LOW DENSITY POLYETHYLENE TAPIOCA STARCH DEGRADABLE BIOFILMS WITH PALM OIL BASED PROCESSING AID FOR BLOWN FILM EXTRUSION

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This thesis is dedicated to my husband, Helmi Hj Haron, mama and abah, super cool siblings; Fina, Baby and Fiq and beloved children, Iman, Fathiyyah and Fayha

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ABSTRACT

In this study, tapioca starch-based polyethylene biofilms with various starch contents, ranging from 5 to 40 wt%, were prepared with added plasticizers and polyethylene-grafted-maleic anhydride (PE-*g*-MA) as compatibilizer by a one-step process. The pellets of tapioca starch-based low density polyethylene (LDPE/TS) were first produced using a twin-screw extrusion process, followed by film blowing extrusion process to produce biofilm samples. Two types of plasticizers, commercial glycerol and palm oil based olein, were added to produce the best formulation for the film blowing process. Palm oil based olein influenced the processing of biocomposites by inducing lower viscosity, better dispersion and flowability. The biocomposites with addition of fixed amount of palm oil based olein displayed excellent film blowing ability compared to glycerol. Scanning electron micrograph of this biofilm with incorporation of starch up to 30 wt% showed good dispersion of starch granular in the polymer matrix. Adding compatibilizer increased the compatibility of the blends, and thus the mechanical properties of tapioca starch-based biofilms were improved. Optical properties, such as haze and gloss of biofilms, decreased as the starch contents increased, coinciding with the starch particle size in the polymer matrix. The barrier properties of tapioca starch-based biofilms, such as water uptake, moisture content and water vapour transmission rate were higher than pure LDPE, due to the hydrophilic characteristics of starch. Biofilms exposed to outdoor weathering, fungi, enzyme and controlled soil burial test demonstrated significant changes on weight loss and surface structure due to photodegradation by sunlight and microorganism activities. Biofilms with starch contents 10 to 40 wt% were determined safe to be used as food plastics packaging for aqueous, non-acidic and acidic foods, oils and processed dry food containing fat and alcoholic ingredients.

ABSTRAK

Dalam kajian ini, biofilem polietilena berasaskan kanji ubi kayu dengan pelbagai kandungan kanji, daripada 5 hingga 40 wt% telah disediakan dengan tambahan pemplastik dan polietilena-tercangkuk-maleik anhidrida sebagai penserasi melalui proses satu-peringkat. Palet polietilena berketumpatan rendah berasaskan kanji ubi kayu (LDPE/TS) telah dihasilkan dengan menggunakan proses penyemperitan skru berkembar, dan kemudian diteruskan dengan proses penyemperitan tiupan filem untuk menghasilkan sampel biofilem. Dua jenis bahan pemplastik digunakan, iaitu gliserol dan minyak sawit berasaskan olein, telah ditambah untuk menghasilkan formulasi terbaik melalui proses penyemperitan tiupan filem. Minyak sawit berasaskan olein pengaruhi pemprosesan biokomposit dengan mendorong kepada kelikatan yang lebih rendah, serakan dan keboleh aliran yang lebih baik. Biokomposit dengan tambahan minyak sawit berasaskan olein pada kadar tetap menunjukkan keupayaan yang baik untuk diproses melalui proses penyemperitan tiupan filem berbanding gliserol. Mikrograf imbasan elektron biofilem ini dengan kandungan kanji sebanyak 30 wt% menunjukkan penyebaran butiran kanji yang baik dalam matriks polimer. Tambahan penserasi dalam adunan telah meningkatkan keserasian adunan, dengan itu sifat-sifat mekanik biofilem berasaskan kanji bertambah baik. Ciri-ciri optik, seperti jerebu dan kekilatan biofilem menurun dengan peningkatan kandungan kanji, bertepatan dengan saiz partikel kanji dalam matriks polimer. Sifat rintangan biofilem berasaskan kanji ubi kayu mengandungi kandungan penyerapan air, kandungan kelembapan dan kadar penghantaran wap air yang lebih tinggi berbanding LDPE tulen, disebabkan oleh ciri-ciri hidrofilik kanji. Biofilem yang terdedah kepada luluhawa, kulat, enzim dan ujian tertanam di dalam tanah yang terkawal menunjukkan perubahan yang ketara kepada penurunan berat asal dan struktur permukaan yang disebabkan oleh aktiviti fotodegradasi oleh cahaya matahari dan aktiviti mikroorganisma. Biofilm dengan kandungan kanji sebanyak 10 hingga 40 wt% berat telah didapati selamat untuk digunakan sebagai pembungkusan plastik makanan bagi makanan jenis berair, makanan bukan berasid dan berasid, makanan berminyak dan makanan kering yang diproses yang mengandungi bahan lemak dan alkohol.

