



A Blend of Green Algae and Sweet Potato Starch as a Potential Source of Bioplastic Production and Its Significance to the Polymer Industry

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Received: 12 November 2012; **Revised:** 1 December 2012 **Accepted:** 8 December 2012

Abstract: Our research focus was to obtain an alternative source of biodegradable plastic from blue green algae and sweet potato starch to obtain a sustainable source of plastic synthesis. Different concentrations of starch and dried green algae were used to produce biopolymers. The amount of algae that produced the best bioplastic was the objective of the research. High percentages of dry algae produced material with high strength with a deep black colour. The concentration in percentage of sweet potato starch was varied from 25-87.5 while the algae powder was varied from 21.-75%. Cross-linking of cellulose polymers together through chemical processes produces tough material, which can be converted to various forms. The manufacture of plastics is a form of polymerization reaction. Bio-plastic or organic plastic is a polymer material obtained from renewable biomass sources such as vegetable oil, corn starch, potato starch, and pea starch unlike fossil-fuel plastics derived from petroleum. Starch is made of long chains of glucose molecules joined together. It contains two polymers: amylose which is straight chain and amylopectin which is branched. When starch is dried from an aqueous solution it forms a film due to hydrogen bonding between the chains. However, the amylopectin inhibits the formation of the bio-plastic. The reaction of starch with Hydrochloric acid breaks down the amylopectin forming an appreciable plastic.

Keywords: Bioplastic, Starch, Polymers, organic plastic and Biodegradable.

INTRODUCTION

The diminishing reserves of oil has prompted the search for sustainable methods of plastic manufacture, petroleum based polymers have been the dominant source of basic requirement for the manufacture of this ubiquitous product. Bio-plastics is a polymeric material obtained by direct processing of naturally

occurring polymers (biopolymers)¹. Plastics are indispensable in our daily life. Approximately 265,000,000 tonnes of them are produced and used annually. Today, bio-plastics from renewable resources only account for a very small share of the total market (<1 percent), but the rapid advances in biotechnology and biochemistry will further push forward this fast growing market. To the present day, bio-plastics production capacities have already expanded with double-digit growth figures every year. Innovative technological approaches like the bio-refinery and the concept platform chemicals will further transform industrial production of renewable plastics.

Organic plastic has the twin advantage of reducing global warming and reducing dependence on fossil fuels. These advantages coupled with the availability of algae and plant starch has led to more research on the field of organic plastic potentials. Biodegradable bioplastics may help towards the goal of a cleaner and greener environment because they are made using renewable materials such as starch/sugars, vegetable oil and wood pulp. Using renewable feedstock for plastic production can reduce the amount of global warming greenhouse gasses (GHGs such as CO₂ and CH₄) released into the atmosphere when compared to conventional plastic production from fossil fuels. In addition, biodegradable bioplastics break down in the environment and are clearly not as persistent as conventional non-degradable petroplastics². The use of algae opens up the possibility of utilizing carbon, neutralizing greenhouse gas emissions from factories or power plants. Algae serve as an excellent feedstock for plastic production owing to its many advantages such as high yield and the ability to grow in a range of environments.

Bio-plastics are manufactured using biopolymers through two routes:

- I. Biopolymers from living organisms- made from cellulose, soy protein and starch.
- II. Polymerizable Molecules – these are typically made from lactic acid and triglycerides,

These molecules come from renewable natural resources, and can be polymerized to be used in the manufacture of biodegradable plastics. Processes by which small molecules generally referred to as monomers undergo repeated combination to form very large molecules is called polymerization. The specific physical and chemical properties of polymers are determined both by the structure and by the degree of organization of the structural units.

The widespread use of polymeric plastic materials that contribute so much to our standard of living has brought with it a pollution problem. A solution to the environmental pollution problem has been the development of biodegradable polymers such as polyesters derived from ϵ -caprolactone and lactic acid³. Most existing international standards require biodegradation of 60% within 180 days along with certain other criteria for the resin or product to be called compostable⁴. Currently, most products are designed with limited consideration to their ecological footprint especially as it relates to their ultimate disposability. Of particular concern are plastics used in single-use disposable packaging and consumer goods. Designing these materials to be biodegradable and/or bio-based and ensuring that they end up in an appropriate disposal system as composting along with other bio wastes is environmentally and ecologically sound⁵.

