

Tapioca Starch Biocomposite for Disposable Packaging Ware

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In this research, the renewable source, tapioca starch (TS) is used as the subject to improve the degradability of injection moulded plastic packaging. The TS blended with low density polyethylene (LDPE) was melt compounded using a twin screw extruder at screw speed at 70-80 rpm, barrel temperature range at 150, 130, 130 and 140 °C and followed by injection moulding process to produce sample. Studies on their mechanical properties and biodegradation were carried out by tensile test and exposure to fungi and enzyme environment respectively. The presence of high starch contents had an adverse effect on the tensile properties of LDPE/tapioca starch blends. In biodegradation studies, fungi test evaluated visually and showed the starch in the sample promoted growths and increased fungi colony. Young's Modulus and tensile strength was found to decrease with the addition of tapioca starch. However, elongation at break of the samples increased slightly when starch is added. The samples become ductile at increasing of TS loadings. A growth of microbes colony can be seen on the surface of LDPE/TS biocomposites indicates that granular starch present on the surface of the samples were attacked by microorganisms, until most of it is assimilated as a carbon source.

1. 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. The usage of excessive plastics in food packaging, plastics bags and plastics gardening film makes the landfill becomes worse once the plastics has become wastes. In Malaysia, plastic waste is the most common solid waste in the country accounting for 7-12 percent by weight and 18-30 percent by volume of the total residential waste generated. The characteristics of plastics that are strong, light-weight, inexpensive, easily processable and energy efficient make degradable being a difficult task (Albertsson and Karlsson, 1995). The most common plastic that was used in many applications is polyethylene (PE) due to its good mechanical properties and low cost (Sailaja, 2005).

There are developments of biodegradable plastics that can reduce the municipal wastes and this development indirectly will prevent the world become waste disposal. Biodegradable polymers and plastics are material that was completely decomposed when exposed and under attack to microorganism, either bacteria or fungi with appropriate environmental condition. Biopolymers from agricultural sources are becoming an interesting alternative for biodegradable films and other plastics stuffs (Gomez-Martinez et al., 2011). By blending polymers and starch the tendency for the product to degrade is become larger. The blending of biodegradable polymer which is starch with inert polymers such as polyethylene has received considerable attention because of the possible application in the waste disposal of plastics (Zeena et al., 2009). The blends between starch and polyethylene also lead to poor mechanical properties and in order to improve the incompatibility between starch and polyethylene this is by addition a compatibilizers (Sailaja and Chanda, 2002). TS are inexpensive, renewable and abundant product. It has good potential as biodegradable fillers to synthetic polymer such as LDPE. Thus, it has been alternatives

to reduce our dependence on depleting petrochemical resources. In LDPE/TS blends, the mechanical properties reduce and drop down up to 50% starch loading (Sailaja, 2005). However, the addition of compatibilizer substantially improved the mechanical properties. Previous studied only focused on LDPE/TS film by blown film at maximum of 50% TS loading and also the compounding of LDPE/TS. In this study, biodegradable LDPE and tapioca starch blends were formulate via injection moulding processes with addition of compatibilizer and glycerol as processing aid. The mechanical, thermal and biodegradability of LDPE/TS blends were discussed besides to optimize the injection moulding process parameters of the blends.

2. Experimental

2.1 Sample Preparation

Tapioca starch (TS) (food grade; particle size of those starches ranged from 9.73 μm to 83 μm with an average particle size of 32.97 μm and moisture content of tapioca starch is average of 11.5%) and low-density polyethylene (LDPE) resin (injection grade (TITANLENE® LOW-DENSITY POLYETHYLENE; density, melt flow index and melting temperature (T_m) of the polymer were 0.922 g/cm³, 7 g/10 min and 110°C respectively) has been prior dried in oven and was then been heated at 82°C for 24 hours. Then, the mixing process has been carried out using high speed mixer with no heat addition. First, dried LDPE been introduced into the high speed mixture and glycerol (industrial grade), maleic anyhydrate, stearic acid and wax had been added continuously. The rotation speed of the high speed mixer had been set up to 30 rev/min and the running time had been considered up to 10 min for each material added. The compositions stated in Table 1.

