



Title of Thesis

Production of Polylactic acid in laboratory scale, and characterising the thermal properties.

Shristi Basnet
2016

DEGREE THESIS	
Arcada	
Degree Programme:	MATERIAL PROCESSING TECHNOLOGY
Identification number:	14235
Author:	SHRISTI BASNET
Title:	PRODUCTION OF POLYLACTIC ACID IN LABORATORY SCALE, AND CHARECTERISING THE THERMAL PROPERTIES.
Supervisor (Arcada):	BJÖRN WIBERG
Commissioned by:	MIRJA ANDERSON
<p>Abstract:</p> <p>This thesis presents findings from experimental research on producing biodegradable plastic from corn starch. A corn consists of many parts, among which starch is used essentially in food and bioplastic products. A starch is extracted from corn, then it is mixed plasticizers and some plastic additives for further synthesis. The synthesis and drying of starch based polymer was performed in Arcada Lab. The thermal analysis of the material were performed in the laboratories of Helsinki University, Department of chemistry. Corn starch based plastic were compared through various material and thermal tests to PLA standard and its material properties as references. Lab experiment closely observes thermal properties and does not include any mechanical test and analysis.</p> <p>The thesis also covers introduction on corn, corn starch as a raw material to produce bioplastic, its application and importance in food packaging. It is suggested that corn starch as a source for renewable and eco-friendly raw material. Application of starch based plastic could address environmental issue that are caused by oil based plastic.</p>	
Keywords:	Starch, Bioplastic, DSC , FTIR, TGA, Hydrolysis
Number of pages:	43
Language:	ENGLISH
Date of acceptance:	

Acknowledgement

I would like to express my sincere gratitude to the Arcada University of applied Science for letting me fulfil my dreams of being a student here. I would also like to thank Mirja Andersson, Department of Material Processing Technology for giving me the opportunity to write an honours thesis. To my supervisor, Björn Wiberg and lab supervisor, Joonas Siirilä from Helsinki University, I am extremely grateful for your assistance and suggestions throughout my project. And I am very thankful for his understandings, wisdom, patience, encouragement and for pushing me farther than I thought I could go.

Mostly I am indebted to my parents, father Late. Mr. Bishnu Basnet for his lifelong support and to my mother Mrs. Geeta Basnet for her immense love and care. I would like to dedicate my thesis to my family and my well-wishers.

Abbreviation

Carbon	C
Carbon dioxide	CO ₂
Corn Sample one	C.S.1
Corn Sample two	C.S.2
Corn Sample three	C.S.3
Degree Celsius	°C
Differential scanning calorimetric	DSC
Fourier transform infrared spectroscopy	FTIR
Glass transition temperature	T _g
Hydrogen	H
Infrared	IR
Mole	M
Maximum	max
Micrometre	µm
Milligram	g
Millilitre	ml
Minimum	min
Percent	%
Ploylactic acid	PLA
Polyethylene terephthalate	PET
Rotation per minute	RPM
Temperature	Temp
Temperature of crystallisation	T _c
Temperature of melting	T _m
Thermogravimetric analysis	TGA
Years	yrs

TABLE OF CONTENTS

Introduction	9
1.1 What is Bioplastic?	9
1.2 Corn.....	9
1.3 Starch Plastic Packaging and Agriculture Applications.....	10
2. Research aim	12
3. Research questions.....	12
2. THEORETICAL FRAMEWORK.....	12
2.1 Starch.....	12
2.2. PLA	13
2.3.1 Thermal Properties of PLA.....	15
2.3.1.1 Crystallization Temperature	15
2.3.1.2 Endothermic	15
2.3.1.3 Exothermic	15
2.3.1.4 Quench Cooling	15
3. DEMARCATION.....	16
4. RESEARCH DESIGN	16
4.1 Material	16
4.2.1 Corn soaking	18
4.2.2 Synthesis of corn starch	20
4.2.3 Heating Process	21
4.4. Reaction.....	22
4.5. Drying process	22
4.6 Curing the bioplastic	25
5. Equipments.....	30
5.1. FTIR	30
5.2. TGA.....	31
5.3. DSC	32
6. Results.....	34
6.1. FTIR Data.....	34
6.2. TGA Data	35
6.3. DSC Data.....	36
7. Data Analysis.....	40
8. Conclusion.....	41
9. Discussion	41
10. Future of Starch	41

References 43

List of Figures

Figure 1 showing corn kernel with its inner components and its uses	10
Figure 2 showing starch application in different fields, 1% in Feed, 29% in other food, 29% in Congruent and paper,32% in Confectionery and drinks, 4% pharma and chemical and 5% other non-food (Europe, 2012).....	11
Figure 3 Chemical formula for starch (AINI, Dec 2010).....	13
Figure 4 (top) showing Zea mays Evarta (popcorn) bought in local supermarket manufactured in Holland.....	17
Figure 5 Showing samples drying on the table	23
Figure 6 Showing sample after several days of natural cooling	23
Figure 7 Showing corn soaking and sample drying in the oven.....	24
Figure 8 CS1, Corn Sample 1 Method 2 (48hrs).	26
Figure 9 CS3 Method 4 (72 hrs).....	27
Figure 10 CS3 Corn Sample 3 Method 1 (48hrs).....	28
Figure 11 CS2 Corn Sample 2, Method 4 (72 hrs)	29
Figure 12 FTIR Instrument (Helsinki University)	30
Figure 13 Showing working principle of FTIR instrument.....	31
Figure 14 TGA Instrument Helsinki University	31
Figure 15 DSC Instrument	32
Figure 16 Showing Comparison of different spectra (from top), PLA filament, CS3 Method 2, Corn starch, Poly (Vinyl Acetate) and Glucose Anhydrous.....	34
Figure 17Figure 14 Showing Comparison of different spectra (from top), Corn starch, CS3 Method 2, D- Glucose Anhydrous PLA filament and Poly (Vinyl Acetate).	35
Figure 18 TGA data curve.....	35
Figure 19 DSC test of PLA (sample references) Showing Glass transition point at 64 and Melting point at 166.56	36
Figure 20 DSC test of CS3, Showing Glass transition point at 64.49 and Melting point at 166.41.....	37
Figure 21 DSC test of CS3, in slow heating cycle, showing glass transition point at 57.04 and Melting point at 166.48	38
Figure 22 Showing Global Bioplastic production	42

List of tables

Table 1. Showing conditions and duration of corn soaking.....	18
Table 2. showing temperature of oven and duration of sample kept for drying.....	24
Table 3. Showing DSC test results of i. PLA (sample reference), ii. CS3 (Corn Sample 3), iii. CS3 slow heating.....	40

Introduction

1.1 What is Bioplastic?

Bioplastic are mainly means two types of plastic, compostable plastic and bio based plastics. The compostable plastic are made up of renewable and non-renewable resources whereas bio based plastic are made up of renewable resources.

There has been various research on bioplastics. Biodegradation is the chemical process in which the material itself decomposes into the nature. The plastic which is made from bio based substance known as bio-based plastic and the plastic which can be decomposed by natural organism is called biodegradable plastic. The fossil fuel plastic are bio degradable, when it is combined with bio based substance and forces them to decompose (European bioplastic, 2015).