Even if some biopolymers are shown to have environmental characteristics that are preferable to conventional polymers, much work needs to be done to bring down the costs of biologically derived materials. Commercially available biopolymers are typically two to five times more expensive than synthetic resins. In only a few specialized applications, such as biomedicine, are the relatively high costs of biopolymer materials not likely to impede market growth. Since many biopolymers are in the early phases of development, it is difficult to determine whether economy-of-scale manufacturing will be able to bring down their current high production costs⁶

PLASTIC SYNTHESIS

The synthesis of plastic is a polymerization reaction. Small units called monomers undergo chemical reactions to form polymers. A general knowledge of polymerization reactions and mechanisms involved is a vital study. In condensation polymers, the monomers bond with the loss of a small molecule. If this small molecule is water, as it is in protein polymerization, then the reaction is called dehydration. Condensation polymers are also known as step-growth polymers. Addition polymers add one monomer at a time at the end of the polymer chain. The end of the chain that is growing will often have a reactive intermediate. There are three types of reactive intermediates that are found at the end of addition polymer chains. The first is a cation, which is a positively charged atom. The second is an anion, which is a negatively charged atom. The third option is a radical, which is an atom with a single non-bonded electron in its valence orbital. Addition polymers are also known as chain-growth polymers. When a polymer is made of 2 or more different monomers it is called a copolymer. Chain branching is caused by hydrogen abstraction where the free radical at the end of the chain in an addition polymer abstracts a hydrogen atom from the middle of the chain causing a branch to form at that point ⁷

ENERGY CONSUMPTION AND THE GLOBAL WARMING IMPACT

The energy consumption of plastic production is significantly high. The total oil consumption in the year 2008 was 87.2 Million barrels a day. The strategic importance of the bio-economy is linked to those areas in which bio-based products and processes can substitute for fossil or mineral-based products and/or chemical processes ⁸. The known oil reserves total 1.24 trillion barrels, which at the current rate of consumption will last for approximately 41 years ⁹. It is estimated that 99% of the plastic feedstock comes from petroleum.

The energy consumption is considerable with an estimated U.S plastic industry consuming about 6% of all the Energy used by the American Industries. With the plastic industry being a heavy energy consumer, the greenhouse effect will continue to impact on the environment. The use of petroleum based resins is an issue that requires attention in order to mitigate the global warming effects. Microalgae can be commercialized for the production of both Energy and Bio-plastic.

The realization that fossil fuels are fast depleting has accelerated the search for an alternative energy source that is renewable, economical, and environmentally friendly. The situation has been exacerbated by global warming which has brought it home to all that there is a need to conserve energy and reduce collectively man's global carbon footprint. The instability in the regions from which the fossil fuels are sourced is another cause for concern ¹⁰.

METHODOLOGY

Algae Production, Collection and Preparation: Green algae were obtained from the University of Eastern Africa, Baraton Dam and small water ponds outside the University. Alga culture concerns mainly microalgae. Seaweeds also have many commercial and industrial uses but due to their size and the specific requirements of the environment in which they need to grow, they don't lend themselves as readily to cultivation ¹¹. The open pond system was employed in the development of algae. The ponds were left undisturbed until a thick mass had formed. This system of cultivation was used as it was relatively cheap compared to other methods like single layer. Those that indicated high levels of growth and photosynthetic activity were obtained. Green algae are one of the largest groups of algae with close to more than seven thousand five hundred species. These algae contain chlorophyll (like in plants) and a large amount of proteins. In addition, under stress conditions they produce starch and oil that are stored inside the cell ¹². Any form of impurity was removed by hand and cleaned with clean water. The fresh samples were air dried for two weeks. After they were very dry, they were crushed into powder form. The

dried samples were weighed and 50ml of distilled water was added to every 100g of the dried algae.

Sweet Potato Flour Collection and Preparation: Sweet potato root tubers were collected from different farms around Baraton. Two species of the potatoes were identified; Red skinned and white skinned. The tubers were cleaned to remove any form of dirt. They were then sliced into small pieces. The sweet potato tubers were sundried for two weeks. The dried tubers were taken for grinding in a mill.

PROCEDURE FOR MAKING BIO PLASTIC FILM

Different weights of sweet potato flour were measured using an analytical balance and placed in a beaker. 50g, 75g, 100g, 125g, 150g and 175g of the flour was weighed and equal amounts of distilled water were added for each weight. After the starch preparations had been weighed and equal amounts of DI water had been added, the beakers were labelled and left for about three minutes to form slurry.