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LIST OF SYMBOLS

µm	-	Micrometer
d	-	Diameter
w	-	Weight fraction
x	-	Average thickness
$P_{\circ}$	-	Partial pressure
α-Amylase	-	Alpha amylase
°C	-	Celsius
°F	-	Fahrenheit
T_g	-	Glass transition temperature
T_c	-	Crystallization temperature
T_m	-	Melting temperature
M	-	Mass of residue
A	-	Total surface area
g-force	-	Gram force
nm	-	Nanometer
mg	-	Milligram
cm	-	Centimeter
dm	-	Decimeter
H_2O	-	Water
NH_3	-	Ammonia
NaOH	-	Sodium hydroxide
CH_4	-	Methane

LIST OF ABBREVIATIONS

PE	-	Polyethylene
TPS	-	Thermoplastic starch
PHA	-	Polyhydroxylalkanoates
PHB	-	Polyhydroxybutyrate
PHBV	-	Polyhydroxybutyrate-co-hydroxyvalerate
PLA	-	Polylactic acid
PCL	-	Polycaprolactones
PEA	-	Polyesteramides
PBSA	-	Aliphatic-co-polyesters
PBAT	-	Aromatic-co-polyesters
PGA	-	Polyglycolic acid
PVOH	-	Poly(vinyl alcohol)
PVAC	-	Poly(vinyl acetate)
PEK	-	Polyethylketone
EAA	-	Poly(ethylene-co-acrylic acid)
PE-*g*-MA	-	Polyethylene-grafted-Maleic anhydride
SEM	-	Scanning electron micrograph
DSC	-	Differential scanning calorimetry
MB	-	Manganese stearate
STAc	-	Starch acetate
EVA	-	Ethylene vinyl acetate
KBr	-	Potassium bromide
WVTR	-	Water vapour transmission rate
TGA	-	Thermogravimetry analysis
FTIR	-	Fourier transform infrared spectroscopy
MI	-	Melt index

BUR	-	Blown-up ratio
LDPE/TS	-	Tapioca starch-based polyethylene
MD	-	Machine direction
TD	-	Transverse direction
STMP	-	Sodium trimetaphosphate
RH	-	Relative humidity

CHAPTER 1

INTRODUCTION

1.1 Introduction

Plastics are man-made long chain polymeric molecules. Plastics have become an essential part of our everyday life. More than half a century ago, synthetic polymers began to be used as a substitute for natural materials in almost every application (Shah *et al*., 2008). The plastics industry has developed remarkably since the invention of various methods of production for synthetic polymers from petrochemical sources, which produce plastics that are valuable and desirable due to special characteristics. Plastics have been approved for use in a range of types and forms, including natural polymers, modified natural polymers, thermosetting plastics, thermoplastics, and more recently, biodegradable plastics (Andrady and Neal, 2009). Plastics have a range of unique properties used at a wide range of temperatures, are chemical and light resistant and durable, and can be easily processed and moulded at a lower cost relative to other materials, such as steel, glass, and paper.

Today plastics are almost completely derived from petrochemicals produced from fossil oil and gas, referred to as synthetic plastics. Synthetic plastics are extensively used in packaging food products, pharmaceuticals, cosmetics, detergents, chemicals, and in agricultural mulching film. This projected growth is mainly associated with an increasing public demand for plastics in many applications. Although hundreds of plastic materials are commercially available, only a few of these qualify as commodity thermoplastics in terms of their high volume and relatively low price. This group of plastics consists of high-density polyethylene (HDPE), low-density polyethylene (LDPE), poly(vinyl chloride) (PVC), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) (Siracusa *et al*., 2008). Their partial consumptions on a global basis are displayed in Figure 1.1.

