

## Preparation and Characterization of Thermoplastic Cassava and Sweet Potato Starches

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### ABSTRACT

Thermoplastics starches are plastics made from renewable resources like plants that are fully bio-based and biodegradable. The aim of this study was to produce and characterize thermoplastic using starches extracted from cassava and sweet potato. The effect of variable amounts of glycerol used as plasticizer and acetic acid used for hydrolysis of the starch polymer were investigated. The intermolecular interaction between the starch and glycerol was ascertained using FT-IR spectroscopy. The biodegradability test conducted on both cassava thermoplastic starch (TPSc) and potato thermoplastic starch (TPSp) were found to lose 36% and 23% respectively of their initial weights after seven days of soil burial. The result showed that as plasticizer concentration increased from 50 to 80%, there was an increase in both moisture and oil uptake but a decrease in water uptake. However, an increase in acetic acid concentration from 2.5% to 7.5% resulted in a decrease in oil uptake, water uptake and moisture uptake of the thermoplastics. Findings in this study reveal increase in the amount of glycerol plasticizer in both thermoplastics increases moisture contents retention however the observed oil uptake and biodegradability properties suggest the thermoplastic starches especially the potato thermoplastic starch is generally suitable for making eco-friendly thermoplastics.

**Keywords:** Thermoplastic starch, Biodegradability, Plasticizer, Moisture uptake, Oil uptake, Water uptake.

### INTRODUCTION

Plastics have become inevitable part of our daily-life and so have diverse uses, they cannot be avoided and have turned into a major threat to the environment by contributing to the major part of land pollution (Modebelu and Edward, 2014). Plastics cover about 25 % of the total volume of landfills (Raaz *et al.*, 2013). Plastics versatility in usage result to their production in excess but poor waste management, deposition in landfills and non-degradability of plastics have worsened environmental pollution (Raaz *et al.*, 2013). The non-biodegradability of petrochemical-based plastics coupled with the reduction in supply of petroleum has necessitated the need for 'green' alternatives such as starch-based biodegradable plastics (Marvizadeh *et al.*, 2017).

Plastics made from renewable resources (plants sources like corn, potatoes, cassava and algae) that are fully bio-based, and/or biodegradable or compostable are called thermoplastics. Starch is an excellent biodegradable filler suitable for thermoplastic production because it possesses well-satisfied thermal stability and hinders interference with melt-flow properties used in the plastic industry. Starch is a natural biopolymer consisting of two types of polymer chains namely amylose and amylopectin. Amylose is a linear polymer of glucose linked together by  $\alpha$ -1, 4 bonds while amylopectin is a branched polymer comprising of both  $\alpha$ -1, 4 and  $\alpha$ -1, 6, glycosidic linkages, with the latter found at branch points (Ming *et al.*, 2011). During the starch extrusion process, the combination of shearing, temperature and plasticization result in the production of a melted thermoplastic material (Averous *et al.*, 2001). These materials are converted to film by means of thermoforming or injection molding. In this regard, starch has been used as

fillers, thermoplastic starch (TPS), in the production of biodegradable synthetic polymer like polylactic acid (PLA), foamed starch and starch-synthetic polymer blends. Hence, the aim of this study is to prepare and characterize cassava and sweet potato starch-based thermoplastics.

### MATERIALS AND METHODS

#### Plant Material and Chemicals

Sweet Potato (*Ipomoea batatas*) and cassava (*Manihot esculentus*) were both purchased from Sokoto local market, in Sokoto State, Nigeria and were washed with running tap water to remove sand particles. All other chemicals used in this study were provided by the Department of Pharmaceutics, Usmanu Danfodiyo University, Sokoto and used without further purification.

#### Starch Extraction

Starches were extracted from the tubers by wet milling processes according to Khoramnejadian *et al.* (2013). The tubers were washed, peeled and soaked in Sodium metabisulphate before grating. The resulting pastes were mixed with water and filtered using a clean cloth. The collected filtrates were then allowed to stand for 6 hours followed by the removal of the supernatant. The white precipitate (starch) was then recovered. The crude starches were purified by using centrifuge at 4000 rpm for 10 minutes. The sediment obtained were further dispersed with 100 cm<sup>3</sup> of distilled water and centrifuged to obtain the pure starches which were then dried in an oven at 50 °C to obtain white powder. The starch powder was stored in polyethylene containers at room temperature (Musa *et al.*, 2013).