Table 1: Samples Formulations

Samples	Tapioca Starch (wt%)	LDPE (wt%)	Glycerol (wt%)	Stearic Acid (wt%)	Wax (wt%)	Maleic Anhydride (wt%)
LDPE/TS:30/70	30	54	7	3	3	3
LDPE/TS:40/60	40	45	6	3	3	3
LDPE/TS:50/50	50	36	5	3	3	3
LDPE/TS:60/40	60	27	4	3	3	3
LDPE/TS:70/30	70	18	3	3	3	3

Compounding of the blended mixture was undertaken on a twin-screw extruder at four step temperatures of 150, 130, 130, and 140°C and 70-80 rpm rotating speeds. Low in viscosity of the samples founded difficulties in injection process. Thus, the sample been prepared by hot press at 165-170°C, with pre heating time of 1 min, heating time of 9 to 10 min and cooling time at 15 min.

2.2 Mechanical Studies

Tensile test had done using Lloyd Universal Test Machine Model 4400 to measure the tensile strength, Young's modulus and elongation at break of the LDPE/TS blends. According to ASTM D638-99, type of dumbel specimens, approximately 3 mm thick and 6.5 cm length had prepared. The cross-head load had used was 250 kg and the extended speed had been set up at 1 mm/min. Seven measurements had been conducted for each formulation, and the results taken were average. The testing had done at room temperature.

2.3 Thermal Analysis

Thermal stability had been measured by means of a Perkin-Elmer DSC-2 on 2-mg samples encapsulated in standard aluminum pans with three holes in the pan cover. The samples been purged with oxygen with flow rate, 50 mL/min and also been heated from 30 to 200°C at a rate of 5°C/min. The melting temperature of LDPE/TS composite had been determined. The standard referred was ASTM D3418.

2.4 Biodegradation Studies

A. Exposure to Fungi Environment

Samples were tested using petri dishes containing sterile nutrient salts agar (pH 6.5) and one 2"x2" piece of each specimen according to ASTM G21. Each sample tested in triplicates. Each replicate of the two samples were inoculated with a fungal suspension that consisted of equal volumes (35.0 mL) of 5 mold suspensions that were at a concentration of 1,000,000 spores \pm 200,000 per ml. The fungal pecies tested included *Gliocladium virens* ATCC 9645, *Aspergillus niger* ATCC 9642, *Penicillium pinophilum* ATCC 11797, *Chaetomium globosum* ATCC 6205 and *Aureobasidium pollulans* ATCC 15233. With the testing it was included three pieces of inoculated sterilized filter paper as positive controls. Two non inoculated tiles

for each type of material were included as negative control as well a set of media blanks as control. Samples were incubated at $27.00\text{C} \pm 2.00\text{C}$ for 28 d maintaining a relative humidity of 85.0 %.

B. Exposure to Enzyme Environment

In vitro, degradation studies were performed by incubating polymeric blends into α - amylase solutions at constant pH (6.8) and temperature (25 ± 0.2 °C). In brief, pre-weighed pieces of blends were added into a 20 ml of enzyme solution containing 6.5 IU/ml of α -amylase. As a result of the degradation of starch content of the blend, a weight loss of the blend occurs, which was periodically recorded at desired time intervals by a sensitive balance. The extent of degradation may be calculated by the final equation:

$$\% \text{ Degradation} = \frac{m_0 - m_d}{m_0} \times 100$$

whereby; m_0 and m_d are the initial and final weights (before degradation and after degradation respectively) of dry polymer blends (Bajpai and Shrivastava, 2005).

3. Results and Discussions

3.1 Fourier Transformed Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectroscopy was conducted to measure the bond vibration frequencies in a molecule and is used to determine the functional groups present in the pure LDPE, tapioca starch and LDPE/TS blends. The characteristic peaks of pure LDPE, tapioca starch and LDPE/TS blends have been given in Table 2. The FTIR spectra of LDPE show the characteristic of C-H stretching at $2,923.67 \text{ cm}^{-1}$ in the range of $2,800\text{-}3,000 \text{ cm}^{-1}$. The spectrum for LDPE/TS are shown as in Figure 1 shows the broad peak of O-H at $3,399.56 \text{ cm}^{-1}$ which the range is within $3,400\text{-}3,300 \text{ cm}^{-1}$. It is shown that the starch is hydrophilic which can absorb more water compared to the LDPE which is hydrophobic.