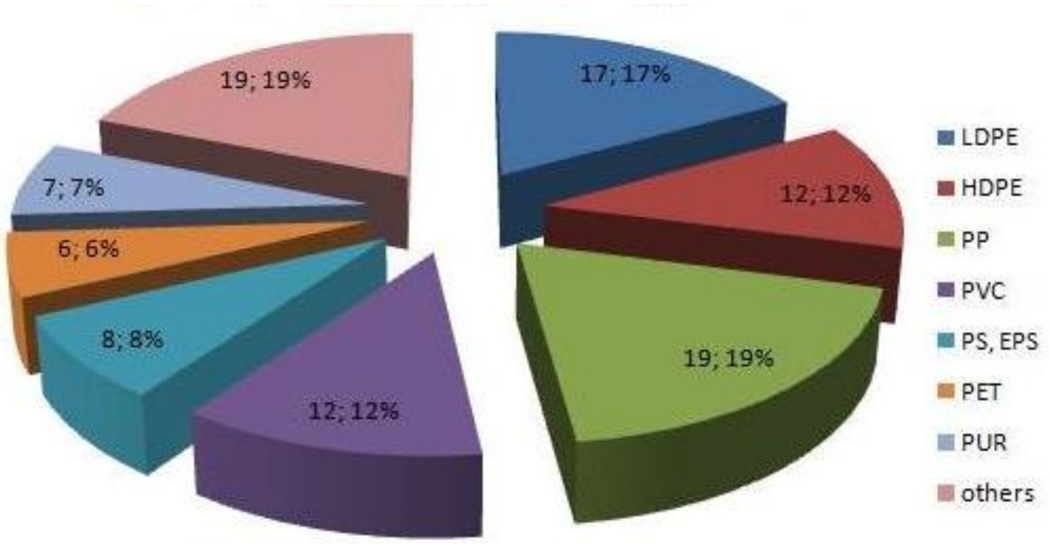

Figure 1.1 World plastic materials demand by resin types in 2010 (Plastics, 2011)

Table 1.1 shows that thermoplastics are extensively used in packaging and fabrication of bottles and films. There are approximately 49.5 million tons of synthetic plastics produced worldwide. Polyethylene represents 29% of the produced synthetic plastics. Half of that quantity, which is 25 million tons, will accumulate in nature and the majority is from the packaging sector. Synthetic plastics that are petrochemical-based, such as polyolefin, polyesters, and polyamides have been increasingly used as packaging materials. These types of plastics were overused in industries due to their availability in large quantities at a low cost and their favourable functionality characteristics, such as excellent tear and tensile strength, good heat-seal ability, and excellent barrier properties against oxygen and aroma compounds (Tharanathan, 2003).

However, these plastics are made of petroleum-based materials that are not easily and readily biodegradable. Synthetic plastics such as polypropylene (PP) and polyethylene (PE) have a very low water vapour transmission rate rendering these materials completely non-biodegradable. Therefore, these materials contribute to environmental pollution, which causes severe ecological problems. Polyolefins are not degraded by microorganisms in the environment, which prolongs their lifetime to hundreds of years. In order to overcome these problems, there has been an increased enthusiasm among researchers in enhancing the biodegradability of synthetic plastics by blending them with low-cost natural biopolymers.

Table 1.1: Main plastics and their applications (Zheng and Yanful, 2005)

Plastics	**Applications**
Low density polyethylene (LDPE), linear low density polyethylene (LLDPE) Poly(vinyl chloride) (PVC)	Films, bags and packaging
Polyethylene terephthalate (PET), PVC, high density polyethylene (HDPE)	Bottles, tubes, pipes, insulation moulding
Polystyrene (PS) polypropylene (PP), PVC	Tanks, jugs, containers
Polyurethane (PUR)	Coating, insulation, paints, packing

Most lightweight synthetic plastic is used for a one-time utilization for packaging and is discontinued when its useful life is over, remaining in garbage deposits and landfills for decades (Volke-Sepulveda *et al*., 1999). These materials are inactive and resistant to the existence of microorganisms, leading to a long duration of shelf life (Arvanitoyannis *et al*., 1998). Even though there have been a lot of new technologies and methods for recycling and reducing plastics waste, the amount of accumulation of waste still increases every year. Replacing plastics with other packaging materials, such as paper, glass, and metals is a less attractive option due to economic factors and the material’s deficiencies as compared to plastic materials. Recycling products also has its limitations, such as the high cost of operation; moreover, recycling technology is still in development. Many packaging materials are not suitable for recycling because of contamination; the cleaning that is necessary prior to recycling can be very expensive.