Bioplastics are a new generation of plastics which are biodegradable and compostable. They are manufactured generally from renewable raw materials like starch from e.g. corn, potato, or plants as a whole is used as a feedstock for bioplastic to get starch ,cellulose, lactic acid etc. which are not hazardous in production and decompose back into carbon dioxide.

1.2 Corn

Corn which is also known as maize in common. In *Zea mays* L. ssp. *mays*, belongs to the grass *Andropogoneae* of the family *Gramineae* (*Poaceae*). It is grown almost all over the countries from centuries. Maize has always even number of rows generally 16 rows. Each kernel of maize is a seed of that maize plant. The Purpose of growing this plant is different from countries to countries It is now grown as food source however corn kernel is also use in different other fields like medicines (Scanlon, 2016).

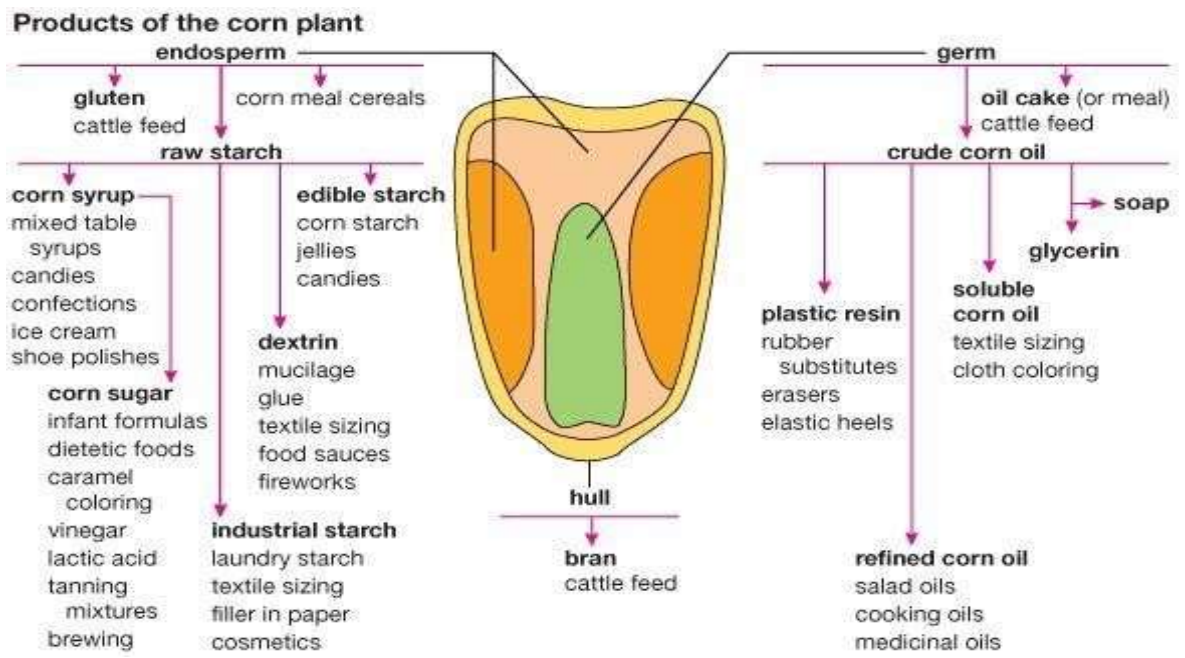


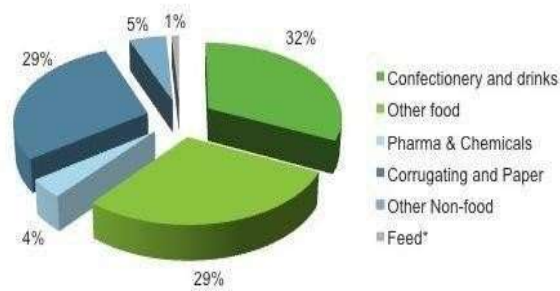
Figure 1 showing corn kernel with its inner components and its uses (Encyclopedia Britannica, 2010)

1.3 Starch Plastic Packaging and Agriculture Applications

The starch is obtained from the endosperm of the corn kernel. Starch has played the most important role from history till now for a food industry, and the demand of starch in food will be only increasing in near future too. The demand of starch is high in many sector not only in food, but also increasing from paper industries to food packaging industries. Starch could provide numerous advantages in various industrial application if a proper production and utilisation of starch can be maintained. Current ice breaking application of starch is also felt in starch based biofuel. For saving environment and safe food packaging system the bioplastic made from starch can be a very wise option. Technology and science is so well advanced now that scientist can alter the molecules separate the elements of food and change the food to food packaging in which the same food comes in. (S.K. Pankaj, 2013)

Low cost, seasonal vegetable and fruits which contain starch has now attracted many scientist to further deep investigate on use of starch in other field. Today, the European starch industry produces 10.5 million tons starch annually. Consumption of starch and starch derivatives was stated to be 9 million tons in 2014 (The European starch industry, 2012). Starch are very versatile and can be modified which has now led to a product like adhesive agents, thickeners, anticaking agents, mold release agents. Modified starch are capable to encapsulate vitamins different flavours and helps in medicine fields

Main starch applications - 2014



Total Market: 9 mio tonnes

Figure 2 showing starch application in different fields, 1% in Feed, 29% in other food, 29% in Congruent and paper, 32% in Confectionery and drinks, 4% pharma and chemical and 5% other non-food (Europe, 2012)

There is upscaling demand of the material and downscaling in its availability due to scarce of oil. Therefore, it is wiser to move towards new organic material rather than using of oil based plastic.

The bioplastic are the best solution for safe disposable of plastic without harming the environment and even marine living creatures. The knowledge of this can contribute a lot in the field of bioplastics. Polylactic acid, PLA is starch based polymer having significant uses in different field of production. PLA can be made to degrade quickly or last for years. It leads to good future possibilities for PLA fibres in textiles manufacturing applications. Use of PLA from renewable raw materials helps preserve natural resources such as oil. In Europe alone, 1.5 million tons of polyester per annum could be replaced by bioplastics in the next 10 yrs. That would be 5% of the European market for plastic packaging (Eur-Lex Access to European Union law, 2013).

2. Research aim

The aim of the research is to manufacture PLA from starch. Process includes the extraction of starch from *Zea mays L. ssp. Mays* and *Zea mays evarta* commonly known as maize and popcorn. To study the thermal properties of starch-based plastic produced in laboratory.

3. Research questions

- Ability to produce PLA from consumer corn
- Identification of produced PLA properties
- Properties of starch based polymers.

2. THEORETICAL FRAMEWORK

2.1 Starch

Starch is a white, tasteless and odourless powder that is insoluble in cold water or alcohol but can dissolve in warm water. Starch is a storage of glucose in plants, mainly starch contains amylose and amylopectin. The glucose units in amylose are 1, 4 alpha D linked chain whereas amylopectin has highly branched glucose chain due to this the mobility of polymer chain gets less. Therefore molecular weight of amylose is less than amylopectin (Chaplin, 2001).

