latifolia*) Composites

ABSTRACT

Fabricating polymer (low linear density polyethylene) with a natural fiber such as *Typha Latifolia*, will provide a new opportunities to the manufacture a green plastic products. In this study, three objectives have been carried out such as characterization of the *Typha Latifolia*, effect of different sizes and loading and influences of NaOH modification on fiber towards LLDPE/*Typha Latifolia* composite. The experimental was prepared by using extruder machine with parameter of $150^{o}C - 160^{0}C$ temperature and speed of 70rpm. The characterization such as tensile properties (tensile strength, elongation at break and Young modulus), X-ray fluorescence spectrometry (XRF), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) on composites were determined. Results indicated that the distribution of the Fine size *Typha Latifolia* was very prominent between 99.19 µm and 447.37µm on particle size analyzer while the coarse in between 1-4 mm. XRF results detected the calcium oxalate monohydrate and potassium, which is accumulated between ultimate *Typha Latifolia* fibers. The incorporation of *Typha Latifolia* into LLDPE found that the reduction on tensile strength and elongation at break except for Young's modulus. However, the fine size of *Typha Latifolia* shows the high value on properties compared with Coarse size at all loading ratios of LLDPE/*Typha Latifolia* composites. The addition of 15% fine size *Typha Latifolia* with 3% concentration of NaOH treatment demonstrated the optimum value in tensile strength and elongation at break of LLDPE/*Typha Latifolia* composites excluding young modulus. It was believed that the hydroxide sodium NaOH on fiber thus improved the tensile properties of the composites. The observation on the morphology of the composites proved that the treatment improved the adhesion between fibers and matrix.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The history of fiber-reinforced plastic began in 1908 with cellulose fiber in phenolics, later extending to urea and melamine and reaching commodity status with glass fiber-reinforced plastics. However the incorporation of natural fiber into plastic started last decade and have been try in many applications. Natural fiber is subdivided base on their origins, coming from plants, animals or minerals. All plant fiber are composed of cellulose while animal fiber consist of proteins (hair, silk and wool). Plant fiber include bast (or stem or soft sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal and straw. Recently, efforts to fabricate practical polymer composites continue apace, but the technology is still in its infancy. However, a pioneering project began to develop novel polymer-based composites that one day could truly revolutionize the automotive industry. Aims to make high-performance polymer composites that could reduce the weight of car structures by one-third or more. Therefore, when the weight becomes less the more composite efficiency will increase this subsequently increase efficiency of device produce such as car, airplane etc.

Linear low density polyethylene (LLDPE) and starch based product have been received promising attention as partial replacement for petroleum based product. Moreover, most of the plastic products are made from petroleum based plastics which are not biodegradable or discompose naturally. Therefore disposing of these materials attracts major attention regarding the sustainability issue and demanding continuous developments of producing new biodegradable or semi-biodegradable end products.

However, contrary to their biodegradable behavior, the mechanical properties of starch based blends are quite poor with increasing starch content. This is attributed to the poor interfacial adhesion due to the incompatibility of hydrophilic starch with hydrophobic synthetic polymer.

1.1.1 The Effect of Combining Natural Fiber and Polymer (Polymer Composite)

Research on polymer composites has shown as the most encouraging and promising area of research due polymer materials for its featuring unique properties in science from the last century (Tanaka and Chujo., 2013). This consequently its gained greater attention due to their potential characteristics of enhancing the mechanical, physical, optical, morphological and barrier properties for different application especially such as construction, cosmetics, medical industry, food sciences in many other composite-based industries (Saba et al., 2014). The composites usually are being processed from polymeric matrix such as thermoplastics and thermosets (Saba et al., 2014). In general, the reinforcement of polymer with natural material or fillers, such as wood, metal, glass fiber, carbon currently designated as a dynamic and active area of research and generally affect the polymer properties, these properties include mechanical (tensile, stiffness etc,), physical (color, orientation etc,), optical and thermal. There are several research communities have work on polymer based reinforcement in quest finding unique properties of composite polymer, among these researchers (Amal and Eman., 2013) conducted experiments to identify loading effect of silicone carbide on epoxy polymer. It found that the strength decreased with further increase in weight percentage of reinforcement and they claimed this is due to the weak of bonding between the matrix and the nanoparticles (Amal and Eman., 2013).

