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Effect of plasticizer on physical and mechanical properties of ldpe/sago starch blend

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Abstract. Starch-based polymeric materials offer a renewable, economical alternative to existing petroleum based, non-renewable or costly polymeric materials. The aim of this study is to develop degradable starch-low density polyethylene (LDPE) composites with enhanced mechanical properties. This research studies the effect of different kind of plasticizer. The compounding of the LDPE with sago starch was performed via a twin screw extruder followed by injection molding. Studies on their physical, mechanical of each formulation were carried out by density, melt flow index (MFI), tensile, flexural, impact. The presence of high starch contents had an adverse effect on the mechanical properties of LDPE/starch blends. However, the addition of compatibilizer or plasticizer improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the blends. After using the proper composition and processing condition, mechanical properties of plasticized LDPE/SS blend are significantly higher than those of the unplasticized LDPE/SS blend with the same starch contents.

1. Introduction

In recent years, there has been growing concern about the disposal of single-use plastics. There are many biodegradable resins now present on the market. However, most of them are very expensive to compete with the petroleum-based products. Plastics are everywhere in contemporary society. They are found in households and are extensively employed in such many industries. Polyethylene is available in many varieties (linear low density, high density, high molecular weight). Low density polyethylene that is used extensively in the rigid packaging industry because of several favourable physical properties. Polyethylene represents 64% of the produced synthetic plastics. Polyethylene is so widely used because of their wide range of physical properties, suitability to most of the commercial thermoplastics fabrication process. In addition, it offers such desirable features as broad range of properties, very good moisture barrier properties, and good chemical resistance and food grades available. The most important properties found in PE resin is because of the cheaper price that can give them a competitive advantage compared to other materials (both polymeric and non-polymeric) [1].

Plasticizer that used in this study like sucrose, urea, glycerol and sorbitol will improve the incorporation of starch in LDPE and enhancing the biodegradability of the blends as well. This kind of additives like plasticizers and fillers are normally susceptible to microbial attack. This will cause to



physical embrittlement of the polymer, leaving a porous and mechanically weakened the polymer. Plasticizers also reduce the brittleness of the blend by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules and increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular volume [1][2].

Blend/mould prepared from native polymers tends to be crack and brittle upon drying. The addition of plasticizer cause the molecular rigidity of a polymer is relieved by lowering the intermolecular forces along the polymer chain. Molecules of plasticizer interact themselves between the individual polymer chains, thus breaking down polymer-polymer interactions, making it easier for the polymer chains to move past each other. The plasticizer improves flexibility and reduces brittleness of the blend. Polyethylene glycol, glycerol, urea, Sucrose, and sorbitol are the most commonly used plasticizers in edible blend production [3]. The amount of plasticizer added can cause adverse effects on blend properties such as increasing mass transfer through the blend. Hence, plasticizers must be used with caution. The amount of plasticizer used in mould or even blend formation should also be small enough to avoid probable toxic effects [2]. The main objectives of this paper were to investigate effect of plasticizer on the physical and mechanical properties of LDPE/sago starch blend.

2. Experimental

2.1 Materials

Sago starch as filler used in this study was food grade stuff. Sago starch 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 . Low density Polyethylene (LDPE) with melting temperature of 140°C, was collected from Petlin Malaysia Sdn Bhd (Malaysia). Sucrose, urea, glycerol and sorbitol was chosen as a plastisizer which supplied by MTBE (M) Sdn Bhd.(Malaysia).

2.2 Sample preparation for sago starch/LDPE blend

The starch and Low density polyethylene was dried before sample preparation in an oven at 70 °C for 24 h and then cooled in a desiccator for 1 h to ensure it was moisture free. The sample was mixed and placed in an airtight plastic container to equilibrate for 12 h at 25 °C and then extruded. The compounding of LDPE/starch blend was done using Brabender twin screw extruder. The compounding process was carried out at a speed of 80 rpm and the temperature was set at 150°C/150°C/140°C/140°C [4]. The sample was fed manually as much as the extruder would process. The extrudates was palletized using a pelletizer machine for each formulation and were stored in an airtight plastic container.