### Preparation of Thermoplastic Starch Films

The method described by Wissinger *et al.* (2016) was adopted. To each of two 100 cm<sup>3</sup> beakers, 1.25 g of starch, 50.00 cm<sup>3</sup> distilled water, 1.2 cm<sup>3</sup> of 5 % acetic acid and 60 % (to the weight of the dry starch) glycerol was added as plasticizer. The mixture was stirred continuously while heating slowly on a hot plate using a magnetic stirrer at a rate of 180 rpm for 10 min. This brings the mixture to a gentle boil. The mixture started out white in coloured suspension and changes to transparent or translucent and thickens until completely gelatinized after which the heat was removed. The prepared thermoplastic starch solutions were then cast by pouring into dried and labelled petri-dishes and were dried in an oven at 50 °C for 24 hours. Similar preparations of thermoplastic starch with 2.5% and 7.5% acetic acid and 50%, 70% and 80% glycerol were carried out to assess their effects on thermoplastic absorption of moisture, water and oil.

### Characterization of Thermoplastic Starches FT-IR Spectroscopy

For each of the potato and cassava thermoplastic starch, 5 mg sample were placed in the sample holder of FT-IR spectrometer and IR spectra recorded at 27 °C from 650 to 4000 cm<sup>-1</sup> range, background scanned at 64, sample scanned at 32, and the resolution was 4, and fitted with a compatible PC running recommended operating system as described by Maulida *et al.* (2016).

### Thermogravimetric Analysis

The thermogravimetric analysis (TGA) examination of the thermoplastic starch films was taken by using computer controlled Thermo gravimetric analysis (TGA) The Temperature range was maintained at 30 °C to 600 °C and the temperature was increased at a rate of 10 °C/min. The flow rate of nitrogen gas was 20 ml/min.

### Physicochemical Properties of Thermoplastic Starches Water Uptake

To test the ability of thermoplastic starch to absorb water, measurement was carried out using standard ASTM techniques (ASTM 2004) at room temperature. Dried thermoplastic starch samples were cut into 10 x 10 mm<sup>2</sup> and weighed for initial weigh. The moisture absorption data of thermoplastic starches were obtained by dipping the samples in a water bath containing distilled water for 24 hours at ambient temperature. After that, the samples were removed and wiped off and immediately weighed again as final weight. The water absorption capacity of the thermoplastic starch was calculated using equation (1).

$$\% \text{ Water uptake} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Final weight}} \times 100 \dots (1)$$

### Oil Uptake Capacity

Oil uptake was determined using the same method described for water uptake but with groundnut oil as the dipping medium. However, the samples were excited and rinsed with absolute ethanol to remove the excess oil and allowed to dry on a clean filter paper for 10 minutes. The oil uptake of the samples was calculated in percentage using the equation:

$$\% \text{ Oil Uptake} = \frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}} \times 100 \dots (2)$$

### Moisture uptake

Two grams of each of the samples was weighed and placed over the surface of a 70 mm tarred petri dish. The samples were placed in a large desiccator containing distilled water in its reservoir at room temperature. The weight gained by the samples at the end of five days was recorded and the percentage amount of water sobbed by the samples was calculated from weight differences:

$$\% \text{ Moisture uptake} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Final weight}} \times 100 \dots (3)$$

### Biodegradability Test

The method described by Khoramnejadian *et al.*, (2013) was adopted in testing the biodegradability of prepared thermoplastic starch. The specimens were cut into pieces of 4.0 cm<sup>2</sup> and 500 g of soil (having slight moisture content) was collected and stored in a 1000 cm<sup>3</sup> conical flask. Each sample was buried inside the soil at a depth of 2 cm for 7 days under the prevailing laboratory conditions. The weight of the specimen was measured before and after the testing. The biodegradability test was measured by using Equation (4)

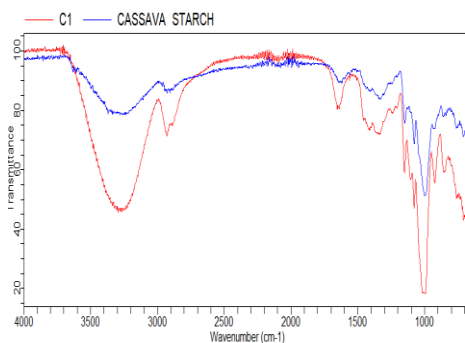
$$\text{Soil biodegradation (\%)} = \frac{W_f - W_i}{W_i} \times 100 \dots (4)$$

Where:  $W_i$  and  $W_f$ , is the initial and final weight of samples.

