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BIO-PLASTICS PRODUCTION FROM STARCH

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The aim of this thesis was researching mainly about bio-plastics and bio-plastic production from starch which is a future alternative to petrochemical plastics and to gain more academic knowledge of bio-plastics production from different types of starch, to discuss the advantages as well as the limitations existing.

The project was approached by related theories, academic explanations and writer's professional opinions including the insight of bio-plastics properties, characteristics, advantages and disadvantages and application of bio-plastics in houseware scale. Particularly science theories prove that it is possible to produce starch-based plastics in different ways in the laboratory and do further research in the future.

Key words
Bio-plastics, bio-polymers, bio-based plastics, starch.

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CONCEPT DEFINITIONS

PE	Polyethylene; most common plastics used in packaging
PP	Polypropylene; a thermoplastic polymer used in packaging and labeling
PET	Polyethylene terephthalate; a form of polyester (clothing fabric) applied in plastic bottle and containers when packaging foods and beverages and other consumer products.
PEF	Polyethylene furanoate; polyester of the future and 100 % bio-based alternative to PET
PA	Polyamide or Nylon; a synthetic thermoplastic
PTT	Polytrimethylene terephthalate; a synthetic polyester used to manufacture carpet fibers
PBAF	Poly (butylene adipate-cobutylene 2,5-furandicarboxylate), the furanoate analogue and fully bio-derived and biodegradable
PLA	Polylactic acid; a thermoplastic aliphatic polyester derived from renewable resources
PHA	Polyhydroxyalkanoate; bio-derived, biodegradable plastic
PBS	Polybutylene succinate; a thermoplastic polymer with biodegradable properties
PBAT	Polybutylene adipate terephthalate; a biodegradable random copolymer
PCL	Polycaprolactone; a biodegradable, semi-crystalline thermoplastics polyester
PDO	Polydioxanone; a colorless, crystalline, biodegradable synthetic polymer
GHG	Greenhouse gas including carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and water vapor (H_2O)

CONCEPT DEFINITIONS

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1 INTRODUCTION

Plastics can be classified as a group of artificial or natural organic materials that can be cast and hardened. Plastics are very common and useful nowadays and are used in almost every place such as; in packaging material, in bottles, cell phones, printers, even in pharmaceutical to automobiles industries. The reason why plastics are a useful option because their structures can be chemically treated with some strength and shape to obtain higher molecular weights, low reactivity and long-lasting substances. In addition, they are durable and cost-effective. Nowadays, people are more aware about the harmful effects of petrochemical derived plastic materials in the environment. Researchers have conducted many studies for managing plastic waste on Earth by finding eco-friendly alternatives to plastics. This ecofriendly alternative is bioplastics, which when disposed in the environment, will easily degrade through the enzymatic actions of micro-organisms. The degradation of biodegradable plastics gives a rise to carbon dioxide, methane, water, biomass, humic matter and various other natural substances which can be readily eliminated (Azios 2007). The impact of renewable material becomes even bigger and leads to a more sustainable way of manufacturing materials. In fact, renewable resources play a very small role in the major chemical product category of plastic. However, a number of bio-based plastics and products have been researched, developed and are growing rapidly. Bioplastics will be a new plastics generation. Renewable raw materials such as corn, potato, or plants are used to manufacture bioplastics. They are a feedstock for bioplastics to get starch, cellulose, lactic acid etc. They are not dangerous, hazardous and very environmentally friendly raw materials to produce.

The important aim for this thesis is to get the professional knowledge about the basic properties of different kinds of biopolymers, bioplastics and to investigate the potential ways to manufacture the bioplastics from potato starch which is replaced to fossil-based plastics, then to understand more about the cost-effective methods for bioplastics production from cheap renewable resources. Moreover, through it to encourage consumers to use the bioplastic alternatives by providing more environmentally friendly material options. Most importantly, people will be aware that environment issues are on an alarm; fossil fuel sources are limited, climate is changing and the problem with greenhouse gases and global warming.

2 GENERAL INFORMATION ABOUT BIO-PLASTIC

Bio-plastics are a type of plastic that is made in whole or in part from polymers which are derived from biological sources such as sugar cane, potato starch or cellulose from plants, straw and cotton. Bioplastics is based on either bio-based, biodegradable, or both of bio-based and biodegradable properties. Several important definitions should be notice.

2.1 Biodegradable plastics

A biodegradable plastic is able to made from renewable resources or fossil fuels. A biodegradable plastic might be broken into smaller particles through the help of micro-organism activity, such as bacteria and fungi. Biodegradable refers to the biochemical processes in which microorganisms that occur naturally in the environment, converted polymers into substances such as water, carbon dioxide and biomass. Depending on the composition and thickness of the material, some biodegradable plastics disintegrate quickly, whilst others take longer. (Gibert 2015.)

2.2 Degradable plastics

Degradability is the process of disintegration of the polymers into smaller fragments by the action of abiotic factors such as UV radiation, oxygen attack, and biological attack. Most degradable plastics are made from polyethylene and contain an additive to speed up the decomposition. They have to change significantly in their physical structure which leads to loss of structure properties. (Gibert 2015.)

2.3 Bio-based plastics

Bio-plastics are plastics derived from natural resources or biomass in some content such as sugar cane, corn or potato corn starch, cellulose and are not derived from petroleum resources. They may or may not be biodegradable but recyclable. Biodegradable property is added in bioplastics at the end of a product’s life. Biodegradation which depends on the chemical structure of the material does not rely on the sources of polymer. Therefore, a bio-based plastic is not necessary a biodegradable plastic, and a bio-based plastic is not necessarily degradable (Kershaw & Gilbert 2015). FIGURE 1 indicates the distinction between bio-based plastics and bio-degradable plastics. (Chen 2010.)

2.4 Compostable plastics

A plastic is capable to decompose biologically and break down into carbon dioxide, water, inorganic compounds and biomass. It is clear that a compostable plastic leaves no toxic residue to the environment. Products can also degrade by the mechanism of enzymes. Currently, on the market, corn starch is the most common raw material to produce the compostable plastics. Potato starch, soybean protein, cellulose as well as petroleum and petroleum by-products are also available for making compostable plastics. Hence, compostable plastics could from polymers derived from both plant-based raw materials and petroleum. (Sarasa, Gracia & Javierre 2008). And conventional plastics are derived generally from non-renewable resources such as petro-based plastics/fossil based, synthetic plastic.

