PREPARATION AND CHARACTERIZATION OF LINEAR LOW DENSITY POLYETHYLENE LLDPE/THERMOPLASTIC STARCH (TPS)/BANANA FIBER COMPOSITES

by

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LIST OF ABBREVIATIONS

LLDPE	linear low density polyethylene
PE	Polyethylene
TPS	Thermoplastic starch
BF	Banana fiber
SEM	Scanning electron microscope
DSC	Differential scanning calorimetric
TGA	Thermogravimetric analysis

Penyediaan dan Pencirian Komposit Polietilena Berketumpatan Rendah Linear/ Kanji Thermoplastik/ Serabut pisang

ABSTRAK

Adunan polietilena linear berketumpatan rendah (LLDPE) dengan kanji termoplastik (TPS) terisi serabut pisang (BF) telah dikaji. Dua jenis adunan disediakan; matriks LLDPE/TPS dengan nisbah adunan yang berbeza, dan komposit LLDPE/TPS (80/20) yang terisi 5-30 wt% serabut pisang. Perubahan morfologi yang diperhatikan melalui mikroskop imbasan elektron (SEM) menunjukkan partikel-partikel TPS tersebar secara sekata di dalam matriks LLDPE. Dalam sistem lain, BF didapati tertanam di dalam fasa TPS, menunjukkan interaksi yang baik di antara fasa BF dan TPS. Pemerhatian ini sejajar dengan nilai modulus Young yang mana meningkat dengan kandungan BF. Peningkatan nilai modulus Young juga disebabkan oleh kesukaran pergerakan rantaian LLDPE/TPS dengan kehadiran BF. Selain itu, kesan kandungan TPS dan BF ke atas sifat-sifat terma matriks LLDPE juga dikaji. Pengukuran dari kalorimeter imbasan pembezaan (DSC) dan analisis termogravimetrik (TGA) membuktikan keberkesanan TPS dan BF dalam meningkatkan tahap degradasi adunan. Komposit LLDPE/TPS/BF menunjukkan kestabilan terma yang lebih baik berbanding adunan LLDPE/TPS, disebabkan oleh kesukaran pergerakan rantaian LLDPE. Kemasukkan BF ke dalam adunan LLDPE/TPS juga didapati menghalang pergerakan rantaian yang meningkatkan kestabilan terma dan membaiki kekuatan adunan.

Preparation and Characterization of Linear Low Density Polyethylene LLDPE/Thermoplastic Starch (TPS)/Banana Fiber Composites

ABSTRACT

The blending of linear low density polyethylene (LLDPE) with thermoplastic starch (TPS) and filled with banana fiber (BF) were investigated. Two types of systems were prepared; the LLDPE/TPS matrix with different blend ratio and (LLDPE/TP) (80/20) composites filled with 5 – 30 wt% of BF. Morphological changes using scanning electron microscope (SEM) were observed and its showed that TPS particles are homogenously dispersed in LLDPE matrix. On the other hand, BF was found to be well embedded in TPS phase, showing the good interaction between BF and TPS phases. This observation show an agreement with the Young's modulus value which is increased with the in cerement of BF contents. The increment in Young's modulus value was also attributed to the difficulties in LLDPE/TPS chains movement with the presence of BF. Besides that, the effect of TPS and BF contents on thermal characteristics of LLDPE matrix was also investigated. The measurements from differential scanning calorimetric (DSC) and thermo-gravimetric analysis (TGA), proved the effectiveness of TPS and BF in improving the blend degradation. The LLDPE/TPS/BF composites showed better thermal stability than the LLDPE/TPS blend, which is reflected to the LLDPE chains movement restriction. The incorporation of BF into the LLDPE/TPS blends was found to restricts the chains movement and resulting in more thermally stable and improving the blends toughness.

CHAPTER 1

INTRODUCTION

1.1 Overview

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 (Feng et al, 2008; Yuan et al, 2010). 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.

The matrix acts as a load transfer medium in the composites. Since the matrix is generally more ductile than fibers and fillers, it is the source of composite toughness (Reis et al, 2008; Saeoui et al, 2010). The matrix also serves to protect the fibers and fillers from environmental damage before, during and after composite processing.

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 (Reis et al, 2008; George and Carol, 2008).

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 (Feng et al, 2008; Yuan et al, 2010). Blending polysaccharide with LLDPE polymer could also be the promising alternative to the commonly used conventional filler reinforce LLDPE. The combination of polysaccharide, i.e cellulose and starch with synthetic polymer to produce biodegradable 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 (Shin et al, 2010; Brindha et al, 2012). 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 (Yuan et al, 2010, Sirisinha et al, 2010). Most of the synthetic polymers are incompatible at molecular level with TPS and leads to poor interfacial adhesion strength. Due to strong intermolecular hydrogen bonding, TPS tend to agglomerate and do not easily disperse in LLDPE matrix. These problems have made the properties of the blends to reduce significantly with increasing TPS content. In order to overcome incompatibility of these blends, the area of study was concentrated on adding banana fiber that can be compensated the deterioration caused by the incorporation of TPS. Therefore, this study performed novel preparation and characterization of linear low density polyethylene LLDPE/thermoplastic starch (TPS)/banana fiber composites for partial biodegradable composite production.

1.2 Biodegradable Materials

A biodegradable material has shown the ability to break down easily by biological means and disappear into the environment without any harm (Vroman and Tighzert, 2009). Putting biodegradable material to polymer blends will help to break up the polymer into small fragments when exposed to microorganisms (Vroman and Tighzert, 2009).

Cellulose and starch are example of many polymers found in nature. Cellulose is made of repeat units of the monomer glucose. This is the same glucose which body metabolizes in order to live, but can't digest it in the form of cellulose. Because cellulose is built out of a sugar monomer, it is called a polysaccharide (Yuan et al, 2010)

Starch is a linear polymer made up of repeating glucose groups linked by glucosidic linkages in the 1-4 carbon positions. The length of the starch chains will vary with plant source but in general the average length is between 500 and 2 000 glucose units. There are two major components in starch namely: amylose and amylopectin. The alpha linkage of amylose starch allows it to be flexible and digestible. Starch-based biodegradable plastics may have starch contents ranging from 10% to greater than 90%. Starch based polymers can be based on crops such as corn (maize), wheat or potatoes. Starch content needs to exceed 60% before significant material breakdown occurs. As the starch content is increased, the polymer composites become more biodegradable and leave less recalcitrant residues. Often, starch-based polymers are blended with high-performance polymers (e.g. aliphatic polyesters and polyvinyl alcohols) to achieve the necessary performance properties for different applications.

Biodegradation of starch based polymers is a result of enzymatic attack at the glucosidal linkages between the sugar groups leading to a reduction in chain length and the splitting off of sugar units (monosaccharide’s, disaccharides and oligosaccharides) that are readily utilized in biochemical pathways. At lower starch contents (less than 40%) the starch particles act as weak links in the plastic matrix and are sites for biological attack. This allows the polymer matrix to disintegrate into small fragments, but not for the entire polymer structure to actually bio-degradable.

There are several categories of biodegradable starch-based polymers including:

- Thermoplastic starch products;
- Starch synthetic aliphatic polyester blends;
- Starch PBS/PBSA polyester blends; and
- Starch PVOH Blends.

1.2.1 Blending of Polyethylene with Starch

The blending of polyethylene starch blends is possible to improve the blend properties and characteristics such as yield stress, modulus, impact strength, and biodegradability by choosing an appropriate combination of blends. For typical semi-biodegradable polymer blends, generally it is composed of the combination between polymer matrices, such as from thermoplastic and/or elastomer and another component as biodegradable agent (Sadiku et al, 2014).

Based on the prerequisite characteristics, common semi-biodegradable materials can be classified as bio-composites, where biodegradable agent act as a filler or secondary blends components when biodegradable agent exist in plasticized form. In this section, the detailed descriptions of blend’s component especially related to the polyethylene and starch is presented. Polymer blends have played significant role in the last few decades in providing high performance alternative to pure polymer. The term ‘polymer blends’ may be defined as a physical mixture of two polymers or two copolymers, giving rise to materials with a range of properties, which could not be delivered by any of the constituents. Polymer blending provides a simple and inexpensive process to combine properties of blend’s components and has the advantages of obtaining them in one product. In addition, the properties of blends can be adjusted by simply changing the blends composition (Margaria et al, 2008;Sadiku et al, 2014).

1.3 Problem Statement

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 will 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 (Shin et al, 2010).

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 in biodegradable material shows great interest since it provides a possible way to produce composites that are degradable at very low cost.

Although natural fibers are abundantly available at low cost, the composite made up from the natural fibers based are not very strong enough to meet the market requirement.

1.4 Objectives

(1) To identify the best mixing proportion between LLDPE and TPS with acceptable mechanical properties.

(2) To examine the effect of different banana fiber blends proportion on the mechanical and thermal properties of LLDPE/TPS blends.

1.5 Scope of Study

(1) Effort will be made to identity the mixing proportion of LLDPE and TPS for better improvement of mechanical, physical and optical properties of LLDPE / TPS / BF composites.

(2) The properties of different mixture proportion of the blend will be tested for surface morphology, mechanical properties, and thermal properties via scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) respesctively.

(3) Justification on optimum condition for the production of the best blend with capable of yielding good mechanical and physical properties will be conducted and be tested using scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetric (DSC).

1.6 Thesis Organization

The thesis background which consists of problem statements, objectives and research scope are presented in Chapter 1. Chapter 2 explored the literature on the linear low density polyethylene (LLDPE), thermoplastic starch (TPS) and banana fiber composites. These included some theoretical aspects of of molecular structures, beginning with the overviews and then examining some of the significant factors that combine to determine the ultimate various mixing proportions. Chapter 3 discusses the methods and efforts used in undertaking the blends preparation, measurement and characterizations approaches. Chapter 4 discusses the results of characterization of the composites and present the results of numerous measurements intended to help in understanding the properties of materials blends. Chapter 5 offers conclusions and recommendations based on the work presented in the preceding chapters.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents the literature reviewed on the current work related to starch and cellulose based polymer blends. The current research is aimed at producing new degradable materials properties which is comparable to their conventional plastic counterparts and coupled with the added advantage of biodegradability.

2.2 Polymer Blends

Polymer blends have played significant role in the last few decades in providing high performance alternative to pure polymer. The term 'polymer blends' may be defined as a physical mixture of two polymers or two copolymers, giving rise to materials with a range of properties, which could not be delivered by any of the constituents (Reis et al, 2008). Polymer blending provides a simple and inexpensive process to combine properties of blend's components and has the advantages of obtaining them in one product. In addition, the properties of blends can be adjusted by simply changing the blends composition (Rohaniet al, 2010).

The development of polymer blends, composites and laminates is a very active area of science and technology; of great economic importance not only for the plastics industry but also for many other industries where the use of such products is becoming increasingly more common (Sadiku et al, 2014). Most pairs of polymers are immiscible with each other. Even worse, in fact that they also have less compatibility and would be required in order to obtain the desired level of properties and performance from their blends, compatibilizers are often used as additives to improve the compatibility of immiscible polymers and thus improve the morphology and resulting properties of the blend. It is often challenging to disperse fillers effectively in the matrix polymer of a composite, or to adhere layers of polymers to each other or to other substrates (such as glass or metals) in laminates (Gad et al, 2010). Continued progress in the development of compatibilization technologies is, hence, crucial in enabling the polymer industry to reap the full benefits of such approaches to obtaining materials with optimum performance and cost characteristics.

The improvement of polymer blends and composites qualities is the great economic importance for the plastics industry and for other industries the use of such products is becoming increasingly. Advanced polymer modification techniques have grown in importance during the last two decades as the "point of diminishing returns" has been approached in improving the performance price balance by altering just the chemical structures of polymers.

The most important polymer modification techniques are blending dissimilar polymers, preparing composites where a matrix polymer is modified by fillers. The objective is to seek synergies between the components so that one can attain better performance without increasing cost or maintain acceptable performance at lower cost.

Polymeric are polymers that can be used (normally in small percentages) as additives to help assemble dissimilar components into polymer blends, composites and laminates with improved properties. These more attractive properties generally result from phase separation on a finer scale (microscale or even better nanoscale, instead of macroscale) along with stronger interconnections between phase domains. Impact modification (toughening) is one major benefit that can often be attained by using polymeric compatibilizers. It can be inferred from the anticipated continued growth of markets for polymer-based heterophasic products that polymeric compatibilization technologies will also continue to grow in importance (Feng et al, 2008; Derrien et al, 2009).

