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Effects of Copolymer blends in the Production and Characterisation of Biodegradable polymer from Agricultural Product-Using Cassava Starch (Manihort Species) as case studies

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High demands and diverse applications of plastic materials had contributed immensely to the social-economic growth of the nations especially in the packaging industry. However, plastics have been a major contributor to the world's present garbage problems especially from the packaging sector of the industry. The menace was traced to non-degradable characteristics of LDPE and HDPP resins often used in the productions, hence, the need for biodegradable polymer blends.;l Co-polymer from Cassava (Manihort Species) starch with glycerol, vinegar and water was formulated to produce slurry, which was heated to about 1000c to form gel, dried to about 12% moisture. The resulting chips were weighed in the ratios of 1:0, 1:3, 1:1, 3:1, 0:1 (wt/wt %) to pure low density polyethylene (LDPE) resins. Each formulation of mixture was extruded at 1600C to produce polymer blends (plastics) in batches. The samples were chipped into same dimensions of 2.0mm thickness, 15.00mm width and 30.00mm and characterized. The mechanical properties of the polymer blends were found to decrease as the Copolymer increased. The best Young modulus was achieved with pure LDPE extrudate having 0.45±0.005 (109N/m,Gpa) and the least in the pure copolymer 0.11±0.005 (109N/m,Gpa). The homogenous dope exhibited compatibility of cassava starch with polyethylene and it took up to 72 hr for each of the samples to cure completely.

INTRODUCTION

The high demand for plastics and their numerous usages had been a major contributor to the world's present garbage problems because of their non-biodegradable characteristics after utilization. The need for such large quantities of conventional plastics and their dominance over other materials is due to their excellent “long life” properties and tenacity. Approximately, ten million tons of plastic products are discarded each year (Halley et al. 2001). Polyethylene is one of common synthetic polymers of high hydrophobic level and high molecular weight (Abd El-Rahim et al., 2004). Petroleum based polymeric plastics, films and materials cannot be degraded by natural processes in a short period of time, hence, they are left as solid waste, causing environmental problems. They find their ways into water channels causing flooding and leading to loss of lives and property. Methods normally used to destroy other types of waste such as burning and burying are not suitable for plastic destruction. When some types of plastics are burnt, they release toxic fumes, posing challenges to human health, so there is need to produce plastics that will disintegrate within a short time. Burying plastics in soil cannot destroy plastics because they are not biodegradable, there is also limited space for landfill. Degradation at high temperature, such as in pyrolysis (burning) tends to cause emission of toxic fumes. Available solutions includes: creation of sanitary landfills in appropriate places; conducting campaigns by creating awareness about the inherent problems caused by indiscriminate plastic disposal to the environment and demanding greater participation of government authorities (Banerjee, Hung and Srivastava, 2014). Adoption of selective collection and recycling programs which includes plastic conversion to oil, synthesis of petroleum based fuel from plastics are front liner solutions (Dipak and Pranav, 2014; Cleetuset al 2013).

Fig 1: A dump site where plastics are burnt releasing toxic fumes.

Recently, public concerns on environmental problem, climate change and limited fossil fuel resource have caused much research and development to be devoted to the study of biodegradable materials to replace the conventional non-biodegradable plastics. Biodegradable plastics are regarded as Copolymers (plastics) with similar properties to conventional plastics, but it can decomposed after disposal to the environment by the activity of microorganisms with end products of CO_2 and H_2O (**Tharanathan**, 2003). A number of aerobic and anaerobic microorganisms have been identified for biodegradation. The use of starch in the manufacturing of bioplastics began in the 70's (Curvelo et al., 2001). Among its advantages, the starch is cheap, abundant and renewable. Besides, it is found in several forms due to the origin of its raw material as filling agent for polyolefin and as a component in synthetic polymers blends. (Lawter and Fischer, 2000).