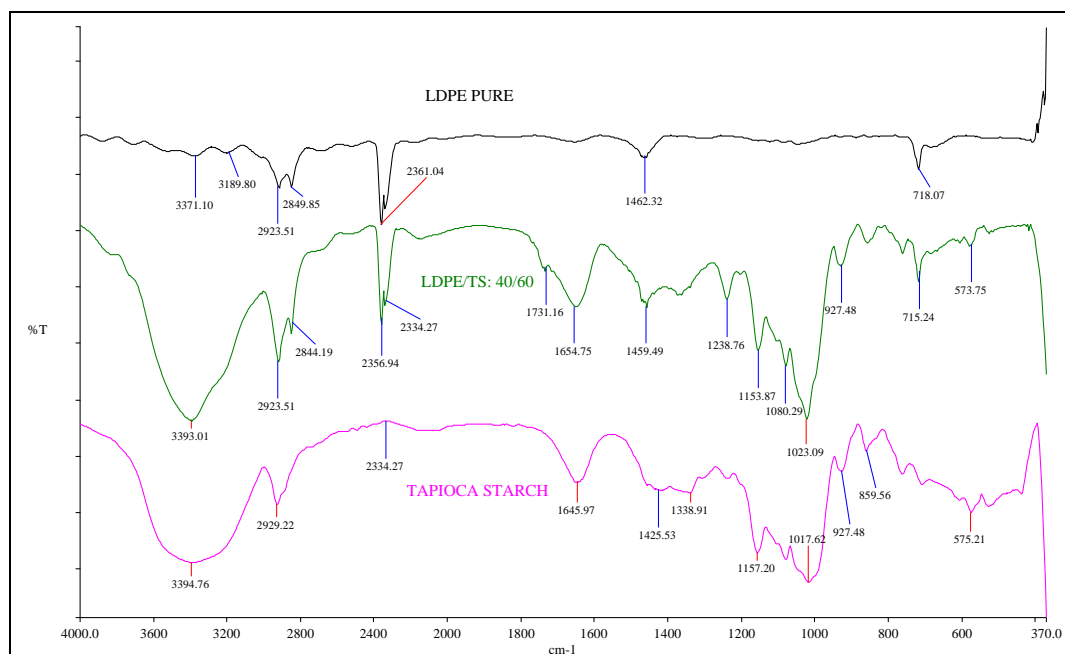


Figure 1: FTIR spectra LDPE, LDPE/TS (40/60) and tapioca starch

3.2 Mechanical Studies

The mechanical properties of TS/LDPE blends were evaluated by tensile properties. Increasing of TS loading lowering the strength and stiffness of the biocomposite. However, it increased the ductility of biocomposites. Based on Figure 2 (a) and (b), increasing of TS loading had lowering the mechanical strength and stiffness of the sample. This had due to the fact that increasing of starch cause the weakness in the bonding between the matrix and the filler. Thus, results in little stress transfer from the matrix to the

filler (Sailaja, 2005). However, the increase of TS loadings had increased the readings of elongation at break as stated in Figure 2 (c). This phenomenon indicated that the increased of elastomeric properties of the sample. Thus, increase loading of tapioca starch had lowering the strength but increase the ductility of the sample.

Table 2: FTIR spectra for LDPE, TS, and LDPE/TS blends

Functional Group	LDPE	Tapioca Starch	LDPE/TS
O-H (alcohol/phenol) Broad : (3610 cm^{-1} -3670 cm^{-1}) to (3200 cm^{-1} -3400 cm^{-1})	Nil	3399.56 cm^{-1}	3439 cm^{-1}
C-O (alcohol/phenol) strong :1190-960 cm^{-1}	Nil	1025.79 cm^{-1}	1020.82 cm^{-1}
C-H (methyl) Strong : 1460 cm^{-1} -1470 cm^{-1} Strong to medium : 2780 cm^{-1} , 2960 cm^{-1} Weak : 1380 cm^{-1}	2915.85 cm^{-1} , 2845.40 cm^{-1} , 1468.39 cm^{-1} , 1374.58 cm^{-1}	2923.67 cm^{-1}	2915.85 cm^{-1} , 2845.40 cm^{-1}
C-C (acyclic) 1645 cm^{-1} -1670 cm^{-1}	Too small	1644.29 cm^{-1}	1639.01 cm^{-1}