## RESULTS AND DISCUSSIONS

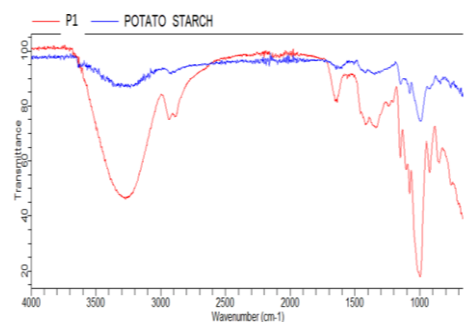
### Chemical Properties of Tthermoplastics

Figures 1 and 2 present the FT-IR spectra of native cassava and sweet potato starches and that of derived thermoplastics. The spectra produced from this study displayed the presence of major absorption peaks - O-H stretch, C-H stretch, C=O stretch and C-O stretch. The major absorption peaks for each of the cassava and potato thermoplastic spectra were found to reduce as compared to that of the native cassava and potato starches. This is an indication that plasticization has really occurred which restrict the free chances of stretching of the compound in the polymer matrices (Szczepanowska and Wilson, 2000).



C1 = cassava thermoplastic starch

**Figure 1:** FT-IR spectra of native cassava starch and cassava thermoplastic starch

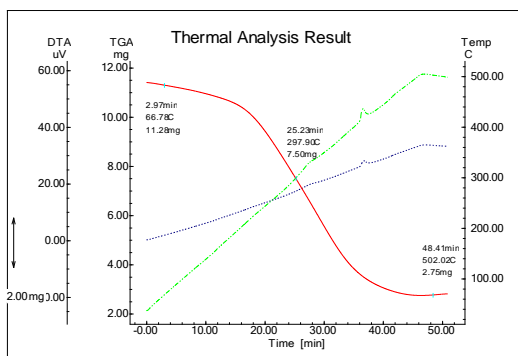


P1 = potato thermoplastic starch

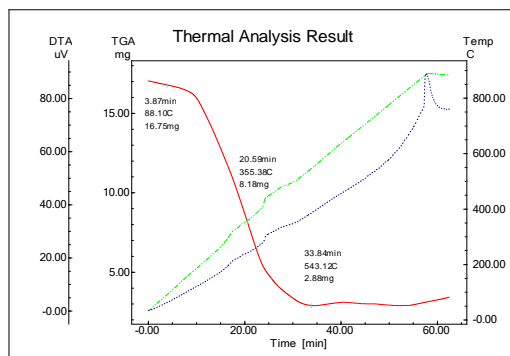
**Figure 2:** FT-IR spectra of native sweet potato starch and potato thermoplastic starch

**Thermogravimetric Analysis (TGA) of Thermoplastic Starch**

Thermo gravimetric analysis (TGA) was used to investigate experimentally the thermal stability of cassava starch-based and potato starch-based thermoplastics. Figure 3 shows the decomposition profile of cassava and potato thermoplastic obtained from thermo gravimetric analysis (TGA). From the graph, the T50% (temperature at which 50% of weight loss occurred) occurred at 18 to 36 minutes and 10 to 25 minutes respectively for cassava and potato thermoplastics. The thermal stability of any polymeric material is largely determined by the strength of the covalent bonds between the atoms forming the polymer molecules. Decomposition temperature decreases with the increase of amylose content in the starch (Monica, *et al.*, 2013). The correlation between decomposition temperature and amylose content signifies the amylose content in potato is greater than in cassava. Wickramasinghe *et al.* (2009) also mentioned in their study that amylose content was found higher in potato than from cassava ranging from 25.9% and 23.5% respectively. This also indicates that potato has greater heat stability compared to cassava (Musa *et al.*, 2013).