2.3 Injection molding

After the storing process, the pallets were injection moulded with injection moulding machine equipped with a diameter 35 mm screw. Dumbbell test specimens were injection moulded for the tensile, flexural and impact measurements. The injection moulding pressure was 1400 bars, and the holding pressure was varied from 600 to 1000 bars. The injection moulded specimens were stored in an airtight plastic container.

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 150°C 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 gasoperated (argon gas) pycnometer (micromeritics, 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 $43 \pm 0.4\%$ relative humidity maintained with saturated potassium carbonate (K_2CO_3) aqueous solution for 1 days until equilibrium was reached. Tensile and flexural properties of specimen were carried out using a Shimadzu tensile machine. The test was 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 was set at 50 mm [5].

Samples for tensile and flexural measurements were testing and five samples were tested for each formulation. The conditioning of tensile specimens was followed accordingly as stated by the standard. Tensile modulus, tensile strength and elongation at break were evaluated from stress-strain data of tensile testing, while flexural strength and flexural modulus was 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 ($25 \pm 2^\circ C$) and $50 \pm 5\%$ relative humidity at 90° swing angle using a 1 J hammer. All samples were tested at least in triplicate.

3. Result and discussion

3.1 Density and Melt Flow Index (MFI)

Results show the MFI value of LDPE is 2.8522. But, the value of the MFI become lower reaching 2.6787 when starch at 10wt% loading is added, compared to native LDPE. The combination of LDPE, 10wt% sago starch and different amount of sucrose at 1wt%, 3wt% and 5wt%, gives MFI value of 2.8648, 2.8431 and 2.8287 respectively. UTPS blends shows MFI values of 2.7851, 2.7471 and 2.7899 respectively. GTPS blends shows MFI values of 2.780, 2.7553 and 2.7325 respectively. The MFI of STPS blends also shows increasing values from 2.7717, 2.9260 and 2.9008 respectively. This shows that plasticizer and starch influenced the MFI values. Sucrose as plasticizer reduced the intermolecular forces between polymer coils and increased the molecular spaces and mobility of polymers [6][7].

As shown in table 1. The movability of the polymer long chain increases with adding of plasticizer into the starch. The secondary bonds are generated between plasticizer and starch molecule: it reduces the binding strength of secondary bonds among the polymer long chains of starch mobility. It is evident that the viscosity of LDPE/SS with plasticizer is far lower the LDPE/SS blends without plasticizer. The descending degree of viscosity increase with the increase of plasticizer content, so the viscosity plasticized LDPE/SS blends is lower than uncompatibilized LDPE/SS blends.

Table 1. Density and Melt flow index values of native LDPE, LDPE/SS and plasticized LDPE/SS blend with different amount of plasticizer.

Sample	LDPE (wt%)	Starch content (wt%)	Plasticizer (wt%)	Density ^a (g/cm ³)		MFI ^b (g/10min)	
				Mean	St.dev	Mean	St.dev
Native LDPE	100	-	-	0.918	0.05	2.8522	0.08
LDPE/SS	90	10	-	0.966	0.29	2.6787	0.36
			Sucrose				
Sucrose	89.5	9.5	1	0.943	0.02	2.8648	0.52
	88.5	8.5	3	0.917	0.01	2.8431	0.30
	87.5	7.5	5	0.905	0.06	2.8287	0.18
			Urea				
UTPS	89.5	9.5	1	0.953	0.07	2.7851	0.24
	88.5	8.5	3	0.947	0.04	2.7471	0.30
	87.5	7.5	5	0.919	0.05	2.7899	0.01
			Glycerol				
GTPS	89.5	9.5	1	0.953	0.09	2.7820	0.65
	88.5	8.5	3	0.938	0.01	2.7553	0.33
	87.5	7.5	5	0.927	0.08	2.7324	0.37
			Sorbitol				
STPS	89.5	9.5	1	0.951	0.10	2.7717	0.11
	88.5	8.5	3	0.935	0.05	2.9260	0.05
	87.5	7.5	5	0.928	0.02	2.9008	0.21

*All analyses were based on two separate experiments with each mean \pm standard deviation being an average of three determinations.