Starch is the least expensive biodegradable materials used for many non-food items such as in paper making, cardboard, textile sizing, and thickening and in adhesives agents. Further applied into making utensils and as raw material for film production. Starch has an advantage of fast degrading properties in polymers and starch based polymers are highly being popular into food packaging, where plastic can degrade along with leftover food Remarkable physical and chemical reaction occurred when the starch is processed to thermoplastic. Melting, crystallisation and water diffusion are common and also involves gelatinisation. Gelatinisation is basis of starch changing into thermoplastic, and related to other reactions. Before gelatinisation, decomposition temperature of starch is higher than of its melting temperature. The main idea is that gelatinisation is irreversible way in which crystalline structure of starch gets destructed. The gelatinisation is a multistage method, which can be tested in DSC instrument (Liu et al., 2009).

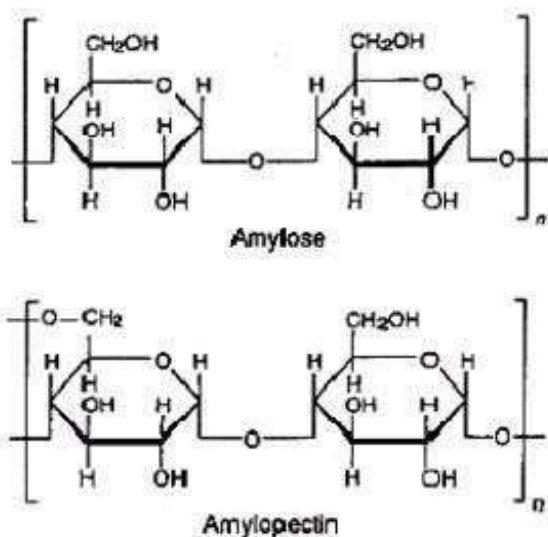


Figure 3 Chemical formula for starch (AINI, Dec 2010)

2.2. PLA

PLA is polymer which has similar properties in compare to PET, but also performs a lot like Polypropylene (PP) in elasticity. Ultimately it may be the polymer with the broadest range of applications because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment. (David E. Henton, 2005)

PLA also has excellent organoleptic characteristics and is suitable for food contact and related packaging applications. PLA is also used in 3D printing because of its low flowing temperature it can flow in laser tip of 3D printer. (Lievendag, 2014)

PLA emits H₂O and CO₂ while degradation that are not hazardous to humans and environment. Thus contributing PLA as an eco-friendly bio materials. PLA is widely used in biomedical materials, like clips and source of medication (David E. Henton, 2005). PLA is popular because of its renewability, transparency, biocompatibility and thermos plasticity (Jamshidian, September 2010).

Although PLA was introduced long time ago, but was not used in many fields. PLA has a very slow degradation process with hydrolysis, which can take several years. It is very brittle and has breaking point less than 10 percent elongation. PLA is considered not to be applicable for mechanical properties. Furthermore, PLA is hydrophobic and has limited gas barrier properties (Singh, August 2003). Since there are wide range of application, where PLA is needed and many researchers believe that PLA can be modified and treated in order to overcome the drawbacks. PLA can be bulk modified, surface treated and physical modification. This helps to have more flexible and crystalline of molecular chain. Starch from corn and potatoes act as a feed for PLA manufacturing.

Starch has high demand and considered as a good diet of food source. However keeping balance in food demand and considering the starch based industrialization could motivate many to make starch

as a multibillion industry. Different starch based bioplastic can be treated and modified. Treatment like Plasma treatment, in order to apply bioplastic as an inner coating in food packaging industries.

Green in environment will be added if maximum use of bioplastic is in use. It can also help in reducing the global warming situation and gives safe food packing with organic material.

Interesting fact about PLA is that it is unaffected by UV light having lesser density than most of the oil based plastic. The thermal bond between monomers can be controlled and the shrinkage rate is also linear compared to other plastic. It has low flammability and outstanding mouldability (James LUnt, n.d.)

A polysaccharide consisting of many glucose units is called starch which is major structural component of plants. These starch are processed chemically and physically to manufacture bioplastics with better material functional properties. Polylactic acid (PLA) is a new type of plastics which is produced by the fermentation of starch. PLA was discovered around 1932 by Carothers. He discovered this PLA by heating lactic acid in vacuum .By this process the production cost would be rather high. Nowadays PLA is made by fermentation of Starch (James LUnt, n.d.) PLA granules are generally from 1 to 100 micron diameter in size when manufactured (Otulugbu, 2012). Many companies use corn starch to produce plastics and can be manufactured for various useful applications.

2.3.1 Thermal Properties of PLA

During the previous studies there are such a detail about the physical properties of PLA. Previous studies shows PLA normally have high molecular weight and it depends on their density, heat capacity and mechanical properties. Normally in solid state PLA can be either amorphous or semi crystalline. The melting point is about 130°C to 230°C depending on the structure and the $T_{(g)}$ around 58°C. The state when PLA behaves as rubber on temperature above $T_{(g)}$ and it also behaves as a semi liquid if more heat is supplied.

When the temperature decreases the PLA behaves as brittle polymer.so PLA have different thermal and mechanical properties respectively (David E. Henton, 2005).

2.3.1.1 Crystallization Temperature

While processing PLA, the crystallinity varies as the cooling occurs. During the crystallization the alfa-crystalline is formed when treated in the temperatures between 130°C 140°C. And the annealing occurs at lesser temperature. The crystal formed during this cooling can diffract the x rays. It can be checked as curve in the DSC instrument (T. Tábi1, 2010).

2.3.1.2 Endothermic

During the endothermic process the curve in DSC is found to be obtained high because during this time there is no crystalline structure is formed and the DSC instrument can easily analyse the PLA (T. Tábi1, 2010).

2.3.1.3 Exothermic

The exothermic is obtained when the cold crystallization occurs above T_g . When it is exothermic the curve of the DSC instrument is absent during this process because the ray of the DSC refracts during the exothermic activities (T. Tábi1, 2010)

2.3.1.4 Quench Cooling

The quench cooling is the process in which the PLA is heated and cooled down using the different cooling rates .this process avoids the crystallite of the PLA so that the curves of the DSC instrument can be easily visible and is not refracted. The rate may by 10 or 5 or 1°C / min (Hitachi High-tech Corporation, 2007)

3. DEMARCATION

This thesis presents findings from experimental research on production of biodegradable plastic from corn starch. Corn starch based plastic were compared through various tests to PLA standard and its material properties as references. In experimental work thermal properties are analysed.

4. RESEARCH DESIGN

4.1 Material

Three different type of corn (popcorn and maize) is taken as a sample to extract the starch from it to create a starch based bioplastic. The starch from the corn is used to make a thin layer of a bioplastic samples.

