Production of Cassava Starch Bioplastic Film Reinforced with Poly-Lactic Acid (PLA)

T. M Ogunrinola¹ U.G Akpan²
Research Scholar ¹, Professor ²
Department of Chemical Engineering
Federal University of Technology
Minna, Niger State
Nigeria

ABSTRACT

Biodegradable thermoplastic starch from cassava starch was produced in this study. The thermoplastic starch (TPS) produced was reinforced with Polylactic Acid (PLA) so as to improve their physical properties. The TPS was produced using a casting method of polymer preparation and later subject to a compression moulding to form a 2 mm film. Glycerol was used as the plasticizer with content varying from 10 to 30% along with the varying amount of water (40 - 60%) and acetic acid (0 – 10%) content. The results show that glycerol has a significant effect on the tensile strength of the material while the effect of water was more significant in the elongation and water absorption properties of the TPS. An optimum value of tensile strength (11 MPa), percentage elongation at break (12%) and percentage water absorption (32%) was derived at 28, 60, and 2% of glycerol, water and acetic acid respectively. Addition of Poly-Lactic Acid (PLA) to the TPS at 10, 20, 30, 40 and 50% results in a significant positive improvement on the tensile strength (11 MPa to 38 MPa) and reduction in the percentage water absorption (30% to 10%) of the TPS with no significant improvement on the percentage elongation of the material. The TPS/PLA composite with higher tensile strength and lower water absorption can be utilized in some applications to replace the non-biodegradable synthetic plastic so as to reduce the unsustainable waste generation from the use of synthetic plastic.

Key Words: Bioplastic, Thermoplastic, Plasticizer, Poly-Lactic Acid.

1. INTRODUCTION

Biodegradable materials are substance that maintains their physical properties during the useful lifetime and degrade rapidly at standard environmental conditions when dispose. Bio plastics have higher percentage of biodegradability than all other synthetic plastic [1], [2], [3]. A synthetic polythene plastic will require a couple of hundred years to degrade under normal environmental condition resulting in high volume of accumulation [4], [5]. Currently synthetic polymers dominate about 90% of the world’s plastic market due to low cost and extensive commercialization in production and processing. Most bio plastic currently developed is inferior in property and with higher cost making it difficult to replace synthetic polymer in many applications. Many researches are focusing on improving properties while keeping the cost low with noticing improvement over the years. One of the most promising biodegradable bio plastic material is Poly lactic acid (PLA) derived from bio feed stock with physical properties close to the conventional plastics currently in use but with slightly higher cost [6]. Keeping cost low as much as possible while maintaining useable properties have been the subject of many recent researches.

Starch bioplastic or Thermoplastic Starch (TPS) is been considered by many researchers as the presently available material to provide a reasonable future solution in the quest for biodegradable plastic [6], [7], [8], [9], [10], [11], [12].
its cheap availability from various plants across the globe. Starch is a polymer containing a continuous chain of amylose and branched chain amylopectin but could not form a real thermoplastic by itself [13]. But in the presence of plasticizer (water, glycerol, sorbitol), high temperature (90-180°C) and shearing it melts and fluidized, thus allow for its process ability into mould and blowing just as conventional plastic [14]. The TPS is inferior in properties when compare with various plastics currently in the market and this is largely due to starch affinity to water making it unusable in many applications. Recently many works have been carried out in an effort to reinforce TPS without compromising its biodegradability thus using various available bio materials protein, fibres and lignin sources [15].

The current advance and breakthrough in producing polyester bioplastic like PLA has allowed for a more promising reinforcement of TPS. This research explored the possibility of blending PLA and TPS from cassava starch in order to reduce cost while maintaining the required properties for its suitability in replacing conventional plastic in some packaging applications in which synthetic plastic currently dominates.

1.2 Statement of the Problem
The enormous availability of starch at low cost makes it an ideal choice of raw material feedstock for the production of biodegradable plastic. Currently the bioplastic produced from starch are of inferior properties and therefore cannot be effectively use in various plastic application. Many attempts have been made to reinforced bioplastic from starch and result shows that starches from various sources performed differently. This prompt the to examine the performance of starch from different sources for production of bioplastic.