2.2.1 Linear Low Density Polyethylene (LLDPE)

Polyolefin are polymer built from high molecular weight hydrocarbons. Polyolefins include linear low density polyethylene, low density polyethylene, high density polyethylene, polypropylene copolymer, polypropylene, and polymethyl pentene. These polymers are the only plastics that have a lower specific gravity than water. When ethylene is polymerized the result is relatively straight polymer chains. From the main chain they can branch out. There are different kinds of polyethylene from the varying degree of branching in their molecular structure. The figure 2.1 to 2.3 showed the brief descriptions on how the polyethylene differs from each other. Low density polyethylene (LDPE) has the most excessive branching. This causes the low density to have a less compact molecular structure which is what makes it less dense. It has a density of 0.910-0.925 g/cm^3. LLDPE based materials are the ideal choice for applications which require significant material flexibility, in addition to strength and durability, combined with outstanding resistance to low temperatures and ultraviolet exposure.

Figure 2.1: Illustrative structure representative of LDPE (Durmus et al, 2007).

HDPE (high density polyethylene) has minimal branching of its' polymer chains and give rigid properties and less permeable when compared to LDPE. It has a density of 0.941-0.965 g/cm^3 as shown in Table 2.1.

Figure 2.2: Illustrative structure representative of HDPE (Durmus et al, 2007).

LLDPE (linear low density polyethylene) has a significant numbers of short branches. Because it has shorter and more branches its' chains are able to slide against each other upon elongation without becoming entangled, like LPDE. This gives LLDPE higher tensile strength and higher impact and puncture resistance than the LDPE. It has a density of 0.91-0.94 g/cm^3.

Figure 2.3: Illustrative the structure representative of LLDPE (Durmus et al, 2007).

Table 2.1: The mechanical and thermal properties of the LLDPE (Feng et al, 2008).

LLDPE Material Properties	Properties	Units
Melt Index	8-1.2	g/10min
Density	0.93	g/cm3
Mold Shrinkage	0.020 - 0.022	in/in
Tensile Strength	1900-4000	psi
Tensile Modulus	25-.5 Gpa	%
Ultimate Tensile Elongation	850	psi
Elastic Modulus in flex	160000	Shore D
Hardness	D48-D56	kJ/m^2
IZOD notched or un-notched	1.86	
Deflection Temperature	45	°C
Dielectric Strength	2500	V/mil
UL Listing	HB	
Thermal Conductivity	-2.55	BTU*in/hr*ft2*ºF
Heat Capacity	0.52	BTU/lb*ºF
Coefficient of Friction	0.55	%
Crystallinity	N/A	
Conditions Favoring Crystallinity	133	°C
Crystalline Melt Temp	120-160	°C
Glass Transition Temp	119	°C
Service Temp range	160-232	°C
Degradation Temp	250	°C
Viscosity at TM	-	

2.3 Starch

Starch is the second most abundant natural polymer, after cellulose. It has a low cost and can be easily extracted from a large variety of plants. Starch is fully biodegradable, like all natural polymers, can be used in many applications for the materials or filler. Starch-containing plastics can be used to make capsules, coatings, garbage bags, flower-pots and many disposable objects. After use, such objects can be disposed of by biodegradation. Both starch and cellulose consist of glucose molecules linked together to form long chains. Starch is the main form of energy storage of plants; cellulose is the main component of wood. Starch is extracted in form of granules that have different shape and size depending on its origin.

Though it is highly hydrophilic, starch is not soluble in water. Differently from cellulose, starch can be found in industrial applications as a thermoplastic polymer. When processed with proper treatments it turns to a true thermoplastic that can be further processed with traditional techniques. The main drawback of starch is its high sensitivity to moisture that renders it not suitable for many applications. Combination of starch with traditional, synthetic plastics allowed overcoming this problem, leading to new materials with properties similar to the main plastics that fulfil the market demand. Such "mixed" plastics may contain as much as 50% of starch.

It can easily be processed and during processing, amylose and amylopectin degradation occurs and this phenomenon is obviously dependent on the thermal and mechanical energy brought to the system. Numerous studies were conducted to determine the degradation mechanism and to understand the contribution of each parameter. Since starch is a hydrophilic material, water is the best plasticizer.

Nevertheless, the water content and thus the plasticized starch properties are strongly dependent on the storage conditions (temperature and atmosphere relative humidity). This drawback is partially solved with the use of less volatile plasticizers, which present lower plasticization efficiency. These compounds bearing hydroxyl groups, can interact with the starch chains through hydrogen bonds. Glycerol is the most common plasticizer.

2.3.1 Chemical Structure of Starch

Starch is a very important and widely distributed natural product, occurring in the leaves of green plants, seeds, fruits, stems, roots, and tubers. It serves as the chemical storage form of the energy of the sun and is the primary source of energy for the organisms on the earth. Starch is composed of two kinds of polysaccharides, amylose and amylopectin, exclusively composed of d-glucose residues with α-(1→4) linkages in a linear amylose and α-(1→4) linkages and ~5% α-(1→6) branch linkages in amylopectin, both combined in a water-insoluble granule that is partially crystalline and whose size, shape, and morphology are dependent on its biological source. Chemically, starch is composed of two different molecules, amylose and amylopectin. In amylose, the glucose molecules are linked in a fashion; however, the tetrahedral chemistry of carbon (and the bond angles that result from this chemistry) gives amylose an overall spiral shape as shown Figure 2.4

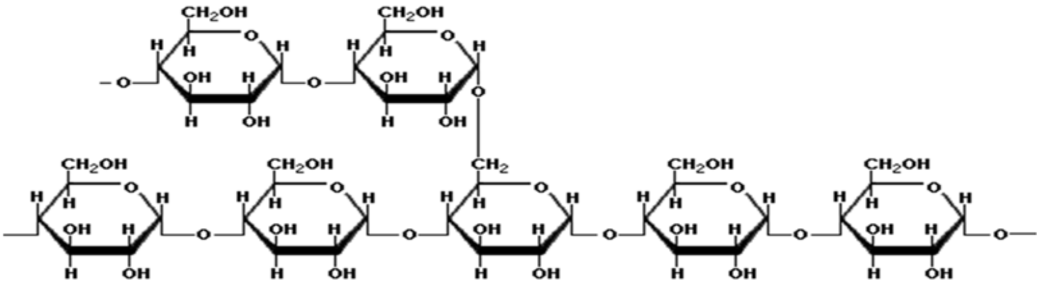

Figure 2.4: Structure of a starch (amylopectin) (Serge Perez and Eric Bertoft ,2010).

2.3.2 Thermoplastic Starch (TPS)

Thermoplastic starch (TPS) have a starch (amylose) content greater than 70% and are based on gelatinized vegetable starch, and with the use of specific plasticizing solvents, can produce thermoplastic materials with good performance properties and inherent biodegradability. Starch is typically plasticized, de-structured and/or blended with other materials to form useful mechanical properties. Importantly, such TPS compounds can be processed on existing plastics fabrication equipment. High starch content plastics are highly hydrophilic and readily disintegrate on contact with water. This can be overcome through blending, as the starch has free hydroxyl groups (OH) which readily undergo a number of reactions such as acetylation, esterification and etherification (Saeoui et al, 2010).

Moreover, thermoplastic starch (TPS) properties can be improved significantly by blending with other polymers, fillers, and fibers. Both natural and synthetic polymers have been used, including cellulose, zein (a protein from corn), natural rubber, polyvinyl alcohol, acrylate copolymers, polyethylene and ethylene copolymers, polyesters, and polyurethanes. Blending is usually accomplished by twin-screw extrusion at elevated temperature. Blends of TPS with other biodegradable polymers, such as polyvinyl alcohol or aliphatic polyesters like polylactic acid, polycaprolactone and poly(3-hydroxybutyrate) are fully biodegradable. For TPS blends with non-biodegradable polymers, it is likely that only the TPS component will biodegrade in a meaningful timeframe. Reinforced, 100% renewable TPS blends can be obtained by including natural fibers, such as wood pulp, hemp and other plant fibers.

2.4 Cellulose

Cellulose is the essential component of all plant fibers. Cellulose is a linear condensation polymer consisting of glucose units jointed together by β-1,4- glycosidic bonds. The formula of cellulose is shown in Figure 2.5. Natural cellulose fibers from different bio renewable resources have become attraction of research community all around the globe owing to their unique intrinsic properties such as biodegradability, easy availability, environmental friendliness, flexibility, easy processing and impressive physico-mechanical properties. Natural cellulose fibers based materials are finding their applications in a number of fields ranging from automotive to biomedical. Natural cellulose fibers have been frequently used as the reinforcement component in polymers to add the specific properties in the final product.

A variety of cellulose fibers based polymer composite materials have been developed using various methods. Seeing the immense advantages of cellulose fibers, the processing of biorenewable natural cellulose fibers; chemical functionalization of cellulose fibers; synthesis of polymer resins; different strategies to prepare cellulose based green polymer composites, and diverse applications of natural cellulose fibers/polymer composite materials are the current focus of research.

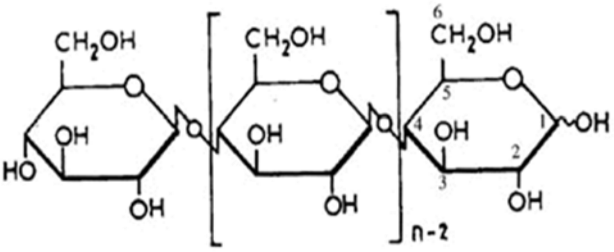

Figure 2.5: Chemical structure of cellulose (Serge Perez and Eric Bertoft, 2010).

The molecular structure of cellulose is responsible for its supra-molecular which determines many of its chemical and physical properties. The mechanical properties of natural fibers depend on its cellulose type and spiral angle, because each type of cellulose has its own cell geometry and geometrical conditions and can determine the mechanical properties. Solid cellulose forms a microcrystalline structure with regions of high order i.e. crystalline regions. Generally, all natural occurring cellulose crystallizes in monoclinic structure.

2.4.1 Physical Structure of Cellulose Fibers

A single fiber of all plant based natural fibers such as banana trunk consists of several cells. These cells are formed out of crystalline micro fibrils based on cellulose, which are connected to a complete layer, by amorphous lignin and hemi cellulose. This structure is a good example of a composite with lignin hemi cellulose matrix and cellulose fiber reinforcement. Strength is supplied by highly crystalline cellulose whereas ductility is supplied by amorphous lignin and other components. Structure of cellulose component, cellulose –lignin/hemi cellulose layers in one primary and three secondary cell walls stick together in a multiple layer composite. These cell walls differ in composition and in the orientation (spiral angle) of the cellulose micro fibers. The spiral angle of the fibrils and the content of cellulose determine mechanical properties of cellulose based natural fibers.

Due to the relatively high cost of synthetic fibers and health concern, it becomes necessary to use natural based fiber as a viable alternative banana fiber (BF). Banana fiber is better than other organic fiber in terms of spin ability and tensile strength. It is blended with other fiber like cotton making it very suitable for making fabric and or polymer composite. It is used for making yarn, fabric and garments. It can be blended with other fibers. In the recent time quest for fibers is increasing and especially fiber extracted from banana varieties and (Saeoui et al, 2010) studied extraction of fiber from banana scoured with 2% NaOH solution at 100ºC for 45min and analyzed for their physico-chemical and mechanical properties. They found out that, the moisture regain, cellulose content, the modulus and tenacity of the fibers of all varieties were increased after scouring process. They conclude that, scouring with 2% NaOH of fibers of banana varieties increases the quality of fiber in terms of their physico-chemical and mechanical properties.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.

2.5 Polyethylene/Starch Blends

There are many methods use for this purpose however; currently two major methods have been developed to incorporate starch into commercial polymers. One is based on using the granular starch as filler and the other is the use of gelatinized starch as one part of the polymer blends. The high viscosity and poor flow properties of starch present the difficulties of processing granular starch based materials. Due to the processing difficulties and significant loss in tensile strength, blending granular starch with other polymers is limited to starch content of 40% or less. However, tensile strength and flow properties of starch based blends can be significantly increased by converting native starch into thermoplastic form.

This structural convention of starch into thermoplastic is well known as a plasticization process. The transform material is normally known by the name thermoplastic starch (TPS). The well-accepted plasticization refers to the process of destruction of the crystalline structure of starch granules, which is an irreversible process and that includes the granular swelling, molecular solubilisation and starch has the properties to flow like synthetic polymers. Starch is a natural polymer synthesized by green plants as energy source. In comparison with low-cost synthetic polymers, starch is inexpensive, abundant and renewableraw material for the development of polymeric sustainable materials. It has be used in its native granular form as rigid filler or transformed in a thermoplastic material for melt blending with synthetic or natural polymers.