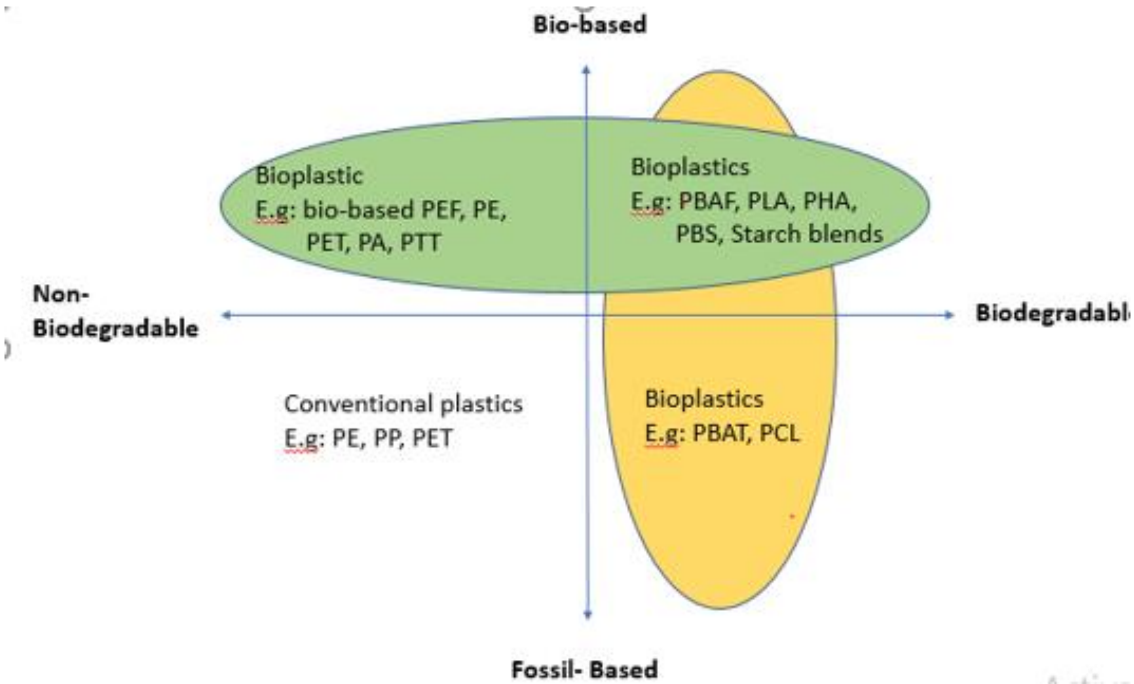

FIGURE 1. Understanding the three different categories of bioplastics (European Bioplastics 2016)

2.5 Advantages of bioplastics

The best advantage of biodegradable plastics is to reduce of permanent garbage. Biodegradable plastics are especially suitable for recycling alongside organic waste, as long as the plastic is compostable. To be assumed that biodegradable plastics should be the best used to substitute the conventional plastics that generate environmental problems both during use and their end-of-life. For instance, plastics for shopping bags are a major reason to pollute the environment because the litter in ocean is from disposable plastic bags which effect the environment especially marine species, and breaks the ecological systems. (Gilbert 2015.)

It is clear that bio-based plastics have much lower carbon footprint. It should be pointed out that the carbon footprint of bioplastic is crucially dependent on whether the plastic permanently stores the carbon extracted from the air by the growing plant. A plastic made from a biological source sequesters the CO_2 captured by the plant in the photosynthesis process. If the resulting bioplastic degrades back into CO_2 and water, this sequestration is reversed. But a permanent bioplastic made to be similar to polyethylene or other conventional plastics stores the CO_2 forever. Even if the plastic is recycled many times the CO_2 initially taken from the atmosphere remains sequestered. (Chen 2014.)

Following the energy efficiency advantage, energy cost will be lower to manufacture than conventional plastics. 4% of the oil every year is used to made plastics. Nowadays, oil becomes scarce, the prices of manufacturing plastics are increasing and fluctuating. (Chen 2014.)

About an independence of the fossil fuel uses, compare to conventional plastics, feedstock of bio-based biodegradable plastics are from biomass that provides potentially for carbon neutrality and reduces green gas emissions. (Yu and Chen 2008). They can contribute to improved resource efficiency through the use of biomass cascades, as they are suitable for recycling and energy recovery after reuse and recycling options. Novel functional properties and low GHG emissions during manufacturing process, as shown in TABLE 1 (Yu and Chen 2008)

TABLE 1. Comparison between Bioplastics and Petro-plastics (Ying, 2014)

Properties	**Bioplastics**	**Petro-plastics**
Renewable resources	Yes and partially	No
Sustainable	Yes	No
Breakdown in the environment	Biodegradable and/or compostable	Some degradable by polymer oxidation
Polymer range	Limited but growing	Extensive
GHG emissions	Usually low	Relatively high
Fossil fuel message	Usually low	Relatively high
Arable land usage	Currently	None

2.6 Disadvantages of bioplastics

Besides many significant advantages of biodegradable plastics, there are still a several disadvantages that need to be noticed. Recycling problem is one of the huge issues. Firstly, uncontrolled disposal of biodegradable plastics leads to pollution of the soil, water and land. Although biodegradable polymers are broken down into smaller particles, there remains the potential harmful to environment when discarding the products. Secondly, biodegradable plastics look similar to the conventional ones, so instruction for clear labelling, disposal and recycling is need. The reason is that these biodegradable polymers can contaminate the conventional plastics during the recycling processes. (Gilbert 2015)

Moreover, bioplastics are two times more expensive than conventional plastics. However, there is an expectation that in the near future, the amount of large-scale industrial production of bioplastics are more common and increasing that leads to a cost reduction. (Ezgi and Havva 2015). They will be competitive to food sources because bioplastics produced from renewable sources might reduce raw material reserves. However, in order to reduce the potential competition with agricultural resources for foods, food by-products are also current trend to manufacture bioplastics (Lagaron and Lopez-Rubio 2011). For example: the technological development in bioplastics industry have shown that biodegradable plastics could be possible to create from hemp, seaweed and other plants. (Innocenti 2008.)