(a) Cassava thermoplastic starch



(b) Potato thermoplastic starch

**Figure 3:** Thermograms of (a) cassava and (b) sweet potato thermoplastics starch

**Effect of plasticizer (glycerol) and acetic acid on Water uptake of thermoplastic starch**

Figure 4 shows the effect of different concentration of glycerol on the water uptake of thermoplastic at (a) 2.5%, (b) 5% and (c) 7.5% acetic acid respectively. From the Figures it can be observed that the water uptake of both cassava starch-based thermoplastic and potato starch based-thermoplastic decreased with increasing glycerol

concentration (50% to 60%, 70% and 80%). This is because the absorption of water may have been influenced by the interaction between hydroxyl groups of starch and glycerol with water molecules which promotes the formation of cellulose particle network that prevents swelling of starch and therefore water uptake as well (Dagang *et al.*, 2010). This observation corresponds with the findings of Gilfillan *et al.* (2012) which suggest decrease in water uptake of

thermoplastics might be due to the formation of hydrogen bonds between the starch and glycerol.

Varying the concentration of acetic acid was found to affect the water uptake of thermoplastic in a manner that suggests increasing concentration of acetic acid from 2.5% to 5% and 7.5%, results in decrease of water uptake of cassava thermoplastic starch for all glycerol concentrations (50 %, 60%, 70% and 80%) as presented in Figure 5. A similar observation was made for potato thermoplastic starch except that at 7.5% acetic acid, increase in water

uptake occurred which may be as a result of high concentration of amylose formed from the converted amylopectin of the starch. Increase in acetic acid led to decrease in water uptake because acetic acid act as a barrier against the diffusion of the water to films. Low water uptake/absorption in the thermoplastic films can also be explained in terms of changes in molecular structure of the starch and protonation that occurred during plasticization of thermoplastics, as the aqueous acetic acid has a plasticization effect which result in reducing the water uptake of thermoplastic starch. (Zhang *et al.*, 2019).

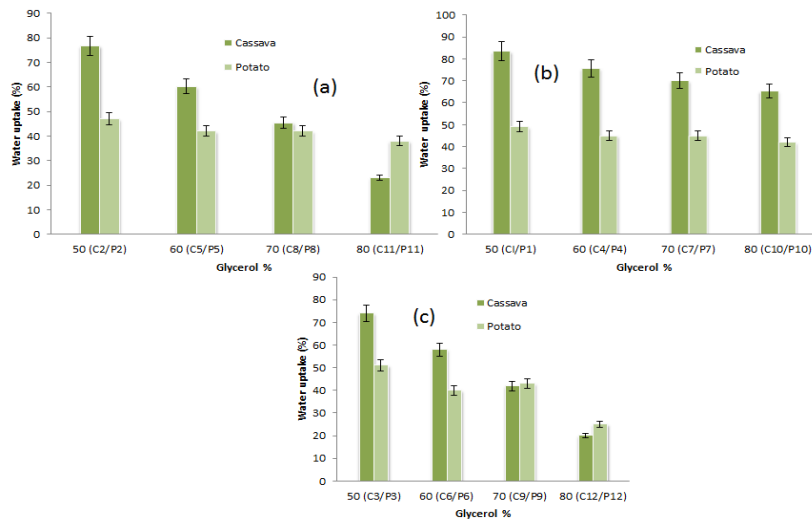


Figure 4: Effect of glycerol concentration on thermoplastic water uptake at (a) 2.5%, (b) 5% and (c) 7.5% acetic acid