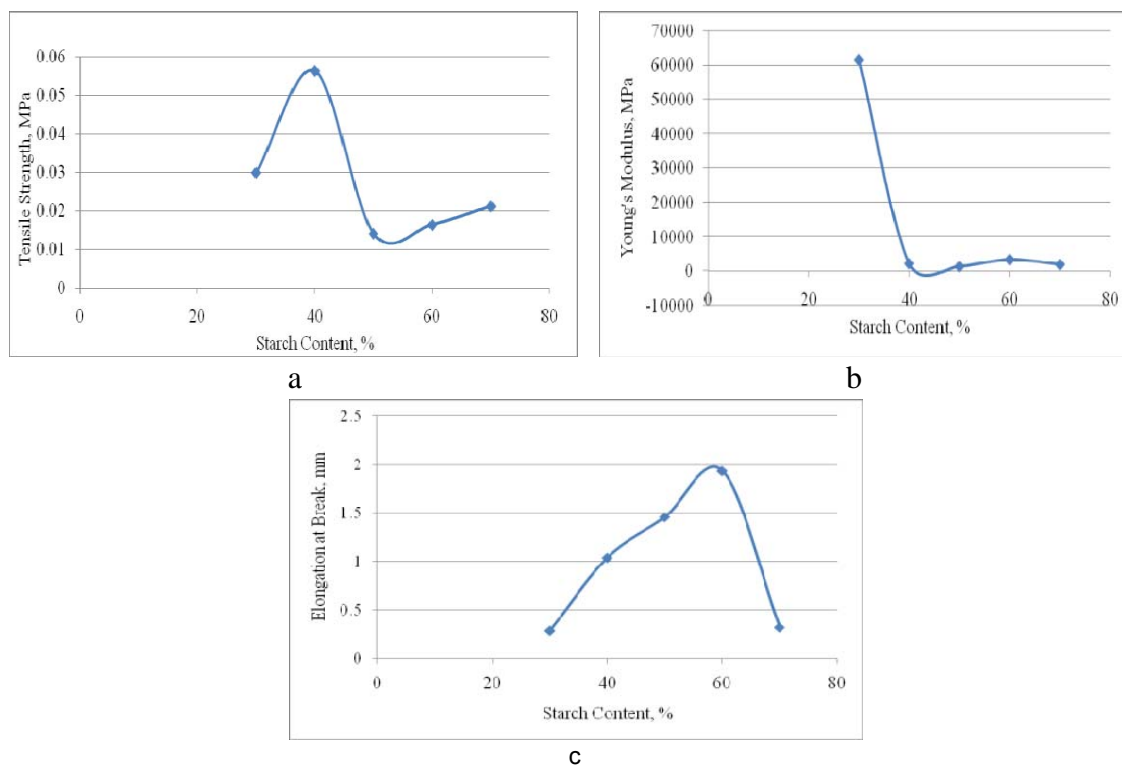


Figure 2: Plot of (a) Tensile strength (MPa) and (b) Young's modulus (MPa) and (c) Elongation at break (mm).

3.3 Biodegradation Studies

There was no fungi growth on the surface of LDPE, due to microbial resistance behaviour presence in the film, as shown in microscopy image analyzed with magnification of 200x (Figure 3). LDPE are form by carbon-carbon (C-C) linkages in which these linkages are not susceptible to microbial attack (Shah et al., 1995). In contrast, after 21 d, the fungi growth was clearly visible for LDPE/TS biocomposites as the incorporation of starch has attracted fungi to attack the samples. Figure 4 shows the fungal growth for various compositions of LDPE/TS biocomposites. Starch loading up to 20 % shows the apparent of fungi growth and as the starch contents increased, more of the samples 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 (Shah et al., 1995).

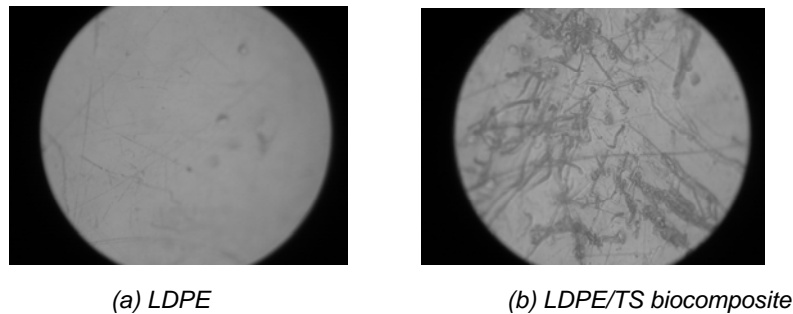


Figure 3: Evidence of fungi growth (*A. Niger*) on surface of LDPE/TS biocomposites with and without starch under microscope magnification 200x.