Biodegradable plastics are plastics that can permit a degradation process. They are defined as plastics with comparable properties to synthetic plastics, but they can be decomposed after disposal in the environment through the activity of microorganisms (Tharanathan, 2003; Raghavan, 1995). Biodegradable plastics can be particularized as plastics wastes that can be processed using thermoplastic processing methods and machineries and can be decomposed when disposed in landfills through the activity of microbes and fungi to produce CO_2 and H_2O (Tharanathan, 2003), microbial cellular components, and miscellaneous microorganism by-products (Raghavan, 1995). Microorganisms break down the polymer chains, molecules and consume the material through several methods, such as microbial degradation, thermo-degradation, chemical degradation, and photo-degradation. Biodegradable plastics provide an alternative option for reducing municipal solid waste through biological recycling in the ecosystem. They can replace conventional synthetic plastic products (Raghavan, 1995). In addition, it is enticing that these biodegradable polymers originate primarily from agricultural or other renewable resources for a sustainable environment.

Polyethylene (PE) is one of the mass-produced non-degradable polymers. Various types of PE are used in many applications including agricultural and packaging films. Among the polyolefins, low-density polyethylene (LDPE) is more susceptible to the attack of microorganisms in certain conditions (Ohtake *et al.*, 1998). Biodegradable polymers are considerably more expensive than conventional non-biodegradable polymers. New mechanisms for production and processing of synthetic polymers and natural polymers from agriculture will be interesting alternatives to reduce the cost of biodegradable polymers in the market. Blending of low-density polyethylene with a low cost and abundant natural biopolymer such as starch will enhance the biodegradability of this material. Incorporating starch will expedite the attack of microorganisms on starch-based LDPE products. Starch is a good choice because it is an abundant and low cost material in the market, which will reduce the cost of production of a starch-based polyethylene biodegradable polymer.

Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Starch satisfies the requirements of adequate thermal stability with minimum interference of melt properties and negligible disturbance of product quality; it has been considered a material candidate in certain thermoplastic applications (Shah *et al*., 1995; Mani and Bhattacharya, 1998). The excellent physical properties of polyolefin make them suitable as packaging and agricultural film materials. Polyethylene (PE) blended with starch is already a potential candidate to replace non-degradable thermoplastics in the areas of packaging and agricultural mulching films. Starch is a hydrophilic polymer, mainly due to the hydroxyls contained in the molecules; in contrast, polyethylene is a hydrophobic material. The blends of starch and polyethylene are immiscible because of this opposite character of the two polymers.

Blending starch with synthetic polymer, such as polyethylene with the addition of glycerol as a plasticizer will improve its immiscibility and also enhance the biodegradability of the blends. Low molecular weight plastic additives like plasticizers and fillers are ordinarily susceptible to microbial attack. This leads to physical embrittlement and fragmentation of the polymer resulting in a porous and mechanically weakened polymer (Sastry *et al*., 1998). The microbes release nonspecific oxidative enzymes that could attack starch-based polyethylene polymers. The addition of palm oil based olein can also function as a plasticizer to blend starch and LDPE, and it can reduce the cost of production. Films of starch-based polyethylene with and without vegetable oils as plasticizers were prepared using a blow film extrusion machine. The degradation of the films increased under thermo-oxidative treatment, ultraviolet light exposure, high temperature, high humidity, and natural ambience (soil burial). It can also be seen that vegetable oil as an additive has a dual role: as a plasticizer it improves the biofilm's quality, and as a pro-oxidant it accelerates degradation of the biofilms (Sastry *et al*., 1998).

Starches are polymers that naturally occur in a variety of botanical sources and are a widely available renewable resource that can be obtained from residuals of harvesting and raw material industrialization. Tapioca starch is a promising starch that can be used in the development of biodegradable polymers. The incorporation of starch, as a naturally biodegradable polymer with synthetic polymers such as polyethylene, will produce a biodegradable film with excellent mechanical properties that can be easily processed through conventional polymer processing techniques.

The addition of plasticizing agents, mainly glycols, will enhance the compatibility of starch-based polyethylene blend systems and will also typically increase their susceptibility to microbial attack (Mali *et al*., 2005). Plasticizers also reduce the brittleness of the film by interfering with hydrogen bonding between the lipid and hydrocolloid molecules, and by improving film flexibility due to their ability to weaken internal hydrogen bonding between polymer molecule chains while increasing molecular volume (Tharanathan, 2003; Mali *et al*., 2005).

