Starch Based Biofilms for Green Packaging

Roshafima R. Ali, W. A. Wan Abdul Rahman, Rafiziana M. Kasmani, and N. Ibrahim

***Abstract*—**This current research focused on development of degradable starch based packaging film with enhanced mechanical properties. A series of low density polyethylene (LDPE)/tapioca starch compounds with various tapioca starch contents were prepared by twin screw extrusion with the addition of maleic anhydride grafted polyethylene as compatibilizer. Palm cooking oil was used as processing aid to ease the blown film process, thus, degradable film can be processed via conventional blown film machine. Studies on their characteristics, mechanical properties and biodegradation were carried out by Fourier Transform Infrared (FTIR) spectroscopy and optical properties, tensile test and exposure to fungi environment respectively. The presence of high starch contents had an adverse effect on the tensile properties of LDPE/tapioca starch blends. However, the addition of compatibilizer to the blends improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the films. High content of starch amount also was found to increase the rate of biodegradability of LDPE/tapioca starch films. It can be proved by exposure of the film to fungi environment. A growth of microbes colony can be seen on the surface of LDPE/tapioca starch film indicates that the granular starch present on the surface of the polymer film is attacked by microorganisms, until most of it is assimilated as a carbon source.

***Keywords*—**Degradable polymer, starch based biofilms, blown film extrusion, green food packaging.

I. Introduction

PLASTICS have been widely used all over the world but it has become a major problem when the plastic cannot degrade even after hundred years. Approximately 140 million tones of synthetic polymers are produced worldwide each year to replace more traditional materials, particularly in packaging. Over 60% of post consumer plastics waste is produced by households and most of it as single use packaging [1]. Plastics are manufactured and designed to resist the environmental degradation and also more economical than metal, woods and glasses in term of manufacturing costs and energy required. Due to these issues, plastics resins have become one of the most popular materials used in packaging.

However, these plastics are made of petroleum-based materials that are not readily biodegradable. Synthetic plastics such as polyethylene and polypropylene have a very low water vapor transmission rate, which are good characteristics as packaging materials. Furthermore, they are totally non-biodegradable, and therefore lead to environmental pollution, which pose serious ecological problems. Polyolefin are not degraded by microorganisms in the environment, which contributes to their long lifetime of hundreds of years. Plastics packaging has a cycle less than a year and continuously enter the waste stream on a short turnout of time. The continuous growing of plastics industries has lead to the increase volume of plastics waste in the landfill. With the growing concern about environmental pollution, the accumulation of plastic waste needs immediate resolution. Biodegradable plastics have been intensively studied in recent years [2] - [6] and have been commercialized into various products such as garbage bags, composting yard waste bags, grocery bags and agriculture mulches.

Biodegradable plastics defined as plastics with similar properties to conventional plastics, but it can be decomposed after disposal to the environment by the activity of microorganisms to produce end products of CO_2 and H_2O [7]. It is also an alternative to the petroleum based non-biodegradable polymers. Biodegradable plastics can be used in hygiene products, household goods, horticultural products, agriculture, medical products and many more. It decreases the solid waste problems created by plastics waste. Biodegradable polymers can be divided to two main categories, which are naturally occurring biodegradable polymers and synthetic biodegradable polymer [8].

Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Technologies have been developed for continues production of extrusion films and injection-moulded plastics containing 50% or more of starch [7]. Starch satisfies the requirements of adequate thermal stability, minimum interference with melt properties and disturbance of product quality [9]. Starch is an abundant, inexpensive, renewable and fully biodegradable natural raw material which has generated a renewed in its use as a component in plastic formulations [10]. Incorporation of starch into the synthetic polymer will increase the biodegradability of synthetic polymer when starch is consumed by microorganisms. It is believed that under a rapid enzymatic hydrolysis, starch will be degraded leading to a void containing matrix, reduced the mechanical properties of the plastics and might be promote the biodegradation of synthetic polymer due to the increased surface area available for interaction with microorganisms [11]. In this present study, low density polyethylene (LDPE)/tapioca starch biodegradable film were prepared by blown film extrusion with the addition of compatibilizer and palm oil based glycerin as processing aids.

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II. Materials and Method

A. Materials

Low-density polyethylene (LDPE) resin grade (TITANLENE® LOW-DENSITY POLYETHYLENE, 71009A, LDF 260GG) supplied by Titan Polyethylene (M) Sdn. Bhd. were used in this research. The density, melt flow index and melting temperature (T_m) of the polymer were 0.922 g/cm^3, 5 g/10 min and 110°C respectively. Tapioca starch, food grade was used as filler in this research. The particle size of those starches ranged from 9.73 ηm to 83 ηm with an average particle size of 32.97 ηm. The moisture content of tapioca starch is average of 11.5%. Palm cooking oil (commercial grade) and maleic anhydride grafted polyethylene; PE-g-MA (DuPont) was used as processing aids and compatibilizer to these blends respectively.