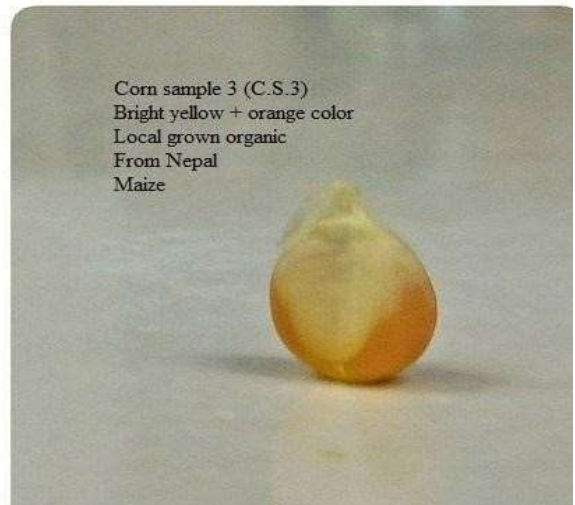


Figure 4 (top) showing Zea mays Evarta (popcorn) bought in local supermarket manufactured in Holland

(Left) figure showing Zea mays Evarta (popcorn) bought in market, manufactured in USA,

(Right) figure showing Zea mays (maize) locally grown, organic from Nepal

4.2.1 Corn soaking

The figure (3) above are three different corn samples

- C.S.1 (Corn sample 1 (Zea Mays Evarta manufactured Holland))
- C.S.2 (Corn sample 2 (Zea Mays Evarta manufactured USA),
- C.S.3 = Corn sample 3 (Zea Mays local organic from Nepal)

Each sample weights 68 gram (g). These samples were soaked in four various methods. The ratio of ethanol, temperature of soaking and time length (hours) of soaking were varied in each methods as a guideline to obtain 24 total samples. Further in each method, samples were soaked for 48 hrs and 72 hrs. First the corn samples were clearly inspected and cleaned before processing. Then corn kernel were kept for soaking.

Method 1. All 3 samples were soaked in purified water at room temperature.

Method 2. The samples were soaked in separate beakers in purified water with 0.1 Mole ethanol at room temperature.

Method 3. All samples were then placed in separate beakers with purified water. Then 0.4 Mole concentrate ethanol was added.

Method 4. The samples were placed in beakers and added with purified water and 0.2 Mole ethanol and kept in the oven at 50 degree.

Table 1. Showing conditions and duration of corn soaking

Methods	Corn Soaking conditions	Hours		Total Samples
		48 hours	72 hours	
Method 1	Soaked in purified water and kept in room temperature	C.S.1 C.S.2 C.S.3	C.S.1 C.S.2 C.S.3	6
Method 2	Soaked in purified water + 0.1 M ethanol and kept in room temperature	C.S.1 C.S.2 C.S.3	C.S.1 C.S.2 C.S.3	6
Method 3	Soaked in purified water + 0.4 M ethanol and kept in room temperature	C.S.1 C.S.2 C.S.3	C.S.1 C.S.2 C.S.3	6

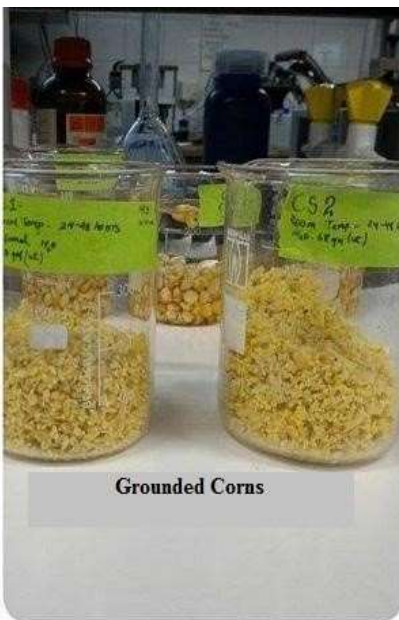
Method 4	Soaked in purified water + 0.2 M ethanol and kept in oven with 50 degree temperature.	C.S.1	C.S.1	6
		C.S.2	C.S.2	
		C.S.3	C.S.3	

After soaking, the corn was lightly grounded and germ were separated from the mixture in centrifuge separator. Centrifuge is a small bench top applied to separate different liquid samples through their density. (For research, training, education, development in field of chemistry, bio-technology and life science.) The centrifuge is supplied with 6*5ml rotor and adaptor available for tubes smaller than 10ml. The centrifuge reaches up to 6500RPM.

The mixture then was washed several time and double grinded finely. Then the starch was extracted by filtration method. Filtration should perform carefully considering wide chances of getting impurities in final solution as direct food was being processed. The collected filtrate was left overnight for starch in beaker to settle down. As a result starch solution was obtained after decantation process. The obtained the starch solution was processed to chemical synthesise to break the glyosidic bonds contain in starch.



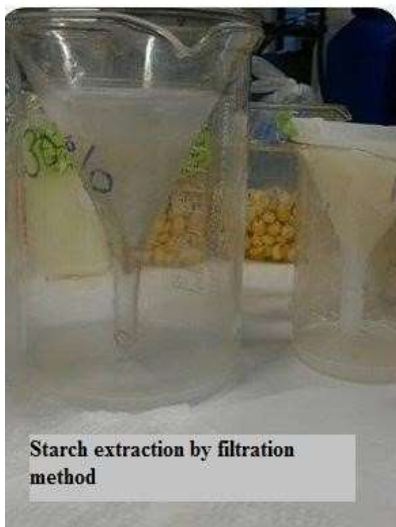
Corn soaked in room temperature



Grounded Corns



Samples in centrifuge Separator



Starch extraction by filtration method



Collected Filtrate



Collected starch at bottom of beakers

Figure 4 showing starch extraction process

4.2.2 Synthesis of corn starch

For the synthesis of polymeric properties the starch was treated with other compound to make the chain of the polymer. Without these additional component the carbon chain in the starch cannot make monomer. Incubation of food containing starch releases amylase which is a natural enzyme to break the glycosidic bonds of starch. HCL was added in order to break the C-O-C bond together with amylase. When HCL was added, the lone pair of oxygen attacks H^+ and made oxygen very unstable. Then the unstable oxygen lets hydrolysis to occur which breaks the starch into the glucose molecules.

To check whether hydrolysis has occurred or not, a few drops of iodine is poured in small amount of sample and tested with litmus paper. If the litmus paper test turned into dark brown-blue in color, it states the sample contains starch in it which is negative result. Whereas, if the test is clear then it states that hydrolysis is completed and starch has break down into glucose molecules.

The obtained 10 ml of starch solution was placed in 150 ml beaker and added to the ingredients mentioned below:-

- 0.5 ml of glycerol 2.12%
- 0.5 ml of glue 2.12 %
- 0.5 g of sugar 2.12%
- 2 ml of 0.1M HCL 0.85%
- 10 ml of deionised water (DI) 42.55%

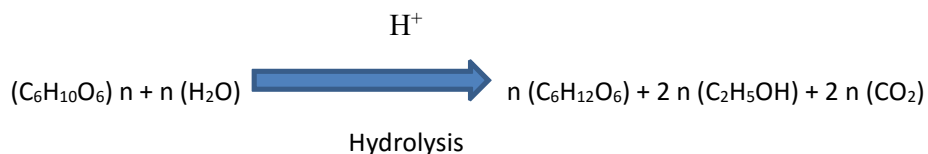
4.2.3 Heating Process

The hot plate with magnetic rotor was used for heating process. The plate was preheated in 100 °C temperature for 5-7 minutes. The solution was then heated and stirred in every 5 minutes and temperature was gradually increased. Then the solution was heated on plate for 20 minutes. The maximum temperature was kept at 145 °C. The solution was heated inside the fume cupboard to avoid toxic fumes.



Figure 5 Synthesis of corn starch

4.4. Reaction



Note, Where,

$C_6H_{10}O_6$ = Starch

$C_6H_{12}O_6$ = Glucose

C_2H_5OH = Ethanol

CO_2 = Carbon dioxide

n = number of moles

- $(-C_6H_{10}O_6-)_n$, represents the polymer Starch with (n) number of molecules and here transformation between starch and glucose lies in the number of hydrogens and the starch is a number of glucose subunits bonded by 1,4 glycosidic linkages.