1.2 Research Problem Statement

Due to the challenges of petroleum based products high cost, environment and health and they need to find renewable resources natural fibers offers cost and energy advantages over traditional reinforcing fibers such glass and carbon. Nowadays research is going on development of bio-composites to replace traditional materials. The combination of different natural fibers found to give better mechanical and physical properties. However, several limitations must be overcome in order to exploit the full potential of natural fibers. At first proper fiber characterization and surface treatment should be developed and implemented. Secondly properties of composites are greatly depend on the volume percentages of fibers and resin. The quality at fiber matrix interface should be improved. The current challenge is to make the cost effective. The efforts to produce economically attractive composite components have resulted in several innovative manufacturing techniques currently being used in the composites industry. Hence, this study proposed a proper characterization, treatment and identification right mixing proportion of *Typha latifolia* fiber mixed with LLDPE (Ray et al., 2002).

Also due to the effect of global warming has forced the researchers to find an alternative material to polymer because most polymers, including poly (ethene) and poly(propene) which are not biodegradable. This means that micro-organisms cannot break them down, so they may last for many years in ground and this will cause the ground to be not fertile for crops cultivation.

Another problem for polymer such as LLDPE, when it is burn, carbon dioxide is produced, which adds to global warming. Toxic gases are produced unless the polymers are incinerated at high temperatures. At the same time, when polymers incorporated with additives are burnt they emit a lot of poisonous gases into the atmosphere - low molecular weight polymers (Polyethylene bags) are difficult to recycle - improper disposal leads to environmental pollution - undergo oxidation and ozonation easily so add natural fiber like Typha latifolia can solve this problem.

1.3 Research Objectives

This study consists of three objectives such as:

1. To characterize the *Typha latifolia* with particle analysis, morphological, TGA, FTIR and XRF.
2. To study the effect of different sizes of on untreated *Typha latifolia* mixed with LLDPE on tensile properties, thermal and morphology.
3. To study the effect of treated *Typha latifolia* mixed with LLDPE on tensile properties, thermal and morphology based on the selected ratio

1.4 Research Scope

The first scope of this research is to identify the best mixing proportion of LLDPE with thermoplastic starch to produce acceptable mechanical, thermal, morphological and optical properties. That will promote the mixing quality between LLDPE and *Typha Latifolia* fiber which will enable to select the best formulation.

The second scope is to perform mixing processes between the polymer matrix and the characterized fiber and fully investigate the effect of different blends proportion on the biodegradability characteristic and properties of LLDPE and *Typha Latifolia* fiber for mechanical, thermal, morphological and optical properties changes using tensile machine, thermo gravimetric analiyzer (TGA), Scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) respectively.

The third scope is to examine the effect of *Typha Latifolia* fiber incorporation on the mechanical and thermal properties of LLDPE and *Typha Latifolia* composite by using tensile machine, Scanning electron microscope (SEM) and Fourier transform.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Composites

Polymer composites are composites that utilize polymer as a matrix with a reinforcement matrix that can consist of another polymer, glass, carbon, metal, natural/bio-based materials (Almeida et al., 2012). Approaches to manufacturing thermoplastic composites are not a simple task. High processing temperatures, high melt viscosity, and the lack of drape and tack of prepregs (pre-impregnated fibers) are complications that occur during processing (Almeida et al., 2012). Other factors such as softening temperature, thermal stability, size and shape should be taken in to consideration when choosing a processing method. Reinforced composites are comprised of high strength additives such as glass, carbon, biomaterials, or fibers that are assorted within the polymer resin. Note, laminar composites can also have additives (Almeida et al., 2012). When integrating composites together, there are various approaches to creating a composite structure.

The fiber orientation is whether arranged in a laminar or reinforced manner can be continues or discontinuous orientated or disorientated or pre-impregnated or non-pre-impregnated to support the fiber treatment for promoting good interfacial adhesion between the fiber and the thermoplastic resin depending on the type of fiber chosen and the nature of the thermoplastic resin (Almeida et al., 2012). These operations often occur during the time of the fabrication process mainly because it reduces the handling of the fibers problem (Almeida et al., 2012). Prepregs are reinforcement materials that are pre-impregnated into a thermoplastic resin matrix which can be woven or uni-directional creating prepregs. The processing temperatures are need to be taken into account because some fibers will degrade at that state. Common prepregs fibers are glass, carbon, aramid fibers, or other thermoplastic resins. The length of these fibers (i.e. short or long) can contribute to the overall properties of the composite (Saba Naheed et al., 2014).