1.4 Aim and Objectives
The research is aimed at producing bio plastic film from cassava starch reinforced with PLA to improve physical properties to meet the criteria for processing in existing plastic processing equipment and replace synthetic plastic in some basic household application. The activities that will be carried out in pursuance of this aim will include:

1. Extraction and purification of starch from cassava tuber
2. Plasticization of the starch using glycerol and water as the plasticizer
3. Processing of the TPS and TPS/PLA composite on a compression moulding machine to produce a bioplastic film
4. Characterization of the film produced for its physical properties

2. METHOD AND PROCEDURES

2.1 Preparation of Cassava Starch
Fresh cassava tuber (Manihot eculante) of TME1 variety having amylase-amylopectin ratio percentage ratio of approximately 40/60% was supplied by the International Institute of Tropical Agriculture, Ibadan, Nigeria. The starch extraction was carried out using the wet milling process as described in many works on starch extraction [15], [16], [17], [18].

2.2 Preparation of Cassava Thermoplastic Starch
Table 3.1 shows the percentage composition of the mixture component used in the formulation of the experiment. Using a combined mixture experiment on Design Expert with the heating time as the process factor combined with three component mixture, a total of 35 experimental runs was generated with three output of tensile strength, elongation at break and water absorption added for analysis.
Table 3.3: High and low value of the mixture component used for the design of experiment

| Component/Factor     | Low  | High |
|----------------------|------|------|
| Water (%)            | 50   | 80   |
| Acetic Acid (%)      | 0    | 5    |
| Glycerol (%)         | 20   | 30   |
| Heating Time (Mins)  | 160  | 200  |

For the preparation of the TPS all component was premeasured according to the formulation. The water was then placed in a 500ml beaker into which the casava starch was added and thoroughly mixed for 30 minutes to obtain a homogeneous mixture. Acetic acid and glycerol was then added and also mixed before placing the beaker on a heating mantle set to 120°C. the mixture was continuously stirred during heating and after the gelatinization of starch, the heating is continued for 160 – 200 seconds depending on the time factor of the experimental run. After heating, the thick opaque mixture formed was casted on an aluminium tray and allowed to dry for 8 days at room temperature.

2.3 Preparation of TPS/PLA Composite

The TPS/PLA mixture was heated and kneaded together thoroughly on the Two Roll Mill Machine to form a composite mixture. The process involves the addition of the TPS/PLA while the rolls were in counter clockwise motion for a period of 10 min and at a temperature of 150°C, the rolls rotate at 500 rpm and allowed to mixed for 5 min until homogeneous mixture was achieved. The composite was then transferred into the mould on the compression machine. In the moulding process, the samples were compressed using hydraulic press machine to achieved definite shape and dimensions of 100 mm X 50 mm X 2 mm.

3.0 RESULTS AND DISCUSSION

Water is the primary plasticizer in binding starch molecules but the thermoplastic produced using only water as the plasticizing agent are highly rigid and usually appears to have various tears in formation as a result of shrinkage as water rapidly evaporate from the material during drying [19]. Glycerol as an oil is less evaporative and allows better inter-alias of the starch molecules during plasticization. From the experiment, the tensile strength values are higher with higher glycerol content. The response shows the highest value of 11 MPa at 30% glycerol content with similar higher tensile strength value from 20% and above glycerol content. This value is close to those obtained in the works of [18], [20], [21]. The results do not quite agree with the recent work of [11] who quoted higher tensile strength value of above 20 MPa but similar elongation at break. This differences can be attributed to the method of polymer preparation used and the usage of the whole cassava tuber (including the peel) in the starch extraction stage of their work.

To deduce the optimal mixture constituent that ensures good physical properties specifically the highest tensile strength, the responses was subjected to a numerical optimization on Design Expert. All mixture content and responses were simultaneously optimized within the upper and lower limits of the experimental range. The goal is to maximize the tensile strength within the experimental range of water, glycerol and acetic acid. Table 4.6 shows the result of the optimized solution along with the experimental value. The desirability obtained was 1.0 and this shows that maximum tensile strength is within the chosen experimental range.

Table 4.6: Results of Experimental and optimised solution

| Process Parameters       | Experimental solution | Optimized Solution |
|--------------------------|-----------------------|--------------------|
| Glycerol (%)             | 0.280                 | 0.300              |
| Water (%)                | 0.600                 | 0.600              |
| Aceti Acid (%)           | 0.020                 | 0.000              |
| Tensile strength (MPa)   | 11.000                | 10.999             |
| Water absorption (%)     | 30.000                | 38.349             |
| Elongation (%)           | 12.000                | 11.373             |
As expected, the addition of PLA causes a direct increase in the tensile strength of the material much because of the ability of PLA to bear more load. As depicted in Figure 4.6 the increase was minima at 10% addition of PLA (TPS₁₀) and gradually increases up to about 250% increment of tensile strength at 50% addition of PLA (TPS₅₀). Significant increase was also observed for TPS₄₀ and TPS₅₀ (about 220% and 250% respectively when compared with the control sample). Similar increase in mechanical properties was observed in the work of [22] in which starch plastic was reinforced with cellulose nanocrystals from rice straw.