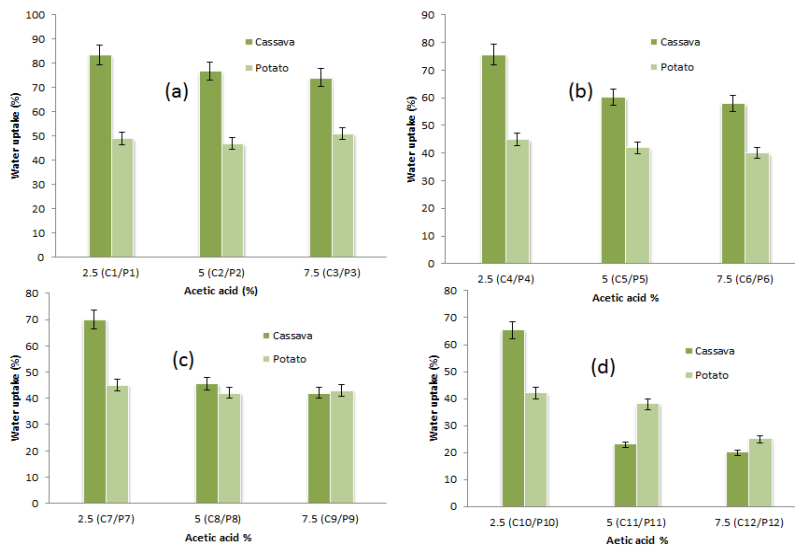


Figure 5: Effect of Acetic Acid concentrations on thermoplastic water uptake at (a) 50 %, (b) 60 %, (c) 70 % and (d) 80 % glycerol

**Effect of plasticizer (glycerol) and acetic acid on oil uptake of thermoplastic starch**

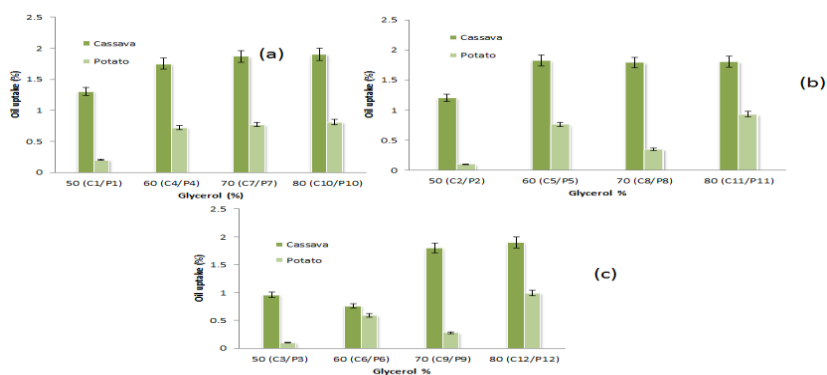
Figure 6 shows the effect of varying concentration of glycerol at 2.5 %, 5 % and 7.5 % acetic acid respectively in thermoplastic uptake of oil. A similar trend in oil uptake was observed for the three concentrations tested; as the glycerol concentration increase, the oil uptake in cassava-based thermoplastic increases from 50% to 70% glycerol concentration and decreased at 80 % glycerol. However, potato starch-based thermoplastic, a reversed interaction was observed; as the glycerol concentration increased, the oil uptake decreases sharply from 50 % to 80 % glycerol concentration.

The results show that the oil uptake for cassava starch-based thermoplastic increased steadily up until at 70% and began to slowly form a curve. Films with high glycerol content absorbed more oil than that with less glycerol content in the following manner: 70% > 60% >50% glycerol. At 80% glycerol concentration, absorption declined

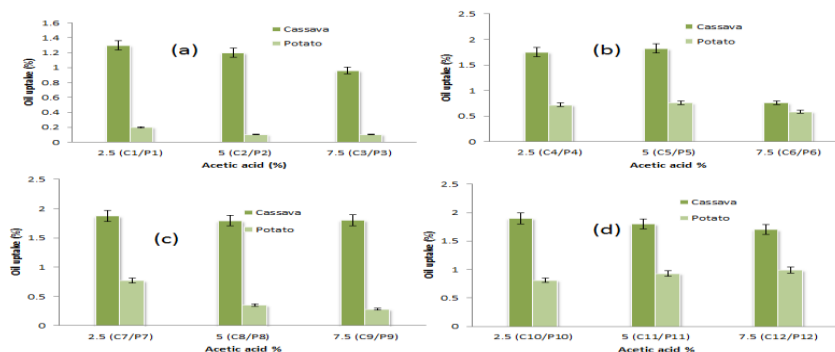
suggesting most of the oil are probably absorbed by the glycerol until saturation. According to Vieira *et al.* (2011), polysaccharides possess a good film-forming property, which provides efficient barriers against oils and lipids.