^{a,b} Mean within same column are no significantly different at ($P < 0.05$)

3.2 Mechanical test

3.2.1 Tensile properties Plasticizing agent is needed to add in the polymer blend to overcome plastic brittleness caused by extensive intermolecular forces. It also increases the mobility of polymer chain and reduces these intermolecular forces. Furthermore, these plasticizers also improving flexibility and extensibility of the blend. Tensile strength represents the maximal force per original cross sectional area that the blend could sustain before breaking, while elongation reflects the extensibility of the material [8]. Generally, all starch blend plasticized with urea, glycerol, sorbitol and sucrose mixture behave like viscoelastic material. Generally, the values of elastic modulus for the plasticized LDPE/SS blends increased with increasing plasticizer content. The values of tensile strength and elongation at break changed concurrently with the values of elastic modulus. Generally, both increased plasticizer content and water content will increase the elongation at break of LDPE/SS blends.

Figure 1, 2 and 3 shows the tensile properties of unplasticized and plasticized LDPE/SS:90/10 blends with sucrose, urea (UTPS), glycerol (GTPS) and sorbitol (STPS) as plasticizer. Tensile properties and elongation at break mean are no significantly different at ($P < 0.05$) for all blend. Both the tensile strength and modulus of LDPE decrease on addition of starch for blends without plasticizer. The decreases of both the modulus and tensile strength are due to the incompatibility of starch with LDPE. However, a small increase in elastic modulus and tensile strength without a change in the stiffness of LDPE was observed for the blend containing 3wt% and 5wt% of different types of plasticizer, indicating the plasticizing effect of this copolymer.

The stiffening effect of the starch granules increase the elastic modulus of the blend, as the starch is stiffer than native LDPE. Since the sago starch contains both amorphous and crystalline regions, the calculated starch moduli are averages which reflect the contribution of each phase. The hydrogen

bonding in the starch gives it much higher elastic modulus than LDPE, which has no hydrogen bonding. Therefore there is a direct relation between the amount of starch in the blends and the increase of the modulus value. In the case of compatibilized LDPE/SS with MA, elastic moduli increased greater in comparison to the LDPE/SS blends due to the reaction between malaeic anhydride, LDPE and starch which improves adhesion, or reduces slippage at the matrix-filler interface [9].

Figure 2 shows the change in elongation at break percentage for the plasticized LDPE/SS blends. There is a clear negative deviation from the mixing additive rule. LDPE/SS incorporated by plasticizer was shown as a brittle glassy material but rigid. The elongation at break of LDPE/SS blends was observed to increase gradually with increase in plasticizer content. The increase in elongation at break in the plasticized LDPE/SS blend is due to the fact that plasticizer acted as a dilutor and lowers the interaction of the molecules. The reason for increasing elongation at break of the plasticized LDPE/SS probably was that the flexible chain $-\text{CH}_2-\text{CH}_2-$ in each plasticizer molecules provided enough room for the movement of the starch molecules. The movement of the segments and macromolecules is improved, which cause to enhance the elongation at break [10].

Generally, elongation at break is considered to be highly sensitive to the interface state. Property modification is one of the principal observed with the addition of an interfacial modifier in synthetic immiscible polymer blends is an increase in the elongation at break. Very high elongation at break values in what appears to be a classic immiscible system of hydrophobic PE and hydrophilic starch is the most unexpected finding of present study. The high elongation at break was maintained even at high thermoplastic starch loadings and in the absence of an interfacial modifier [11].

