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STUDY THE PHYSICAL, MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF LDPE/SAGO STARCH BLEND

Shaharuddin Kormin¹, Faridah Binti Kormin¹, Mohammad Dalour Hossen Beg¹, Mohd Bijarimi Mat Piah¹²Faculty of Mechanical Engineering, University Tun Hussein Onn (UTHM), 86400 Batu Pahat, Johor, Malaysia²Faculty of Science, Technology and Human Development, University Tun Hussein Onn Malaysia (UTHM), 86400 Batu Pahat, Johor, Malaysia¹Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang Lebuhraya Tun Razak, 26300 Kuantan, Pahang, MalaysiaE-Mail: faridahk@uthm.edu.my

ABSTRACT

A variety of low density polyethylene (LDPE)/sago starch compounds and degradable sago based moulds with various sago starch contents to enhance their mechanical properties were prepared by twin screw extrusion with the addition of additives. Biodegradable and compostable plastics based on renewable resources from the agricultural industry are an essential innovation which offers significant impulses for the future technologies. In this study, sago starch was physically blended with LDPE and few additives to produce plasticized starch biodegradable polymer. LDPE with different percentage sago starch loading were shaped processed by conventional extrusion, injection moulding. Studies on their characteristics, mechanical properties were carried out using SEM and universal mechanical tester machine respectively. The addition of starch to LDPE reduced the MFI values, the tensile strength and the elongation at break, whereas the modulus increased. However, the density increases with the addition of sago starch. The presence of high starch contents had an adverse effect on the impact and flexural properties of LDPE/sago starch blends. Water adsorption was increased with increasing of sago starch loading. Scanning electron microscopy (SEM) shows agglomeration of the starch granules and hence, poor wetting between the starch granules and LDPE matrix. For thermal stability, it was found that the LDPE with 30wt% sago starch loading had the highest thermal stability.

Keywords: Low density polyethylene • Sago starch • Biodegradable mould •

INTRODUCTION

Disposal of used plastic products made from petroleum has become a public concern due to their non degradability and their potentially hazardous to the environment. The effect of disposable plastic products in the waste management system has been of serious concern to environmentalists hence was got enough publicity from media. It was about 23000 tonnes of expandable polystyrene loose fillers are consumed annually (Frey et al., 1998). Considerable effort has been made to produce environmentally friendly alternatives to plastic products (Fang et al., 2001).

In the past decades, the researcher have been focused on generating new materials by the blending of stable synthetic polymer with natural biopolymers, such as starch, cellulose, and chitin to produce biodegradable polymer. Biodegradable polymer is an important material innovation because it decreases dependence on petroleum and reduces the amount of synthetic polymer (Pranamuda et al., 1996) (Lawton et al., 1994). Blends of starch converted to a thermoplastic material offers a materials partially or totally biodegradable is an interesting

alternative for synthetic polymers while it reduces the consumption of petro-chemical resources.

Interest in the usage of biopolymers especially starch, are driven by their plentiful sources, cheap, and renewable characteristics (Vroman and Tighzert, 2009). In addition, starch have the unique characteristics of biodegradability properties as a carbon source and easily dissolve in water. A number of study was successfully done on blends of starches and synthetic polymers (Arvanitoyannis et al., 1999, Graaf et al., 2001). Some of researcher used rice starch (El-Rahim et al, 2004), potato starch (Borgheti et al. 2010) and sago starch (Abdul Rahman, et al. 2006) (Danjaji et al. 2001, 2002) as starch sources.

Sago as starch sources had been widely studied by many researcher on investigation the influences of sago starch content on the mechanical and biodegradation properties (Hoque et al., 2013). However, too little attention had been paid so far on morphology properties. Therefore, the focus of the study was to determine the optimum loading of sago starch (up to 30%) in LDPE that can give good mechanical properties for moulded items and biodegradability along with morphology of LDPE/sago starch blend.