The most popular method in preparation of starch and polyethylene blends was the conventional extrusion with the addition of processing aid to enhance the compatibility of the two materials. (Shah et al, 1995) have prepared detailed experimental approach for blending modified starch with LDPE. The blending of polymers with starch under controlled conditions leads to co-polymerization that in turn results in high molecular polymers with thermoplastic properties. The starch is not really thermoplastic, but, in the presence of a plasticizer (water, glycerin, sorbitol, etc.), high temperatures (90 - 180°C) and shearing, it melts and fluidizes, enabling its use in injection, extrusion and blowing equipment, such as those for synthetic plastics. It is necessary that the starch maintains its semi-crystal granular structure and that it behaves in a way similar to that of a melted thermoplastic, obtained through a mono- or twin-screw extrusion with the use of mechanical and thermal energy (Lourdin et al., 1999). However, it is necessary to add an additional plasticizer besides water, such as polyol or destructurating compounds such as glycerol, carbamide, etc. with hydrophilic properties which will be only slightly influenced by the atmospheric conditions in the sorption -desorption mechanism and allow a melting phase at a temperature lower than that of the starch degradation (Averous, 2002).

Starch is the principal source of food calories for people globally (Jeffry Grotto 2013). Starch consists predominantly of two types of glucose polymers namely, amylose and amylopectin. In nature, these two polymers are organized in the semi-crystalline structure packed in the starch granule. The granular structure of starch is quite strong; it possesses high thermal stability with a decomposition temperature as high as 22^{0}C (Shogren, 1993).

The use of cassava would not only create an economic alternative for cassava agriculture but would also lead to a reduction in the impacts caused by the intense use of packaging plastics derived from petroleum oil (polyethylene, polystyrene, etc.). The structure of Cassava root tuber is shown in Figure 2.

Figure 2: Cassava root-tubers (*Manihort esculential* L)

Nigeria being the world largest producer of cassava, production of biodegradable packaging materials is thus, feasible. Starch is readily dispersed in cold water and thickens as the starch/water mixture is heated to near boiling point to give a thickened, colloidal solution that gels on cooling. This process is known as destructuration since it involves destruction of the granule crystallites. Polymer blends can be distributed or transported to normal plastic converters, which can process the blends to products using normal injection or blow moulds. The objectives of this research work is to produce and characterize a biodegradable plastics from cassava starch.

MATERIALS AND METHODS

The materials used were, powdered cassava starch, glycerol, vinegar and low density polyethylene obtained from Ojota market, Lagos, Nigeria. De-ionsed water was used in all formulation as it played two major roles of breaking the structure of the native granule and the bonds of hydrogen chains, and as a plasticizer. The experiments were conducted at Federal Institute of Industrial Research Oshodi (FIIRO).

The moisture content of the powdered cassava starch was first determined using a moisture analyzer model AND MS 70 in which cassava starch was scanned for 30mins. This was done to ensure that the starch moisture content did not exceed the acceptable limit of 13% because higher moisture content causes loss of starch structure due to invasion by microbes. Solutions of different measure of cassava starch in the range of 1.0 to 1.6 Kg were respectively dissolved in 1 Litre of water, 200 ml of vinegar and 200 ml glycerol, while the magnitude of the cassava starch were kept constant. Each mixture recipe were stirred continuously and heated to 100^{o}C over a hot plate till the mixture turned from white suspensions to clear, consistent gel-like mass dope. The dope were removed from the hot plate and extruded into pellets of about 30.0mm x 15.0mm x 2.0mm dimensions and allowed to dry at ambient temperature of about 27^{o}C till a constant weight is attained . Two other batches of 100% polyethylene and 100% starch plastics were also produced separately to serve as the control experiments. Other blends were constituted in the ratios of 25/75; 50/50; and 75/25 cassava starch to polyethylene.

The extruded and dried samples were processed with low density polyethylene resins at 160^{0}C to produce plastics in three different batches in a twin screw extruder with a melt flow of 5g/10min. Mechanical properties of the biodegradable polymer were determined and recorded. The tensile test of the samples was carried out using testometric universal tensile testing machine M500-25KN at a cross-head speed of 10mm/sec. The method used is in accordance with ASTM. The assay was repeated three times and the average results computed for analysis.

For biodegradability test, 1g each of the all batches was weighed and buried in a bucket of soil; they were brought out after 30 days and carefully examined, observations were recorded.