Polymers filled with dry starch granules behave as typical composite materials where modulus increases and ductility decreases due to the stiffening effect of the starch granules. An important disadvantage showed by polymeric composites filled with granular starch is the low starch content that can be added, especially for application where high ductility is required . In contrast to the ordered structure of starch molecules in granular starch, thermoplastic starch (TPS) is an amorphous material that can flow and be deformed as any synthetic polymer. Crystalline of starch granules is destroyed by the application of heat and shear in the presence of moisture during the gelatinization process.

The addition of a good plasticizer, such as glycerol, allows TPS to be extruded at the processing temperatures of most commodity polymers . Mechanical performance of TPS material blended with synthetic polymers depends on a series of parameters including blend morphology (particle size and shape, and particle dispersion and distribution), interfacial adhesion and the intrinsic characteristics of TPS. It has been reported that melt blending of TPS with synthetic polymer is an excellent alternative for the development of sustainable and more environmentally friendly product.

Additionally, starch is one of the most abundant polymers in the world. Starch is found in a wide variety of naturally grown products, including rice, maize (corn), potato, tapioca and beans. Starch is made up of a repeated glucose chain. The gelatinization of starch occurs when the starch granules swell and cross-link. In the presence of excess water, a three dimensional matrix of swollen gelatinized starch granules forms, increasing the stiffness of the starch,this thickening activity allows starch to be used as a resin.

Research using starch as a resin for “green” composites is relatively new, and due to its worldwide abundance and biodegradability, it was used in this study. Starches have been studied in polymer blends, but only as an additive to other polymer. (George et al, 2008; Chand et al, 2012)studied a polymer blend of low density polyethylene (LDPE) and tapioca starch. It was found the addition of tapioca starch to the LDPE martix improved the mechanical properties of the blends, as compared to LDPE alone . However, unlike starch, LDPE is not biodegradable, environmentally friendly, sustainable or available in abundance. In this study, starch is examined as the main ingredient of the blends (Ning, et al, 2007). Additionally, it is used with other sustainable ingredients in order to keep both the blends and the composite “green”.

2.6 Polyethylene/Cellulose Composite

The use of polysaccharide-like cellulose as natural filler in various polymer composite systems has been widely investigated by many researchers. This is due to the fact that the cellulose is one of the most abundant polymers on the earth, which is also low-cost, non-toxic, renewable, environmentally friendly and biodegradable. The utilization of cellulose woven as filler in polymer bio-composites is very promising due to its strength, stiffness and the structural stability of the products. Besides that, the preparation of polyethylene PE cellulose woven bio-composites may also possibly be used in the production of diverse products with biocompatible and biodegradable properties. Nevertheless, the compatibility and adhesion between the natural fillers and the PE in the bio-composite systems is very low, thus resulting in reductions in their performance, particularly tensile properties and other correlated characteristics of the final natural filler-reinforced composite products.

Composites from polyethylene and cellulose are perceived as a viable alternative over other polymers in various applications such as, biomedicine, packaging and construction etc. This interest arises from the remarkable mechanical properties by cellulose filler based polymers. Some experimental aspects regarding the preparation and the characterization of polyethylene composites with cellulose filler have carried out by many researchers (Pielesz et al, 2010). Morphological changes of polyethylene matrix when cellulose is added filler are pointed out by electronic microscopy, by mechanical and dielectric characterization. Polymer composites from polyethylene and cellulose filler show improved mechanical and dielectric properties compared to polyethylene and traditional other composites. Polymer composites constitute a broad group of materials, composed of the macromolecular matrix and various fillers. Currently the filler market for plastic composites is dominated by calcium carbonate (40%) and glass fiber (31%) and some other inorganic filler such as talc, mica and clay. Although the conventional fillers offer property changes in the composites, their high density is not beneficial to fuel savings in automotive applications (Pielesz et al, 2010).

Polymer composites with cellulose fillers are growing rapidly, mainly in the construction and automotive industry.

2.7 Incorporation of Banana Fiber in the Polyethylene Matrix Blends

Many researchers has claimed that blending polyethylene/TPS/cellulose fibre could also be the promising alternative to the commonly used conventional filler reinforce composite polymer. The combination of polysaccharide, i.e cellulose and starch with synthetic polymer to produce a new material 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. 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.

Accordingly, in the starch based polymer blend, the overall properties and characteristics depend upon the dispersion of the dispersed size. Since the mixing of starch with secondary polymer is limited by the agglomeration of starch particle at higher concentration, most of the previous works have used starch as a dispersed phase in which the concentration is in the range of 5% - 30% (Serge Perez and Eric Bertoft, 2010).

The incorporation of banana fiber in thermoset plastics was reported by (Joshi et al, 2004), their showed in their investigation of banana fiber with polyester composites and obtained the specific modulus of the composites is 2.39 which are of the same order as that of glass fiber plastics. Further the scanning electron microscope study of banana fiber cotton fabric shows the specific modulus of the composite are also the same order of glass fiber reinforced plastic (Joshi et al, 2004). It was suggested by them, that the use of banana fiber reduces the water absorption and steam absorption to a great extent along with increase in mechanical properties like Young's modulus, hardness, and impact strength.

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 (Torres and Aguirre, 2003; Awal et al, 2010).

A significant literature was found on the thermal study of natural fiber (NF) and 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 tensile strength and specific gravity of BF are considerably less than those of glass fibers. However, cost considerations make bamboo an attractive fiber for reinforcement (Torres and Aguirre, 2003; Awal et al, 2010).

Ortega and co- workers, 2010 explored the compression molding technique (CMT) and roller mill technique (RMT) in combination with the alkaline treatment for extracting the BF. Okubo et al. (Awal et al, 2010). used mechanically rubbing to reduce diameter 10–30 lm after steam explosion technique for the extraction of BF as reinforcement for polypropylene (PP). These techniques give fiber bundles which create a problem in dispersion.

Most of the studies made on natural fiber composites reveal that their mechanical properties are strongly influenced by a number of parameters such as volume fraction of the fibers, fiber length, fiber aspect ratio, fiber-matrix adhesion, fiber orientation and stress transfer at the interface. Therefore, both the matrix and fiber properties are important in improving mechanical properties of the composites (Awal et al, 2010). A number of investigations have been made on various natural fibers such as kenaf, hemp, flax, bamboo and jute to study the effect of these fibers on the mechanical properties of composite materials.

CHAPTER 3

METHODOLOGY

3.1 Materials

Linear low density polyethylene (LLDPE) granulates with density 0.92 g/cm^3 was supplied by Titan Chemicals, Malaysia. Tapioca starch used was a food grade and obtained from Thye Huat Chan Sdn Bhd., Malaysia. Reagent grade glycerol was obtained from Merck, Darmstadt, Germany and used as received. The flow chart of the study was in the Figure 3.1

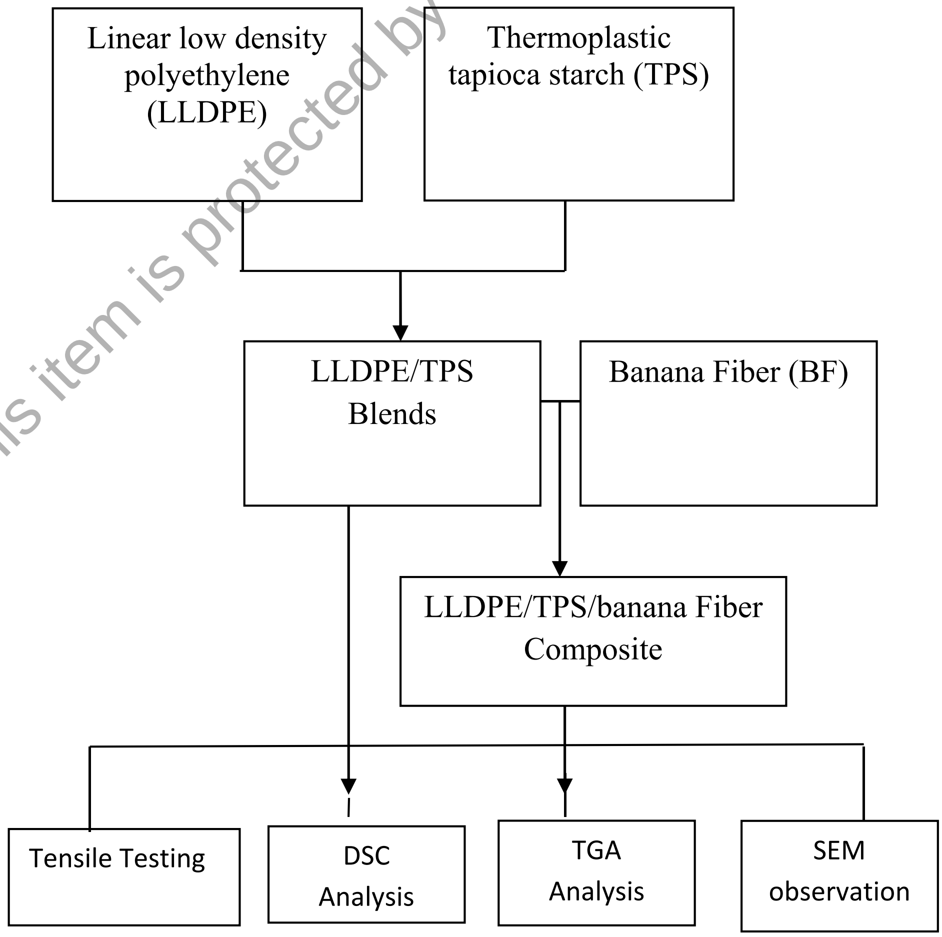

Figure 3.1: The flow chart of LLDPE/ TPS/BF composites preparation

3.2 Preparation of Thermoplastic Tapioca Starch (TPS)

Tapioca starch was dried at 80 °C in vacuum oven for 24 hours. Tapioca starch was first pre-mixed with 35wt% of glycerol using high speed mixer (3000 rpm, 2 min) until a homogenous mixture was obtained. Then, the mixture was stored overnight in a desiccator. Later the mixture was processed using heated two-roll mill at the temperature of 150 °C and the mixing time was 10 min.

3.3 Preparations LLDPE/TPS Blends

The blends will be conducted by melt blending of LLDPE/TPS in a suitable mixer equipped with roller rotors that will promote homogenous blend. The mixing was carried out at a temperature of 150 ^{0}C and rotor speed was fixed between 55-65rpm with various mixing ratio as shown in Table 3.1. The LLDPE will first be kept into the mixing chamber for 3-5 minutes and followed by TPS and the process continued until the desired blend is obtained.

Table 3.1: The mixing ratio of LLDPE/TPS blends

Sample	Ratio	LLDPE(g)	TPS (g)
1	100:0	40	-
2	90:10	36	4
3	80:20	32	8
4	70:30	28	12
5	60:40	24	16

3.4 Preparations of LLDPE/TPS/BF Composites

The blends were prepared by melt blending LLDPE/TPS/BF in a HaakeRheomix 600 mixer equipped with roller rotors. The mixing was carried out at temperature 150°C and rotor speed was fixed at 55rpm with the ratio presented in table 3.2. The LLDPE was first charged into the mixing chamber for 3 min and followed by TPS. Then, the mixing time was continued for 4 minutes before mixed with banana fiber and the process continued until plateau torque was reached. The whole process proceeded for 12 min. The blend was converted into 1mm sheet using a hydraulic hot press Gotech Testing Machine. The hot press procedures involved by preheating at 150°C for 6 min and followed by 2 min compressing at the same temperature, subsequent cooling under pressure for 4 min (Figure 3.1).

Table 3.2: The mixing ratio of LLDPE/TPS/BF composite.

Sample	LLDPE/TPS (80:20)	Banana fiber
1	100	0
2	95	5
3	90	10
4	80	20
5	70	30

3.5 Testing

3.5.1 Differential Scanning Calorimetry (DSC)

Thermal analysis of LLDPE/TPS blends and LDPE/TPS/BF composites were performed using a Mettler Toledo Differential Scanning Calorimetry TS0800GCL under nitrogenatmosphere at scan rate 10°C/min. The samples were heated from ambient temperature to 190°C and held at this temperature for 3 minutes to eliminate thermal history and destroy the polyethylene nuclei. Then, samples were slowly cooled at 10°C/min to room temperature before the crystallized samples were subsequently heated to 230°C at the same heating rate. The melting temperature (T_m) and the heat of fusion (ΔH_{exp}) were determined from the endothermic peak integration during the second heating.

3.5.2 Thermogravimetric Analyses (TGA)

The thermogravimetric analyses of the blends were operated using a Perkin Elmer Pyris 6 machine. Samples were tested at heating rate 10°C/min from ambient temperature to 600°C. Two types of samples were studied: LLDPE/TPS blends and LLDPE//TPS/banana fiber composites. The weight loss was calculated from the initial and final weight of the thermograms obtained as follows;

$$\text{Weight loss (\%)} = \frac{\text{Initial weight - final weight}}{\text{Initial weight}} \times 100\%$$

3.5.3 Tensile Testing

Measurements of the tensile properties were performed by using an Instron Universal Testing Machine (model 3366), with crosshead speed 50 mm/min. Dumbbell sample (1mm thick) with 50 mm gauge length were tested according to ASTM D 638. The mean value, out of five samples was reported with standard deviation to show the error range.