Thermoplastic such as LLDPE composites are composed of a thermoplastic polymer matrix reinforced with another polymer, fiber or material. The nature of the composite's matrix and reinforcing material distinguishes which processing method should be used. Traditional processing methods such as extrusion and injection molding can be utilized in the fabrication of a composite; but other processes like consolidation, prepregging, and joining are more innate with the special characteristics of a thermoplastic composite (Almeida et al., 2012).

Linear low density polyethylene (LLDPE) has interesting mechanical properties which provide good tensile properties, dimensional stability and high thermal and chemical resistance. Incorporation of thermoplastic starch (TPS) as disperse phase in LLDPE matrix is due to the high demand in green technology approach. Currently there are many intensive study on the biodegradable plastic based on the natural resources due to the many environmental downsides caused by conventional plastics such as LLDPE, starting from the production of plastics until the problem of waste disposal. Among the concerns for the environmental issues, blending synthetic polymer with a cheap natural biopolymer such as starch, provide new attention to manufacture biodegradability products. Blending polysaccharide with LLDPE polymer could also be the promising alternative to the commonly used conventional filler reinforce LLDPE

(Almeida et al., 2012). The combination of polysaccharide, i.e cellulose and starch with synthetic polymer to produce newer materials that are competitive with synthetic polymer reinforced with conventional filler such as glass fibre, glass bead, carbon black, silica, etc, is gaining attention over the last decade.

The advantages of natural filler from the renewable plant source over the conventional fillers are as follows: lightweight, low cost, abundantly available, ease for separation, acceptable mechanical strength and biodegradable. Environmental friendly materials have the potential to be the new materials in the future and could be the partial solution to the many environmental problems Most of the synthetic polymers are incompatible at molecular level with thermoplastic starch (TPS) and leads to poor interfacial adhesion strength. Due to strong intermolecular hydrogen bonding, thermoplastic starch tend to agglomerate and do not easily disperse in LLDPE matrix. These drawbacks cause the properties of the blends to reduce significantly with increasing thermoplastic starch content. In order to overcome incompatibility of these blends, there was a study by adding banana fiber that can be compensated the deterioration caused by the incorporation of TPS (Almeida et al., 2012).

The LLDPE mechanical properties of starch based blends are quite poor with increasing starch content. This is attributed to the poor interfacial adhesion due to the incompatibility of hydrophilic starch with hydrophobic synthetic polymer. Cellulose reinforced composites have shown interesting properties and generally, natural fiber has shown a growth of due to the economic and environmental advantages and the attractive specific properties. Therefore, applying natural fibers material such as *Typha Latifolia* is of great interests since it provides a possible way to produce composites that are mechanically strong at very low cost. Although polymer are abundantly available at low cost, the structure made up from the pure polymer based are not very strong enough to meet the market requirement (Almeida et al., 2012).

2.1.1 Implications of Polymer Composite

Natural based component have short coming such as the effect of weather conditions on natural based composite one of major problem also polymer composites absorb moisture in humid atmosphere and when exposed to environment. The effect of absorption of moisture leads to the degradation of fiber matrix interfacial region thus creating poor stress transfer efficiencies resulting in a reduction of mechanical and dimensional properties. One of the main concerns for the use of natural fiber reinforced composite materials is their susceptibility to weather conditions and the effect on physical mechanical, physical and thermal properties (Amal and Eman., 2013).

Natural fiber reduction of the mechanical properties is due to the poor bonding between the fiber and matrix. It is well known that natural fiber hydrophilic in nature, while plastic resin is hydrophobic. The incompatibility leads in poor interfacial bonding between them due to this the composite material can not be used for high impact application (Bogren et al., 2006).

The primary effect of the absorption is on the resin itself through hydrolysis, plasticization, saponification, and other mechanisms, which cause both reversible and irreversible changes in the polymer structure. In some cases, the moisture wicks along the fibermatrix interphase and has been shown to cause deleterious effects to the fiber-matrix bond, resulting in a loss of integrity at that level (Krupaa et al., 2001). Generally, the properties of the polymer composite material significantly improved by adding fibers to the polymer matrix since the fibers have high strength and stiffness values are higher than those matrix (Navin et al., 2012).