RESULTS AND DISCUSSION

The quality of the plastics produced, in terms of strength, flexibility, transparency and texture depends on the proportion of the materials and additives used. Cassava starch was the only material that was varied while other materials were kept constant. The different formulations experimented were carefully observed and it was found that the first formulation produced the best result due to its stability, and that was what was used for the blends of five batches.

It took up to 72hr for each of the samples to dry completely. The exercise showed the compatibility of cassava starch with polyethylene. The different formulations experimented were carefully observed and it was found that the first formulation with the last cassava blend produced the best result due to its stability, and this was used for the blending of five batches. The mechanical property of samples was observed to decrease with the increasing cassava quantity. This sample texture is shown in Figure 3.0.

Fig 3: Structure of the blended PET-Cassava Macromolecules

The 100% polyethylene possessed better mechanical properties than the blended biodegradable plastics which also possessed good mechanical properties. Results also showed that polyethylene can be used to improve the mechanical properties of cassava starch.

The glass transition temperature (Tg) of pure, dry starch is above the decomposition point, so it does not soften and flow. This "thermoplastic starch" (TPS) will flow at elevated temperature and pressure and can be extruded to give both foams and solid molded articles. Unfortunately, the properties of these simple thermoplastics tend to be disappointing. For example, TPS plasticized with water has poor dimensional stability and becomes brittle as water is lost, and the properties of water- and glycerol-plasticized TPS are poor at high humidity which necessitated the blend of cassava starch with polyethylene.

The tensile strength test carried out showed that tensile strength, elongation and modulus decrease with increase in cassava starch in all the blends which means that polyethylene possessed good mechanical properties. The 100% polyethylene possessed better mechanical properties than the blended biodegradable plastics which also possessed good mechanical properties; it also shows the compatibility of cassava starch with polyethylene. Results also showed that polyethylene can be used to improve the mechanical properties of cassava starch.

The products are formed by the swelling and expansion of starch through the action of high temperature and water vapour. The biodegradability test revealed 100% cassava starch plastic showed decrease in weight 0.2g, which is an indication of microbial attack in the soil. The other batches did not show any form of reduction for that period of 30 days.

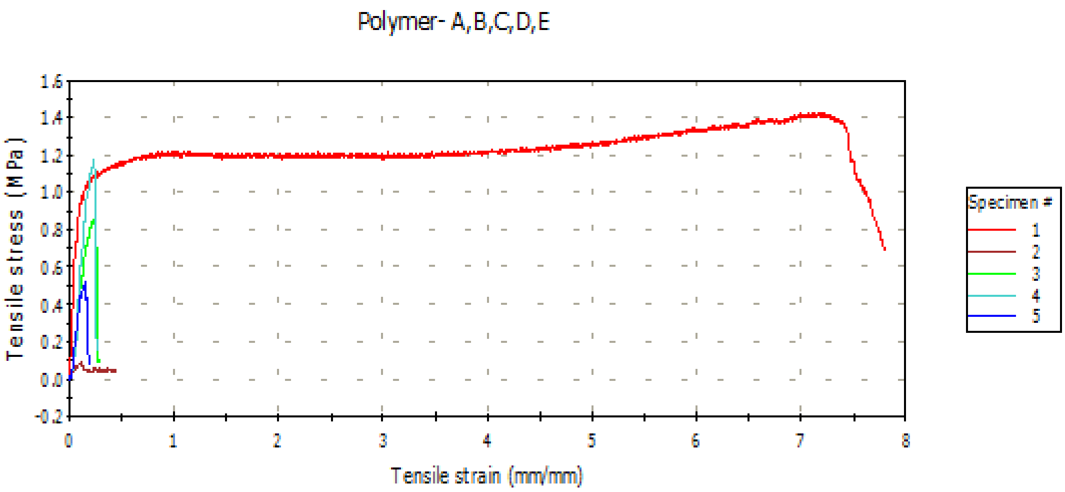

Figure 4: Young Modulus Responses of Biodegradable Polymer Blend with Polyethylene