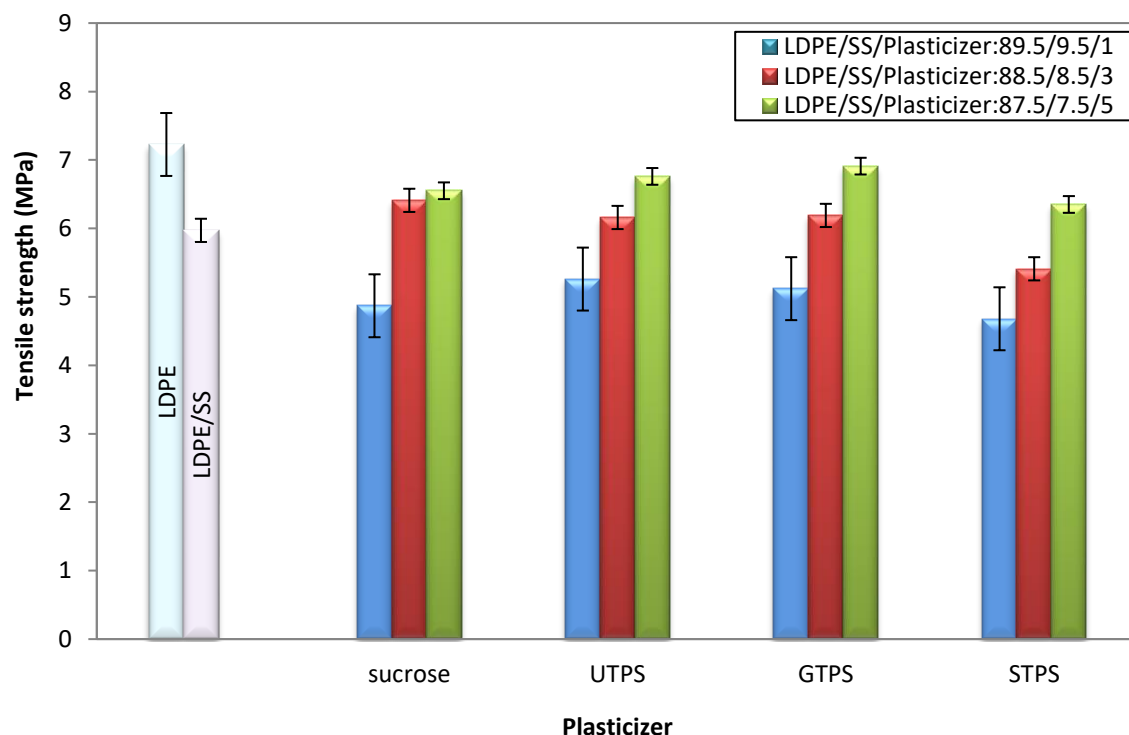


Figure 1. Effect of different plasticizer with different ratio on tensile strength of LDPE/SS blend.