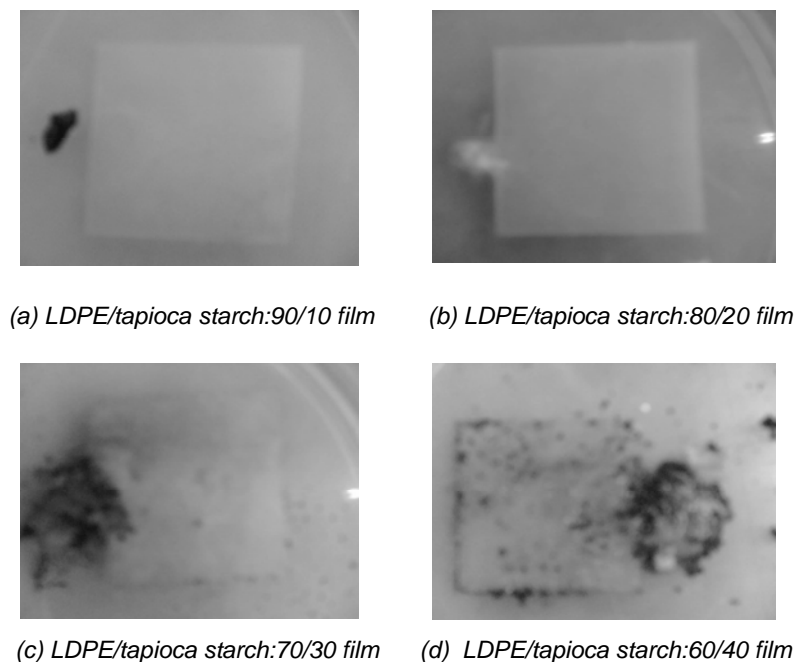


Figure 4: Fungal growth for various compositions of LDPE/starch blends

Enzyme studies were done by technique of diffusion of enzyme molecules into the blends of TS/LDPE at different percentage of loading. In this studies mechanism, the α -amylase molecules were diffused into the blends network and cause degradation. Based on Figure 5, showed that the percent degradation was constantly increase with increasing starch content in the blend. This could be explained by the fact that as the amount of starch increases in the blends, the blends acquires sufficient molecular compactness, and the volume fraction of the polymer being increased with starches resulting in an active diffusion of α -amylase molecules into the network (Bajpai A. K., Shrivastava J.; 2005). This is also proved by the statement from Sailaja R.R.N. (2005) said that higher starch and the compatibilizer used increase the

adhesion of the blends. Since the starch is biodegradable, it would be metabolized by a wide array of organisms (Peter and Avérous, 2009). Thus, higher tapioca starch loading had increase the reactivity of α -amylase.

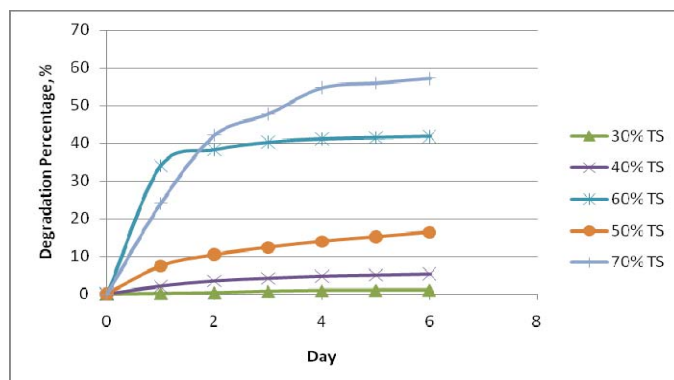


Figure 5: Enzyme test for the LDPE/TS biocomposites

4. Conclusions

LDPE/TS biocomposites were prepared via injection moulding machine and their mechanical properties and biodegradability were measured and correlated to their composition. Increasing of TS loading lowering the strength and stiffness but increased the ductility of biocomposites.. Starch loading up to 20% shows the apparent of fungi growth and as the starch contents increased, more of the samples surfaces were covered by fungi growth, as the incorporation of starch has attracted fungi to attack the film, shows that this biocomposite is degradable. This starch based biocomposite can be decomposed after disposal to the environment by the activity of fungi and microorganisms. Tapioca starch based biocomposites can be use as an alternative to the petroleum based non-degradable polymers. It can be used as degradable plastics for food packaging and many more.

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