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EXPERIMENTAL

Materials

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). Maleic Anhydride Grafted Polypropylene (MAPP) was chosen as a coupling agent which supplied by MTBE (M) Sdn Bhd.(Malaysia). *Aspergillus niger* was purchased from National Pharmaceutical Control Bureau (Malaysia).

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 a airtight plastic container to equilibrate for 12 h at 25 °C and then extruded. Table 1 represents the different composition of the blend. The compounding of LDPE/starch blend will be done using Brabender twin screw extruder. The compounding process will carried out at a speed of 80 rpm and the temperature will be set at 150°C/150°C/140°C/140°C (Shah et al., 1995). The sample was fed manually as much as the extruder would process. The extrudates will be palletized using a pelletizer machine for each formulation and were stored in a airtight plastic container.

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 a airtight plastic container.

Table-1. Composition (w/w) of LDPE/Sago starch blend

No	Samples	LDPE (w/w %)	Sago Starch (w/w %)
1	Native LDPE	100	-
2	LDPE/SS:99/1	99	1
3	LDPE/SS:95/5	95	5
4	LDPE/SS:90/10	90	10
5	LDPE/SS:85/15	85	15
6	LDPE/SS:80/20	80	20
7	LDPE/SS:70/30	70	30

Water absorption

Water absorption test was carried out according to ASTM Standard D750-95 (Chandra. et al. 1999) The mould item products, in the size of 2.0 x 3.5 cm, 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. The samples were periodically weighted every 2 days to record any change in their weights. 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.

Melt Flow Index (MFI) Determination

Melt flow index will be 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 will be measured and the melt flow of the samples will be 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).

Density

The density of a material is the mass per unit volume. Three replicates of density analysis were performed for each sample. Sample was weighted approximately about 2g and measured by a digital weighing balance with four decimal. The volume of a sample (V , cm^3) was measured using a gas-operated (argon gas) pycnometer (micromeritics, AccuPyc II 1340 gas pycnometer).

Determination mechanical properties

Mechanical properties of LDPE/sago starch specimen measured were tensile, flexural and impact property. 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. Gauge length will be set at 50 mm and the crosshead speed of testing will be fixed at 5 mm/min. 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 ($25 \pm 2^\circ\text{C}$) and $50 \pm 5\%$ relative humidity at 90° swing angle using a 1 J hammer. All samples were tested at least in triplicate.



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Thermogravimetric Analyzer (TGA-DTA)

The thermal properties of thermoplastic (TPS) were measured by thermogravimetric analysis (TGA). TGA measurements were carried out using thermogravimetric analyzer (TA instruments, TGA Q500). Each specimen weighed about 10mg (± 5 mg) at scanning temperature range of 25°C-600°C and heating rate of 10°C/min. The sample size was kept nearly the same for all the tests. TGA was conducted with the samples placed in platinum crucible in nitrogen atmosphere at flow rate of 40ml/min to avoid unwanted oxidation. The TGA technique is used to determine the percentage weight loss (%wt) and decomposition temperature (T_d) of the polymer

Morphological studies

Morphological studies were carried out on the tensile surface of test specimen. The surface of the samples before and after biodegradation was studied by Scanning Electron Microscopy (SEM). Test samples were first sputter-coated with gold to prevent any electrical discharge during testing. The coated sample was then taken for microscope images using EVO 50 (ZEISS brand) at 300KV. By observing the surface of composites specimen, the microstructures were compared.

RESULT AND DISCUSSION

Water absorption

Starch content influences the water absorption of LDPE/Sago starch blend. This phenomenon can be observed through Figure 1 that shows the variation in water absorption with time of immersion. Water absorption increased with immersion time and increasing sago starch content.

Rapid water absorption was observed for all samples within the first few days of immersion and 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.