Algae slurry was prepared by weighing 150g, 125g, 100g, 75g, 50g and 25g of algae powder was poured into four different beakers labelled A, B, C, D, E and F, 20ml, 30ml, 40ml, 50ml, 60ml and 75 ml of distilled water was added to the green slurry. The slurry is heated with stirring and the starch slurry is added with constant stirring. 3cm³ of 3M Hydrochloric acid is added and 5ml, 10ml, 15 ml, 20ml, 25ml, 30ml and 0 ml of Propane-1, 2, 3-triol as a plasticizer was added according to the weight of the slurries. The mixtures are carefully brought to boil gently for 15minutes. The concentrations of the sweet potato flour and algae were varied to obtain desired strengths and the effect of the plasticizer on the elasticity and moulding ability. An anhydroglucose molecule of starch contains two secondary and one primary hydroxyl group. These hydroxyls can react easily with a wide range of compounds such as acid anhydrides, organic chloro-compounds, aldehydes, epoxy, and ethylene compounds. Chemicals of these classes having two or more of the reactive groups may react with two or more hydroxyls of the starch molecules. The products are called cross-linked starches. Cross-linking results in a reduction of the solubility in water and to thickening, leading to higher viscosities¹³.

Starch-based bio-plastics strength can be improved by employing different processes which can be summarized as follows; Acetylation which is carried out by dissolving the starch in water, adjusting the pH to 8.0 through the addition of 1M sodium hydroxide, stirring the mixture while adding acetic anhydride, lowering the pH to 4.5 with 0.5M hydrochloric acid, filtering the slurry, washing the slurry with water, then drying the slurry with air. Oxidation is carried out by dissolving the starch in water, raising the pH to 9.5 via the addition of 2M sodium hydroxide, slowly adding NaOCl to the slurry at 30°C, then adjusting the pH to 7 with the addition of 1M sulphuric acid, filtering, washing with water, and finally air-drying. Acid thinning is carried out by creating slurry of starch in 0.15M hydrochloric acid, stirring the slurry for eight hours at 50°C, filtering, washing with water, and then air-drying.

Once the mixture is homogenous and viscous, pour it into well-labelled Petri dishes and spread it to dry, it takes about one day or two days at room temperature.

RESULTS AND DISCUSSION

Different strengths of polymers were achieved with different concentrations of the Propane-1, 2, 3-triol and the weight of the flour and algae. The product obtained from high 75% algae and 25% starch with 0 volume plasticizer produced poor plastic material. Propane-1, 2, 3-triol was added as a plasticizer, from the products obtained, the biopolymer obtained without the plasticizer was brittle and rigid. The polymers obtained from high concentrations of algae showed relatively high strength and a deep black colour. The durability and elasticity varied as per the amount of algae used. It was evident that high algae levels produced quality organic plastics. High sweet potato starch content in the organic plastic produced a white thick film suitable for food packaging. The high algae plastic could be commercialized for the production of materials, which require relative strength.



Fig.1: Photographs of Bioplastic obtained from Sweet Potato Starch and Algae.

Table- 1: Table of different Concentrations of the Bioplastic Raw Materials and the Weight of the Products

% Sweet Potato Starch	% Algae	Volume Of the Plasticizer	Volume of Water	Weight of the Product (g)
87.5	12.5	5	20	3.2183
25	75	10	30	13.7873
37.5	62.5	15	40	9.83
50	50	20	50	9.0373
62.5	37.5	25	60	9.1656
75	25	30	20	9.8371
25	75	0	75	24.142

From the results it was observed that, bioplastic from algae and sweet potato starch can be commercialized and used to replace the conventional petroleum plastics. With a few modifications, these polymeric materials can be converted to different shapes. The bioplastics formed did not degrade at room temperatures which could indicate their significance and ability to withstand humidity and microbial decay at normal storage conditions. The products obtained from the research can be a breakthrough as building blocks for other forms of polymer industry. Bioplastic starch can be produced from polylactic acid which has the advantage of biodegradation. The various routes to bioplastics fabrication can conceptually be classified into a chemical and/or fermentation route to produce the six basic petrochemical feedstock, which can then be transformed into traditional plastics (e.g., bioethanol, bio ethylene, or biopolyethylene), gasification of bio-based feedstock (syngas, methanol, olefins, and polyolefin), and design and development of new building blocks or molecules based on renewable bio sources using chemical and/or fermentation routes (e.g., PLA, PHA, or CO₂ polymers)¹⁴.