The hydrolysis of starch occurs in the presence of H^+ ion from the acid so it breaks down into simple sugar and ethanol. The oxygen plays vital role to protonate the oxygen and it pulls electron away from the carbon. That electron is pulled by the water in oxygen. This oxygen from the water pulls electron and makes it away from its hydrogen atom. In this whole reaction the proton is released. The acid is used as catalyst which is also known as S_n1 mechanism.

4.5. Drying process

After heating process the solution was poured in aluminium foil. Then poured solution was slightly spread with spatula. The samples were left to dry in lab. The layer of the transparent or yellow colored thin sheet bioplastic was expected to appear as it dries.



Figure 5 Showing samples drying on the table

Sample was dried for almost 10 days in room temperature, still they were sticky and wet. It may be due to the sugars present in starch solution or due to the excess water molecules in the sample.

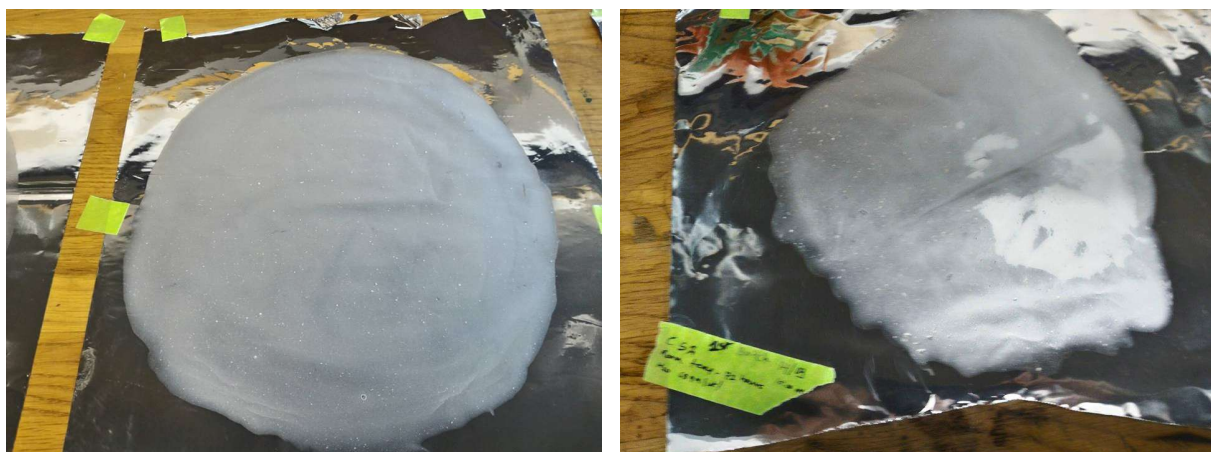


Figure 6 Showing sample after several days of natural cooling

Then the samples were treated in oven. To find the right temperature CS2, CS3 from Method 1 and CS3 from method 2 were treated in temperature 30-40 for 100 hrs increased to 60-80 for 33 hrs. Then CS2, CS3 from method 3 was treated in temperature 80-130 for 30 hrs. Then the samples were decarbonized in some parts. Then CS1, CS2 from method 2 were dries in temperature 80-130 for 24hrs.



Figure 7 Showing corn soaking and sample drying in the oven

Table 2. Showing temperature of oven and duration of sample kept for drying.

Samples	Temperature(°C)	Mid temperature(°C)	Duration (hours)
CS3 No.1	30-40	20	100
	60-80	50	33
CS3 No.2	30-40	20	100
	60-80	50	33
CS2 No.1	30-40	20	100
	60-80	50	33
CS3 No.3	80-130	105	30
CS1 No.2	80-130	105	24
CS2 No.2	80-130	105	24
CS2 No.3	80-130	105	24

Note * No.1 = Method 1

No.2= Method 2

No.3= Method 3

After hours of treatment and observation, Temperature was gradually increased. When first few sample were completely dry all the other samples was dried with oven treatment maintaining the mid temperature of 105⁰ C for 24 hour.

4.6 Curing the bioplastic

The layer of starch based sheet was very thin, which lead big difficulty in curing the samples from the foils. Different tools like knife, scalper, used in lab were used to obtain the samples. Then the samples were carefully took out of the foil and placed in sample zip files. Therefore thin sheet of plastic was not obtained as expected.



Figure 8 CS1, Corn Sample 1 Method 2 (48hrs).

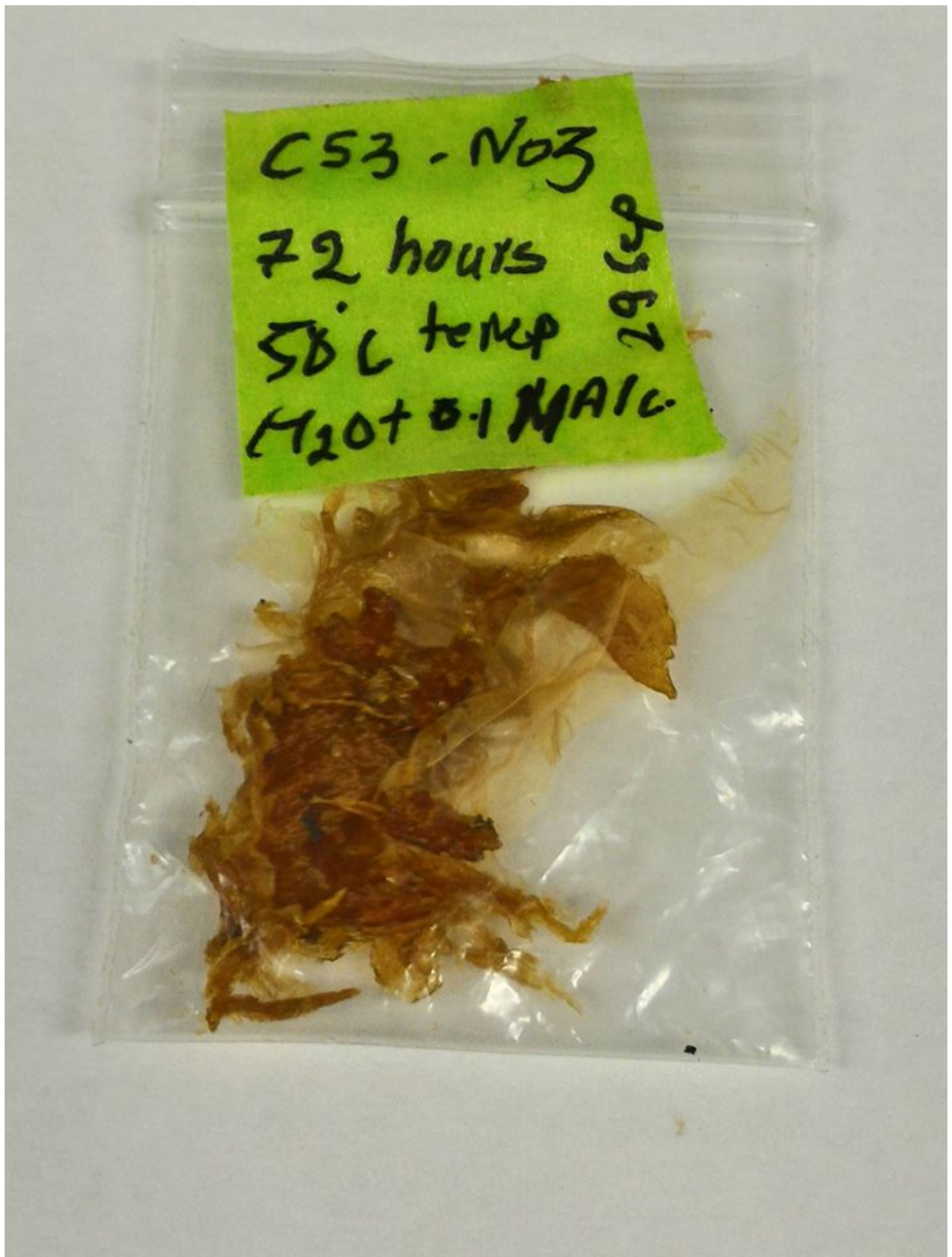


Figure 9 CS3 Method 4 (72 hrs).