B. Sample Preparation

Low-density polyethylene and tapioca starch was dried in an oven for 24 hours at 80°C before pre-mixing and compounding to remove moisture. The compounding of LDPE/tapioca starch at different blend ratios were done using twin screw extruder with the addition of palm cooking oil (PCO) (5 wt% phr) as processing aids and PE-g-MA (5, 10, 15 and 20 wt% phr) as compatibilizer. The compounding process was carried out at a screw speed of 80 rpm and temperatures were set at 150°C/150°C/140°C/140°C from feeder to die. The strands were then cooled using water through, then passed through the pelletizer and palletized. The pellets were collected and used for film blowing. The prepared pellets of different composition, as indicated in Table I, were put in the feed hopper with the temperature setting at 115°C/120°C/130°C/130°C/ 120°C/120°C (from feeder to die). The films of LDPE/starch blends were blown at a drawer screw of 50 rpm and extruder screw speed of 120 rpm.

TABLE I
The Abbreviations of Blends

Samples	LDPE (wt %)	Tapioca starch (TS)(wt%)
LDPE	**100**	**0**
LDPE/TS:90/10	**90**	**10**
LDPE/TS:80/20	**80**	**20**
LDPE/TS:70/30	**70**	**30**
LDPE/TS:60/40	**60**	**40**
LDPE/TS:50/50	**40**	**50**

C. Fourier-transform Infrared

Fourier-transform spectroscopy (FTIR) (Perkin Elmer System 2000) was used to obtain some qualitative information about the functional groups and chemical characteristics of the LDPE/tapioca starch blends after the addition of processing aid. Small amount of samples was scanned using ATR mode and spectra were interpreted by OMNIC software.

D. Optical Property

Using ZLR 1050 Glossmeter, this optical property was conducted at angle, 20^o and 60^o. Ten reading were recorded for each formulation and the average value has been taken.

E. Mechanical Test

The tensile strength and elongation at break of sample films were determined by using tensile testing machine, Lloyd. The films were cut out into uniform shaped according to ASTM D882-02. The test was carried out at a crosshead speed of 50 mm/min. At least five samples were tested for each formulation.

F. Biodegradability

In this test method, samples films was inoculated with *Aspergillus Niger (A. Niger)* on a medium and incubated at surrounding temperature (25^{o}C - 37^{o}C) for 21 days [4], [11]. Samples were cut (2.5cm x 2.5cm) and faced on the surface of mineral salts agar in a petri dish containing no additional carbon source. Before faced the samples, agars surfaced were cultivated with *A. Niger* from the tapioca slices. Thereafter, the films were examined for evidence of colony growth.

III. Results and Discussions

A. Fourier Transformed Infrared Studies

Fig. 1 shows representative FTIR spectra for LDPE, tapioca starch and LDPE/tapioca starch (90/10) films. The existence of peaks at 2650 cm^{-1}, 2018 cm^{-1}, 1902 cm^{-1} and 1265 – 1400 cm^{-1} show the characteristics bands of LDPE. LDPE/tapioca starch films showed a broad O-H stretching absorbance in the 3600 – 3000 cm^{-1} region and strong set of C-O stretching in the 1190 -960 cm^{-1} region indicated the characteristic bands of starch [11]. The result indicated that the starch is distributed uniformly in LDPE matrix. There is no shift in starch peaks in LDPE/tapioca starch blends, inferring that the LDPE/tapioca starch systems were immiscible blends and no chemical modifications occurred in this physical blending.

B. Mechanical Test

The tensile strength, which is a measure of the resistance to direct pull, is of importance in machinability and packaging applications. Tensile properties of different LDPE/tapioca starch blend extruded films were measured and shown in Fig. 2 (a). It was observed from graph that the tensile strength of LDPE gradually decreased with addition of 40% tapioca starch in LDPE/tapioca starch blends. The decrease in tensile strength observed for the films containing the fillers as the addition level increases has been attributed to possible increasing filler-filler interactions at the expense of filler-polymer interactions [12]. This is also due to incompatibility of hydrophilic tapioca starch with hydrophobic LDPE. In fact, addition of starch generally results in an increase in stiffness, which corresponds to decreasing tensile strength as well as elongation at break [11]. Incorporation of starch had also reduced the elongation at break of all LDPE/tapioca starch blends as shown in Fig. 2 (b). Reduction in elongation at break of the LDPE/tapioca starch film was due to no chemical interaction between starch and LDPE, as been proof from the FTIR result. Starch incorporation produced discontinuity in the film matrix resulting in lower elongation [13].