Starch based synthetic materials tend to absorb water because the hydroxyl group in starch can form a hydrogen bond with water. Since the starch is hydrophilic, it has a highly tendency to attract water molecules. There are also high amylopectin in sago starch (73%) that influenced the water absorption. researcher reported that the starch blends containing high amylopectin content absorbed more water (Mani et al., 1998).

Melt flow Index

Native LDPE had a higher MFI than starch filled LDPE the measurements were done using a load of 2.16 kg. Table 2 shows the melt flow index (MFI) values of LDPE/Sago starch composites decreased as the content of starch increased. Reduction in MFI values indicate the viscosity of composite increased. Whereby the MFI of starch composite decreased as the filler loading increased (Mani et al., 1998. Rosa et al., 2005). As the content of starch is increased, the interaction among the granules was increased and contributes to the higher viscosity.

For higher loading of starch, the spaces between particle-particle were small. If the particle-particle interactions are stronger than particle-matrix interaction, agglomeration of particles may occur and result in the immobilization of more matrix molecules (Mali et al., 2005). The matrix molecules become trapped in filler particles as the size of agglomerates rise and flows have been confined. Decreasing of MFI is also due to the fact that starch particles are more viscous than LDPE. This can be observed from Table 2 below; MFI of native LDPE is higher than LDPE/SS:90/10.

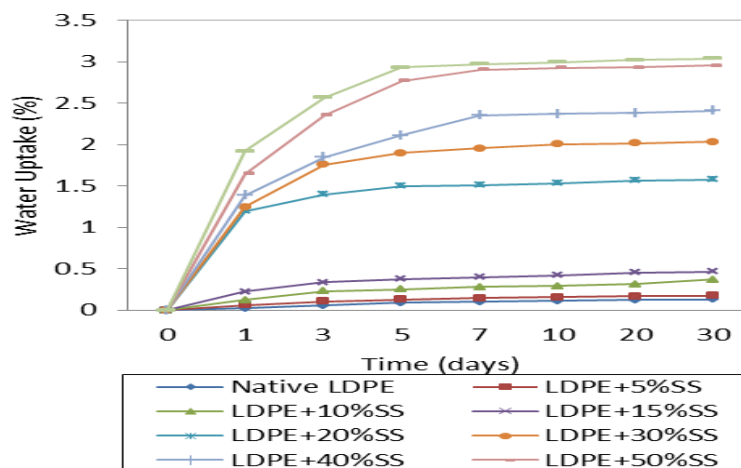


Figure 1 Percentages of water absorption for LDPE/Starch blend with time of Immersion



Table-2. Density and Melt flow index of LDPE/Sago starch blend.

Samples (wt%)	LDPE/Starch Blend*	
	Density** (g/cm ³)	MFI (g/10min)
Native LDPE	0.9188	2.9522
<i>Sago starch</i>		
LDPE/SS:99/1	0.9297	2.8405
LDPE/SS:95/5	0.9577	2.7986
LDPE/SS:90/10	0.9664	2.6787
LDPE/SS:80/20	1.0109	2.2827
LDPE/SS:75/25	1.0346	2.1138
LDPE/SS:70/30	1.0556	1.8937

Density

Table 2 describes the density of LDPE/SS composites. Based on Table 2, the density LDPE was influenced by the increase of sago starch concentration. The density was lower than the control limit value which is 1.46g/cm³. Previous researches proved that the increase of fillers content caused a better interfacial bonding between LDPE and sago starch (Thakore et al., 1999). The lower density values were attributed to the presence of void within filled composites.

Mechanical properties

Tensile strength

Tensile strength decreases with increase in sago starch concentration as shown in Figure 2(a). Reduction of tensile strength was probably caused by less effective cross sectional area of LDPE matrix (i.e. continuous phase) toward spherical particulates starch granules as the starch contents rose. Subsequently resulting in reduce of tensile strength. Low tensile strength of LDPE/Sago starch composite also occurred because of the weakness of interfacial adhesion in which probably attributed to hydrophilic nature of starch, which was not compatible with hydrophobic polymers (Rosa et al., 2005, Thakore et al., 1999). The decreasing of tensile strength occurred due to weakness of interfacial adhesion between starch-polymer. Besides, it was observed the presence of bubbles in the samples. It showed the possibility of reduction of tensile strength was also due to the presence of moisture at the LDPE starch interface.