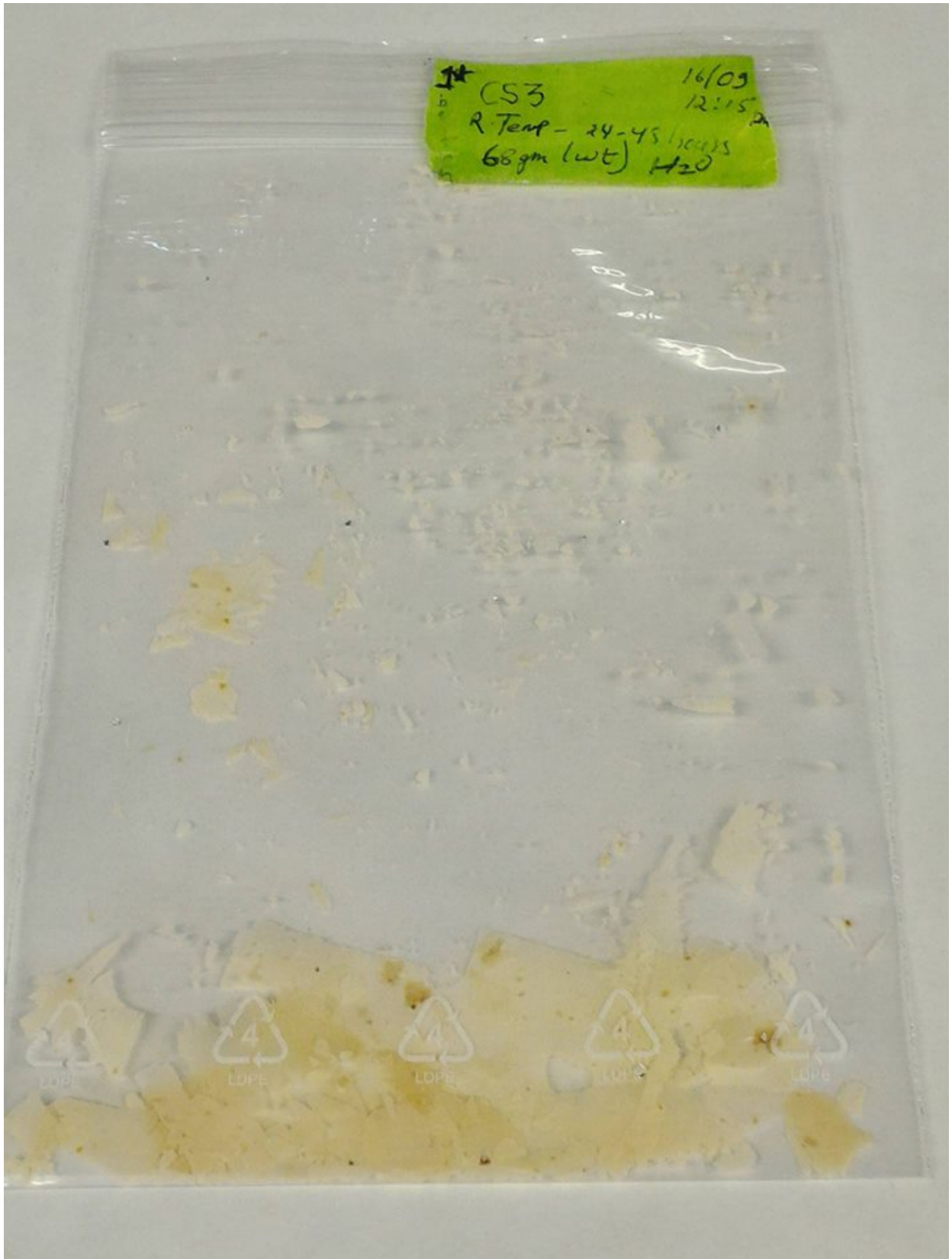


Figure 10 CS3 Corn Sample 3 Method 1 (48hrs)



Figure 11 CS2 Corn Sample 2, Method 4 (72 hrs)

5. Equipments

FTIR, TGA and DSC instruments were used to examine the material properties of the sample. All the tests were carried out at University of Helsinki, Department of Chemistry. PLA filament of 1.75 mm diameter was taken as a sample reference for test from Arcada Lab. The supplier of the PLA filament was Minifactory Oy.

5.1. FTIR



Figure 12 FTIR Instrument (Helsinki University)

Fourier transform infrared spectroscopy, it is technique used to find different composition of compounds in a sample. Which can be further analytical in chemical reaction properties of the sample. FTIR is used to verify organic and polymeric materials. While performing test the sample needs to be placed FTIR instrument so that spectrum passes to sample during the test first step was to collect the background spectra, to make sure if test can be started or not. The instrument also provides the unique chemical bonds and molecular structure of the sample. Different types of bonds, and thus different functional groups, absorb infrared radiation of different wavelengths. The simple working principle of FTIR includes, source of light, stationary mirror, moving mirror, beam splitter, sample and detector. First light source passes through the beam splitter and goes to stationary mirror and moving mirror. Then the light beam comes back and combines, again passes through the sample. Moving mirror is always moving and stationary mirror at rest throughout the process.

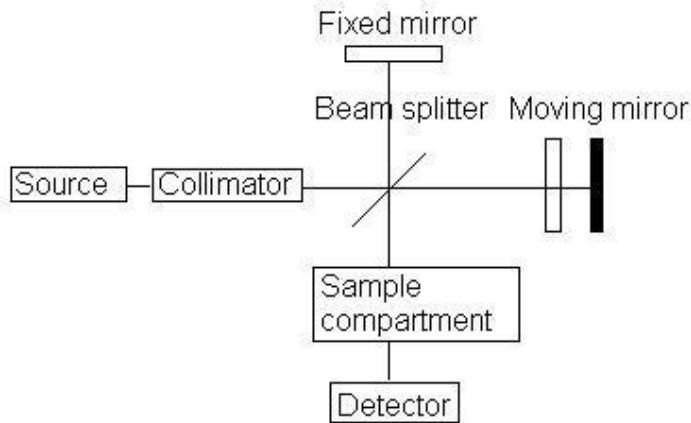


Figure 13 Showing working principle of FTIR instrument

Three corn samples and one PLA sample was tested. First small piece of sample was placed and the instrument was manually operated to enclose the sample. The instrument only consist of one moveable handle. It is very easy to operate but should be very careful.

