Physical and mechanical properties of LDPE incorporated with different starch sources

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Abstract. In this study it was investigated the incorporation of different starches, such as sago starch, corn starch, potato starch, tapioca starch and wheat starch, in low-density polyethylene matrix (LDPE) to enhanced mechanical properties and to obtain partially biodegradable product with the aim to reduce the plastics wastes in the environment. For comparison, virgin LDPE, LDPE with different sources of starch blends were prepared and characterized under the same conditions. The starches were mixed to the LDPE using a twin screw extruder to guarantee the homogeneity of the formulations. The compound were shaping processed by injection moulding. The characterization of those compounds was done by physical (density, MFI), mechanical (Universal tensile machine). The addition of starch to LDPE reduced the MFI values, the tensile strength, elongation at break and impact strength, whereas the elastic modulus, flexural modulus and flexural strength increased. LDPE/SS show the good mechanical behavior compared to other formulation. The physical and mechanical properties were evident when 5 and 30 wt% were added. Water uptake increased with increased starch content and immersion time. The time taken for the composites to equilibrate was about one month even when they were immersed completely in water.

1. Introduction

The disposal of plastics in an ecologically sound manner has resulted in the evolution of new growth industries named Biodegradable Plastics. Most of the raw materials used in the plastic products are derived from petroleum based material. Among them are polyethylene (PE). Polyethylene is the most produced polymer globally. It is utilized for many applications such as in packaging, electrical insulations, construction and daily consumer products. Unfortunately, PE is the worst offender and is highly resistant to biodegradation. This petroleum based products will not environmentally friendly and mostly disposed off as garbage in landfill disposal areas. Incineration of these materials poses other
environmental and health related issues as a result of release of flue gases (NOX and SOX) as well as dioxin, the by-products from the process. This has prompted the incorporation of starch to serve as biodegradable filler for PE and to produce eco-environmentally composites. Two major technologies for starch addition to plastics have been developed. One is based on the use of gelatinized starch molecules as an integral part of the polymeric structure, and the other is based on the use of granular starch as filler. (otey et al) Several different starches are available on the market, including corn, cassava, wheat, rice, tapioca, wheat, and each type has specific properties and, hence, special application [1]. Many researches have been done to analyze the properties of starch-based plastic composites. Over the last 50 years, starch-filled polyethylene plastics have been reported by many researchers [1][2]. Although starch has been studied as a filler in plastics before, degradable starch plastic composites with good mechanical properties only came into existence in the mid-1970s following the work of Griffin [3].

With the development of the plastic industry, starch/polyethylene plastics with good degradability and compatibility are increasingly desired [4]. Granular starch has been incorporated into low-density polyethylene (LDPE) as biodegradable filler. Several starches such as maize, wheat, tapioca, and potato have been successfully incorporated into LDPE. Biodegradable starch based plastic were produce not meant totally replace synthetic polymer. The use of a biopolymer such as starch can be interesting solution because this polymer is renewable, quite cheap, biodegradable, abundant and recyclable. Thus, the main objectives of this work were to compare and characterize the physical, thermal, mechanical and morphological properties of sago, corn, potato, tapioca and wheat starch filled LDPE.

2. Experimental

2.1 Materials
Sago starch (SS) was purchased from G-far keropok Enterprise (Malaysia). The moisture content of the starch was 13% and the granule sizes ranged from 9 µm to 35 µm. Corn starch (CS), wheat starch (WS), potato starch (PS) and tapioca starch (TS) was purchased from Sigma Aldrich Co. (Malaysia). Low density Polyethylene (LDPE) with melting temperature of 140°C, was collected from Petlin Malaysia Sdn Bhd (Malaysia).