The changes in EB with increase in starch content are shown in Figure 2(b). It is evident that EB decreases with increase in sago starch content. Similar to tensile strength, decreasing of elongation at break occurred because of the weakness of interfacial adhesion between starch-LDPE. In synthetic polymer blends, the addition of the immiscible component to a ductile matrix generally decreased the elongation properties at break. The elongation will therefore depend on the state of the interface (Rosa et al., 2005, Thakore et al., 1999). In cases such as when 20% of the dispersed minor phase has been added, highly deformable matrix materials are transformed into fragile materials. In this study, the optimum was at 10% loading.

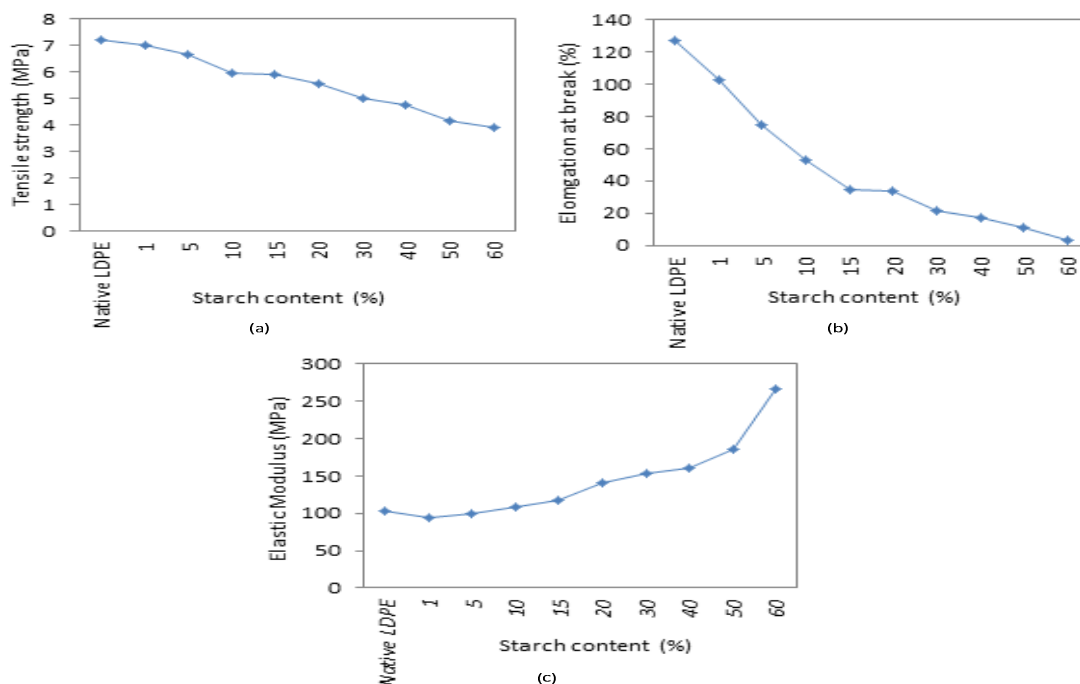


Figure 2 Effect of sago starch content on LDPE a) Tensile strength b) Elongation at break c) Elastic modulus.