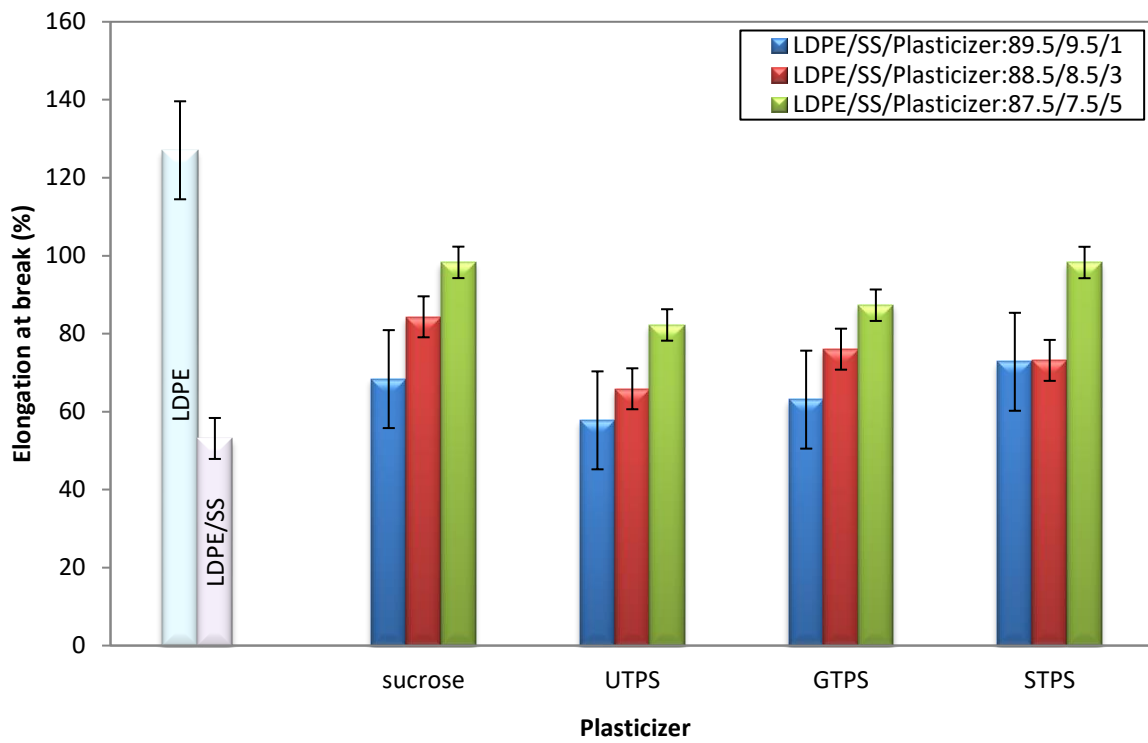


Figure 2. Effect of different plasticizer with different ratio on elongation at break of LDPE/SS blend.

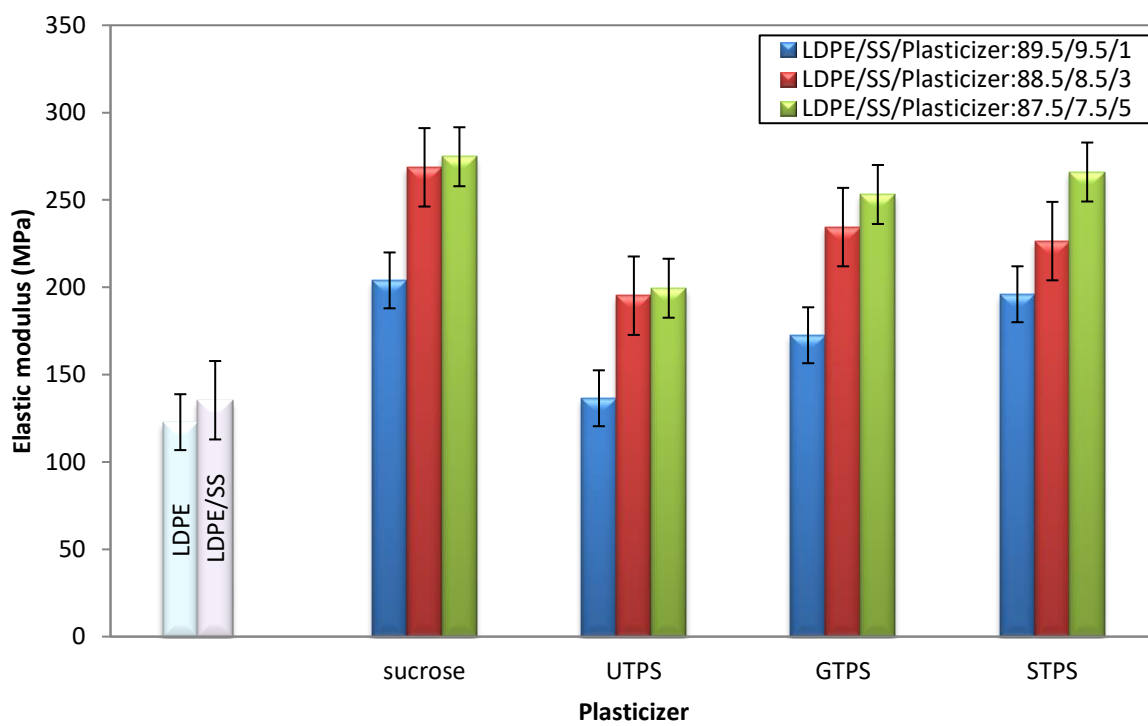


Figure 3. Effect of different plasticizer with different ratio on elastic modulus of LDPE/SS blend.

3.2.2 Flexural properties Figures 4 and 5 show the effect of various kind of plasticizer content on the flexural properties. The flexural modulus indicates as a measure of the stiffness during the first or initial part of the bending process. Flexural strength can be determined as the ability of the material to withstand bending forces applied perpendicular to its longitudinal forces [12].