2.2 Blend preparation
Starch was dried to moisture content below 10% for 12 h in an oven at 70°C to avoid the formation of the porous blend. The moisture content of the starch was approximately 10% to enhance processability and no additional water or other plasticizers were added to the compound. Several types of starch (SS, CS, PS, TS, and WS) blend with LDPE were made at the same processing conditions for comparison purposes. Compound formulation containing different sources of starch and LDPE were made at 5, 10, 15, 20% wt. of starch to study the effect of starch content on the properties of the sample. The dried starch and LDPE was mixed according to the formulation and placed in airtight plastic container to equilibrate for 12h at 25°C and then extruded. LDPE with different sources of starch blends were prepared continuously in an extruder. The extruder machine used in the blending was a laboratory scale twin screw extruder (Brabender instrument). Extrusion was carried out at a screw speed of 60 rpm and the temperature will be set at 150°C/150°C/140°C/140°C in all blends [5]. The sample was fed manually as much as the extruder would process. The extrudates will be pelletized using a pelletter machine for each formulation and were stored in a airtight plastic container.

2.3 Injection molding
After the storing process, the pelletized blends were injection moulded into tensile, flex bars and impact bars as per the specification outlined in the ASTM test method D638, ASTM D790-97 and D256 using Toyo Plastar injection moulding machine with reciprocating screw. The injection moulded specimens were stored in airtight plastic container. A number of parameters, such as melt temperature, mould temperature, mould cooling time and injection speed could affect the mechanical properties of the sample.
However, to keep this study manageable, samples were injection moulded using the conditions summarized in Table 1.

### Table 1: Injection Moulding conditions for starch blends

| Processing parameters     | LDPE/Starch blend |
|---------------------------|-------------------|
| Melt temperature (ºC)     | 140               |
| Mould temperature(ºC)     | 40                |
| Screw speed (rpm)         | 100               |
| Back pressure (MPa)       | 0.5               |
| Injection pressure (Mpa)  | 8                 |

#### 2.4 Physical characteristic

Physical characteristic of extrudates measured were density and melt Flow index. Melt flow index (MFI) were determined using Melt flow Indexer according to ASTM D1238. The temperature of 150ºC and load of 2.16kg will be used. The time taken for the interval is one minute. The weight of extrudates were measured and the melt flow of the samples were calculated. The MFI corresponds to the mass of polymers that passes through a standard capillary, in an interval of 10 min, at a given applied pressure (load).

The density of a material is the mass per unit volume. Three replicates of density analysis were performed for each sample. Each sample was weighted approximately about 2g and measured by a digital weighing balance with four decimal. The volume of a sample (V, cm³) was measured using a gas-operated (argon gas) pycnometer (micrometerics, AccuPyc II 1340 gas pycnometer).

#### 2.5 Mechanical test

Mechanical properties of LDPE/starch specimen measured were tensile, flexural and impact property. Before the mechanical property measurements were conducted, all specimens were conditioned in a desiccators at 43±0.4% relative humidity maintained with saturated potassium carbonate (K₂CO₃) aqueous solution for 1 days until equilibrium was reached. Tensile and flexural properties of specimen will be carried out using a Shimadzu tensile machine. The test will be done according to ASTM test method D-638 and D-256 respectively. Tensile testing was performed using a crosshead speed of 3 mm/min while a crosshead speed of 9 mm/min was used for flexural testing. Gauge length will be set at 50 mm.

Samples for tensile and flexural measurements will testing and five samples will be tested for each formulation. The conditioning of tensile specimens will be followed accordingly as stated by the standard. Tensile modulus, tensile strength and elongation at break will be evaluated from stress-strain data of tensile testing, while flexural strength and flexural modulus will be evaluated from stress strain data of flexural testing.

Impact test was carried out according to ASTM D-256-93. The Izod specimens were notched (45°) to a depth of 2.6 mm. The specimens were notched with Davenport notch cutting apparatus. The test was conducted using an Izod impact machine (Toyoseiki) at room temperature (25 ± 2°C) and 50 ± 5% relative humidity at 90° swing angle using a 1 J hammer. All samples were tested at least in triplicate.