1.2 Problem Statement

The use of plastic packaging is widespread and due to this there is a growing interest in the use of biodegradable polymers that can help minimize the environmental impacts of plastics. Lack of degradability of existing synthetic plastic materials and the shortage of landfill sites, as well as growing water and land pollution problems, have led to concerns about plastics (Shah *et al*., 2008). Synthetic plastics are used in packaging products like food, pharmaceuticals, cosmetics, detergents, chemicals, and agricultural mulching film. Approximately 30% of plastics are used worldwide for packaging applications. Most are short-duration applications where the plastic packaging is used one time before being discarded and disposed to a landfill. Increasing public concern over dwindling landfill space and the accumulation of surface litter has promoted the development of degradable plastics. Biodegradable plastics offer one solution to managing packaging waste.

In the last 20 to 30 years there has been an increased interest in the production and use of fully biodegradable polymers with the main goal being replacement of non-biodegradable plastics commercially, especially those used in packaging materials. However, although these polymers possess the required properties and can be used for the production of blown film, they are not widely used due to their high cost. Commercially available biodegradable polymers are estimated to be four to six times more expensive than polyethylene and polypropylene, which are the most widely used plastics for packaging applications. Consequently, many researchers have focused on studies of biodegradable polymers based on the utilization of natural and abundant polymers such as starch, cellulose, lignin, and chitin. These materials are very cheap, abundant, and produced from renewable and natural resources (Bikiaris and Panayiotou, 1998). However, due to their deficiency in mechanical and thermal properties, these materials are not suitable for most uses in the plastics industry. Blending natural polymer with synthetic polymer will improve the mechanical properties of this material.

The incorporation of starch in polyethylene blends will increase the biodegradability of the biofilm, and at the same time enhance the mechanical properties of this material making this material suitable for the packaging industry. Many researchers have concentrated on blending corn, wheat, rice, and whey starches with low-density polyethylene to produce biodegradable polymers. Tapioca starch has been seen as potential natural polymer for the development of biodegradable polymers because of its fully biodegradable properties and low cost of production. Tapioca starch has been widely studied by many researchers in edible films and coatings used to protect food products (Flores *et al.*, 2007; Fama *et al.*, 2005).

The addition of starch to polyethylene results in a drastic decrease of its tensile strength and elongation at break (Willet, 1994). For processing starch, it is necessary to destruct starch granules under the gelatinization process, which involves high temperature and extensive shear stress conditions or the addition of plasticizers (Rodriguez-Gonzalez *et al*., 2004). This process results in a molten-like material called thermoplastic starch (TPS). TPS will behave like typical synthetic polymers that can be processed into various products by conventional polymer machinery processes such as extrusion, injection moulding, film blowing, compression moulding, and others.

To process starch, it is necessary to improve its process ability, which involves destroying the molecular order within the granules. The gelatinization process under shear stress will disrupt the granular structure of starch. The extrusion process involves high shear and high-pressure conditions achieving gelatinization of the starch. During extrusion, starch granules will become progressively more mobile and eventually the crystalline region of the starch granule will melt. The starch would be expected to show the usual viscoelastic behaviour exhibited by thermoplastic melts (Liu *et al*., 2009). Plasticizers also usually have a large influence on the shear viscous properties of starch polymer melts. The addition of plasticizers to the blend would not only influence the granular transformation and macromolecular degradation during processing, which affects the viscosity, but also assists the movements between starch inter- and intra-molecular chains, which also reduces the viscosity.

The process of blown film extrusion can be used to produce biodegradable starch biofilm in a mass quantity production. During the extrusion, the disruption of starch granules yields a homogenous and fluid material. This material, when expanded by blowing into a tubular matrix form, produces rigid films. The addition of suitable plasticizers increases the flexibility of the films because its presence among the starch chains reduces their intermolecular interaction by separating them, which increases their mobility (Mali *et al*., 2005). Many other low molecular weight substances have been utilized as plasticizers for starch polyolefin blends. Palm oil based olein is a vegetable oil-based plasticizer. Adding palm oil based olein weakens the interaction of starch molecules and improves the plasticization of starch.

Palm oil based olein as plasticizer lead to more homogeneous biocomposites, which may lead to better properties than those produced with commercial glycerol. A plasticizer is a small molecule of volatility, that when added to polymeric materials, modifies the three-dimensional organization, decreases attractive intermolecular forces, and increases free volumes and chain mobility (Swain *et al*., 2004). This plasticizer also contributed to a higher expandability during the blowing process. High melt tenacity would allow palm oil based plasticizer to produce thinner film and also lead to higher production rates of biofilms produced by film blowing process. In this study, tapioca starch-based polyethylene biofilms with various starch content, were prepared with added palm oil based olein plasticizer and compatibilizer by a one-step twin-screw extrusion process. The biocomposites undergo the film blowing process to produce biofilms with the addition of a compatibilizer to enhance its mechanical properties and were incorporated with antimicrobial agent to establish its smart packaging characteristics.