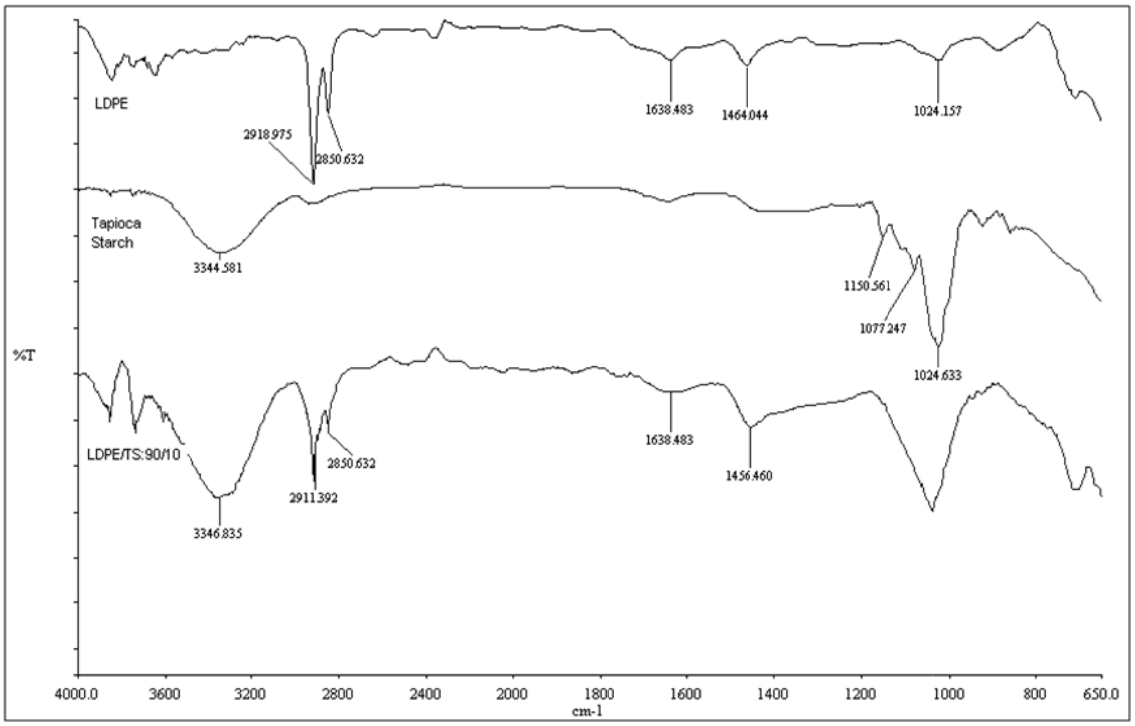
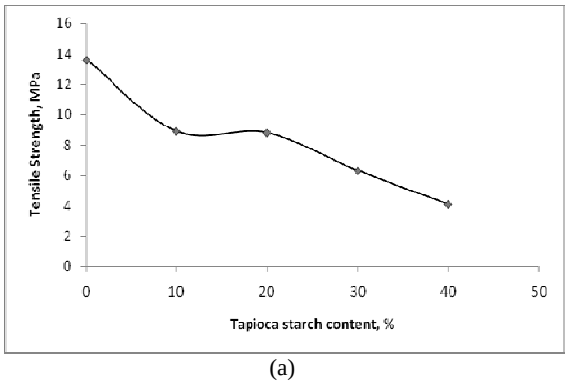
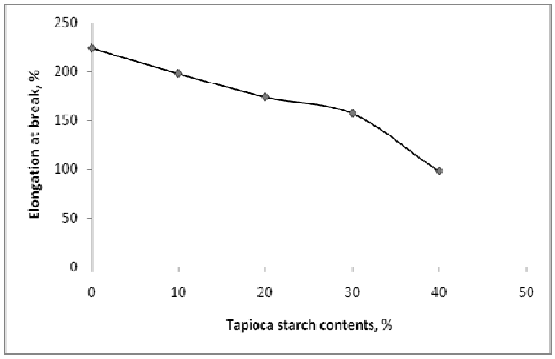


Fig. 1 FTIR spectra for LDPE, tapioca starch and LDPE/tapioca starch (90/10) films