3.5.4 Scanning Electron Microscopy (SEM)

Fracture surface of the samples were performed with a Leo Supra – 3SVP Field Emission Scanning Electron Microscopy at an acceleration rate of 20kV. The fracture surfaces of the specimen were mounted on aluminum stubs and sputter coated with thin layer of gold to avoid electrostatic charge during examination.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mechanical Properties and Surfaces Morphology of LLDPE/TPS Blends

Measurement of the tensile properties of polymer blends is vital in order to understand the mixture integrity in term of acceptable mechanical strength and the homogeneity of final blends. In this system TPS plays as a function of biodegradable agent in LLDPE matrix. The blends were varied from 100 % of LLDPE to a ratio of LLDPE/TPS 60/40 in order to observe the mechanical behaviour (Figure 4.1 – 4.3) of the blends with incorporation of TPS. At low TPS contents, TPS phase existed as a dispersed phase, and thus the deformation behavior of the blends depends on the LLDPE phase. Up to 20 % of TPS contents, the tensile strength of the blends is identical to the virgin LLDPE value. As increasing TPS contents, TPS phase changed from the small size dispersed phase into agglomerate TPS phase, and thus LLDPE plastic response decreased as indicated by decrease in tensile strength and Young's modulus values . At higher TPS loading tensile strength shows marked decrease and therefore, LLDPE/TPS with a blend ratio of 80/20 was chosen for the further study. The mechanical properties of the composite based exhibit a great difference before and addition of banana fiber, this claim was also reported by (Maleque et al, 2006). The modulus of the pure composite also showed significant improvement.

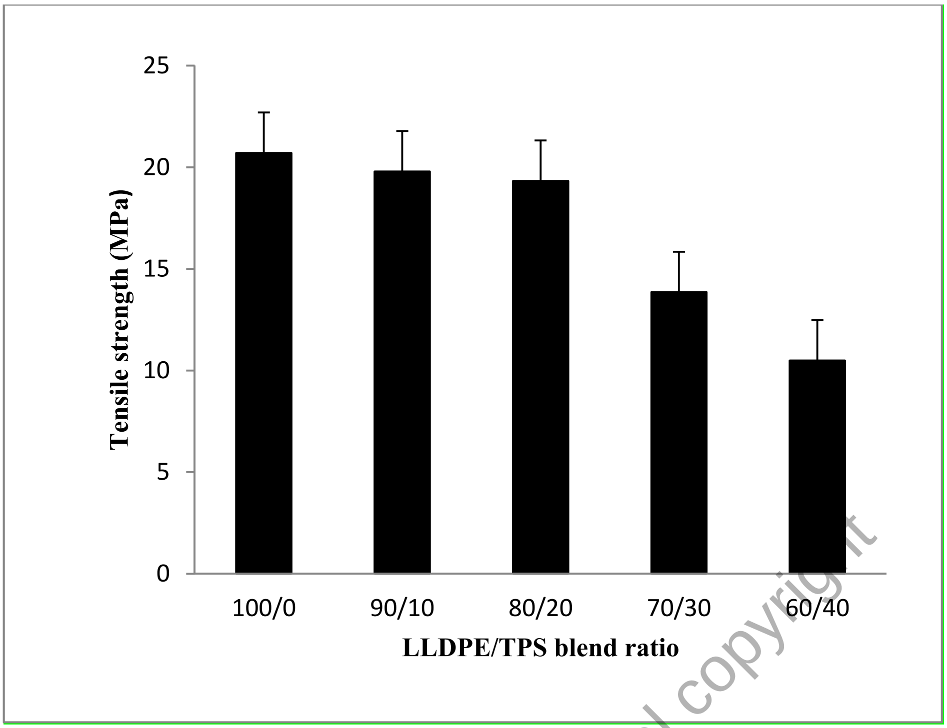

Figure 4.1: Variation of tensile strength in LLDPE/TPS blends at different blend ratio.

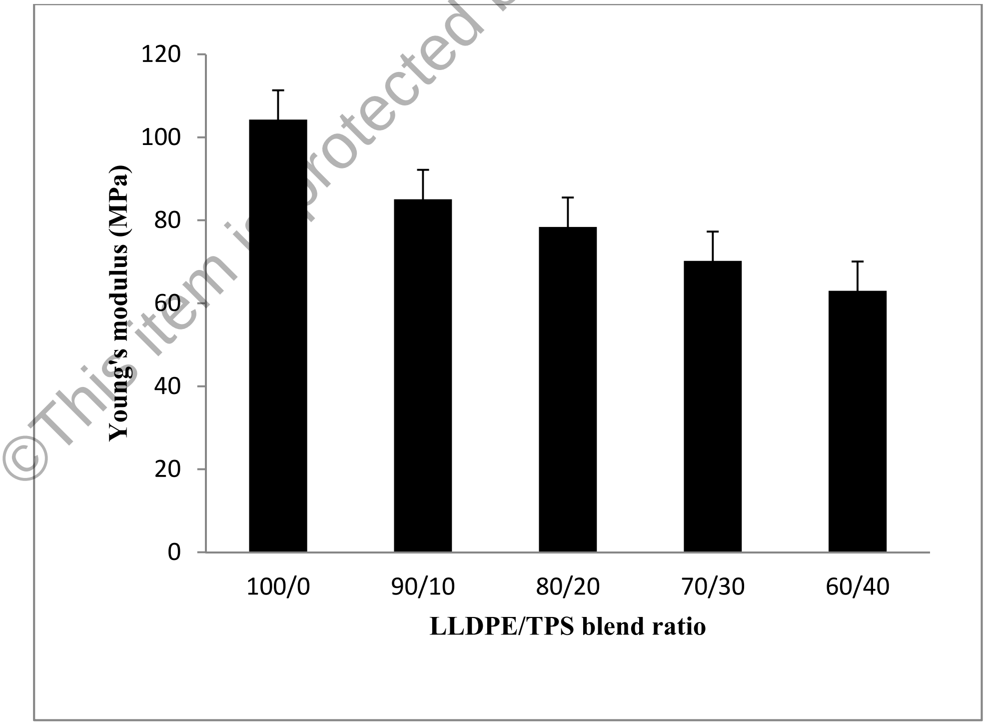

Figure 4.2: Variation of Young's modulus in LLDPE/TPS blends at different blend ratio.

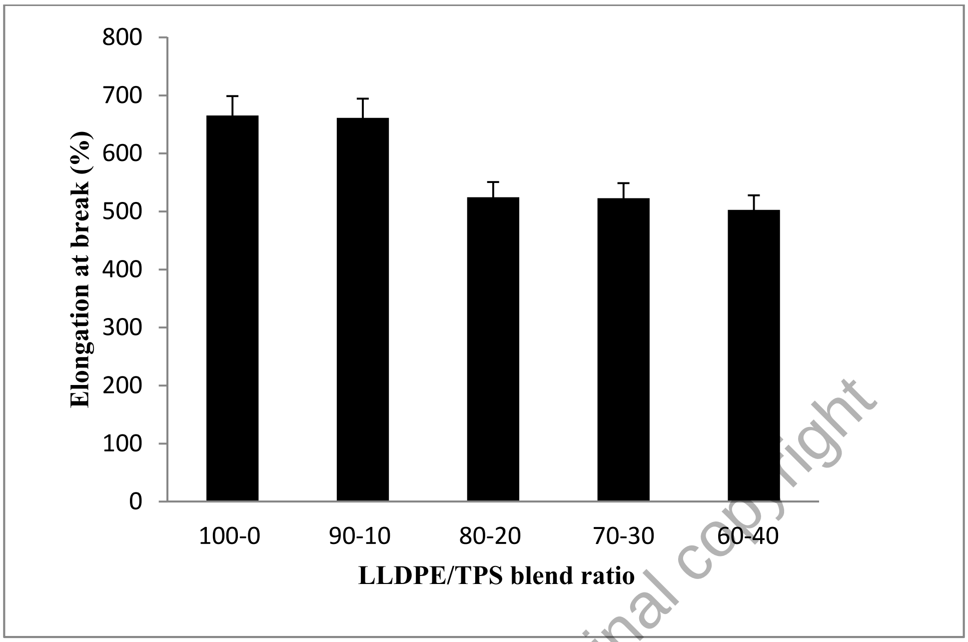

Figure 4.3: (c) Variation of elongation at break in LLDPE/TPS blends at different blend ratio.

4.2 SEM Micrographs for LLDPE/TPS Blends

SEM micrographs of LLDPE/TPS blends at different blend ratio were given in Figure 4 .4 to 4.7. Morphological surface disclose that the TPS was well distributed in LLDPE phase with the droplet dispersion size ranging from 20 µm to 30 µm. The surfaces of TPS were quite smooth and there was no matrix resin adhering to the TPS which indicated the weak interfacial interaction between TPS and LLDPE phases. However, as can be seen in Figure 4.4 to 4.7, the blends with higher TPS contents showed rougher surfaces when compared to the LLDPE/TPS (100/0) and (90/10) blends (Figure 4.4 and 4.5). This observation can be correlated with the failure resistance when the force was applied to the blends.

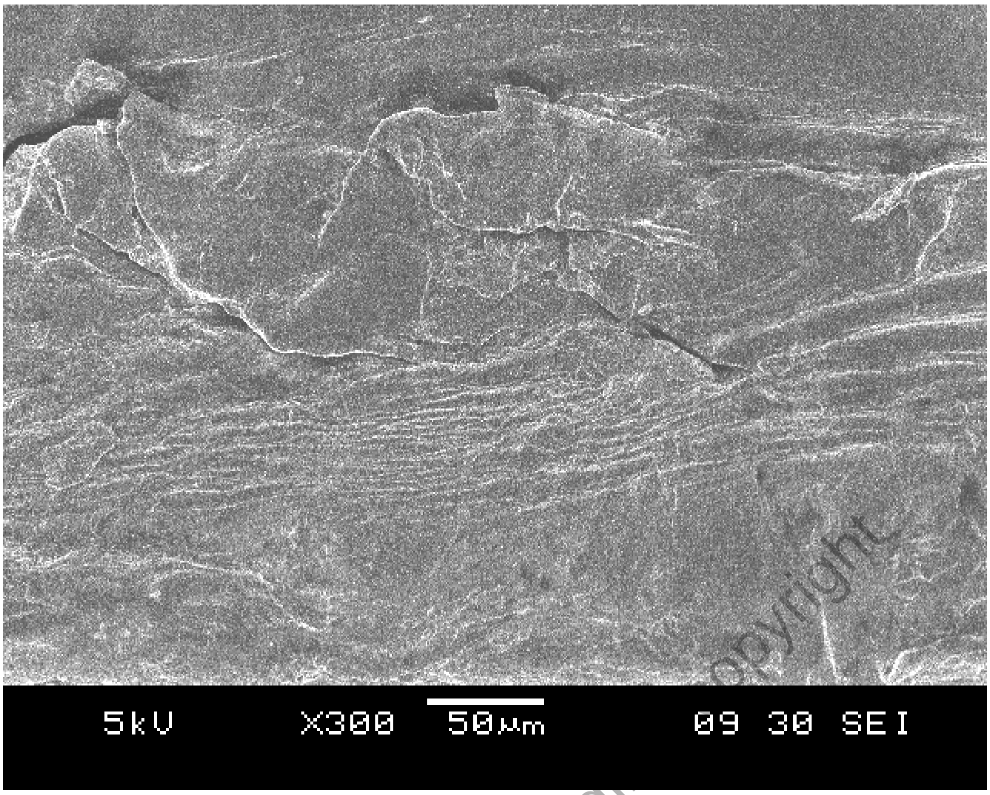

Figure 4.4: SEM micrograph of LLDPE/TPS (100/0) at 300 X magnification.