As seen in Figure 2(c) the Elastic modulus of the LDPE/sago starch blend increase with increase in sago starch loading. Starch incorporated into LDPE still retained their granular shape after processing. These granules are stiff and act as rigid fillers (Mani et al., 1998). Thakore et.al reported that the incorporation of sago starch into LLDPE has led to an increase in the modulus of the composites because of the starch granules are stiffer than the LLDPE matrix in which they are dispersed

In general, modulus is closely related to the hard domain of the material. As the starch content increases, the hard domain content increases, as does the tensile modulus of the blend. As starch is partially crystalline, there was possibility of increasing modulus attributed to crystalline. Crystallinity brings about an increase in modulus. Incorporation of crystalline starch into binary PE-starch blend shows an increasing in modulus with increasing starch contents (Rosa et al., 2005)

Flexural properties

Figure 3 shows the flexural properties of LDPE/Sago starch with varying amounts of starch loading. From Figure 3(a), a rise was observed in flexural strength by about 8%, upon addition of 5wt% sago starch into the blend. At 5wt% sago starch loading, the flexural strength of the blend was quite closer to that of native LDPE. The influence of sago starch content on flexural modulus of LDPE/sago starch blends are shown in Figure 3(b). Addition of sago starch resulted in a progressive increase on flexural modulus. The result illustrated the fact that the properties of binary LDPE/sago starch blend depend on the properties of the blend constituents.

Impact properties

Figure 4 shows the notched Izod impact strength of LDPE/Sago starch blends. The plot indicates that native LDPE exhibited extremely higher impact property, which higher than LDPE with 5wt% sago content. It proven that the LDPE/sago starch is lower than pure LDPE. Theoretically, pure LDPE has high ductile strength and

elasticity. However, the improvement of impact strength was relatively low owing to the incompatibility of sago starch and LDPE. The impact strength of all the blends decreased with increasing starch content, indicating that sago starch behaved as nonreinforcing filler. This may be due to the low interfacial interaction between starch and LDPE, which would lead to mechanical rupture at the blend interface. Further increase in sago starch loading causes the impact strength of the blends to decrease owing to the aggregation sago starch that leads to poor adhesion with LDPE. The results are in agreement with SEM observations.

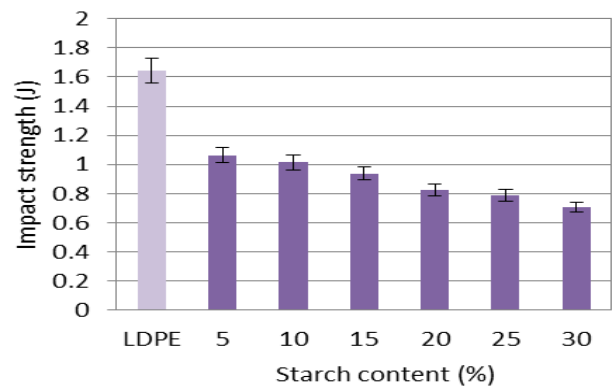
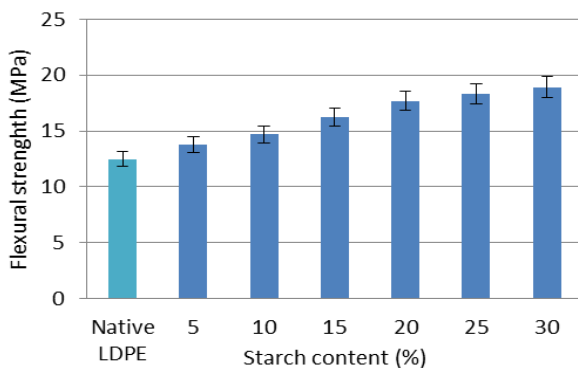


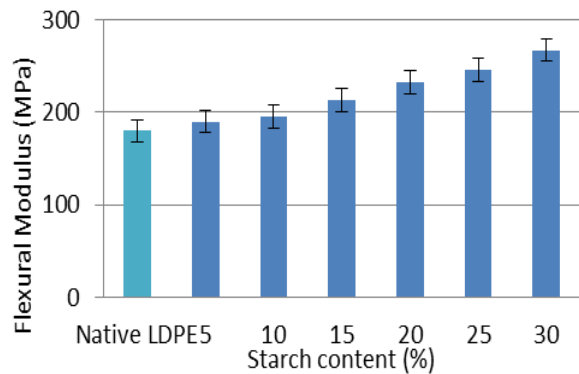
Figure 4 Effect of sago starch content on impact strength of LDPE