**Effect of acetic acid concentration on oil uptake of Thermoplastic Starch**

As presented in Figure 7, both cassava starch-based thermoplastic and potato starch-based thermoplastics show a very slight decrease in oil uptake as the concentration of acetic acid increase. Although, very little uptake of oil was observed, all thermoplastic derivatives possessed a very good oil barrier, and as such do not absorb much oil when immersed for 24 hours, thus increasing the concentration of acetic acid has the effect of reducing the capacity of thermoplastics to absorb more oil. This may be due to the strong intermolecular forces of attraction within the thermoplastic-derivatives that hinders the interaction between them.



**Figure 6:** Effect of varying concentration of glycerol on thermoplastic oil uptake at (a) 2.5 %, (b) 5 % and (c) 7.25 % acetic Acid



**Figure 7:** Effect of acetic acid concentration on thermoplastic oil uptake at (a) 50 %, (b) 60 %, (c) 70 % and (d) 80 % glycerol

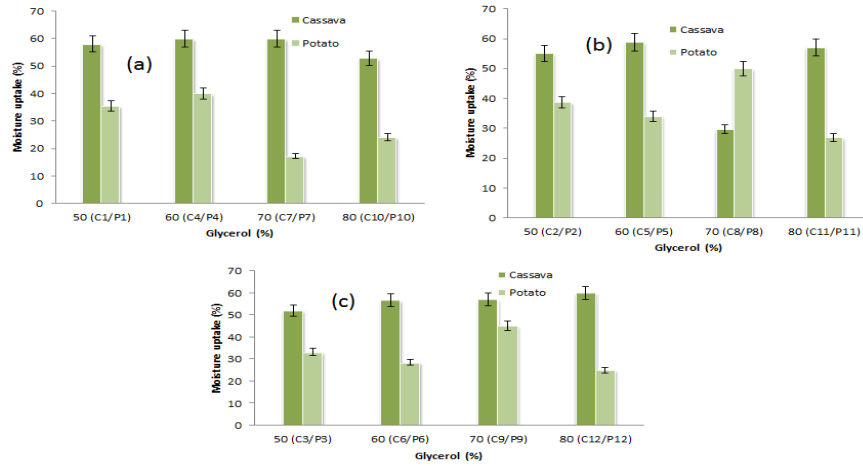
**Effect of glycerol on Thermoplastic moisture uptake**

Figure 8 indicates the effect of varying concentration of glycerol at (a) 2.5%, (b) 5% and (c) 7.5% acetic acid

respectively on thermoplastic moisture uptake. Increasing the concentration of glycerol from 50% to 60% and 70% resulted in the increase in moisture uptake of cassava

thermoplastic starch and when increased to 80%, the moisture uptake decreased. However, potato thermoplastic starch moisture uptake increased by increasing the glycerol concentration from 50% to 60% but dropped to 70% then goes up again at 80%. The moisture content in starch films

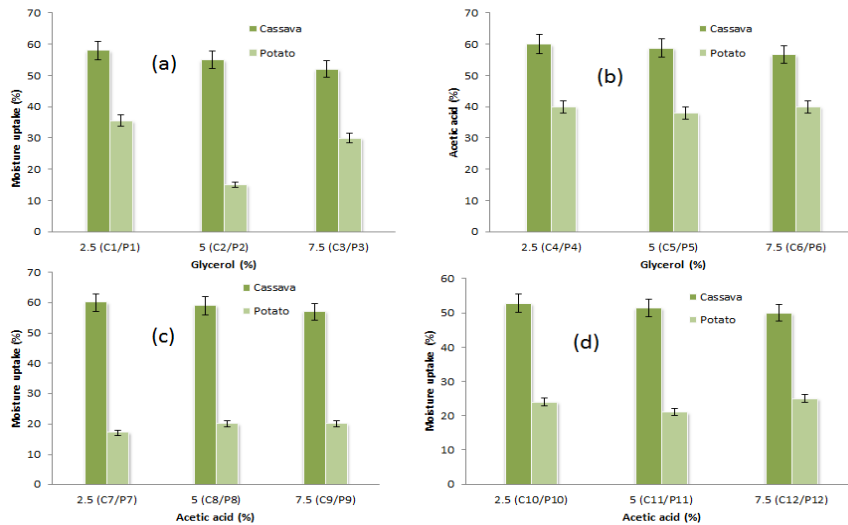
can significantly affect the physical and barrier properties of starch-based thermoplastic films. The results obtained showed films with high glycerol concentration were more hygroscopic.