![Figure 4.6: Influence of PLA addition on the tensile strength of TPS](image)

Even though the results of tensile strength observed in this work differs significantly from some previous studies mostly due to the differences in the sources of starch used and processing method employed, the increase observed with the addition of a reinforcement agent shows similar proportion of influence basically limited by poor alignment of starch molecules to either fiber or polyesters [14]. Figure 4.7 compares the influence of reinforcement addition on starch plastic in this work with other previous studies of [16], [17], [24].

![Figure 4.7: Comparison of tensile strength increase with PLA addition](image)
The result also shows a reduction in the percentage elongation of TPS. This can be associated to the improper alignment of the composite matrix. Even though the material tensile strength increase, the material becomes more brittle and easily snap to breakage at the point of maximum stress. The result is in close agreement with previous works of [18], [24]. This negative influence on TPS percentage elongation is mostly associated with the poor formation of the composite matrix during blending of TPS with the reinforcement material [15].

The percentage water uptake of the TPS was largely reduced as more PLA is added to the composite. This is expected giving that PLA do not readily absorb water thus improving the water resistance of the material. The rate of water absorption is critical in determining the usability of plastic materials in various applications. Many approaches have been taken by various research over the years in an attempt to shield TPS from absorbing water so as to widen its usability. Reference [25] utilize polycaprolactone, hemicelluloses and zein composites on TPS made from cornstarch. The result shows that the composite percentage water absorption drops as more amount of TPS is been replaced. The rapid biodegradability of TPS as compare to synthetic plastic is majorly boosted by the ability to easily absorbed water when dispose in a natural environment. Therefore, when proposing an additive to improve TPS resistance to water absorption such an additive should also be easily degraded so as not to sacrifice degradability for improvement in properties. Reference [26] reported similar results of improvement in water resistance when TPS was reinforced with nanoclay.

4.0 CONCLUSION
The physical properties of cassava starch thermoplastic are close in value to that of TPS from other sources of starch like corn, rice and wheat. Therefore, cassava starch can be adequately use as a feedstock for the production of bioplastic. Addition of PLA to the TPS improves the physical properties of the material. This TPS/PLA composite material can be utilized in various applications where synthetic plastic currently dominates at a competitive cost considering the cheap availability of cassava starch.

5.0 ACKNOWLEDGMENT
Thanks to Mallam Abdullahi Isiaka of the Institute of Leather Research and Polymer Technology for his contribution to this work.

REFERENCES
[1] H. K. Ahn, M. S. Huda, M. C. Smith, W. Mulbry, W. F. Schmidt, and J. B. Reeves, “Biodegradability of injection molded bioplastic pots containing polylactic acid and poultry feather fiber,” Bioresour. Technol., vol. 102, no. 7, pp. 4930–4933, 2011.
[2] O. Udensi, E. V Ikpeme, E. A. Uyoh, and E. A. Brisibe, “Evaluation of Starch Biodegradable Plastics Derived from Cassava and Their Rates of Degradation in Soil,” Nig J. Biotech., vol. 20, p. 2833, 2009.
[3] S. Godbole, “Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films,” Bioresour. Technol., vol. 86, no. 1, pp. 33–37, 2003.
[4] K. Madhavan Nampoothiri, N. R. Nair, and R. P. John, “An overview of the recent developments in polylactide (PLA) research,” Bioresour. Technol., vol. 101, no. 22, pp. 8493–8501, 2010.
[5] N. Rajendran, S. Puppala, S. M. Raj, and R. B. Angeeleena, “Seaweeds can be a new source for bioplastics,” J. Pharm. Res., vol. 55, no. 33, pp. 1476–1479, 2012.
[6] C. Bastioli, “Global status of the production of biobased packaging materials,” Starch/Staerke, vol. 53, no. 8, pp. 351–355, 2001.
[7] B. R. Mose and S. M. Maranga, “A Review on Starch Based Nanocomposites For Bioplastic Materials,” J. Mater. Sci. Eng. B, vol. 1, no. B, pp. 239–245, 2011.
[8] D. Ačkar et al., “Starch modification by organic acids and their derivatives: A review,” *Molecules*, vol. 20, no. 10, pp. 19554–19570, 2015.

[9] L. Fama, S. K. Flores, L. Gerschenson, and S. Goyanes, “Physical characterization of cassava starch biofilms with special reference to dynamic mechanical properties at low temperatures,” *Carbohydr. Polym.*, vol. 66, no. 1, pp. 8–15, 2006.