3 POTENTIAL BIOPLASTIC IN HOUSEWARE APPLICATIONS

Starch-based bioplastics can be divided into two groups. The first group is bioplastic produced from starch itself and the second group is manufactured from fermentation processes with starch sugar. Bioplastics based on starch are used to produce all kinds of applications similar to the original polyethylene and polystyrene. Disposable cutlery, plastics bags and food packaging are typical products. Most commonly known starch-sugar based bioplastics are polylactic acid (PLA) and polyhydroxyalkanotes (PHA) (Barker & Stafford 2009, 62- 63; Momani 2009, 16). However, in this chapter, three materials will be considered to be the most potential houseware applications including polyactic acid (PLA), bio-based polyamides (bio-PA), and bio-based poly trimethylene terephtelate (PTT).

3.1 Polylactic acid or PLA

PLA is referred to as a biodegradable bioplastic because of its environmentally friendly material. PLA is manufactured from renewable resources such as corns, potatoes, and sugar cane. It has characteristics similar to polypropylene (PP), polyethylene (PE), or polystyrene (PS) and easily converted by injection molding, blow molding and deep-drawing machines that are used for the conventional petrochemical plastics. PLA plastics are normally used for packaging like yogurt cups, deli, takeout containers and fresh produce packaging. (Platt 2006, Sturzel 2011)

A great advantage of PLA plastic is its versatile properties might change with additives that leads to the variety of products it can be used in. Besides, PLA's biodegradability is natural when it exposes to the environment. For example, a PLA bottle left in the ocean typically degrade in six to 24 months. (Creativemechanismsblog.com 2018). However, PLA plastics have some disadvantages, especially softening at 60°C. Higher softening temperatures can be achieved by copolymerization with a more heat resistant polymer or by adding fillers. According to research, PLA plastics are reinforced with glass fiber providing the great improvement in mechanical and thermal properties as shown in TABLE 2. (Bioplastics.org 2011.)

TABLE 2. Comparison of 30% Glass Fiber Reinforced Compounds

Mechanical and thermal properties	**Unmodified PLA**	**30% GF PLA**
Tensile Strength	9 000 psi 62 Mpa	16 500 psi 114 MPa
Flexuaral Strength	15 700 psi 108 Mpa	21 000 psi 145 MPa
Flexural Modulus	555 000 psi 3828 Mpa	1 630 000 psi 11 239 MPa
Heat Deflection Temperature (455 kPa)	124 °F 51 °C	320 °F 160 °C

3.2 Bio-based polyamides or nylons

Bio-based amides or nylon are thermoplastics with a long-chain polyamide [-CO-NH-] in their polymer chain. Castor oil as their feedstock is used for many grades of bio-based polyamides. The most benefit of bio-bases nylons is that castor oil is derived from castor plant with high bio content from 48% to 99%, which is not competitive with food crops for land. FIGURE 2 showns the chemical structure of bio-based polyamide from castor oil. (Sturzel 2011)

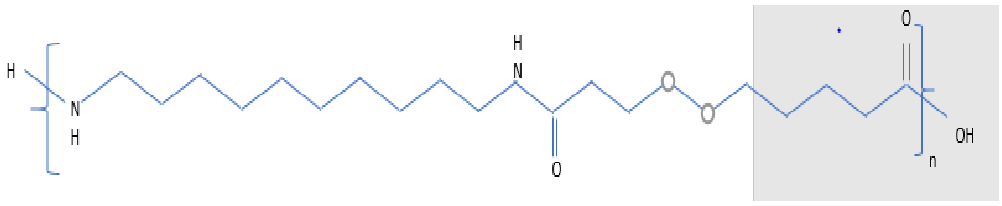

FIGURE 2. Chemical structure of bio-based polyamide from castor oil (Sturzel 2011)

There are similar properties between bio-based nylons and petroleum-based plastics. They are used in the same application such as the handle parts of houseware products are not required to be made from safe materials in contact with food, only blade parts are required food contact safety. (Wolf 2005, 105.)

3.3 Polytrimethylene terephtelate - PTT from bio-based PDO

PTT is an aromatic polyester, which is combinated by 1,3- propanediol (trimethylene glycol or PDO) with terephtalic acid (PTA) or dimethyl terephtelate (DMT). Bio-based PDO is derived from renewable feedstocks such as corn, sugar cane or potato starch. The structure of PTT is shown in FIGURE 3 (Wolf 2005, 67).

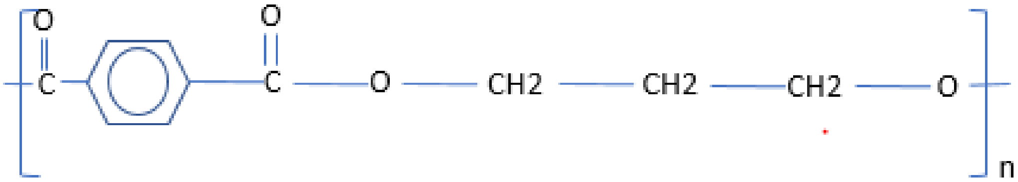

FIGURE 3. Polytrimethylene terephthalate (PTT) chemical structure (Wolf 2005, 67)

"Growing demand for polytrimethylene terephthalate is expected to drive the 1,3-propanediol market." Bio-based PDO is expected to grow fast globally of 10,4 % from 2014 to 2021 and $621.2 million by 2021 in market value. Chemical synthesis and fermentation are the main processes to manufacture bio PDO. Their application is utilized in manufacturing PTT, cosmetics, personal care and cleaning products. (Chen 2010.)

PTT's features are rigidity, heat resistance and strength which can be compared with the characteristics of PET. PTT is applied in the carpet production and industrial textiles. Besides, PTT is mixed with other resins to enhance their tensile strength and is more suitable for molding and injection molding applications. (Wolf 2005, 67)

3.4 Other potential bioplastics

There are several types of bio-based plastics chosen to be mentioned shortly in this thesis because of not containing sufficient information about the mechanical and chemical properties used for household, or non-commercial applications for manufacturing.

Bio-based PE is produced from ethanol which is fermented by renewable feedstocks of corn, potato or sugar cane. There is the same chemical and physical characteristics of conventional PE and starch-based PE. Therefore, it is not biodegradable but can be recycled. Nonetheless, bio-based PE is more environmentally friendly than petro-based PE.

Bio-based PHA is a biodegradable plastic manufactured from renewable feedstocks with bacterial fermentation mechanism. It would be a good alternative in various applications such as films, fibers, molded articles and coating materials. Well-known PHA products include garbage bags, packaging and disposable food containers (Cheng 2010, 251-253)

Cellulose acetate is a natural plastic and a modified polysaccharide with feedstocks from wood pulp or cotton linters. There is a tensile strength between cellulose acetate and polystyrene (PS). Mostly cellulose acetate is used in coatings, adhesive tapes, tool handles and spectacle frames (Moore, Saunders 1997,25).