**Figure 8:** Effect of varying concentration of glycerol on thermoplastic moisture uptake at (a) 2.5 %, (b) 5 % and (c) 7.25% acetic acid

In addition, glycerol had an important favorable effect on the equilibrium of water as its concentration is enhanced. These results may be related to the higher hygroscopic nature of glycerol. Higher levels of plasticizer increased the films moisture affinity and this could be attributed to the hydrophilicity of the plasticizers with accessible hydroxyl groups capable of interacting with water by hydrogen bond

formation. Glycerol molecules are small with high capacity to interact with starch chains, increasing molecular mobility and enhancing free volume in the film network. Furthermore, glycerol has a more hydrophilic nature and the combined effects increases water affinity of glycerol plasticized thermoplastic films (Sothornvit and Krochta, 2001).



**Figure 9:** Effect of Acetic Acid on thermoplastics moisture uptake of at (a) 50 %, (b) 60 %, (c) 70 % and (d) 80 % glycerol

**Effect of Acetic Acid on moisture uptake of Thermoplastic**

As shown in Figure 9 acetic acid increase from 2.5%, 5% to 7.5%, the moisture uptake of cassava starch-based thermoplastic decreases slightly. In potato starch-based thermoplastic, decrease in moisture uptake was observed when acetic acid was increased from 2.5% to 5% but increased subsequently as acid was increased from 5% to 7.5 %. Thermoplastics have a high moisture uptake value at 2.5 % acetic acid because the acetic acid will increase the physical interactions that allow the formation of hydrogen bonds into more chains of starch which increases the moisture uptake of the thermoplastic. When the acetic acid percentage increased to 7.5%, acetic acid will loosen

the bonds between molecules in thermoplastics thereby reducing the moisture absorption capability of the thermoplastics (Martha *et al.*, 2018).

**Biodegradable properties**

Table 1 shows the weight loss of cassava and potato thermoplastics after 7 days soil burial test. The weight loss of thermoplastic sheets during burial in soil indicates the degree of degradation in natural environment by action of microorganisms. The starch content degraded by soil microorganism fractures the polymer chain thus causes biodegradation (Khoramnejadian *et al.*, 2013).

**Table 1:** Biodegradation analysis of Cassava and Potato based thermoplastics with conventional petroleum-based plastic

TPSc	TPSp			Petroleum-based plastic					
	Ini (g)	Fin.(g)	Wt. loss (%)	Ini (g)	Fin.(g)	Wt. loss (%)	Ini (g)	Fin.(g)	Wt. loss (%)
1	1.08	0.72	33	1.05	0.69	34	1.00	0.00	0.00
2	1.12	0.69	38	1.20	1.06	12	1.00	0.00	0.00
<b>Avrg.</b>	1.10	0.71	36	1.13	0.88	23	1.00	0.00	0.00

TPSc.=Cassava thermoplastic starch, TPSp.=Potato thermoplastic starch, Ini.=Initial weight, Fin.=Final weight

The average percentage weight loss of cassava starch-based thermoplastics was found to be 35.5%, which indicates higher degree of biodegradation when compared with that of potato probably attributable to the different nature of starch in cassava and potato. The amount of starch in the Potato has more complex starch polymer compared with cassava thus requires a relatively longer degradation time (Moongngarm, 2013).

**CONCLUSION**

This study demonstrates the production of thermoplastic starches from cassava and sweet potato starches plasticized with glycerol and acetic acid. Glycerol and acetic acid used in the thermoplastic preparation enhances moisture and water uptake while the oil uptake capacity is low in both thermoplastics but much lower for potato thermoplastic starch. While increasing the amount of glycerol in both thermoplastics increases moisture contents retention capacity, the results for oil uptake and biodegradability however suggests the thermoplastic starches especially potato thermoplastic starch are generally suitable for making eco-friendly thermoplastics useful as edible coatings for fruits and vegetables as well as packaging material for oily foods as the thermoplastics absorb less oil.

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