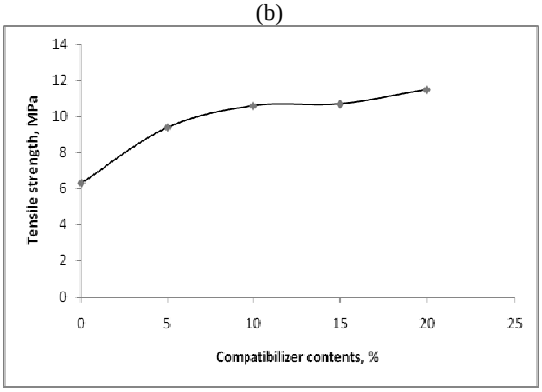
In order to enhance the compatibility between two immiscible polymers, an increased interest has appeared in the use of polymers containing reactive groups, such as, maleic anhydride as compatibilizer. Addition of PE-g-MA to this blends, showed a significant increased in tensile strength of LDPE/tapioca starch blends (Fig. 2 (c)). Tensile strength of LDPE/Starch: 70/30 (30 wt% of tapioca starch content in the blends) film increased as the compatibilizer contents rose.



(a)



(b)



(c)

Fig. 2 (a) Tensile strength of LDPE/tapioca starch based films with various starch contents, (b) Elongation at break of LDPE/tapioca starch based films with various starch contents, and (c) Tensile strength of LDPE/tapioca starch based films with various compatibilizer contents

It was discovered that anhydride groups could react with hydroxyl groups in starch to produce chemical bonding, thus improving the dispersion of starch, the interfacial adhesion, and subsequently the mechanical properties of the blends [12].

C. Optical Property

The control of surfaces gloss is very important in order to achieve the desired visual effect. The gloss level is determined by the degree of specular reflection. Table II shows the measurement level of glossiness of neat LDPE and LDPE/tapioca starch blends with various compositions. The gloss unit value at 20^{o} and 60^{o} of all the LDPE/tapioca starch blends decreased from 40 to 3 and 72 to 8 respectively, with increase in starch content in LDPE/tapioca starch film from 0 to 40%. The reduction in optical properties after incorporation of starch could be due to scattering of light radiation by starch particles [13]. This is also indicates that starch-LDPE systems were immiscible blends because these blends are generally translucent or opaque in nature.

TABLE II
GLOSS MEASUREMENTS

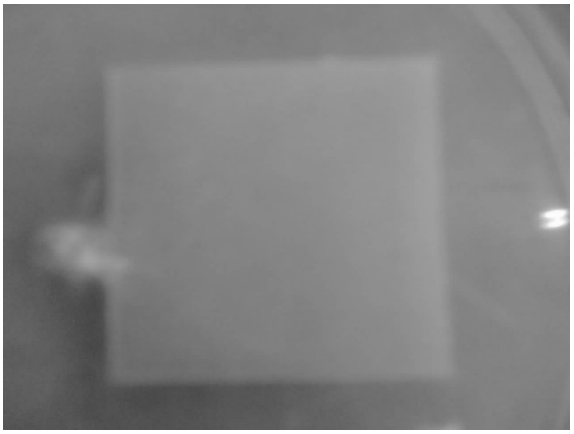
LDPE/tapioca starch films (%wt)	20^{o}(GU)	60^{o}(GU)
100/0	39.5	72.2
90/10	8.8	30.4
80/20	5.6	20.5
70/30	3.3	13.1
60/40	2.6	8.2

D. Biodegradability Study

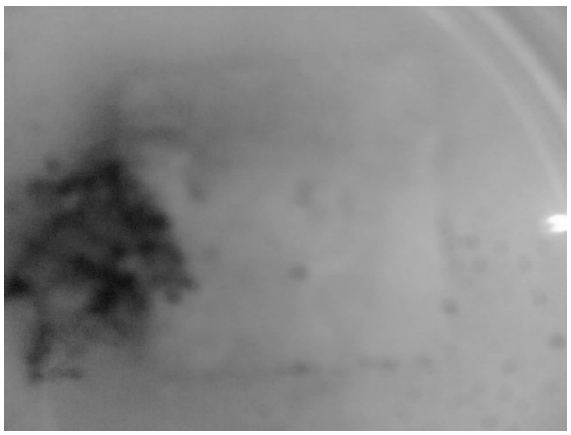
Fig. 3 shows the fungal growth for various compositions of LDPE/starch blends. There was no fungi growth on the surface of LDPE, due to microbial resistance behavior presence in the film, as shown in microscopy image analyzed with magnification of 200x (Fig. 4). LDPE are form by carbon-carbon (C-C) linkages in which these linkages are not susceptible to microbial attack [9]. In contrast, after 21 days, the fungi growth was clearly visible for LDPE/starch films as the incorporation of starch has attracted fungi to attack the film. Starch loading up to 20% shows the apparent of fungi growth and as the starch contents increased, more of the film surfaces were covered by fungi growth. This indicated that the growth of *A. Niger* colony increases as the starch content is increased. The granular starch present on the surface of the polymer film is attacked by fungi. This weakens the polymer matrix and increases the surface volume ratio, hydrophilic and permeability of the film [9].