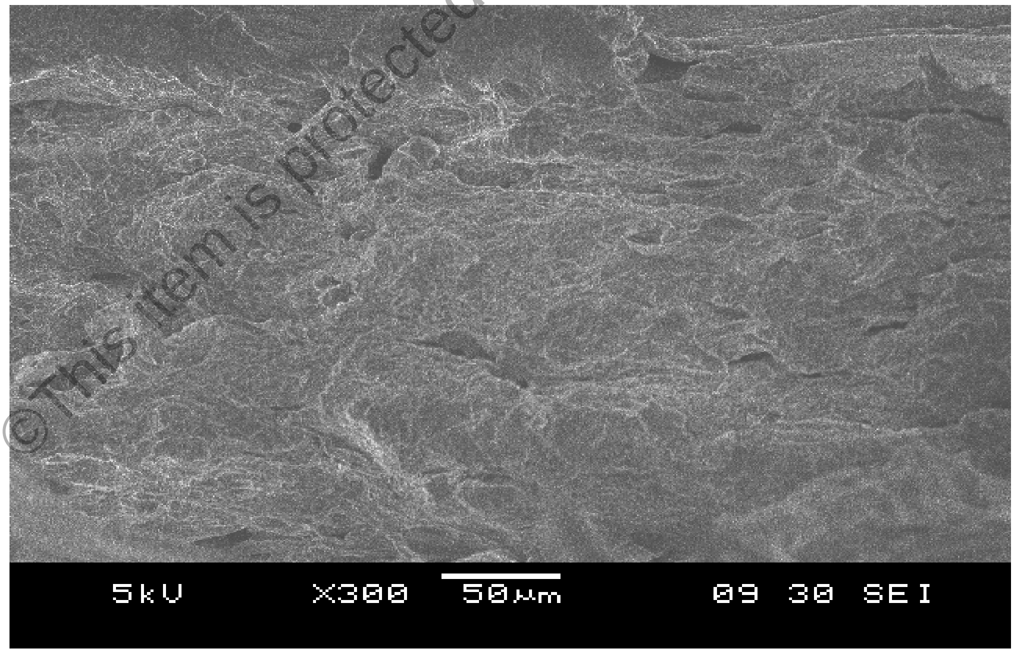

Figure 4.5: SEM micrograph of LLDPE/TPS (90/10) at 300 X magnification.

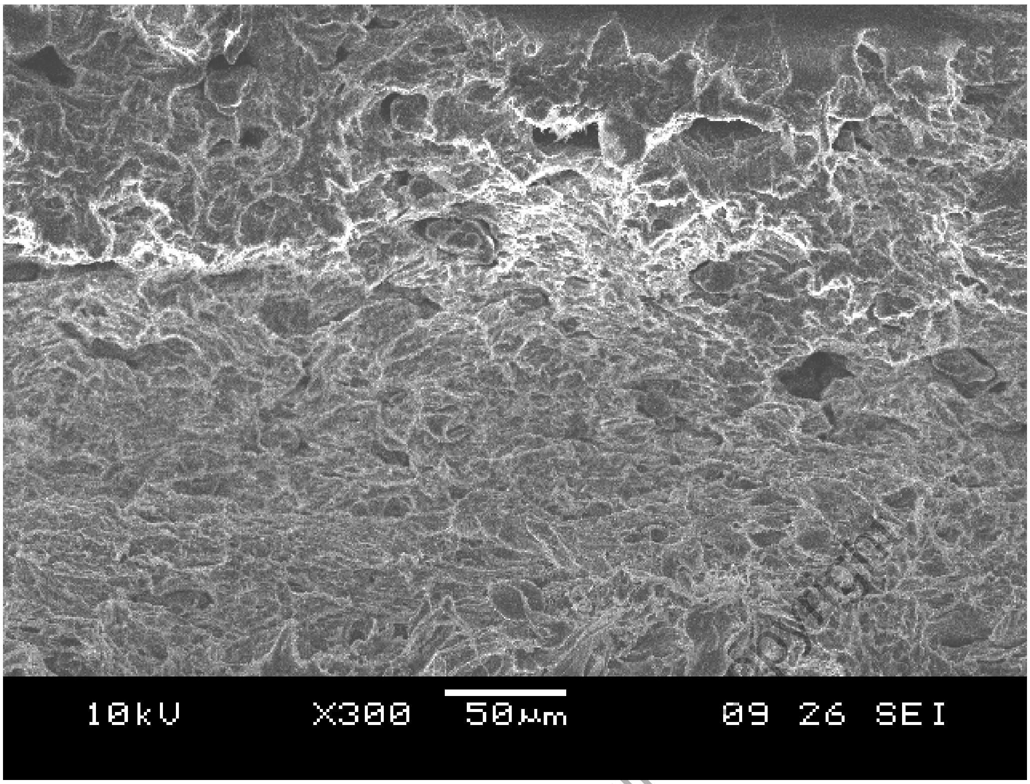

Figure 4.6: SEM micrograph of LLDPE/TPS (80/20) at 300 X magnification.

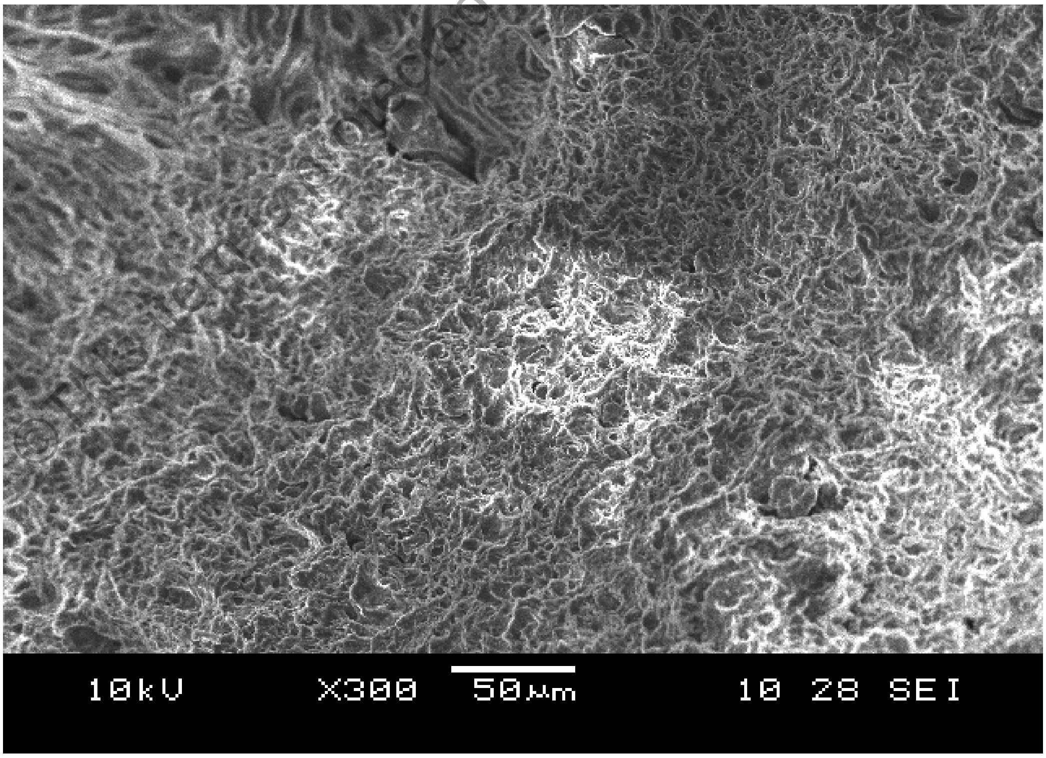

Figure 4.7: SEM micrograph of LLDPE/TPS (70/30) at 300 X magnification.

4.3 Themogravimetric Analysis for LLDPE/TPS

The LLDPE/TPS blended thermo gravimetric analysis is conducted using TGA. The continues mass loss throughout volatilization of the degradation samples was measured as the function of temperature. The TGA and DTG experimental results of LLDPE/TPS and The TGA and DTG experimental results of LLDPE/TPS blends are shown in Figure 4.8. It can be observed in the TGA curve that the materials degradation for pure TPS starts at temperature of 480^{0}C for pure LLDPE and the degradation start as low as 150^{0}C this indicate the addition of TPS has promote degradation properties of the blend and this might due to volatilization of moisture when the TPS is added since TPS is soluble in water causing the molar mass of pure TPS gradually decreases, which is due to the volatilization of glycerol added on it, this claimed is also reported in previous work (Maleque et al, 2006).

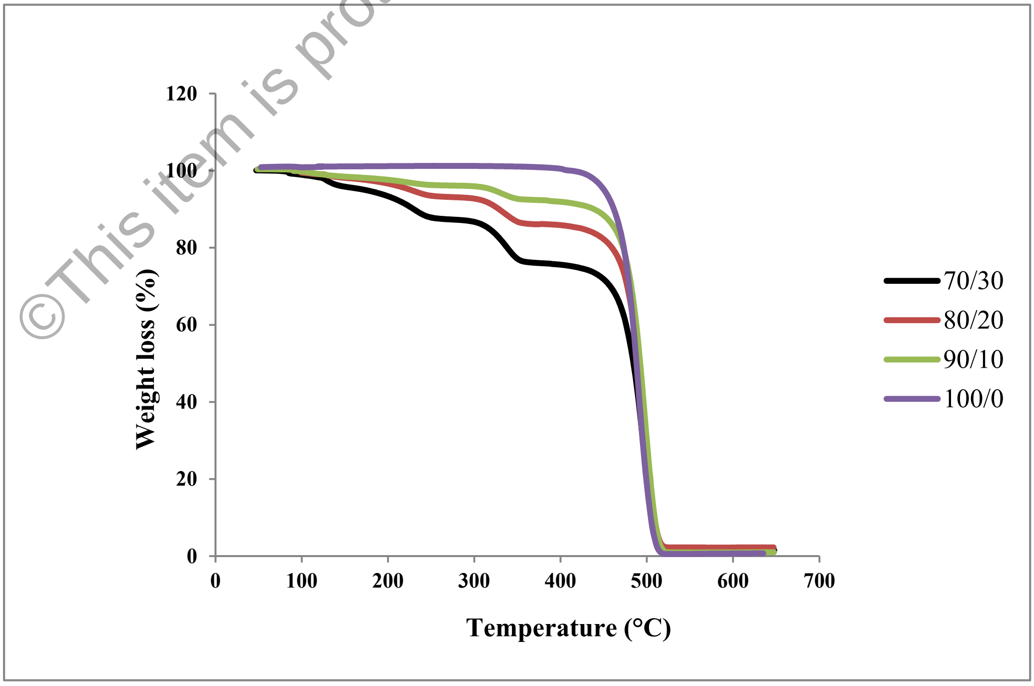

Figure 4.8: Themogravimetric curve of LLDPE/TPS blends

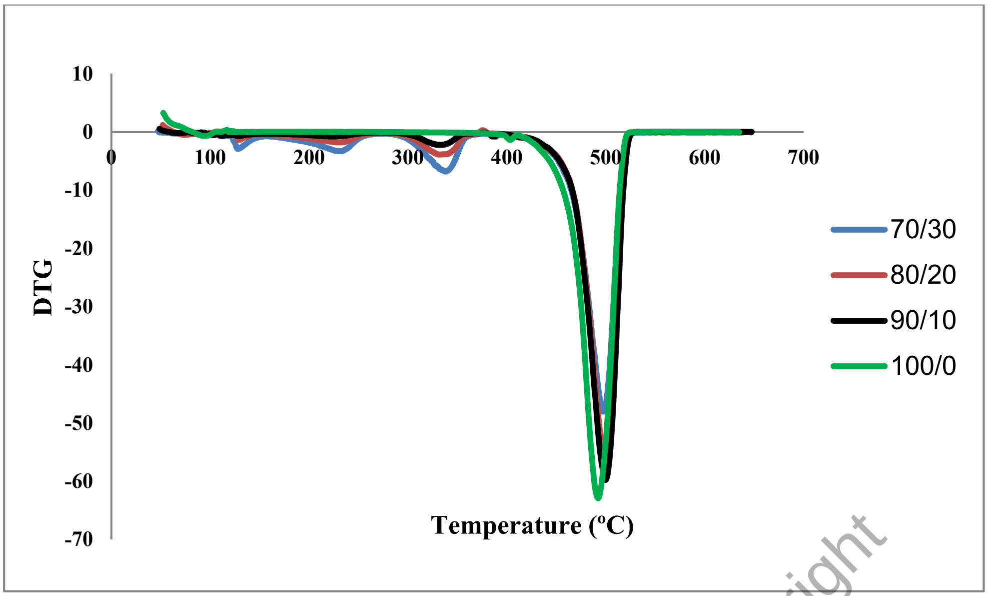

Figure 4.9: DTG curve of LLDPE/TPS blends

In Figure 4.9 DTG thermo grams of LLDPE/TPS blends show the decomposition point for all the 10%, 20% and 30% TPS loading shifting to higher decomposition temperature this equally indicated its disperse nature. When the LLDPE was pure at 100% with 0% TPS, the blends shows slow and steady initial weight loss until major weight loss is detected at approximately temperature 470^{0}C, the following show similar trend in previous study (Maleque et al, 2006).