[10] F. M. Fakhoury, S. Maria Martelli, L. Canhadas Bertan, F. Yamashita, L. H. Innocentini Mei, and F. P. Collares Queiroz, “Edible films made from blends of manioc starch and gelatin - Influence of different types of plasticizer and different levels of macromolecules on their properties,” *LWT - Food Sci. Technol.*, vol. 49, no. 1, pp. 149–154, 2012.

[11] S. L. Ezeoha and J. N. Ezenwanne, “Production of Biodegradable Plastic Packaging Film from Cassava Starch,” *IOSR J. Eng.*, vol. 3, no. 10, pp. 2250–3021, 2013.

[12] K. Lewis and E. Simon, “Bioplastics Simplified: Attributes of Biobased and Biodegradable Plastics,” *Spira - bioplastics* division, no. February, 2016.

[13] O. Vilpoux and L. Averous, “Starch-based plastics,” *Technol. use potentialities Lat. Am. starchy tubers*, pp. 521–553, 2002.

[14] J. J. G. van Soest and P. Essers, “Influence of Amylose-Amylopectin Ratio on Properties of Extruded Starch Plastic Sheets,” *J. Macromol. Sci. Part A*, vol. 34, no. 9, pp. 1665–1689, 1997.

[15] M. G. Lomeli-Ramirez, S. G. Kestur, R. Manriquez-Gonzalez, S. Iwakiri, G. B. De Muniz, and T. S. Flores-Sahagun, “Bio-composites of cassava starch-green coconut fiber: Part II - Structure and properties,” *Carbohydr. Polym.*, vol. 102, no. 1, pp. 576–583, 2014.

[16] E. De Morais Teixeira, A. L. Da Roz, A. J. F. De Carvalho, and A. A. Da Silva Curvelo, “Preparation and characterisation of thermoplastic starches from cassava starch, cassava root and cassava bagasse,” *Macromol. Symp.*, vol. 229, pp. 266–275, 2005.

[17] E. de M. Teixeira, D. Pasquini, A. A. S. Curvelo, E. Corradini, M. N. Belgacem, and A. Dufresne, “Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch,” *Carbohydr. Polym.*, vol. 78, no. 3, pp. 422–431, 2009.

[18] E. de M. Teixeira, A. A. S. Curvelo, A. C. Corrêa, J. M. Marconcini, G. M. Glenn, and L. H. C. Mattoso, “Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid),” *Ind. Crops Prod.*, vol. 37, no. 1, pp. 61–68, 2012.

[19] A. M. Nafchi, M. Moradpour, M. Saeidi, and A. K. Alias, “Thermoplastic starches: Properties, challenges, and prospects,” *Starch/Staerke*, vol. 65, no. 1–2, pp. 61–72, 2013.

[20] J. González-Gutiérrez, P. Partal, M. García-Morales, and C. Gallegos, “Effect of processing on the viscoelastic, tensile and optical properties of albumen/starch-based bioplastics,” *Carbohydr. Polym.*, vol. 84, no. 1, pp. 308–315, 2011.

[21] O. O. Oladayo, Q. C. Umunna, O. S. Joseph, and W. Oluwasegun, “Physicochemical properties of cassava starch and starch-keratin prepared biofilm,” *Songklanakarin J. Sci. Technol.*, vol. 38, no. 4, pp. 349–355, 2016.

[22] N. L. Garcia, L. Ribba, A. Dufresne, M. Aranguren, and S. Goyanes, “Effect of glycerol on the morphology of nanocomposites made from thermoplastic starch and starch nanocrystals,” *Carbohydr. Polym.*, vol. 84, no. 1, pp. 203–210, 2011.

[23] Y. E. Agustin and K. S. Padmawijaya, “Effect of glycerol and zinc oxide addition on antibacterial activity of biodegradable bioplastics from chitosan-kepok banana peel starch,” in *IOP Conference Series: Materials Science and Engineering*, 2017, vol. 223, no. 1.

[24] M. Gáspár, Z. Benko, G. Dogossy, K. Réczey, and T. Czigány, “Reducing water absorption in compostable starch-based plastics,” *Polym. Degrad. Stab.*, vol. 90, no. 3, pp. 563–569, 2005.

[25] H. Suryanto, P. T. Hutomo, R. Wanjaya, P. Puspitasari, and Sukarni, “The stucture of bioplastic from cassava starch with nanoclay reinforcement,” in *AIP Conference Proceedings*, 2016, vol. 1778.