In order to evaluate the flexural properties of the incorporation of different kind of plasticizer into LDPE/SS blend, repeated measures of flexural test were done for LDPE blends. In fact, flexural strength is maximum stress developed in a sample just before it cracks or breaks in a flexural strength. Both figure 4 and 5 show the flexural properties of native LDPE and LDPE/SS:90/10 blends plasticized with varying amounts of Sucrose, urea, glycerol and sorbitol (1wt%, 3wt% and 5wt%). It can be seen that both flexural strength and flexural modulus also increased as the plasticizer content increased but the effects were not as pronounced as those of unplasticized blends.

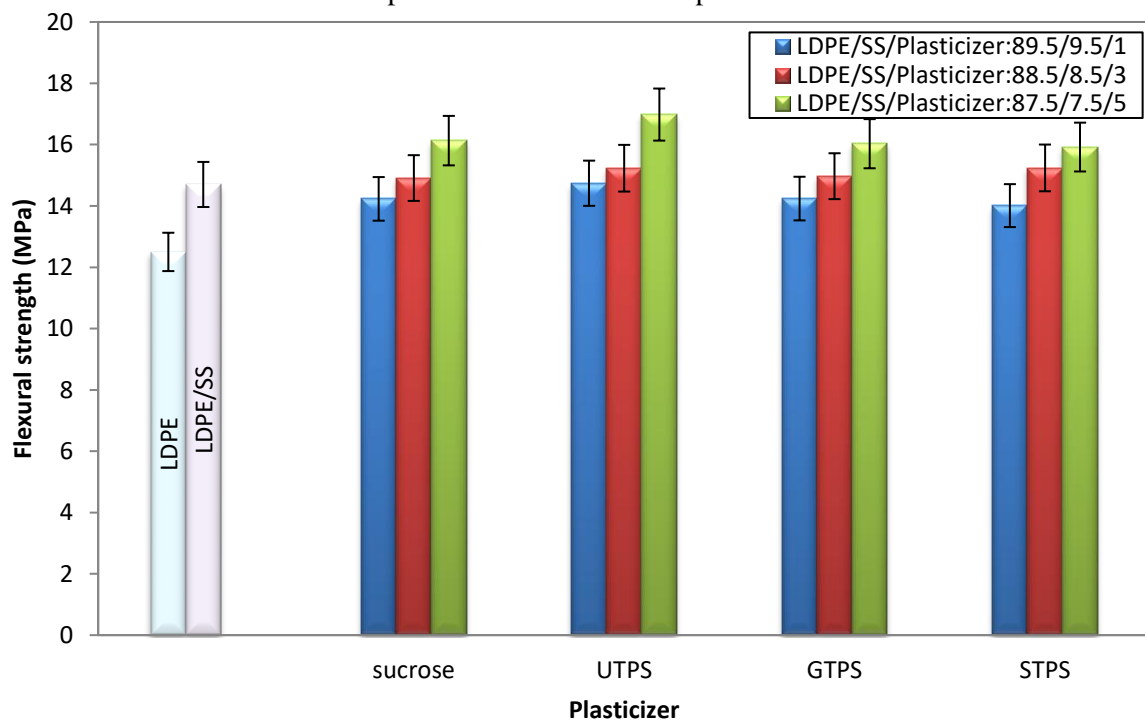


Figure 4. Effect of different plasticizer with different ratio on flexural strength of LDPE/SS blend.