However, due to the number of processing steps, the comparative cost of making PLA is high and a cheaper and more sustainable alternative is thermoplastic starch (TPS). This is formed by integrating small charged organic compounds into the starch structure. Examples of suitable compounds are water, glycerol and urea¹⁵. Organic plastics can be obtained from different sources including the agricultural feedstock as shown by the closed loop life cycle diagram in figure 1. Biopolymers have existed since time immemorial however; the method of production and handling has been a challenge to the research world. There have been a lot of prospects to develop a durable bioplastic with the feature more less the same as the conventional petroleum polymers with the advantage of biodegradation.

Plastic is said to be biodegradable under the European Bioplastic Scope of testing under

EN 13432 / EN 14995 standards if it meets the following criteria⁴:

- (i) **Chemical test:** Disclosure of all constituents, threshold values for heavy metals are to be adhered to.
- (ii) **Biodegradability in watery medium (oxygen consumption and production of CO₂):** Proof must be made that at least 90% of the organic material is converted into CO₂ within 6 months.
- (iii) **Disintegration in compost:** After 3 months' composting and subsequent sifting through a 2 mm sieve, no more than 10% residue may remain, as compared to the original mass.
- (iv) **Practical test of compostability in a semi-industrial (or industrial) composting facility:** No negative influence on the composting process is permitted.
- (v) **Compost application:** Examination of the effect of resultant compost on plant growth (agronomic test), ecotoxicity test.

The world economy is partially sustained by this important asset, which has a functionality that cannot be replaced by other materials. Most plastics are robust and last for hundreds of years. They have replaced metals in the components of most manufactured goods, including for such products as computers, car parts and refrigerators, and in so doing have often made the products cheaper, lighter, safer, stronger and easier to recycle. Plastics have taken over from paper, glass and cardboard in packaging, usually reducing cost and carbon emissions while also providing better care of the items that they protect. In spite of these numerous advantages, conventional plastic offers counterbalancing disadvantages such as, Plastic litter disfigures the oceans and the coastlines, Plastics use valuable resources of oil, the plastics industry uses large amounts of energy, usually from fossil fuel sources which therefore adds to the world's production of greenhouse gases, The manufacturing of conventional plastics uses substantial amounts of toxic chemicals and plastics leach small amounts of pollutants, including endocrine disruptors, into the environment. These chemicals can have severe effects on animals and humans. Bioplastics - partly or wholly made from biological materials and not crude oil - represent an effective way of keeping the huge advantages of conventional plastics but mitigating their disadvantages. Some bioplastics degrade in the open air, others are made so that they compost in an industrial composting plant, aided by fungi, bacteria and enzymes. Others mimic the robustness and durability of conventional plastics such as polyethylene or PET. Bioplastics can generally be directly substituted for their oil-based equivalent. Indeed, they can generally be made to be chemically identical to the standard industrial plastics ¹⁶.

WORLD BIOPLASTIC

Global demand for bioplastics, plastic resins that are biodegradable or derived from plant-based sources, will raise more than fourfold to 900,000 metric tons in 2013, valued at \$2.6 billion. Bioplastics sector registers continuous growth: As estimated by IBAW, pan-European consumption of bioplastics

in 2003 was at 40,000 tons. This indicates that consumption has doubled from 2001. Compostable waste bags and starch based loose fill had the biggest share of overall consumption in Europe. For the first time bio packaging made a substantial contribution to market growth. Especially in Great Britain, Italy and the Netherlands the market development was dynamic ¹⁷. Growth will be fuelled by a number of factors, including consumer demand for more environmentally-sustainable products, the development of bio-based feedstock for commodity plastic resins, and increasing restrictions on the use of non-degradable plastic products, particularly plastic bags. Most important, however, will be the expected continuation of high crude oil and natural gas prices, which will allow bioplastics to become more cost-competitive with petroleum-based resins ¹⁸. The production of bioplastics is small but growing. The world produces over 260 million tonnes per annum (tpa) of plastics. Europe consumes approximately 53 million tpa and, specifically, the UK processes around five million tonnes per annum of plastics. At the moment bioplastics make up only approximately 0.1-0.2% of European plastics consumption (at around 60-100 ktpa). Worldwide bioplastic production is approximately 300 thousand tonnes per annum which equates to about 0.1% of world plastic production capacity. European Bioplastics predict that the worldwide bioplastics market will exhibit a six-fold expansion by 2011 ¹⁸. A hundred billion tons of biomass is produced by plants per year. To put that in perspective the global consumption of plastics is 200 million tons ¹⁹.