4 STARCH BASED PLASTICS

Starch is an agricultural and biodegradable feedstock biopolymer found in a variety of plants such as wheat, corn, rice and potato. Polymers based on starch are an attractive alternative to polymers based on petrochemicals. Simple starch consists of α-D-glucose units (polysaccharide) that is literally formed by one highly branched/polysaccharide- amylopectin in FIGURE 5 (Zia, Zuber, Kamal, & Aslam 2015) and one linear/polysaccharide- amylose polymer with some minor components such as lipids and proteins shown in FIGURE 4 (Zia et al. 2015). Amylose is mainly a linear molecule of (1→4)-linked α-D-glucopyranosyl units and their molecular weights ranging from 10^5 to 10^6 $gmol^{-1}$ (Buleon, Colonna, Planchot & Ball 1998). Amylopectin consists of hundreds of short chains of (1-4) linkages but with (1-6) linkages at the branch points. Their molecular weights are from 10^6 to 10^8 $gmol^{-1}$. Depending on the source type, the ratio of these polymers is different. Typically, the level of amylopectin is 70% (Hedley 2002). For instance, potato starch accounts of 20% amylose and 80% amylopectin (Tarté & Rodrigo 2009).

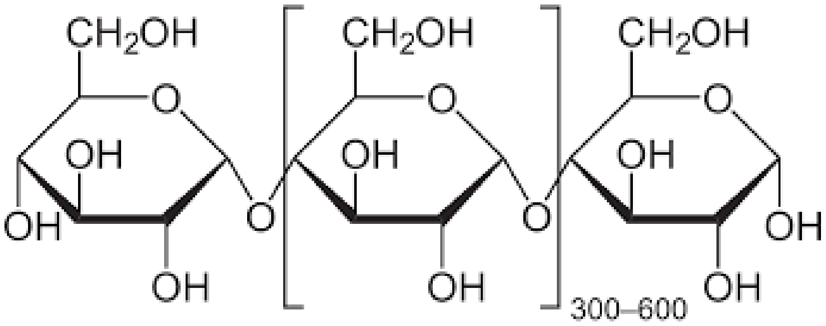

FIGURE 4. A section of the amylose molecule (Zia et al. 2015)

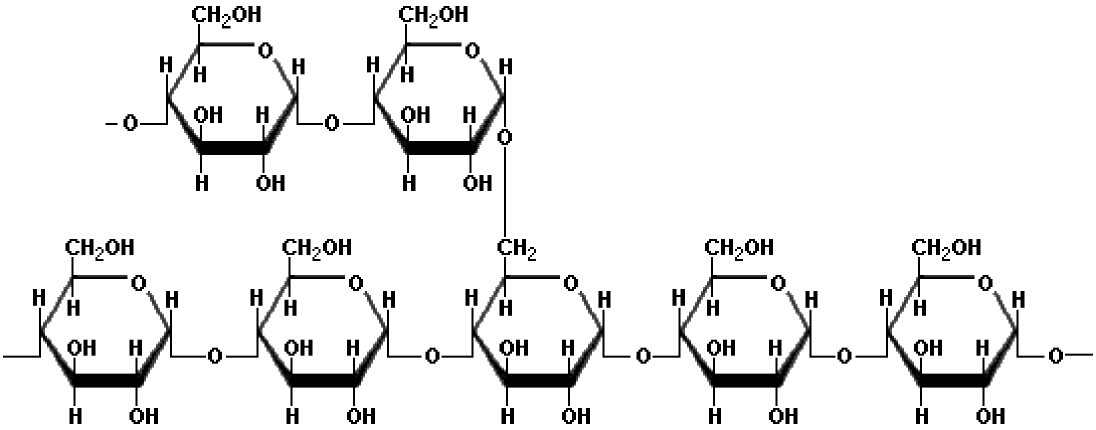

FIGURE 5. A section of the amylopectin molecule (Zia et al. 2015)

According to statistics, in the year of 2002, starch polymers were produced about 30000 metric tons per year. 75% of starch polymers are used for packaging applications, including soluble films for industrial packaging and films for bags. (Innocenti & Bastioli 2002.)

A range of small and large companies all over the world have utilized different types of starch in bioplastics production. For example, Novamont, BIOP Biopolymer Technologies, Biotec, Rodenburg Biopolymers, Green Light Products, National Starch and Chem and Earthshell (Van Beilen & Poirier 2007). Currently, the main raw material for producing starch polymers is corn. However, the European Companies BIOP Biopolymer (Germany) and Rodenburg Biopolymers (the Netherlands) use potato starch. The Rodenburg company received its source directly from the waste stream of a local potato processing. Peels of potato what are considered as waste at the factory used in manufacturing bioplastics. (European Commission 2005)

5 PRODUCTION OF STARCH POLYMERS

FIGURE 6 illustrates the main processing steps producing starch polymer (Shen, Haufe & Patel 2009). According to FIGURE 6, there are three key starch groups from the primary processing step including partially fermented starch polymers, pure starch polymers and modified starch polymers.