#### 2.6 Water absorption

Water absorption test was carried out according to ASTM Standard D750-95 [6]. Samples with size of 2.0 x 3.5 cm were used for water absorption study. The samples were dried for 6 hours at 50°C before they were cooled and weighed. The samples were soaked in distilled water at 23±1°C. Samples were periodically removed from the water, blotted with tissue paper to remove surface moisture and immediately weighed. The samples were periodically weighted every 2 days to record any change in their
weights. The samples were then returned to the water baths. The percentage of the water absorption by films was then calculated using the following formula:

\[
\% W_f = \frac{W_w - W_c}{W_c} \times 100
\]

Where \( W_f \) is the final increased weight percentage, \( W_w \), the wet weight and \( W_c \), the conditioned weight of the testing samples.

3. Result and discussion

3.1 Physical properties

Table 2 indicate that the different starch content affected the LDPE density and Melt flow index of the extruded blend. It should be noted that the results for the experiments with 0% starch content, native LDPE, were included in table 2 for comparison purpose. From the data shown in Table 2, it can be seen that the increased extruded blend density obtained with the increases in all kind of starch content was probably the result of poor bonding between the starch and LDPE. This is because starch is a polar compound, while LDPE is a non-polar compound. Hence, this explains poor bonding between the filler and the matrix. On the other hand, this poor interface is believed to provide channels for gas loss that caused contraction of mould [7]. In other words, when the interface was reduced, these channels were improved, then diffusivity of \( \text{CO}_2 \) through the composite was increased, and as a consequence, the amount of lost gas increased. Another contributing factor could be that the poor bonding between filler and plastic results in easy rupture of cell walls, due to poor wetting of plastic on the filler. The samples containing sago starch (LDPE/SS) loading showed highest density at 30% starch loading compare with other types of starch with 1.0556 g/cm\(^3\). Followed by wheat starch (LDPE/WS), tapioca starch (LDPE/TS) and potato starch (LDPE/PS) loading with 1.0554, 1.0432, 1.0229 and 1.0133 g/cm\(^3\) respectively. The melt flow index (MFI) values of different composites recorded during the MFI tests are given in Table 2. It shows that the melt flow index (MFI) values of LDPE/starch composites decreased as the content of starch increased. The MFI value was increased between 15 to 30% loading for all types of starch loading. Comparing the different types of starch used in the formulations, for the blend containing corn starch (LDPE/CS), the melt flow index show the highest value compare with other types of starch loading.

Table 2: Physical properties, density and Melt flow index (MFI) of LDPE/starch blend.

| Samples (wt%) | LDPE/Starch Blend | Density (g/cm\(^3\)) | MFI (g/10min) |
|---------------|-------------------|----------------------|--------------|
| Native LDPE   |                   | 0.9188               | 2.9522       |
| Sago starch   |                   | 0.9577               | 2.7986       |
| LDPE/SS:95/5  |                   | 0.9664               | 2.6787       |
| LDPE/SS:90/10 |                   | 1.0109               | 2.2827       |
| LDPE/SS:80/20 |                   | 1.0556               | 1.8937       |
| Corn starch   |                   | 0.9354               | 2.9021       |
| LDPE/CS: 95/5 |                   | 0.9567               | 2.8191       |
| LDPE/CS: 90/10|                   | 0.9843               | 2.7893       |
| LDPE/CS:80/20 |                   | 1.0133               | 1.9029       |
| Tapioca starch|                   |                      |              |
The MFI value of polymer-filled starch is lower than MFI value of neat polymer [8]. This is similar to the obtained results shown in Table 2. The reduction may probably due to the starch granules can still retained their shape and functioned as rigid particulate fillers when processed. The flows of matrix LDPE were restricted by the starch particles and thus, increased the viscosity of composite. In addition, decreasing of MFI also due to the fact the starch particles are more viscous than LDPE [9]. This can be observed from the data illustrating MFI of neat LDPE is higher than samples containing starch loading. Starch granules are partially crystalline and have higher molecular weight than LDPE. As the content of starch is increased, the interaction among the granules was increased and contributes to the higher viscosity.