5.2. TGA

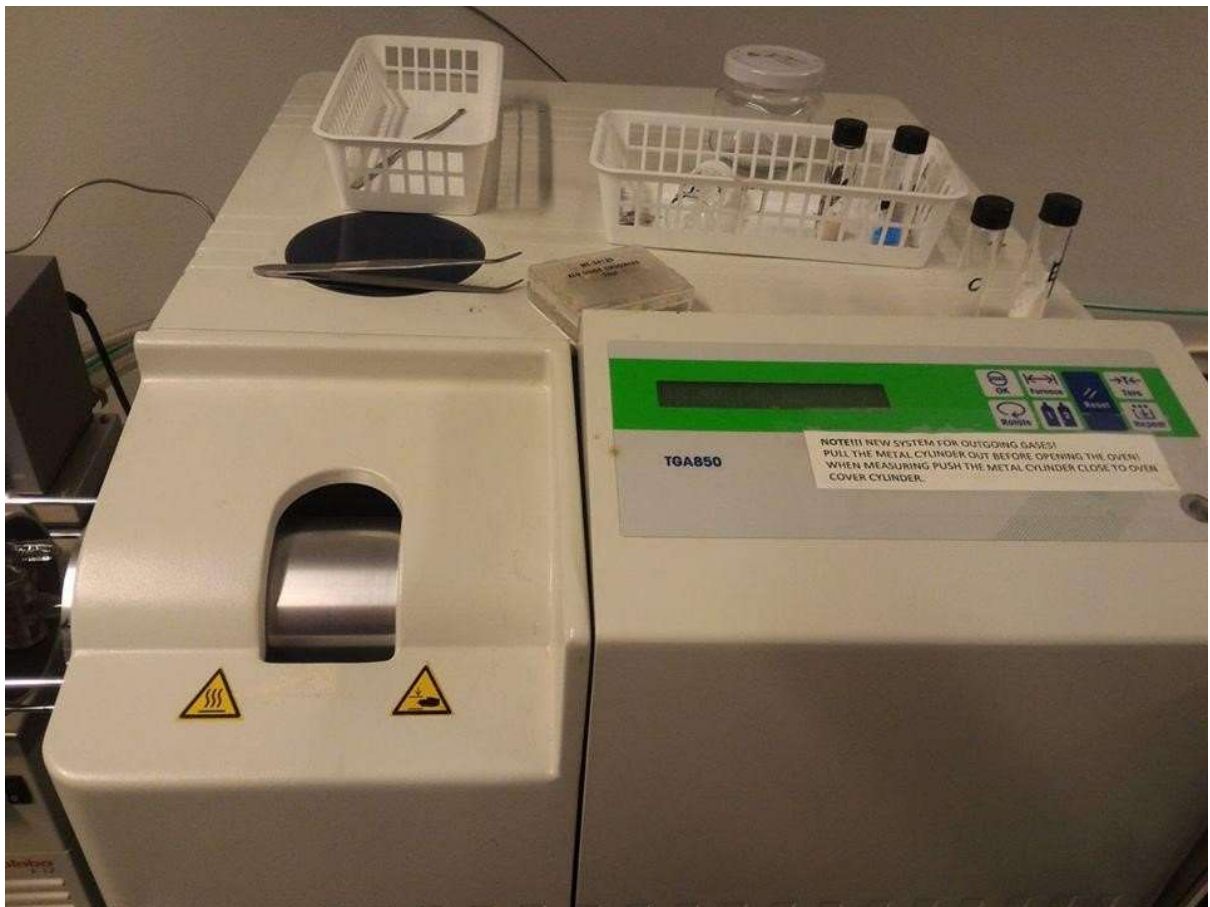


Figure 14 TGA Instrument Helsinki University

Thermogravimetric analysis is a technique that has the sample mass degradation constantly. The heat is applied constantly until the sample is destroyed completely. This is done in presence of nitrogen and in absence of oxygen. The result can show amount of mass destroyed in each stage of testing the sample. Only one sample was tested during the test.

Decomposition of samples identified from weight loss is often not very precise because mass change characteristics of a material are strongly dependent on the experimental conditions employed. Factors such as sample mass, volume, physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber, and the scanning rate have significant influences on the characteristics of the recorded TGA curve.

The sample pan was cleaned and carefully placed with tweezers onto the sample platform. It took few minutes to TARE the instrument. There sample were placed in the centre of the pan. The appropriate inputs were entered into Q50 TGA programme as dictated by the experiment parameters. A sample was destroyed in presence of nitrogen and in absence of oxygen. Green button on the top-left corner is pressed to run software. Once, the run is accomplished, the pan is carefully cleaned with propane torch to avoid any residue.