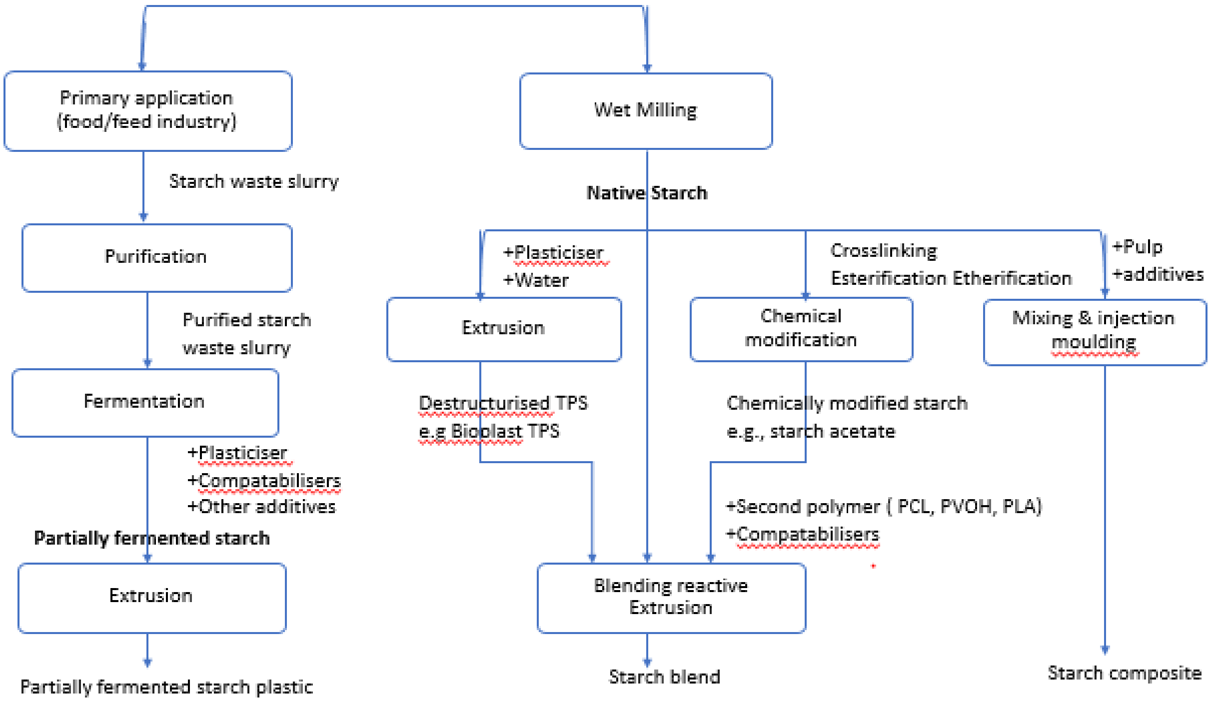

FIGURE 6. Starch plastic production technology (Shen, Haufe & Patel 2009)

In the case of Rodenburg Biopolymers company (Rodenburg, 2003), in partially fermented starch polymers group, feedstock is the waste slurry of potato from food industry. This sludge mainly consists of starch, protein, fat and oil, inorganic ingredients and cellulose with the percentage of 72%, 12%, 3%, 10% and 3%, respectively. After that, slurry is kept in silos for about two weeks to allow stability and partial fermentation. During the fermentation process, a part of starch is converted to lactic acid with the help of lactic acid bacteria that is present in the material. Then the product is dried to get 10% of water content and extruded to get the thermoplastic. (Platt 2006; Shen, Haufe & Patel 2009.) In addition, palm oil and additives such as titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$) are added to improve the product. Finally, another drying step is utilized to stabilize the material. (Shen et al 2009)

5.1 Native starch

All starch plastics start from native starch that is obtained from wet milling process such as the example of corn as the production of native starch. Starch is extracted from the kernel by wet milling. Firstly, kernel is immersed in a diluted acidic to soften. The coarse fraction is ground to split the kernel and to remove the oil-containing germ. Finer milling separates the fibre from the endosperm which is then centrifuged to separate the less dense protein from the denser starch. The starch slurry is then washed in a centrifuge, dewatered and dried prior to extrusion or granulation. (National Starch and Chemical Company 2003.)

5.2 Destructurised starch/ Thermoplastic starch, TPS

Starch is not a real thermoplastic. Thermoplastic is formed through processing native starch in an extruder. In the presence of a plasticizer (or other plasticizing additives), under certain condition of temperature (90 to 180 °C), pressure, shear, limited water and sufficient time, the crystalline structure of starch is destroyed and it forms an amorphous thermoplastic starch (TPS). (Halley & Averous 2004.) Plasticizers are commonly used for TPS including water, glycerol, sucrose, fructose, glucose, glycols, urea, formamide, ethanolamine, ethylene bisformamide, and amio acids (Zang & Rempel 2012). These contribute to the flexibility and mechanical properties of the finished product and reduce the intermolecular hydrogen bonds to product propertie. (Gozzo & Glittenberg 2009). PTS is formed through the destructuration processes including the loss of crystallinity of the granule, then a heat absorption when starch shape is changed, the hydration of starch as accompanied by swelling of granules, a reduce in the rest time of water molecules, the loss of molecular order, and the leaching of linear molecules (amylose) from ruptured granules. (Halley & Averous 2004.)

Thermoplastic products are homogeneous which contains both amylose and amylopectin dispersed uniformly through the material. They have a relatively high molecular weight amylopectin, and superior mechanical properties. However, PTSs are extremely sensitive to water that might suffer from change of molecular weight on extrusion. Therefore, PTS has somewhat limited practical value. (Shen et al 2009.)

5.3 Chemically modified starch

Modified starch has been processed in a number of ways to improve the its properties. Starch plastics containing high native starch are highly hydrophilic and readily disintegrate when contacting water. Therefore, modified starch has to be manufactured by treating with chemicals that lead to hydroxyl groups replace by ester or ether groups. Properties of starch might reduce hydrophilicity as well as alter rheologically, physically, and chemically at very low levels of chemical modification. Cross-linking, in which two hydroxyl groups on the adjacent starch molecules are chemically linked, is also a chemical modification. Crosslinking inhibits swelling of gelatinized granules and increases acid stability, heat treatment and cutting force (Foostarch 2008). For instance, starch acetate is a type of chemically modified starches. Starch acetate is used to produce packaging foams in laboratory, then mixed with PLA, Master-bi or EastarBio and with natural fibers (Guan & Hanna 2006). Studies show that it is quite expensive in production of acetate starch and not very widespread. However, nowadays with the development of research, scientists discovered a way to reduce the production is to add more heterogeneous catalysts. (Hanna 2008.) There are some common types of chemically modified starch, distinguishing properties and their application, as summarized in TABLE3.

TABLE 3. Types, properties and uses of chemically modified corn starch (Daniel et al 2000)

Type	**Distinguishing properties**	**Non-food uses**
Acid- modified	Reduced hot-paste viscosity compared to unmodified starches.	Textile sizing agents such as making in binding cardboard.
Cross-linked	Peak viscosity reduces while increasing paste stability	Ingredients in antiperspirants and printing paste
Ester (acetylated)	Extremely good paste clarity and stability; good freeze; hydrophobic for higher level of alternative starch acetate.	Low level of substitution: Wrap sizing in textiles; forming sizes; and surface sizes in paper making High level of substitution: thermoplastic molding.
Phosphate, monoesters (ester)	Gelatinization temperature and retrogradation reduces.	Additives in wet-end process of paper making
Hydroxypropyl (ether)	Paste clarity increases, but good freeze and retrogradation decreases.	Wet-end in paper making. Using as warp sizing in textiles.