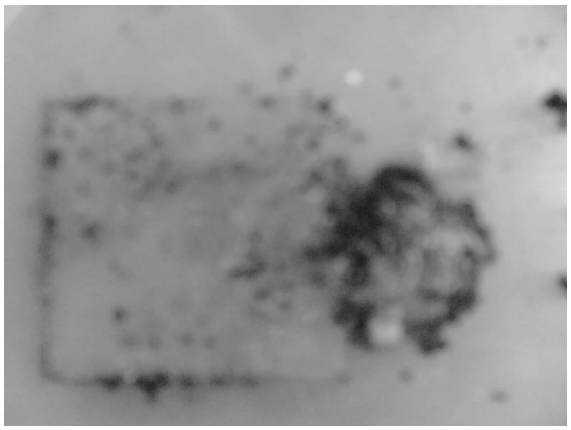
(a) LDPE/TS:90/10



(b) LDPE/TS:80/20

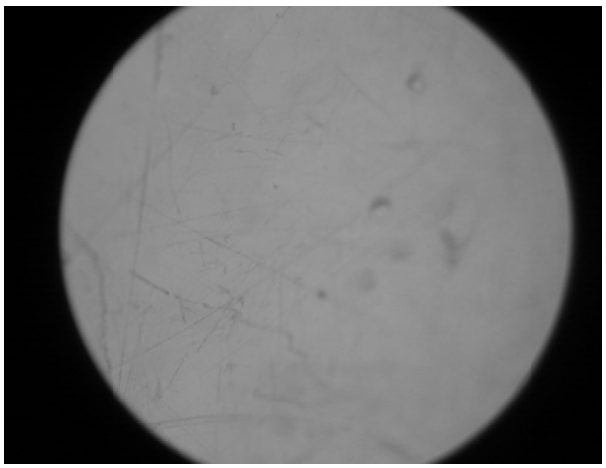


(c) LDPE/TS:70/30

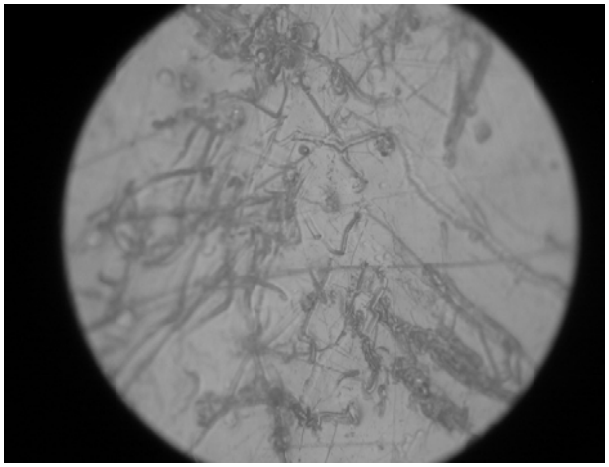


(d) LDPE/TS:60/40

Fig. 3 Fungal growth for various compositions of LDPE/starch blends



(a) LDPE film



(b) LDPE with incorporation of tapioca starch biofilms

Fig. 4 Evidence of fungi growth (A. Niger) on surface of LDPE films with and without incorporation of starch under microscope magnification 200X.

IV. Conclusion

LDPE/tapioca starch based biofilms were prepared and their optical, mechanical properties and biodegradability were measured and correlated to their composition. The addition of palm cooking oil as processing aid, improved processability of the blends, thus, degradable film can be processed via conventional blown film machine. Incorporation of polymer containing reactive group, PE-g-MA as compatibilizer improved the dispersion of starch, interfacial adhesion between starch and LDPE, subsequently the mechanical properties of the resultant blends. The LDPE/starch systems is an immiscible blend, also results in reduction in optical properties. Starch loading up to 20% shows the apparent of fungi growth and as the starch contents increased, more of the film surfaces were covered by fungi growth, as the incorporation of starch has attracted fungi to attack the film.

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