4.4 Differential Scanning Calorimetry (DSC) Analysis for LLDPE/TPS

The DSC heating and cooling curves of the LLDPE/TPS are shown in Figure 4.10 and 4.11. The LLDPE/TPS endothermic melting peak is at 110°C for the composition of (70:30) wt%, while (90:10) wt% and (100:00) wt% both melt around 112°C. The LLDPE/TPS blends show one peak for all composition corresponding to the melting points of the single polymer; this is might be due to mixing homogeneity. A well-defined transition is seen to occur between the temperatures of 80 ºC and 110ºC for the ratio of (80:20) with a heat flow 4.8w/g. so it can be concluded that the transition on the graph is the melting of the sample (Krupaa and Luyt (2001).

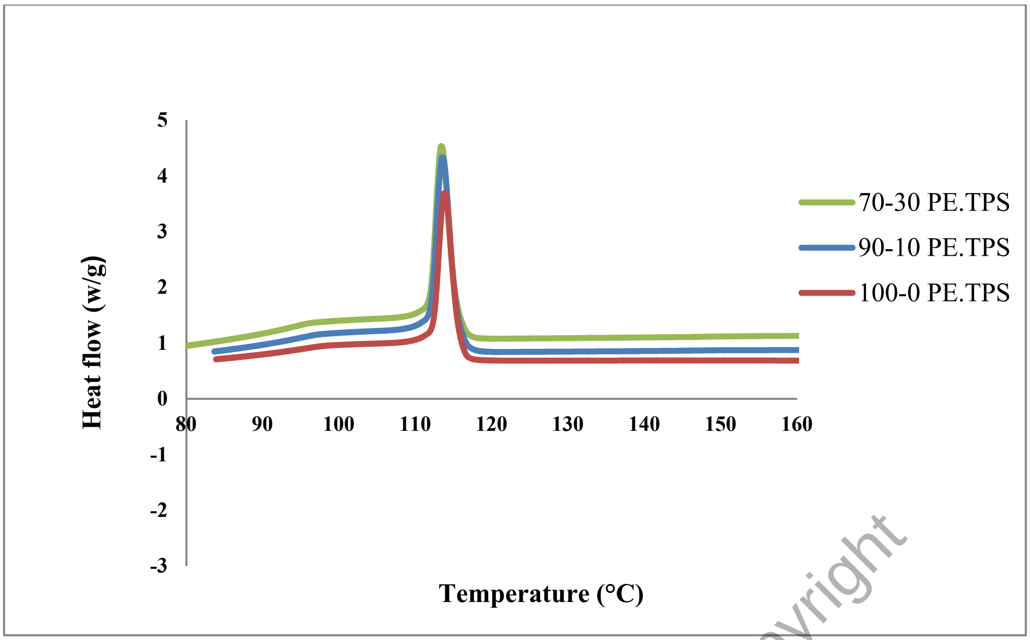

Figure 4.10: DSC curves of the LLDPE/TPS blends (heating)

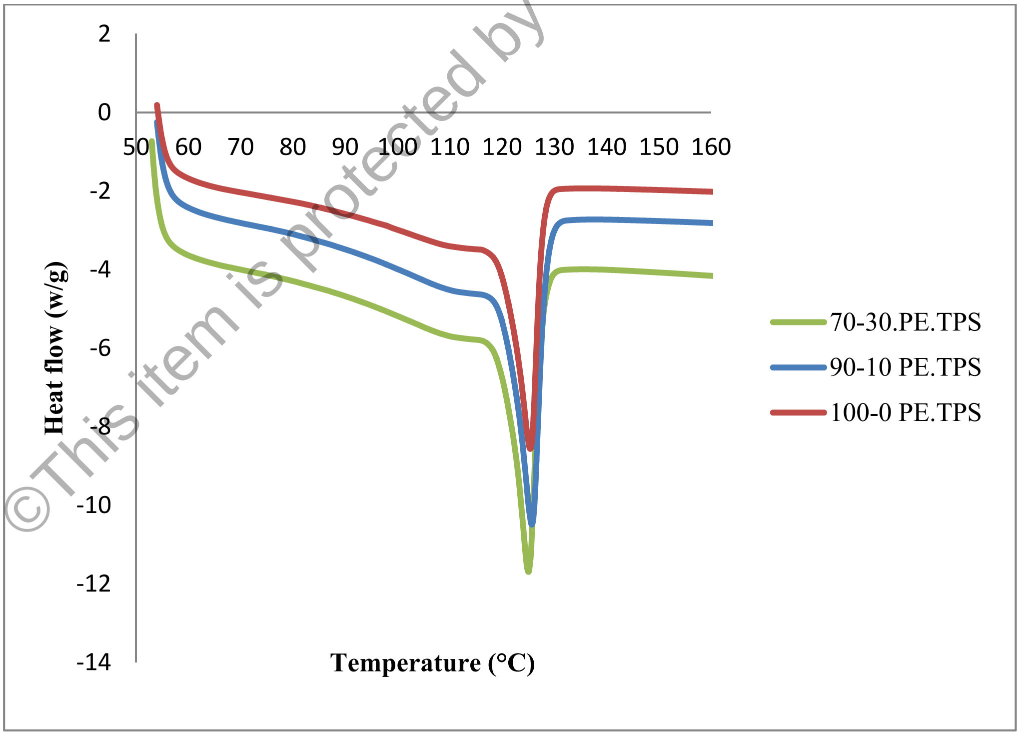

Figure 4.11: DSC curves of the LLDPE/TPS blends (cooling).

The DSC cooling curves of the samples are shown in Fig 4:11. The crystallization of the blends is different The DSC cooling curves of the LLDPE/TPS. The LLDPE/ TPS crystallization for 70:30, 90:10, 100:0 compositions are at 115, 117 and 120^0C respectively. The DSC curves of all the samples, both pure LLDPE and blends. Since these peaks were observed for both pure LLDPE and the blends, it is probable that its origin is partly in the LLDPE structure (Krupaa and Luyt, 2001) .

4.5 Mechanical Properties and Surfaces Morphology of LLDPE/TPS/BF Composites

The effect of BF incorporation into tensile strength of LLDPE/TPS (80/20) was shown in Figure 4.12 The graph exhibited that the tensile strength decrease sharply at initial addition of BF component and the value remains unchanged up to 10 % BF. The possible explanation for this observation was due to the dilution effect as hygroscopic BF component was generally incompatible to the LLDPE phase. Further addition of BF up to 30 % showed mark decrease in tensile strength, indicated that the optimum BF loading was achieved, reason for this is explained in next section. On the other hand, the Young's modulus values were strongly affected by the increment of BF loading in the LLDPE/TPS blends Figure 4.13. The values increased linearly with the BF weight fraction. Its can be explained by the interlocking mechanism between BF surface with LLDPE chains. As expected that the increment in Young's modulus values was proportionally inverse to that elongation at break values Fig. 4. 14. Insufficient interaction at the BF-LLDPE interphase and high amount of BF contents (30 %) might result in early sample failure. This is because LLDPE can form miscible blends with polymers which contain an appropriate functional group i.e. hydrogen bonding or donor-acceptor interactions. The properties of blend films with various proportions of starch are identical. A single glass transition temperature is obtained for all the samples, which are semi-crystalline. The tensile strength was optimum for a LLDPE/PTS/BF ratio of 80/20 (% wt/wt). In this particular case, an advantageous cost reduction and an improvement of mechanical properties compared to LLDPE/PTS blend are obtained. LLDPE/PTS blends had poor mechanical behavior because of a poor adhesion between the starch granules and the polymer matrix. It can be conclude that, the acceptable mechanical strength of LLDPE/TPS-BF composites is only feasible at lower BF content, and from graphs, it can be approximated at around 10-20 % BF portion.

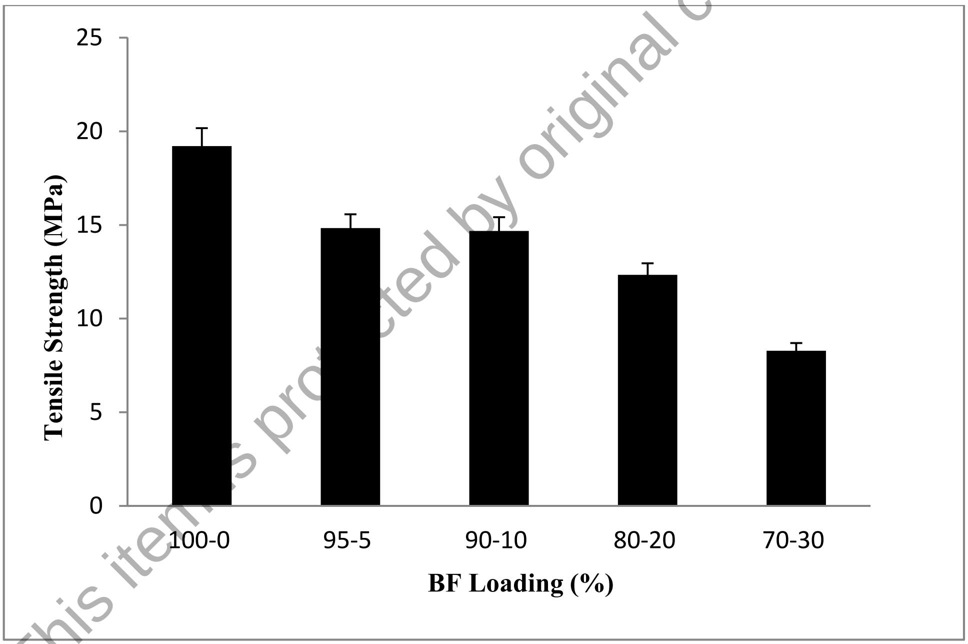

Figure 4.12: Variation in tensile properties of LLDPE/TPS blends with different BF contents.

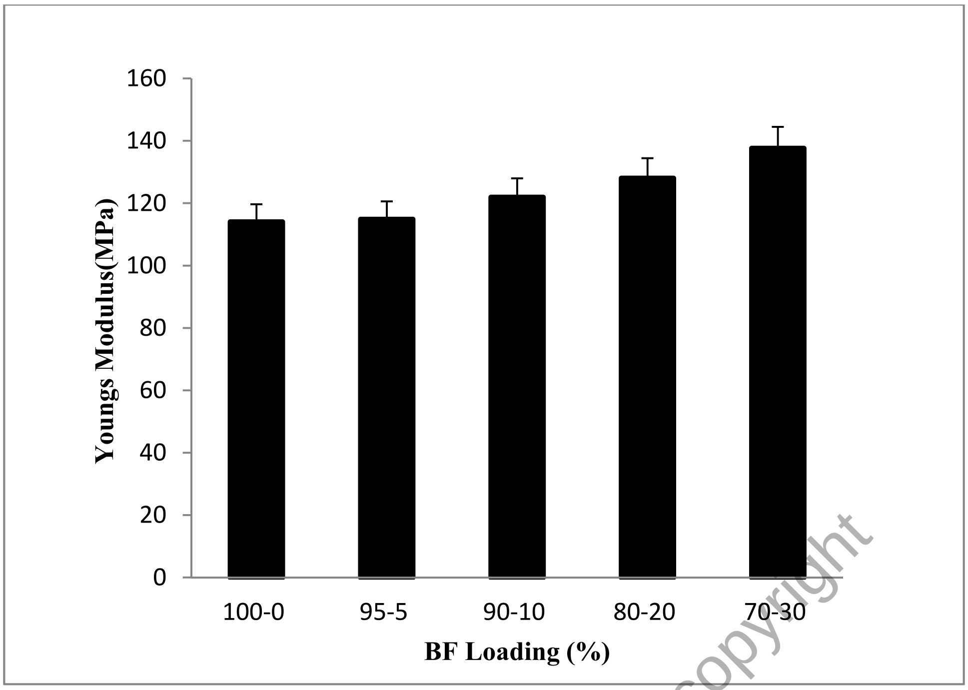

Figure 4.13: Variation Young's modulus in LLDPE/TPS-BF blends at different BF contents.