5.4 Starch blends

Starch blends are the combination of destructurized starch (TPS), chemically modified starch, petrochemical, bio- based or inorganic compounds into a homogeneous material. Nowadays, there are many companies producing the starch blends at a large scale such as Novamont, Biotec, BIOP, and Cereplast. (Shen et al 2009.) Depending to the end application, the composition of starch in a blend will range from 30% to 80% by mass. Starch blends are mostly produced based on partially bio-based and fully biodegradable (e.g., Mater-Bi, BIOPar, Bioplast) because many co-polymers are from fossil fuel feedstocks. TABLE 4 shows a list of co-polymers to combine with starch plastics.

TABLE 4. Typical non-bio-based and biodegradable co-polymers used in starch blends (Shen et al.2009)

Co-polymer	**Trade name**	**Company**
PBS/A (polybutylene succinate/adipate)	Bionolle	Showa highpolymer
PBSL (polybutylene succinate-co-lactate)	GS Pla	Mitubishi Chemical
PBAT (polybutylene adipate-co-terephthalate)	Ecoflex	BASF
PBAT (polybutylene adipate-co-terephthalate)	Biomax	DuPont
PCL (poly-**ε**- caprolacton)	CAPA Tone Celgreen	Solvay Union Carbide Daicel
PVOH (polyvinyl alcohol)	Celvol	Celanese

In a recent research, petrochemical polymers (PP and PUR) were used as the co-polymer in starch blend. These plastics are partially bio-based, but not biodegradable. Their main objective is to replace of petrochemical plastics in the market of durable plastic (e.g., cars). For instance, Cereplast Hybrid or Biopropylene account for approximately 50% starch and 50% polypropylene which focuses on the plastic market of cars (Cereplast 2008).

FIGURE 7 illustrates an overview on how to prepare starch blends. Reacting between a functional group with native starch can be synthesized the starch blend. To obtain functional plastic, firstly a grafting agent reacts with plastic polymers. Taking the synthesis of a starch-PBS (polybutylene succinate) blend as an example. The PBS segment is reacted with maleic anhydride (MA) to create MA-grafted PBS as the functional group. After that, MA-grafted PBS is combined with native starch to form the plastic blend which is called starch-MA-grafted PBS blend. However, there is another way to obtain the starch blend by grafting at the monomer level then polymerizing the grafted monomers. (Narayan, Krishnan & Dubois 1999.)

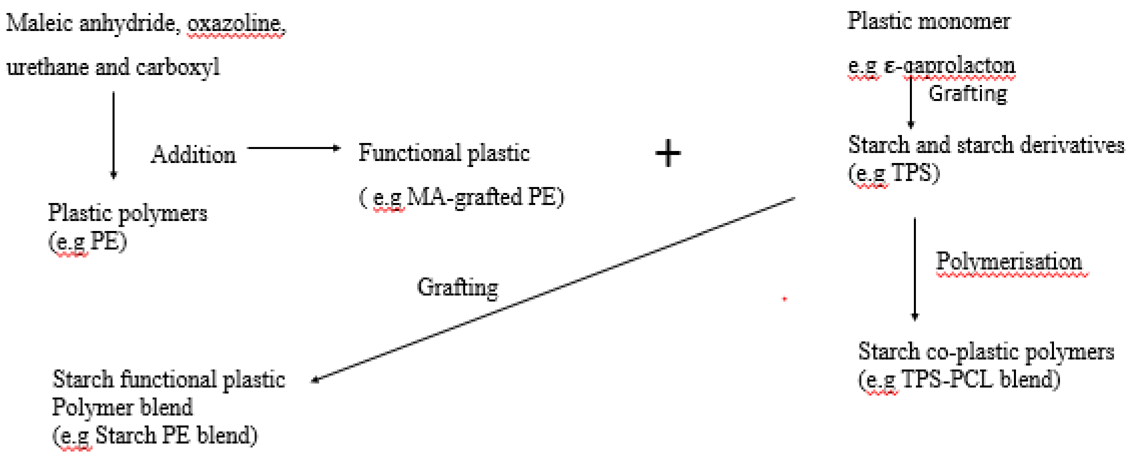

FIGURE 7. Synthesizing the reactive starch blends (Kalambur & Rizvi 2006)

5.5 Starch composites

A starch composite is also produced from native starch with the combination of one or more different materials. PaperFoam® is a commercial product that belongs to this group. PaperFoam® is manufactured from potato starch, paper fibres and added with additives. Then it is formed to product by an injection-moulding process. Composition of final product includes 70% of starch, 20 % of paper pulp, and 10% of additives. (Huisman 2007). In fact, the starch composite market is small when comparing to the market of starch blends. However, this industry scale is growing very fast to replace the durable plastic market such as packaging of CD/DVD or electronic materials. There are several conversion technologies applied to produce the starch polymers including film blowing, extrusion, thermoforming, injection moulding and foaming.

6 POTATO PLASTIC PRODUCTION IN LABORATORY SCALE

This thesis researches the experimental production of biodegradable plastic from potato starch in laboratory at Centria University of Applied Sciences. FIGURE 8 shows the overall process of potato-based plastic manufacturing. Generally, there are 3 main steps to produce potato starch-based plastic:

1. Potato starch extraction
2. Starch-based polymer production
3. Bioplastic production

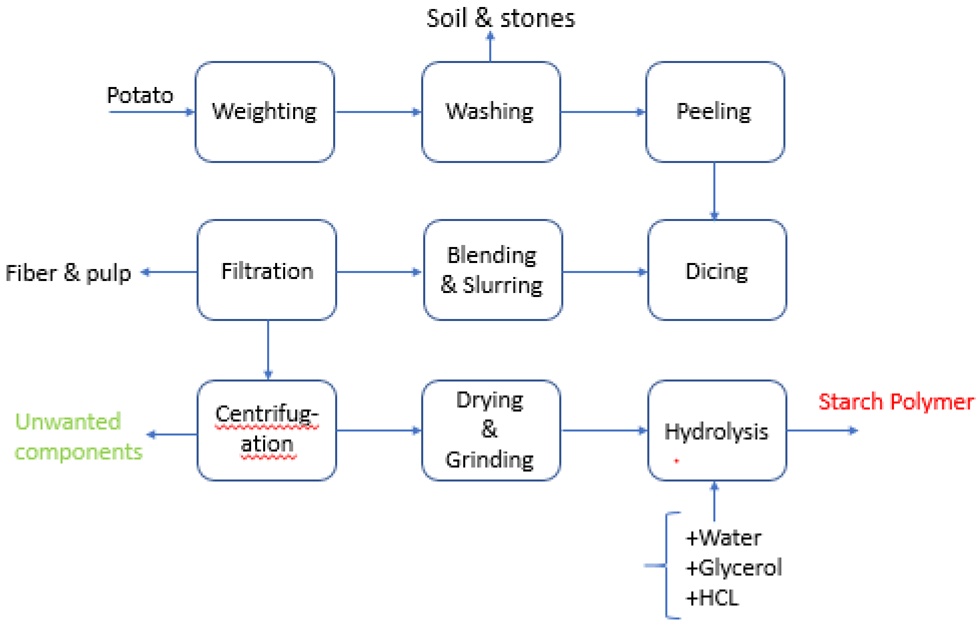

FIGURE 8. Bioplastic production steps

6.1 Main equipment and chemicals

Equipment was prepared to extract the potatoes including a knife, a blender and a filtrate or a double-layered fabric. A knife was used to peel the potatoes and cut them into the small pieces. The potatoes

were then mixed thoroughly with a blender to separate the starch grains as much as possible. At the end of extraction process, potato starch was extracted by a filtrate or a double-layered fabric
Producing the starch-based plastics in laboratory, equipment and chemicals were applied as follow. Equipment used were 250 cm^3 beaker, watch glass, a heater plate, a magnetic stirrer, tripod and gauze, stirring rod, petri dish or white tile, indicator paper, eye protection and cylinders, and main chemicals included the potato starch, propan 1,2,3-triol (glycerol), hydrochloric acid 0,1 mol/dm^3, and sodium hydroxide.

6.2 The potato starch extraction

Starch was extracted from potatoes which were bought in S-market in Finland. To extract the starch, the potatoes had to be crushed and grinded then the starch grains were released from the destroyed cells. Firstly, potato starch was extracted had to processed in various steps such as preparing the potatoes by weighting, washing, peeling and dicing; slurring diced potatoes and then filtrating, shown in FIGURE 9, FIGURE 10, FIGURE 11, FIGURE 12, FIGURE 13 and FIGURE 14.

6.2.1 Weighing

At the beginning, the selected potatoes were weighed to obtain the initial mass of tubers. In the extraction, the total weight of potato tubers was used approximately 1 kilogram. Difference in the weight before and after washing was determined the impurities of the potatoes.

6.2.2 Washing

After that, selected potatoes were washed with water carefully to remove the unwanted materials such as dirt, and soil. Washing step plays an important role because leftovers will affect to the final output of the tuber. Besides, many impurities are similar to starch at specific weights and sizes, so washing properly is the only way to remove them.

6.2.3 Peeling

After washing, potatoes were hand peeled carefully by a knife. Peeling unnecessarily of the potato cells might be one of the reasons for losing the pulp and starch granules. If a large amount of starch granules were damaged by peeling, it also causes changes in physical and chemical properties of potatoes. The wasted peels from the potato can be used as an organic fertilizer for agricultural lands. Therefore, this could reduce the costs of farmers plated.

6.2.4 Dicing

Then, the peeled potatoes were diced carefully by hand to smaller regular size. Care was taken to avoid damage of starch granules in the potato. Following by blending and slurring were water slurring; filtration; and final starch processes.

6.2.5 Blending and slurring

This step was obtained in water by using a blender. This type of slurring is done for the potato because according to the research, the tissues of tuber are soft. So potatoes do not need to grind or mill as compared to hard plant tissues such as grains, cereals and legumes. (Thava Vasanthan 2001).

The ratio of the tuber to water was determined 1:>10 which would be explained in more detail by empirical experiment. For example, there were 890g of diced potato, so water was added up to 9790 g which is eleven times more water by weight. During this process, heat was released. Therefore, ice is added to the mixture to avoid damage to starch granules. (Thava Vasanthan 2001)

6.2.6 Filtration

Double-layered fabric was used in this filtration procedure to let the slurry pass through it. At the end of the process, starch granules were extracted and separated from the residue of the potato. The solution was filtered again to gain as much the starch from potato as possible.

FIGURE 9. Weighting & Washing

FIGURE 10. Peeling

FIGURE 11. Blending

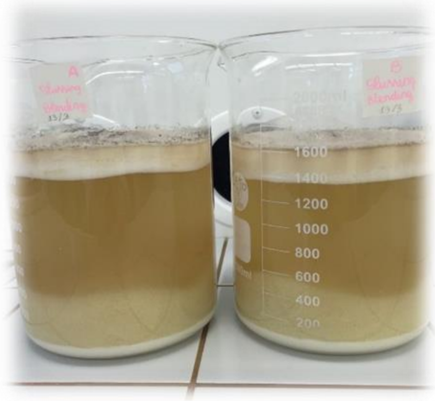

FIGURE 12. Water slurring

FIGURE 13. Wet potato starch

FIGURE 14. Dry potato starch

6.3 Bio-plastics manufacturing steps

At the beginning, 2.5 grams of potato starch was weighed and diluted with 25 ml distilled water in a 250 ml beaker. Then, the beaker was placed on a heater plate set at 100 °C with a magnetic stirrer. Make sure it does not boil dry. Mixture was followed by adding 3 ml of 0,1M HCl. An indicator paper was used to measure the pH level. Then mixture had to be neutralized with the same amount of sodium hydroxide as acid volume at the beginning (around 2 ml). The mixture which was allowed to heat for about 15 minutes, took about 1 hour to form an opaque gel, as shown in FIGURE 16. The mixture was spread on a petri dish and allowed to dry about 1 day on a radiator or 3-4 days at room temperature. Ultimately, potato-based plastic was completed shown in FIGURE 17.

FIGURE 15. Potato starch mixture

FIGURE 16. The opaque gel after 15 minutes boiling

FIGURE 17. Bioplastic based on potato starch

7 RESULTS

In this study, there were different chemicals such as water, hydrochloric acid, glycerol and sodium hydroxide use to create the potato based plastic The reason why these chemicals were applied instead of others will be clearly clarified to understand their importance.

7.1 Water medium

According to the research, water, alkali or enzymatic are three common mediums used to extract the potato starch. Water is the most common medium which is applied in this experiment as well. The reason water is chosen is that starch extraction rate is enhanced compared to alkali medium (Moorthy 1990). According to Kallabinski study, there is a rise in extraction rate from 90% to 93% if enzymatic is used to extract the starch. However, this medium requires high energy and specific parameters of process such as the temperature and pH (J. Kallabinski, 1991).