Scanning Electron Microscopy

Scanning electron micrographs of mould surfaces of native LDPE and sago starch filled LDPE blend at 0, 10, 20 and 30wt% starch loading are shown in Figures 5(a - f). It can be seen that the distribution of sago starch on LDPE matrix is worse with increasing amount of sago composites. This is due to the hydrophilic nature of starch that leads to poor adhesion (miscibility) with LDPE, which are hydrophobic in nature.



(a)



(b)

Figure 3: Effect of sago starch content on LDPE a) Flexural strength b) Flexural modulus.



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Table 3: Effect of sago starch content on the onset of degradation temperature and percentage of weight loss for LDPE blend

Samples (wt%)	onset T _d (°C)		Weight loss (%)		Residue at 510°C
	First	Seco nd	at	at	
			330 °C	450° C	
Native LDPE	-	419.8	-	39.5	0.6
LDPE/SS :95/5	311.7	454.8	5.4	10.1	0.9
LDPE/SS :90/10	311.5	454.5	7.2	15.7	1.1
LDPE/SS :80/20	311.0	454.2	11.1	21.2	2.2
LDPE/SS :70/30	309.8	454	10.1	20.0	1.6

The effect of low mechanical properties of blend was influenced by the presence of moisture in the granules. Water vapour will form around the granules due to prolonged heating at higher temperatures during molding. This results in voids around the granules so that minimum contact exists between the granules and the matrix. This will affect their modulus as a result lower modulus, the granules effectively function as a voids as they are unable to resist any stress.

Thermogravimetric Analysis (TGA)

The effect of sago starch content on the thermal degradation behaviour of the LDPE/starch blends is presented in **Figure 6**. It can be seen that the initial decomposition temperature of the blend composites reduces with increasing sago starch loading. Obviously, the LDPE/starch blends degraded in two stages. The first one around 300-340°C is due to starch decomposition. With a further rise in temperature to 600°C, the entire

blend exhibited no substantial weight changes up to *ca.* 440°C.

The second stage of thermal decomposition began near 450°C with the weight decreasing rapidly at 500°C. This higher thermal decomposition is owing to the sago starch content. Table 3 summarises the onset of degradation temperature T_d (onset) for both stages and also percentage of weight loss and residue at the specific temperatures for all of the blends. As listed, less than 2.5% residue was left at 510°C. Clearly the first T_d (onset) shifted towards low temperature as the amount of sago starch increased.

The LDPE with 5wt% starch started to degrade at 311.7°C, whereas the blend containing 30wt% starch loading began to degrade at 309.8°C. Certainly, the sago starch content affected the amount of weight loss of the composites blend at this stage. For example, at 330°C and 450°C, weight loss of the composites increased as function of starch content. These results confirm that the both stage of temperature, the weight loss must be due to the decomposition of sago starch.

CONCLUSION

The thermal stability of LDPE increased upon starch blending especially at higher starch content (30wt%). The morphology of the blends was found to change with increase in sago starch content and extrusion process in the blend was evident. Water absorption after sample immersion in water was found to increase with increase in sago starch content due to hydrophilic properties of the starch were found to be of reasonable mechanical strength and the recommendation of coupling agents and other additives was suggested to improve mechanical properties.