Bioplastic is one of the breakthroughs of polymer research. Resorting to bio-based polymers and sustainable sources of plastics has led to reduction in carbon emissions. The Kyoto Protocol outlined the need for countries to embrace environmentally friendly sources of energy in order to cut down on the carbon footprint. The biodegradation processes occurs in three steps: Fragmentation (Physical Degradation), Mineralization-Conversion of Organic Carbon, and Standardization ¹. The organic plastic produced from the sweet potato starch and algae was left for more than a year away from direct sunlight, water and under room temperature. It was observed that, if the product is commercialized, it will last if

used on indoor applications. The process of biodegradation of a material varies considerably depending on the environment in which it takes place (e.g. industrial composting plant, soil, fresh water, and marine water). Conditions such as temperature, humidity and the combination of micro-organisms play an important role if a certain degradation level is required within a given timeframe. The temperature for industrial composting might be around 60 °C compared to only about 20 °C in fresh water or soil

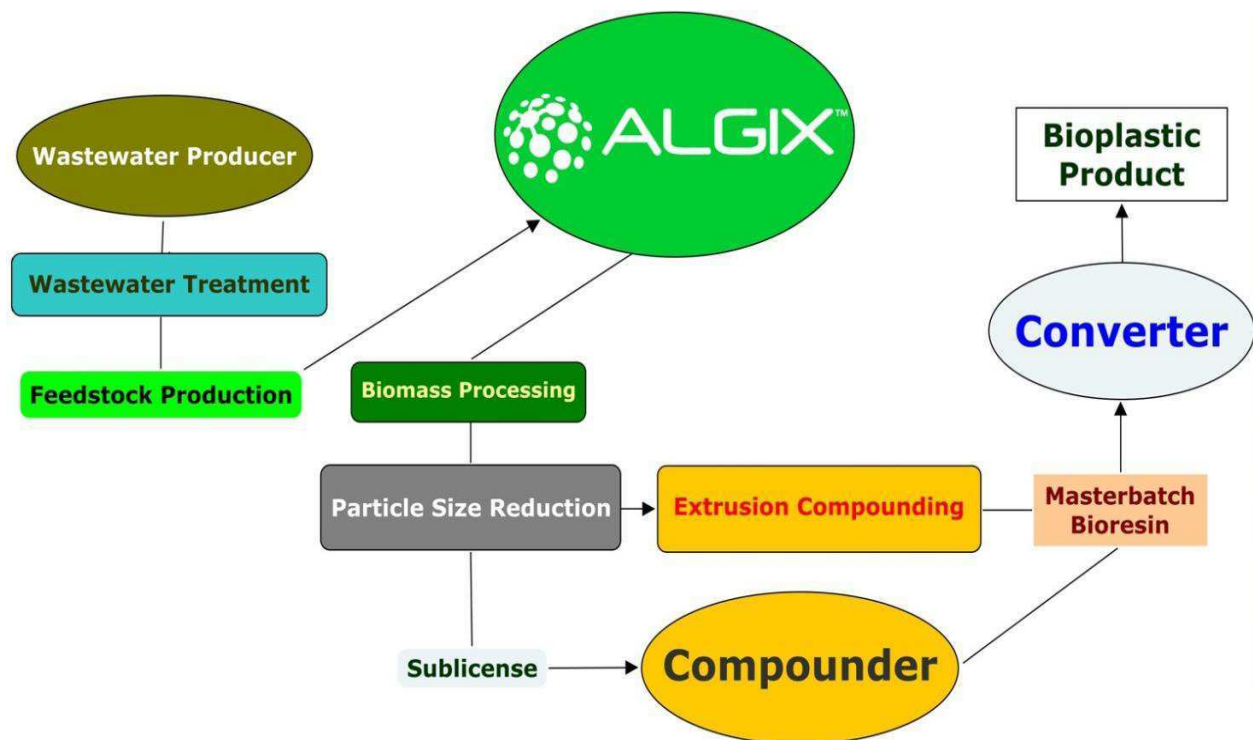


Fig. 2: Algal Biorefinery Flowchart Courtesy of Algix

Algae are preferred as a bioplastic feedstock as its advantages outweighs the disadvantages.

Aquatic Biomass is very attractive for use as feedstock for organic plastics because it has:

- High growth rate of all plants
- Natural protein and carbohydrate-based polymers
- Can remediate Wastewater and CO₂ emissions as a nutrient source
- Frequent harvesting and can be grown year around in warm climates
- Does not compete with Food production

By the year 2011, there was a projected growth of 28% increase to 40% in demand of biobased plastic from the previous 12% demand in 2010. Durables like electronics parts will account for 40% of the world demand of these noble products, which are biodegradable²⁰.