7.2 Dilute hydrochloric acid

In this case, dilute hydrochloric acid HCl was added into aqueous solution with concentration of 0,1 mol/L. This concentration level is low hazard. Thank to HCl, amylopectin molecules were broken down to amylose molecules (the branched molecules to straight chained molecules). 2 M was the concentration of HCl at the beginning. Then HCl 2M was diluted to 0,1 M by pouring 5 ml of HCl 2 M into 100 ml of water H_2O.

$c_1V_1 = c_2V_2$

c_1: Concentration of the initial HCl 2 M

V_1: Volume of the initial HCl 5 ml

V_2: Volume of water 100 ml

c_2: Concentration of diluted HCl

$$\Rightarrow \; c_2 = \frac{c1V1}{V2} = \frac{(2\ \mathrm{M}).(5*10^{-3}\mathrm{L})}{0{,}1\mathrm{L}} = 0{,}1\ \mathrm{M}$$

7.3 Glycerol $C_3H_8O_3$

When the solution is heated, the starch becomes soluble in water and loses its semi-crystalline structure as the starch particles bulge with water. This creates a highly viscous mixture and this process is called gelatinization. As the solution becomes cooler, the water is expelled and the hydrogen-linked amylose molecules form a semi-crystalline structure again that leads to brittle plastic film. To improve the flexibility of the samples, other chemicals can be added to the solution before heating. Glycerol is a molecule that has ability to attract water. When glycerol is added to the starch mixture, it holds water in the starch chain making it less crystalline, and thus less brittle. (Keshav 2016.)

7.4 Starch content of raw potato

From the results that were collected in this experiment, the average mass of extracted starch from the original potato ranged from 10,9 to 12,3 grams. This figured out overall percentage (10% to 12,3%) of the total initial potato used. From the literature review, 100 grams of potato represents around 15% of starch. In fact, 100 grams of potato contains 15% of starch and 2 % of fiber (Nutrient data laboratory 2014).

This means that there was a loss of about 3,5 % of extracted starch from the original. It might the starch still left in peels or due to water medium used. According to Kallabinski, the extracted starch rate can increase by 90% to 93% if enzymatic medium is applied instead of using water or alkali. The results of extracted starch from potato is shown in TABLE 5 and FIGURE 18.

TABLE 5. Extracted starch by blender

Examples	**Potato mass (gram)**	**Extracted starch (gram)**	**Ratio of starch extracted(%)**
1	270,03	29,5	10,9
2	270,05	33,35	12,3
3	269,9	30	11,1
Average			11,43

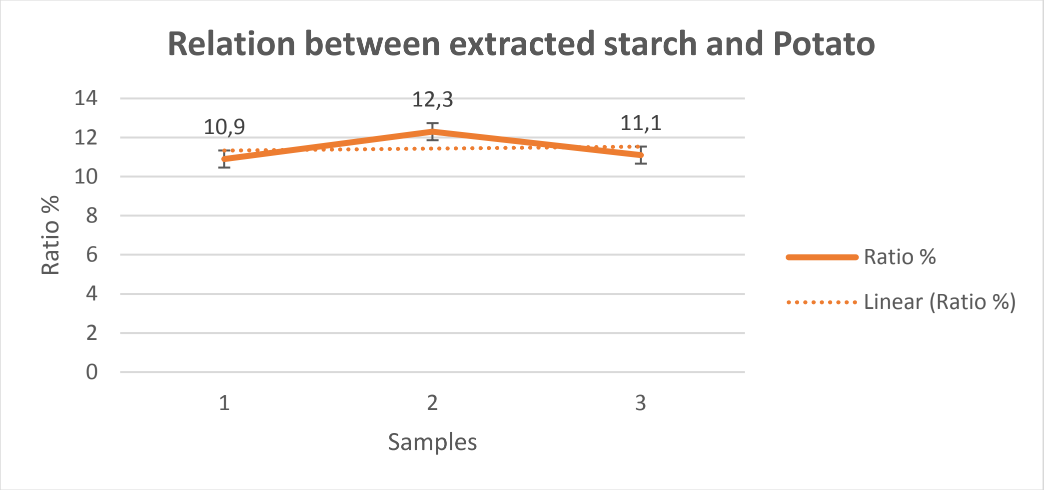

FIGURE 18. Average the extracted starch from potato

8 CONCLUSION

This study showed the potential production purposes of starch-based plastics including a much lower carbon footprint, lower production energy than conventional plastic, or non-fossil fuel plastics. However, there are still several disadvantages that exist when using the bio-plastics become the competition with food sources. Additionally, bio-plastics derived from agricultural resources may affect the production of bioethanol. Other options to produce bioplastics from biomass feedstock is investigated in cost effective way. On the whole, bioplastics will be for sure that the green future market, that is dramatically increasing due to its sustainability. The main challenge could be how to convince consumers use the environmentally sustainable bio-plastic materials instead of the cheaper traditional ones.

With the development of bioplastics, researchers have been conducted many methods to make the starch more useful. Natural starch (potato, corn, sugarcane) is blended with other plastics like polythene to make the overall product more biodegradable than polythene on its own. Unfortunately, the plastics tend to be less biodegradable than ordinary starch. Recently, Catia Bastioli who is a Italian scientist created the starch-based plastics as the way and mixed it with the polymer PVA. As result, bioplastic is biodegradable and soluble in water. This means that its use is limited not used for packaging drinks, fresh food and plants and could be used for packing dry goods, dried food, protective packaging (RSC 2015).

Starch was extracted and filtrated by mainly hand equipment while processing. Many impurities can be seen and still lie in the sample. The variation of temperature point indicates impurities. Furthermore, personal skills and equipment might not reach the standards. However, based on the sample properties, potato-based plastics can be more physically and chemically adjusted in order to apply in several fields such as food packaging, medicine or houseware equipment. Therefore, starch-based plastics can be created in injection molding, extruding or 3D printing manufacturing process, too.

At the moment, the global bioplastics are growing so fast. International companies are shifting from using conventional plastic packaging to the environmentally friendly alternatives. Scientists have been researching bioplastics in laboratory to move towards the sustainable future. Undoubtedly, there is a major demand to apply it in various fields including electronics automobiles and consumer goods manufacturing (European bioplastics 2015). Nowadays, not only potatoes or corns are chosen to manufacture bioplastics, but also fruit and vegetable are also certain to join the group of global industries of starch.

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