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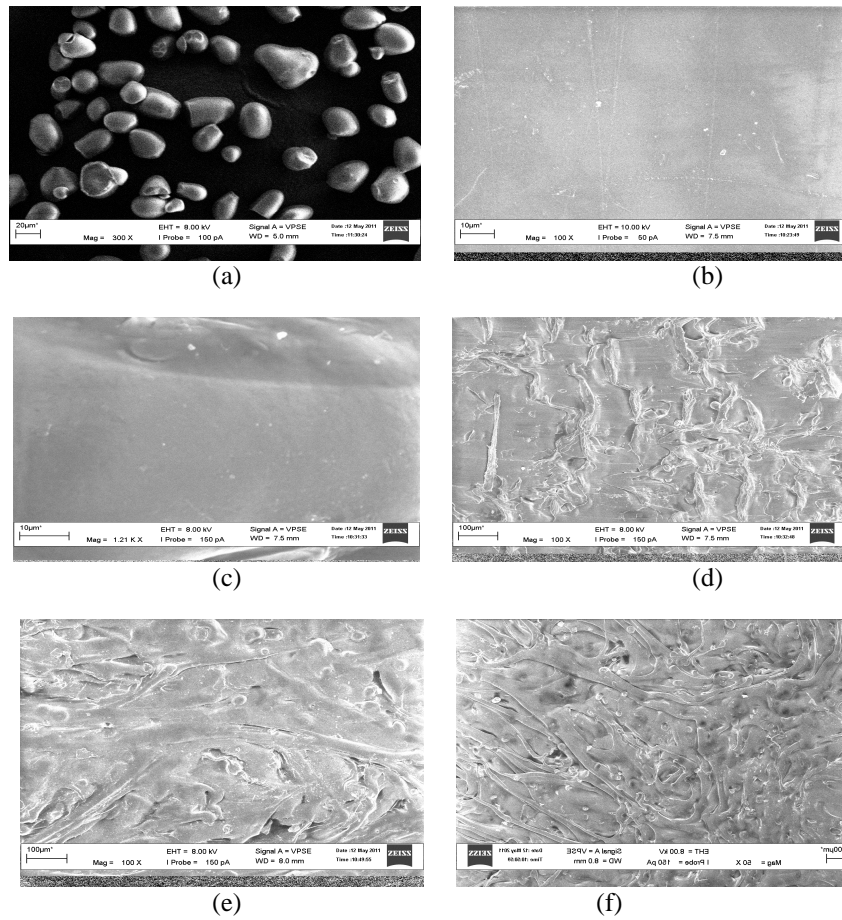


Figure 5. SEM micrographs of a) sago starch granule b) native LDPE c) LDPE/SS:95/5 d) LDPE/SS:90/10 e) LDPE/SS:80/20 f) LDPE/SS:70/30

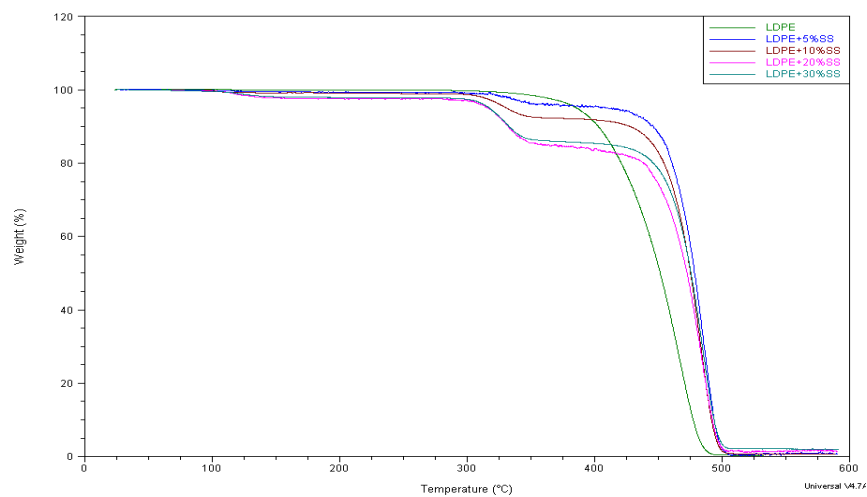


Figure 6 Effect of sago starch content on the TGA thermograms of LDPE



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