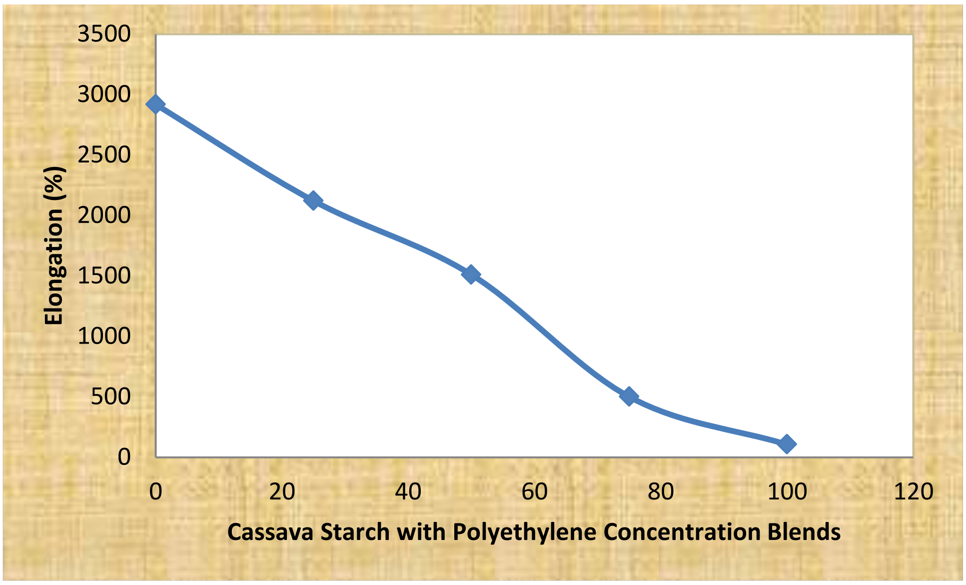

Figure 5: Elongation percentage of Biodegradable Polymer Blend with Polyethylene

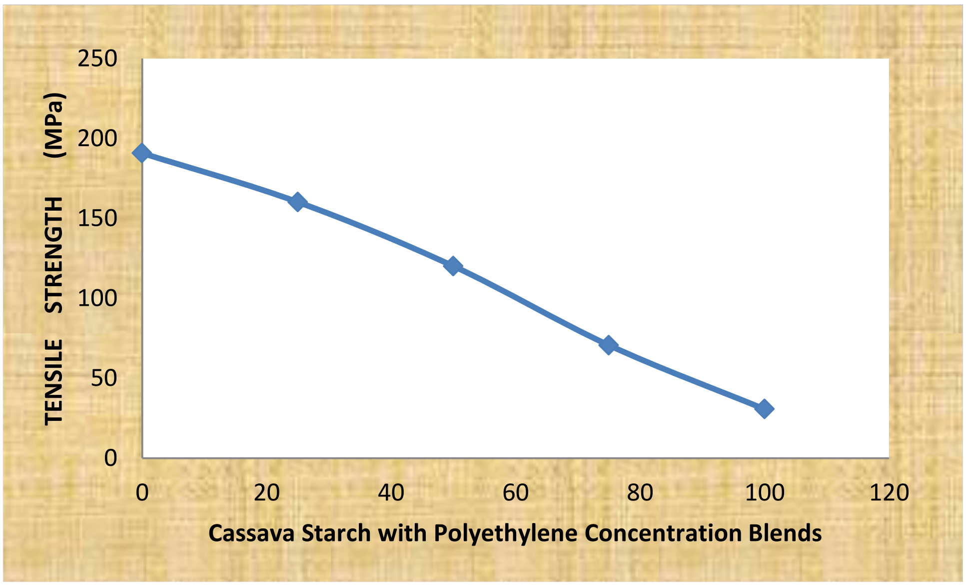

Figure 6: Tensile Strength Responses of Biodegradable Polymer Blend with Polyethylene

CONCLUSION

This study has shown that the development of starch-based biodegradable plastics looks very promising given the fact that starch is inexpensive, available throughout the year, and biodegradable in various environments. This research shows that cassava starch based plastics can compete with petroleum based plastics if well plasticized, even though results in this work showed that 100% polyethylene plastic possessed tensile strength higher than polyethylene - cassava starch plastics, but with time and continuous research in this direction, 100% biodegradable plastics will displace conventional plastics in different areas of applications, so research and development must continue in this direction in order to get rid of petroleum based, non biodegradable plastics for a more friendly environment

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