CONCLUSION

Organic plastics can play a vital role as an environment friendly, biodegradable alternative compared to conventional plastics. Algae based bio fuels are often quoted as the only plausible bio fuel solution to the world's oil crisis. But the economic viability of algae fuels is still in doubt. Exploring the production of

nonfuel products such as bio plastics could play a major role in shaping the economics and viability of algal plastic solutions. There is high potential in the algae plant ranging from bioplastics, food supplements to biofuel production. More research work ought to be undertaken to ascertain the significance of the starch-algae plastic, viable applications and Strength.

The technology routes for the production of algae based bio plastics are still under the research phase, and are far from commercialization. It is hoped that the significant advances made in the bio plastics industry in general will benefit algal bio plastics industry as well and will make algae organic plastics a reality in the not-too-distant future.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support from the Department of Chemistry, University of Eastern Africa, Baraton and our spouses, Mrs. Chelagat Magut and Mrs. Vivian Terer, for their moral support during this research work. May God bless all those who made this research successful.

REFERENCES

1. Kržan Andrej .Bio-based Polymers, National Institute of Chemistry Laboratory for Polymer Chemistry and Technology Ljubljana, Slovenia. 2009.
2. B.Myles and Richard S. Industrial uses for crops: markets for bioplastics HGCA, Caledonia House, 223 Pentonville Road, Kings Cross, London, N1 9HY. 2009.
3. Bright Alexandre, Bioplastics. Enviromental Biodegradable Resins and Additives, Admira Limited, Hong Kong, 18-23 Middle Line, Middvale Village, Clear View , 2010.
4. Narayan Ramani & Patel Martin. Review and Analysis of Bio-based Product LCA's. Department of Chemical Engineering & Materials Science, Michigan State University, East Lansing MI 48824. 2002.
5. Herdman Roger C. *Biopolymers: Making Materials Nature's Way*.U.S Congress, Office of Technology Assessment, U.S.A. 1993.
6. L.G.Wade, Organic Chemistry 6th Edition, Pearson Prentice Hall, U.S.A, 2006. 1233-1236.
7. United Nations industrial Development Organization (UNIDO). Industrial Biotechnology and Biomass Utilization Prospects and Challenges for the Developing World, Vienna.2007.
8. U.S. Department of Energy and The society of the Plastics Industry, Inc *Improving Energy Efficiency at U.S. Plastics Manufacturing Plants*. 2003.
9. Achara Nnorom . Biofuel from Algae. Journal of American Science 8(1). MDPGA, Ministry of Defence, Wethersfield Braintree, United Kingdom. 2012.
10. Demazel Delphine .Use of algae as an energy source. Central Nantes. 2008. Pp 1-26.
11. Hans Wolkers, Maria Barbosa, Dorinde M.M. Kleinegris, Rouke Bosma, René H. Wijffels, Microalgae: the green gold of the future. Propress, Wageningen, 2011.
12. Sugih Asaf Kleopas . Synthesis and Properties of Starch Based Biomaterials. University of Groningen. 2008. 1-155.
13. Swamy & Singh (.Bioplastics and global sustainability. Chemical Market Resources Inc. Webster/Houston, TX, U.S.A. 2010.
14. Abbott, A.P., Ballantyne, A.D., Conde, J.P. *et al.* Salt modified starch: sustainable, recyclable plastics. *J.Green Chemistry*. 2012 **14**: 1302-1307.
15. Goodall Chris Bioplastics: an important component of global sustainability. White Paper, UK. 2011,11-12.
16. Goodall Chris .Bioplastics: an important component of global sustainability. White Paper, UK. 2011. 11-12.
17. <http://www.freedoniagroup.com/brochure/28xx/2823smwe.pdf>. Bioplastic. Beta Drive.2009

18. European Bioplastics. Proceedings of the Third European Bioplastics Conference.2008.
19. Momani Brian .Assessment of the Impacts of Bioplastics: Energy Usage, Fossil Fuel Usage, Pollution, Health Effects, Effects on the Food Supply, and Economic Effects Compared to Petroleum Based Plastics, Worcester Polytechnic Institute.2009.
20. Lunt Jim. The World of Bioplastic, Jim Lunt &Associates .2012.

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