1.3 Objectives of the Study

The main objective of this study is to develop biodegradable tapioca starch-based polyethylene biofilm with enhancing mechanical properties via the film blowing extrusion process. This objective is divided into multiple aims:

- To develop a tapioca starch-based polyethylene biofilm formulation with addition of glycerol and palm oil based olien as plasticizers and compatibilizer;
- To characterize and analyse the physico-mechanical and thermal properties of tapioca starch-based polyethylene biofilm,
- To analyse the barrier properties, morphology, and optical properties of tapioca starch-based biofilm,
- To investigate the biodegradability of tapioca starch-based biofilm,
- To enhance the properties of biofilm as an antimicrobial packaging material.

1.4 Scope of the Study

The scope of this study includes:

- Formulation development of tapioca starch-based polyethylene biocomposites with various starch contents ranging from 10 to 40 wt% using a one-step process. A gelatinization of tapioca starch under shear stress conditions and a compounding process using twin-screw extrusion process was used to produce biocomposites, followed by production of the biofilms via the film blowing extrusion process. The addition of glycerol and palm oil based olein was used to study the effect of plasticizers on blends, ranged from 5 to 20 wt%. The effect of compatibilizers to enhance the blends' immiscibility was investigated by the incorporation of polyethylene-grafted-maleic anhydride at various contents, from 5 to 20 wt%.

- The characterization of tapioca starch biofilms was evaluated using Fourier transformed infrared spectroscopy and density measurement. Thermal properties and thermal degradation of biofilms were examined by differential scanning calorimetry and thermogravimetry analysis. The melt flow index of biofilms was determined to show their process ability. Mechanical properties of the biofilms, such as tensile and tearing strength, were investigated using tensile test and the Elmendorf tearing test, respectively.

- Barrier properties of tapioca starch-based polyethylene biofilms, such as the percentage of water absorption, moisture, water vapour, and food compatibility to acidic, alcoholic, and aqueous food types were analysed using water and moisture content analysis, water vapour transmission rate analysis, and food stimulants compatibility analysis, respectively. Morphology of tapioca starch-based polyethylene blends and the optical properties of the biofilms were examined by scanning electron microscopy and an optical microscope; and transparency, gloss, and haze meters respectively.

- The biodegradability of tapioca starch-based polyethylene biofilm was investigated by microbial degradation and photo-degradation. Biofilms were exposed to an enzyme-containing environment to study the effect of α-amylase enzymatic hydrolysis on the starch content in the film. Microbial degradation of biofilms was evaluated by exposure of biofilms to a fungal environment and soil burial analysis. Photo-degradation of tapioca starch-based biofilms was examined by exposure to natural weathering.

- The antimicrobial properties of tapioca starch-based polyethylene for packaging were investigated by the addition of an antimicrobial agent to the blends and antimicrobial analysis.

1.5 Significance of the Study

Plastics are used in our daily lives in a number of applications, from building and constructions, automotive, electrical and electronics, agricultural mulching to the packaging films, bags and containers. Majority of plastics used are discarded after one-short application especially the packaging materials and disposed to the landfills. Most plastic films used in packaging and agricultural mulching are not biodegradable; and in fact extremely durable and inert to the microorganisms. The significance of this study is to develop a formulation of biodegradable film suitable for plastics packaging and agricultural mulching films.

In this study, suitable plasticizer was added eased the process-ability and enhanced the immiscibility of starch and polyethylene. This study also focused on the production of tapioca starch-based biofilms via film blowing processing. A good formulation of tapioca starch-based blending improved the melt strength and bubble stability of the film blowing process. Hence, smooth and continuous biofilms with constant thickness along the bubble formation were produced. The tapioca starch-based polyethylene can be processed and produced using conventional plastic processing machineries.

The physic-mechanical and thermal properties of the tapioca starch-based biofilms were also important to established excellent materials for plastics packaging, as an alternative to the current non-biodegradable plastics. The properties of the biofilms must be acceptable or at comparable as the conventional synthetic polymers. Besides the excellent mechanical properties, the tapioca starch-based films prepared in this study proved to be biodegradable. Furthermore, addition of antimicrobial agent has prepared this biofilms to be a better material for food packaging.

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