Several studies have been presented in application of natural fiber reinforced polymeric composites and its sensitivity to mechanical impact and thermal properties variation to moisture uptake can be reduced by the use of coupling agents or fiber surface treatments. Weather conditions diffusion in polymeric composites has shown to be governed by three different mechanisms. The first involves of diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and third due to the rearranging the fiber orientation and cause flaws at the interfaces between fibre and the matrix (George et al., 2008).

In order to improve materials usability, lightweight, high-strength and stiffness of composite materials have been identified as a key cross-cutting technology for reinventing energy efficient transportation, enabling efficient power generation, providing new mechanisms for storing and transporting reduced carbon fuels, and increasing renewable power production. Fiber reinforced polymer composites can be used in vehicles, industrial equipment, wind turbines, compressed gas storage, buildings and infrastructure, and many other applications Amal and Eman (2013).

In general, high fiber content is desirable for the purpose of achieving a high performance short fiber reinforced polymers composite. its often been noted that the presence of fibers or other reinforcement in polymer matrix composites pose strength and modulus (Navin et al., 2012). Thus, the impact of fiber content on properties of fiber reinforced composite is interesting and the interests of many researchers. The silk mat instead of hemp and polypropylene fibers in various parts of the mixed and hot pressed to make composite materials. The effects of flax fiber content and not isotropy assessed on the basis of the nature of the resulting voltage composite materials (Navin et al., 2012). Type of fiber and orientation play an important role in determines the tensile strength material. The fiber in the direction perpendicular, tend to decrease with increasing the fiber content for sample study in hemp (maximum reduction of 34% on 70% of hemp). Meanwhile, the tensile strength, the fibers in a parallel direction, showing different trends and the maximum value is found with increased fiber load. It was found that the tensile strength of composites with fibers in a direction perpendicular is 20-40% lower compared to composites with fibers in a parallel direction. Since the fibers put perpendicular to the direction of the load, they can not act as a load containing the elements in the composite matrix structure but becomes a potential defect that could cause a failure.

In the recent time quest for fibers is increasing and especially fiber extracted from banana varieties and adhesion between fiber and LLDPE is achieved via different routes through the interface region. Interface refers to the boundary between two phases, namely fiber and matrix. Bonding between fiber and matrix is accomplished through the interface with different bonding mechanisms. The fiber or filler interfacial adhesion plays an important role in determining the mechanical properties of a polymer composite. A better interfacial bond will impart composite improved properties such as inter laminar shear strength, fatigue and corrosion resistance (Tanaka Kazuo and Chujo Yoshiki,2013).

The matrix acts as a load transfer medium between fibers or fillers. Since the matrix is generally more ductile than fibers and fillers, it is the source of composite toughness. The matrix also serves to protect the fibers and fillers from environmental damage before, during and after composite processing. Polymer composite may be defined as materials made up of two or more components and consisting of two or more phases. Such materials must be heterogeneous at least on a microscopic scale. A polymer composite consists of fibers or fillers embedded in or bonded to a matrix with distinct interfaces between the two constituent phases. The matrix must keep fibers or fillers in a desired location or orientation, separating fillers and fibers from each other to avoid mutual abrasion during periodic straining of the composites (Almeida et al., 2012).

2.1.2 Polymer Composite Processing and Characterization

The compatibility of natural fibers composites depends on the interaction between the fibers and matrix which ultimately depends on the chemical structure of fibers (Awal et al., 2010). In the case of polymer blends containing crystalline polymer, the melting and crystallization temperature depression was observed by mixing with other polymers. The compatibility affects the percentage crystallinity, mechanical properties, thermal stabilities and other thermal related properties (Awal et al., 2010).

A significant literature was found on the thermal properties of natural fiber (NF), such as flour (like wood, wheat straw, etc.) composites (Torres and Aguirre, 2003; Awal et al., 2010; Ortega et al., 2010) used the differential scanning calorimetry (DSC) to study the thermal properties of banana fibers composites. Thermal decomposition behavior of various natural fibers including bamboo-fibers (BFs) was studied by using thermogravimetric (TG) analysis . Among the well-known natural fibers (jute, coir, straw, banana, etc.), bamboo has low density and high mechanical strength. The specific