### 3.2 Mechanical properties

#### 3.2.1 Tensile

The characterization of the biocomposites reveals that the starch content is having significant effect on the mechanical properties of composites. It can be observed in Figure 1 the mechanical behaviour of LDPE/starch compounds. As expected, tensile strength and elongation at break of LDPE/starch blends decreased as the starch content increased. Tensile strength measurements indicated that the more the starch content in the samples increase, the more the mechanical properties values decline. In contrast, elastic modulus increases as the starch loading is increased. Starch incorporated into LDPE still retained their granular shape after processing.

Comparing the different types of starch used in the formulations, for the blend containing sago starch, the tensile strength and percent elongation was decreased between 15 to 30% starch loading. In cases such as when 20% of the dispersed minor phase has been added, highly deformable matrix materials are transformed into fragile materials [8]. In this study, the optimum was at 10wt% starch loading. The samples containing sago starch showed good mechanical properties compared with other types of starch, in terms of absolute values, for mechanical properties.
In all cases, the decrease of both tensile strength and percent elongation was higher in the LDPE blends containing sago starch. LDPE was rigid and fragile with high tensile strength and elongation at break, but poor in elastic modulus.
3.2.2 Flexural properties

The flexural strength and flexural modulus of all different sources of starch were higher than native LDPE. Figure 2(a),(b), LDPE/Sago starch compound show the highest value flexural strength and flexural modulus compare to other types of LDPE/starch compound loading. The highest flexural strength reading was achieved at 18.9MPa for sago starch loading compared to 10.2MPa for wheat starch at 30wt% loading. The flexural modulus value for LDPE/SS also show the highest reading followed by LDPE/PS, LDPE/TS, LDPE/CS and LDPE/WS at 30wt% loading respectively. The LPDE/sago starch flexural modulus reading was achieved at 267.2MPa moduli. In contrast, LDPE/WS show the lowest values flexural modulus reading with 220.8MPa moduli. It is suggested that the weak interfacial bonding between starch interaction with LDPE matrix polymer, cause imperfect alignment between starch and LDPE matrix in terms of void and dispersion, consequently reduce the degree of molecular orientation of composite [10][11].

![Figure 2: Effect of starch content on flexural properties of different sources of starch/LDPE blend: (a) Flexural strength; (b) Flexural modulus.](image)

3.2.3 Impact properties

The effect on impact strength of composites for notched samples was shown in Figure 3. Based on research studies [12], impact strength decreased by increasing fibre loading due to poor interfacial bonding between the filler and the matrix polymer causes micro-crack to occur at the point of impact, which causes the cracks to easily propagate in the composite without any compatibilizing agent [11].
3.3 Water adsorption

Starch based materials tend to absorb water because the hydroxyl group in starch can form a hydrogen bond with water. Influence of the starch type on water absorption of these blends as a function of time is shown in Figure 4. Starch content influences the water absorption of LDPE with different types of starch blend. Water absorption increased with immersion time and increasing starch content. Rapid water absorption was observed for all samples within the first few days of immersion, but this decreased slowly with time. This phenomenon has been observed at different relative humidity. The absorption of water is related to its rate of diffusion into the composites.

![Figure 3: Effect of starch content on impact strength of different sources of starch/LDPE blend.](image3)

![Figure 4: Effect of starch content on water uptake of different sources of starch/LDPE blend at 10wt% loading.](image4)
Conclusion
The work reported here indicates that the addition of starch alters the physical and mechanical properties of low density polyethylene (LDPE). Optimization of compounding conditions was necessary to produce bubble-free blend in extrusion process. The addition of different sources starch usually caused a negative impact on mechanical resistance and elongation at break, if compared with pure LDPE, probably due to the generation of internal strain forces and by a poor matrix starches interface. Materials manufactured from different starch-based blends, exhibit significant differences in their mechanical behavior, which might make them suitable for different particular applications. Apart of mechanical properties, this condition also contributes to reduction of melt flow index (MFI), in such way that rigid particles restrict the flow of matrix. Sago, corn, tapioca, potato and wheat starch blend did not differ among them in its water uptake after immersion in the water and the differences in physical and mechanical properties were small. This occurred because, in general, all samples were processed in a same condition, with higher stability.

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