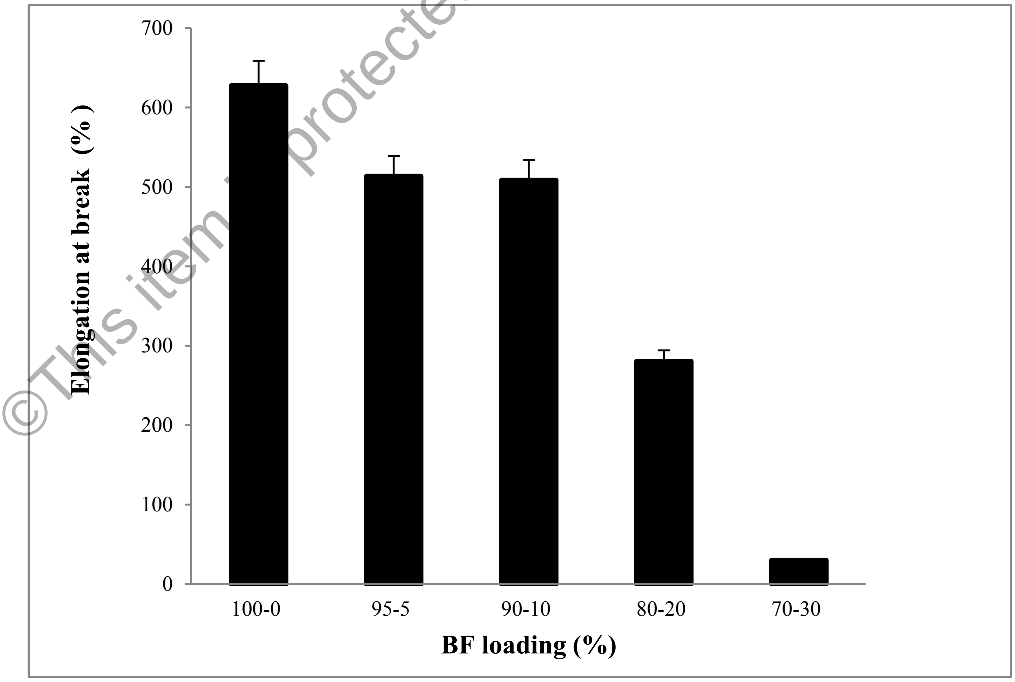

Figure 4.14: Variation elongation at break in LLDPE/TPS-BF blends at different BF contents.

4.6 SEM Micrographs for LLDPE/TPS/BF Composites

SEM images of LLDPE/TPS blends containing 10 % and 30 % of BF were given in Figure 4.15 and 4.16. The micrographs at 300 X magnification revealed that BF was well embedded in TPS phase. At higher BF levels, a very important decrease in mechanical properties is noticed and it has been shown that thermal properties of blends could be improved by crosslinking of composite. This observation was expected due to the BF and TPS have almost similar characteristics in nature. At the higher BF loading Figure 4.9, the fracture surface of the LLDPE/TPS blends become coarser indicating better resistance to the force applied to the blends. This observation can be correlated with Young's modulus value where it increases in figure 4.13 for when (10-30%) BF was introduced to the LLDPE/TPS blends.

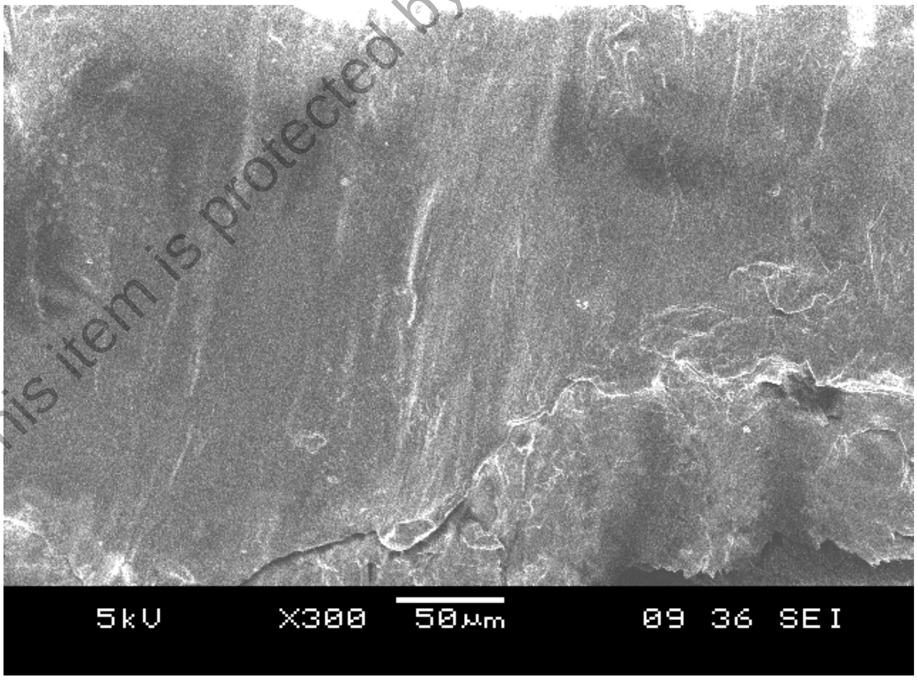

Figure 4.15:SEM micrograph of LLDPE/TPS 10 % BF at 300 X magnification.

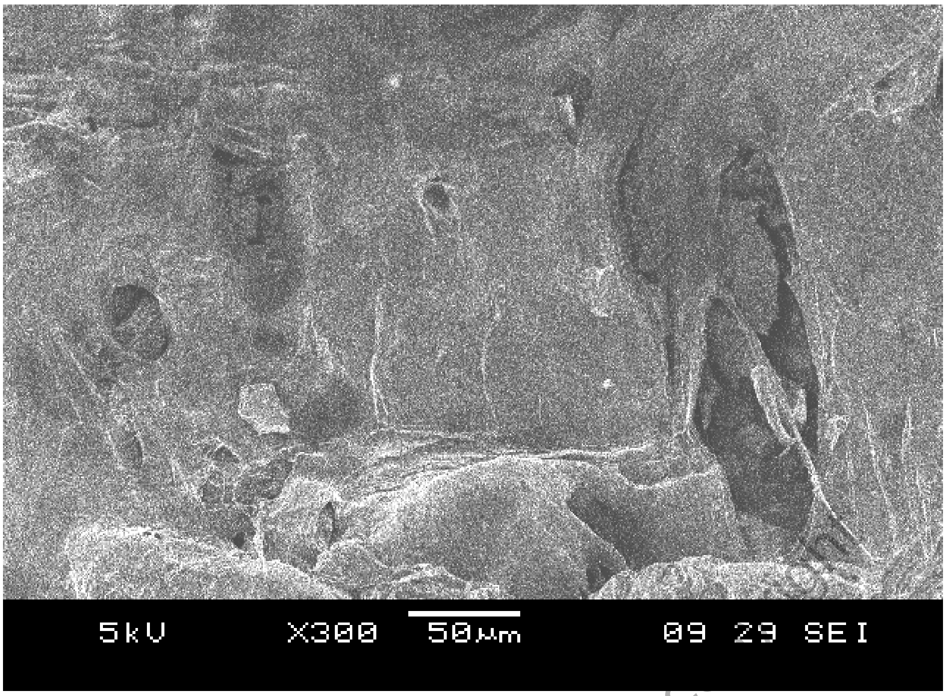

Figure 4.16: SEM micrograph of LLDPE/TPS 30 % BF at 300 X magnification.

4.7 Differential Scanning Calorimetry (DSC) Analysis for LLDPE/TPS/BF Composites

The figure 4.17 shows LLDPE/TPS/BF endothermic melting peak is at 110°C for the composition of (70:30) wt%, (90:10) wt% and (100:00) wt% all melt around 120°C, this indicate the mixing homogeneity for the mixtures. The DSC cooling curves of the LLDPE/TPS/BF are shown in Fig. 4.18. The LLDPE/TPS/BF crystallization for 70:30, 90:10, compositions are at 117°C both. However, it is worthy to note the crystallization 100:0 composition is around 120^0C. There was a small increase in the crystallization temperature of the LLDPE/TPS/BF for 100:0 while that 70:30 and 90:10 remained lower. At the lower, BF content, it seems there is a clear interaction between LLDPE directly with BF. The study demonstrates a preparation and characterization of TLLDPE/TPS/ BF composite. In conclusion, the composites showed better properties than the LLDPE/TPS blend, as a result of the stronger interfacial interaction and the LLDPE/TPS/BF composites are more thermally stable than LLDPE/TPS blend.

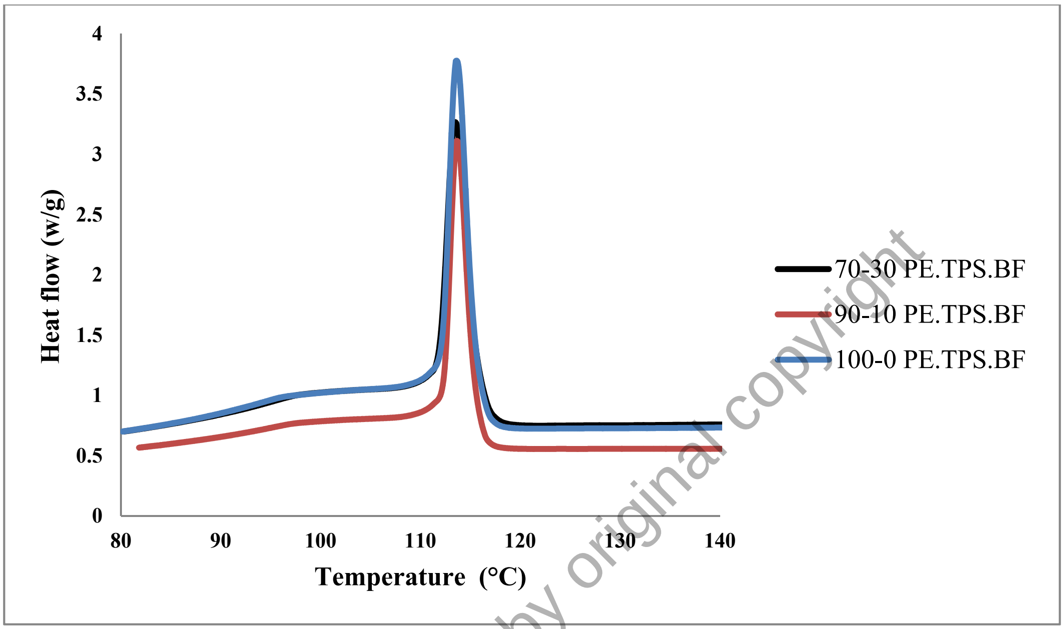

Figure 4.17: DSC curves of the LLDPE/TPS/BF composites (heating).

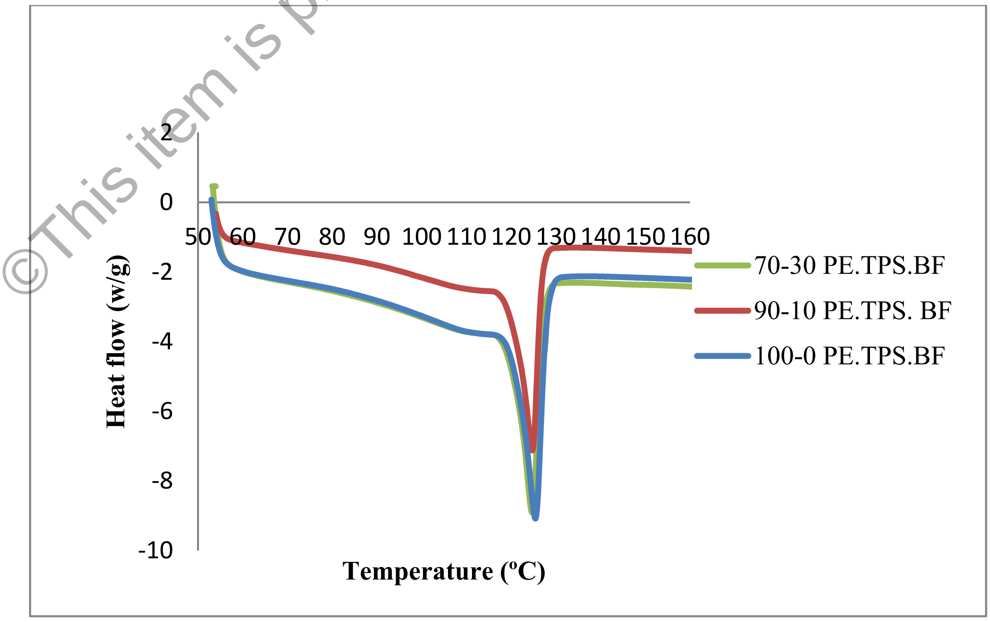

Figure 4.18: DSC curves of the LLDPE/TPS/BF composites (cooling).

4.8 Differential Scanning Calorimetry (DSC) Analysis for LLDPE/TPS/BF Composite

The LLDPE/TPS/BF BF composite thermo gravimetric analysis is conducted using TGA. In this second curve it can be observed the that it can continues mass loss throughout volatilization of the degradation samples was measured as the function of temperature. The TGA and DTG experimental results of LLDPE/TPS/BF and the TGA and DTG experimental results of LLDPE/TPS/ BF composite are shown in Figure 4.19. It can be observed in the TGA curve that the degradation of 100:0, 90:10 80:20 and 70:30. The 100:0 show no degradation until 470^0C. As the content of BF increases the degradation start as early at 100^0C, this indicates the addition of BF has improved degradability of the blend.