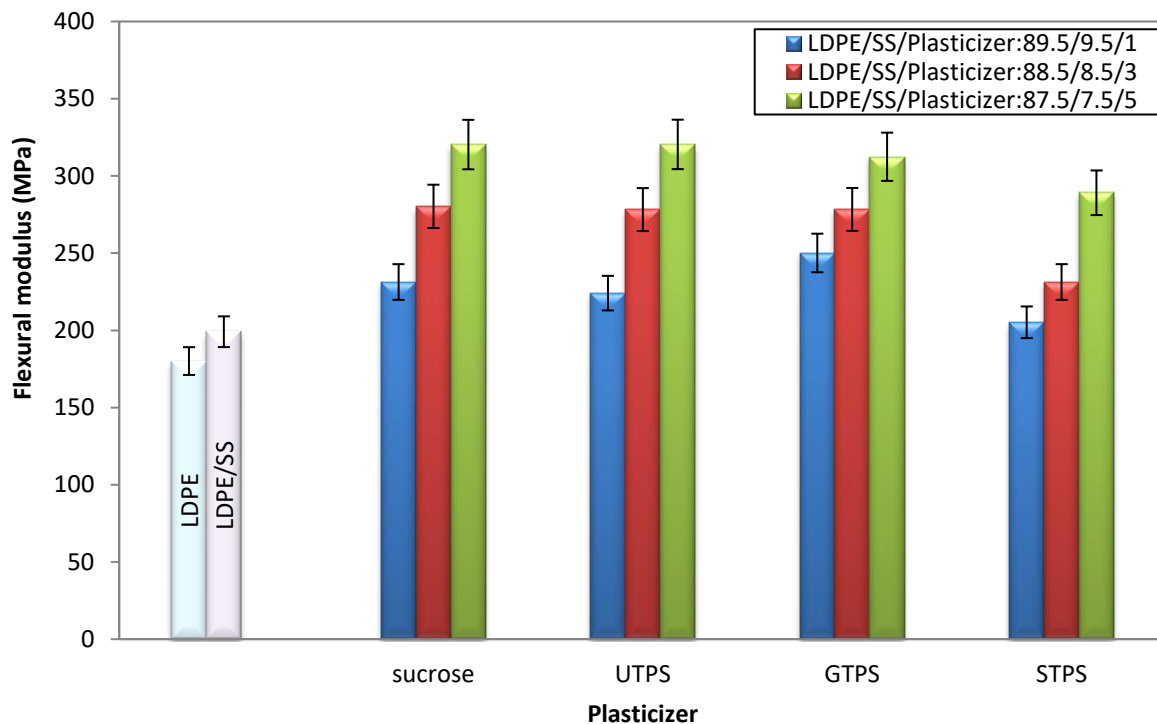


Figure 5. Effect of different plasticizer with different ratio on flexural modulus of LDPE/SS blend.

As seen in the both figures, the flexural properties among all plasticized LDPE/SS blend show no significant different. Those plasticized blend behave quite similar result. Flexural properties were poor with low plasticizer, as the TPS acts merely as a stiff particulate. It increased with increasing plasticizer, with high-amylose starches showing remarkable flexural properties even with small increases in plasticizer. Very high levels of plasticizer produced excellent extension, as the TPS elongated along with the LDPE but provided little mechanical support.

Urea has some small molecules chain $-\text{CO}-\text{NH}-$ functional group which proved to be as plasticizer for the native starch. However, a solid with little internal flexibility and hence urea-plasticized TPS became rigid and brittle. The plasticizer effectively decreased internal hydrogen bonding while increasing intermolecular spacing, therefore decreasing brittleness and increasing permeability of the blend materials. Sorbitol and glycerol are homogeneously incorporated within a network of hydrogen bonds between the starch molecular chains, which makes the blend more flexible, soft, and transparent [12]. This indicate the effectiveness of sucrose, urea, glycerol and sorbitol as plasticizing agent and flexural modifier by enhancing the interfacial adhesion between the sago starch and LDPE polymer, thus better mechanical properties was produced.

3.2.3 Impact properties Figure 6 shows the impact strengths of LDPE/SS:90/10 blends as a function of plasticizer content. Addition of plasticizer increased the impact strength, which continued to increase as plasticizer content increased. The results revealed the positive effect of stronger interfacial interaction on the Izod strength. The impact strength was affected by improving interfacial adhesion between plasticizer and LDPE/SS blend, which also increase the toughness (ductility) of the blend [10].

Figure 6 illustrates the plots of impact strength against the LDPE/SS blend plasticized with different plasticizer (Sucrose, urea, glycerol and sorbitol) with different amount of plasticizer in the blends (1wt%, 3wt% and 5wt%). The impact strength of all the blends before addition with plasticizer decreased with increasing starch content, indicating that sago starch behaved as nonreinforcing filler.

This happens because of low interfacial interaction between starch and PE, this would cause mechanical rupture at the interface of the blend. However, this property improves by the addition of 1wt% plasticizer of all plasticized LDPE/SS blend (Sucrose, UTPS, GTPS and STPS) when compared with the LDPE/SS blend without plasticizer. Although 1 wt% of plasticizer brings increased impact strength, this effect decreases with increasing sago starch concentration. The blend of sorbitol plasticized LDPE/SS (STPS) exhibits the highest impact strength compared to other plasticized blends. Further increase in starch loading causes the impact strength of the blends to decrease owing to the aggregation of TPS and plasticizer that leads to poor adhesion with LDPE. The LDPE/SS/plasticizer (88.5/8.5/3) was chosen as the optimum blend composition due to the balanced mechanical properties and cost effectiveness.

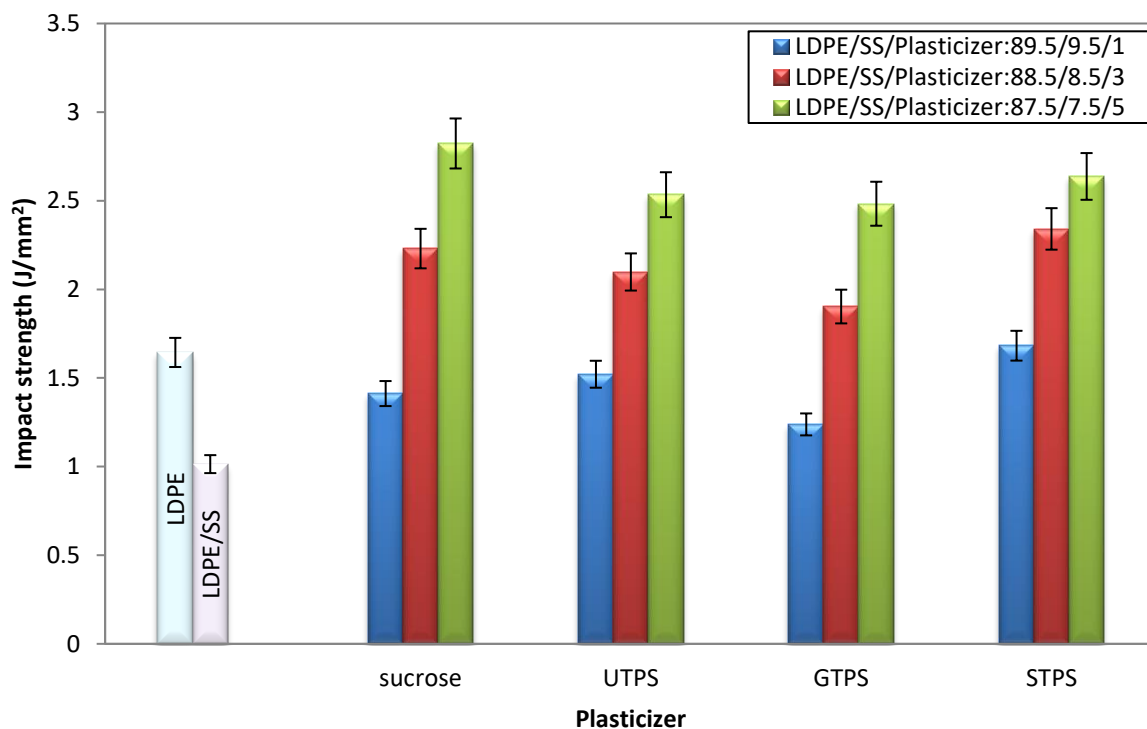


Figure 6. Effect of different plasticizer with different ratio on impact strength of LDPE/SS blend.

4. Conclusion

This research developed starch filled-LDPE blends via twin screw extruder and injection moulding. The properties of injection moulded starch blend with low density polyethylene (LDPE) were investigated. The effect of the addition of plasticizer on the LDPE/SS blends have been clearly investigated. Based on this study, there is an effective conclusion that starch are strongly affected the physical and mechanical properties of LDPE/starch blends. Mechanical properties of LDPE were found to decrease when filled with sago starch. However by addition of plasticizer are found successfully improved the interfacial adhesion between starch and LDPE matrix. The more plasticizer content will have much better performance. In addition, MFI value of plasticized LDPE/SS blend is higher compared to unplasticized LDPE/SS blends.

5. References

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