In Figure 4.20 DTG thermo grams of LLDPE/TPS/BF composite show the decomposition point for 10%, 20% and 30% BF added loading shifting to higher decomposition temperature. When LLDPE/TPS/BF was pure at 10% with the blends shows slow and steady without weight loss until the major weight Loss is pronounced at temperature 460 °C.

As indicated above, the Figure 4.20 show curve indicating initiation temperature around 40, maximum temperature 700, and The thermal degradation of LLDPE 100 in only one stage which started around 400, like wire for 90:10 show similar behavior. However, for 80:20 and 70:30 appear to be in three steps. This can be explained as formation of intermediate products due to crosslinking and branched chains that compete reaction. The degradation of LLDPE/TPS/BF at higher is not a single step decomposition process but seems to follow a more complex degradation pattern. However, the addition of lower improves the thermal stability as shown in TGA curve of LLDPE/TPS/BF (80:10). There must be some interaction between the intermediate component of LLDPE/TPS/BF. It shows a two-step degradation process, clearly reflecting each degradation process of the BF and LLDPE ingredients.

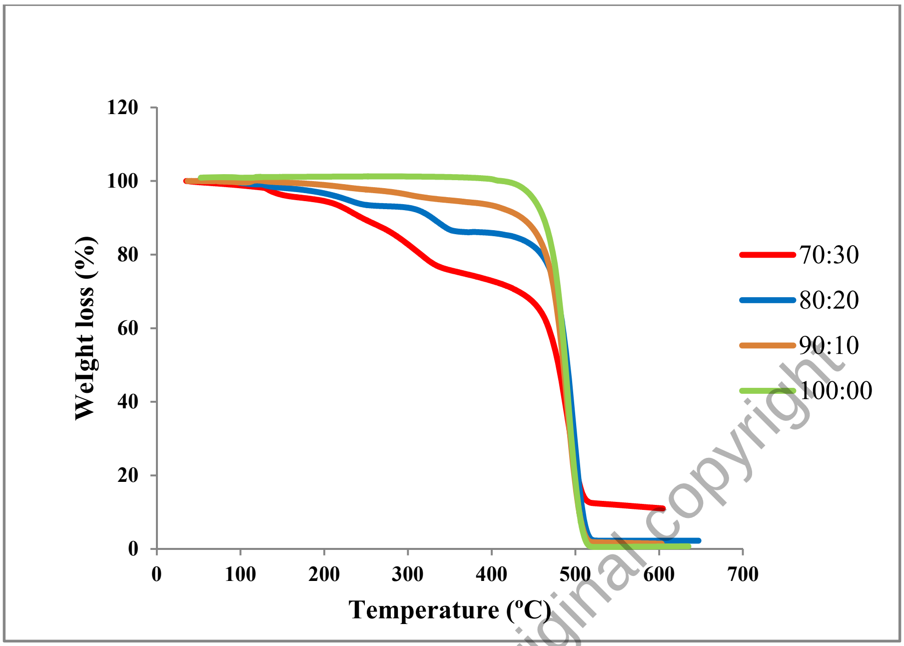

Figure 4.19: Themogravimetric curve of LLDPE/ TPS/BF composite.

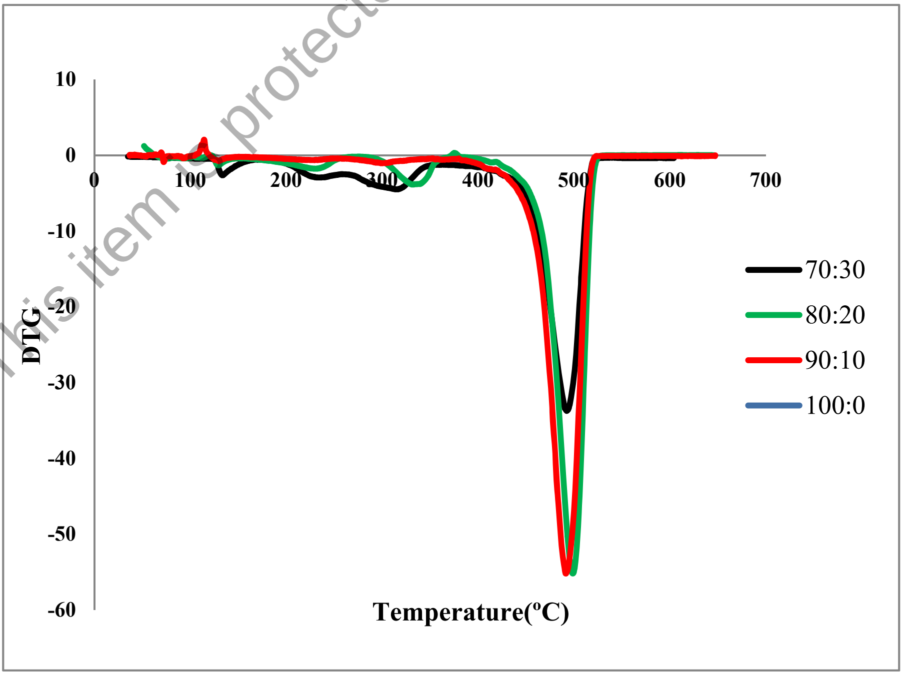

Figure 4.20: DTG curve of LLDPE/ TPS/BF composite.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The preparation and characterization of linear low density polyethylene (LLDPE) thermoplastic starch (TPS) and BF composites were successfully conducted with several characterization methods. The blends were prepared in two different systems, the optimum contents of TPS and BF in LLDPE matrix, the blends properties were assessed in terms of mechanical properties such as tensile strength and Young's modulus. The mechanical data was also correlated with the blends morphologies in order to understand the interaction behavior between LLDPE, TPS and BF. In general, the tensile strength was decreased as increased in TPS and BF contents, but the Young's modulus values showed good increment as BF contents was increased. SEM micrographs showed that BF has good adhesion with TPS and also well embedded in TPS phase. At low banana fiber content, the composite shown good interaction between the BF and TPS resulted in better failure resistance when load was applied to the blends.

On the other system, BF was introduced into LLDPE/TPS matrix as a reinforcing agent in order to promote better mechanical properties of the LLDPE/TPS blends. In the presence of the BF, LLDPE chains are difficult to form crystal due to the interfering chains alignment from the neighboring components. TGA and DTG thermograms displayed the effect of BF in LLDPE/TPS blends. The shift of thermal stability for compatibilized blends towards higher temperature also can be explained by the increase in interfacial interaction between BF and TPS. In conclusion, the optimum mixture for LLDPE/TPS is found to be 80:20 composition and low BF around 10 to 20% composites showed better thermal properties than the LLDPE/TPS blend, as a result from the stronger interfacial interaction between BF and TPS and the influence of BF on the LLDPE chains alignment.

5.2 Recommendations

Banana fiber 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 in biodegradable material is of great interests since it provides a possible way to make composites that are degradable at very low cost. Although natural fibers normally present lower strength than traditional fibers used in current composites, the natural fibers are not very strong enough as reinforcements for making composites used in packaging, construction etc. To improve its process ability and the mechanical property we recommend the fiber treatment and process optimization through adjusting the mixing ratio.

The addition of different compitibilizers with the smaller-scale fillers can provide additional reinforcement to the composite. In addition, the aligned smaller-scale filler can provide possibly easier orientation for the fillers by forming smooth orientated composite. Therefore, future studies using different compitibilizers together with the combination of orientation processes are recommended.

References

Almeida A., Brabant L., Siepmann F., De Beer T., Bouquet W., Van Hoorebeke L. (2012) Sustained release from hot-melt extruded matrices based on ethylene vinyl acetate and polyethylene oxide, *European Journal of Pharmaceutics and Biopharmaceutics*, 82 (3) pp. 526–533

Awal, A., Ghosh,SB., Sain M., (2010) Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers. *Journal of Thermal Analysis and Calorimetry*, 99:695–701

Brindha D., Vinodhini S., Alarmelumangai K., and Malathy N.S. (2012) Physico-Chemical Properties of Fibers From Banana Varieties After Scouring, Indian *Journal of Fundamental and Applied Life Sciences* Vol. 2 (1) 2231-6345

Chaudhary, D.J. (2004) Recycling rice hull ash: A filler matrial for polymeric composites? *Advances in Polymer Technology*, 23: 147-155

Derrien, K., Gilormini, P. (2009) The effect of moisture-induced swelling on the absorption capacity of transversely isotropic elastic polymer matrix composites.*Internationaljournal Solids Structure*., 46, 1547-1553.

Durmus, A., Kasgoz, A., Macosko, C.W. (2007) Linear low-density polyethylene (LLDPE)/clay nanocomposites, Part I-structural characterization and quantifying clay dispersion by melt rheology. *Polymer* 48, 4492.

Feng S. Y., Lauke X. Q., Mai, B., Y. W. (2008) Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate polymer composites,*Composites Part B: Engineering*, 39, 933-961.

Gad, Y. H.,Magida, M. M., El-Nahas, H. H. (2010) Effect of ionizing irradiation on the thermal blend of waste low density polyethylene/ethylene vinyl acetate/bitumen for some industrial applications, *Journal of Industrial and Engineering Chemistry, 16, 1019-1024.*

George, R. N. Carol, D. S. (2008) Poly(amidoamine), polypropylenimine, and related dendrimers and dendrons possessing different 1-2 branching motifs: An overview of the divergent procedures,*Polymer*, 49, 1-173.

Krupaa I., Luyt A. S., (2001) Thermal and mechanical properties of extruded LLDPE /wax blends, Polymer Degradation and Stability 73, 157–161.

Ortega, Zaida, Benítez, Antonio N., Monzón, Mario D., Hernández, Pedro M., Angulo, Inés, Marrero, María D (2010) Study of Banana Fiber as Reinforcement of Polyethylene Samples Made by Compression and Injection Molding, *Journal of Biobased Materials and Bioenergy,Vol. 4(2)* 114-120(7)

Navin C., Suresh C. P., Singh R.K., (2012) Development and characterization of sisal nanofibre reinforced polyolefin composites, *Journal of Scientific Research and Reviews* Vol. 1(3), pp. 026 – 032.

Ning, W., Jiugao, Y., Xiaofei, M., Ying W., (2007) The influence of citric acid on the properties of thermoplastic starch=linear low-density polyethylene blends. *Carbohydrate Polymers* 67, 446–453.

Pielesz A., Binias W., Pielesz and Binias, (2010) Cellulose acetate membrane electrophoresis and FTIR spectroscopy as methods of identifying a fucoidan in Fucusvesiculosus Linnaeus *Carbohydrate Research*, 345 (18) pp. 2676–2682

Reis K.C., Pereira J., Smith A.C., Carvalho C.W.P., Wellner N., and Yakimets I., (2008) *Food Journal of Engineering*, 89, 361

Rohani A. M., Hanafi I., Razaina M. T., (2010) Effects of Polyethylene-g-maleic Anhydride on Properties of Low Density Polyethylene/Thermoplastic Sago Starch Reinforced KenafFibre*Composites Iranian Polymer Journal* 19 (7), 501-510.

Sadiku-Agboola, Sadiku, O. E.R. Sadiku-Agboola and Sadiku, (2014) Chapter 3– Theoretical modeling of nanostructured formation in polymer blends, S. Thomas, R. Shanks, S. Chandrasekharakurup (Eds.), *Nanostructured polymer blends*, William Andrew Publishing, Oxford, pp. 33–99

Saeoui, P., Sirisinha, C., Sanguanthammarong, P., Thaptong, P. (2010) Properties and recyclability of thermoplastic elastomer prepared from natural rubber powder (NRP) and high density polyethylene (HDPE). *Polymer Test*. 29, 346-351.

Shin, T. J., Lee, B., Seong, B. S., Han, Y. S., Lee, C. H., Song, H. H., Stein, R. S., Ree, M. Composition dependent phase segregation and cocrystallization behaviors of blends of metallocene-catalyzed octene-LLDPE(D) and LDPE(H).*Polymer*. (2010) 51, 5799-5806.

Sirisinha, K., Boonkongkaew, M., Kositchaiyong, S. (2010) The effect of silane carriers on silane grafting of high-density polyethylene and properties of crosslinked products.*Polymer test*. 29, 958-965.

Torres F.G., Aguirre M. (2003) Rotational moulding and powder processing of natural fibre reinforced thermoplastics, *International Polymer Processing* 18 (2) pp- 204–210.

Vroman I. andTighzert L. (2009) Biodegradable Polymers, Materials, 2, 307-344

Yuan, Q, Yang, Y., Chen, J., Ramuni, V., Misra, R. D. K., Bertrand, K. J. (2010) The effect of crystallization pressure on macromolecular structure, phase evolution, and fracture resistance of nano-calcium carbonate-reinforced high density polyethylene. *Material Science Engineering*: A. 527, 6699-6713.