5.3. DSC

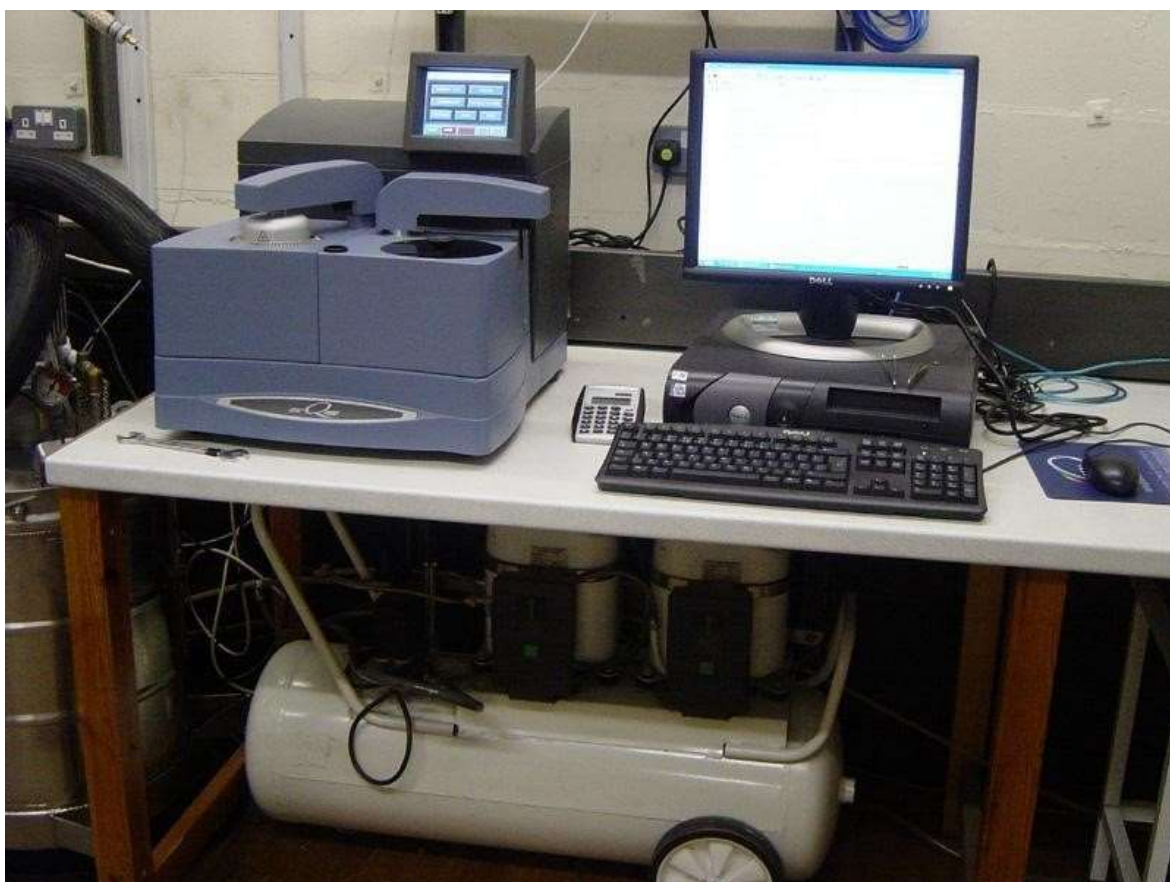


Figure 15 DSC Instrument

DSC instrument provides very precise data, and can be very trustful in terms of measuring any melting point or other properties of Polymers. There is mainly two types of DSC methods, power compensated DSC and heat flux DSC. In power compensated method the sample material and reference materials are held in a separate, self-contained calorimeter each, with its own heater element. And in the heat flux method, the material is placed in an aluminium and empty pan itself act as a reference. Heat flux method was used for test, two pans also connects with heater which provides same temperature for material and reference. The advantage of using power compensated over heat flux DSC is that, the masses of the individual furnaces are much lower.

The heating rate for test was 10°C /min and 20°C / min and mass of sample was 2.42 mg.

6. Results

6.1. FTIR Data

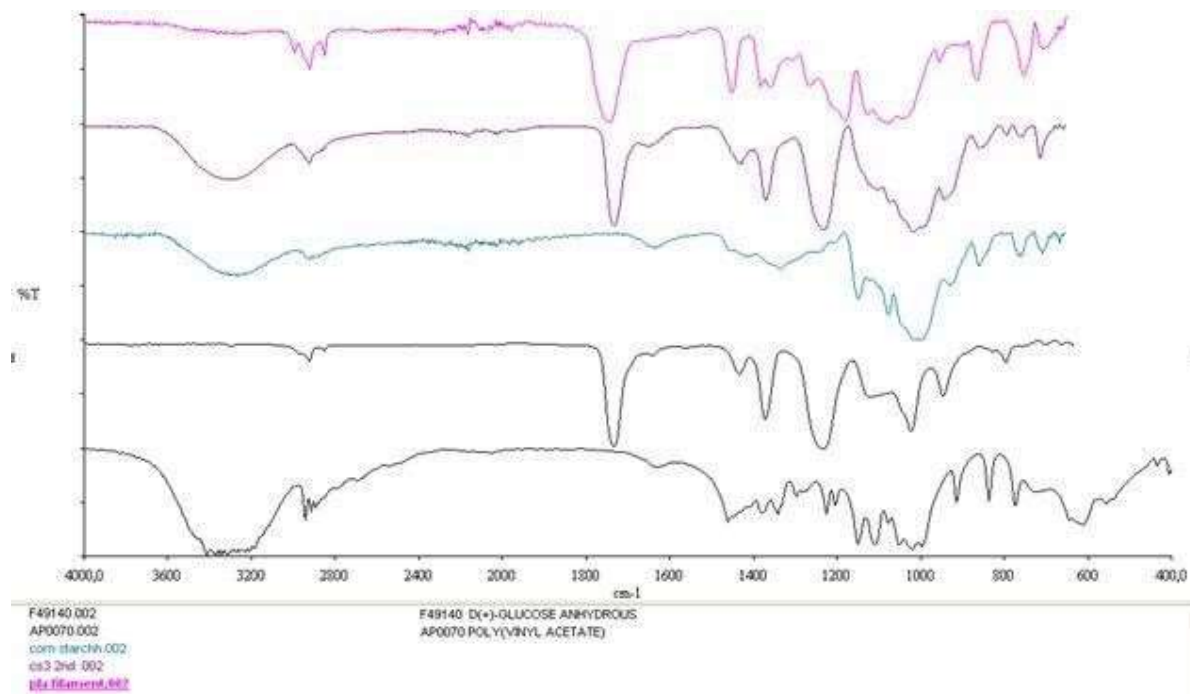


Figure 16 Showing Comparison of different spectra (from top), PLA filament, CS3 Method 2, Corn starch, Poly (Vinyl Acetate) and Glucose Anhydrous

Three sample, CS1, CS2, and CS3 were tested first, the graph of three samples were similar, and therefore it was decided to test only CS3 for further testing. In the above graph, it shows the comparison of IR graphs of CS3 (2nd method) with other spectra like, Glucose anhydrous, polyvinyl acetate, corn starch, and PLA from bottom to top respectively. In a sample spectra, the initial degradation shows the O-H stretching and it's due to hydrolysis, a large number O-H groups absorbed energy in the starting phase. After that the small peak shows the stretching of C-H bond. The later peaks are quite similar to PLA.

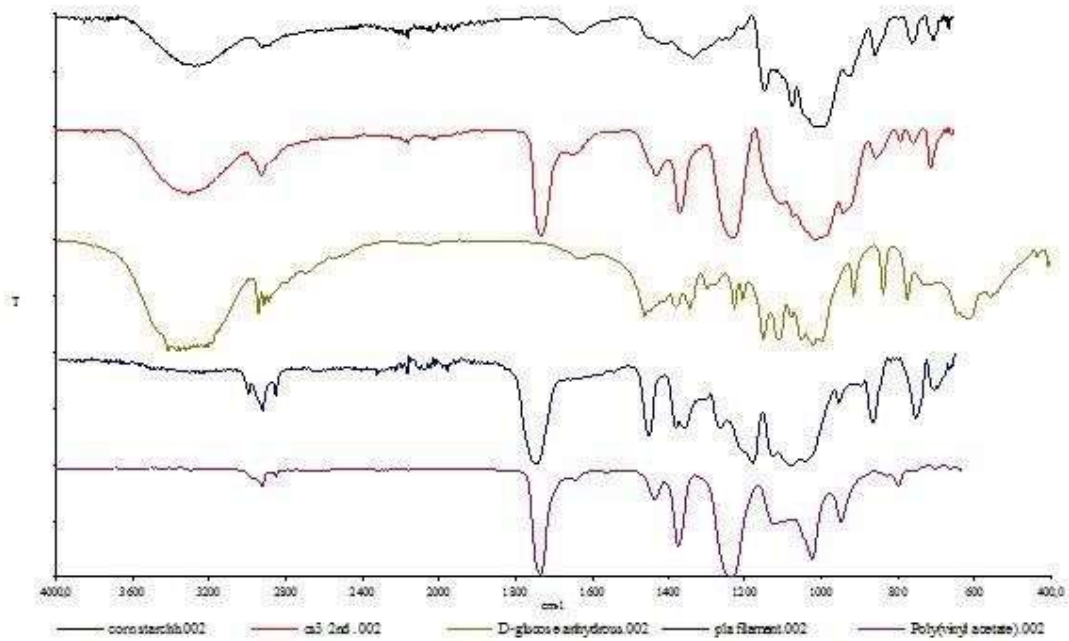


Figure 17 Figure 14 Showing Comparison of different spectra (from top), Corn starch, CS3 Method 2, D- Glucose Anhydrous PLA filament and Poly (Vinyl Acetate).

6.2. TGA Data

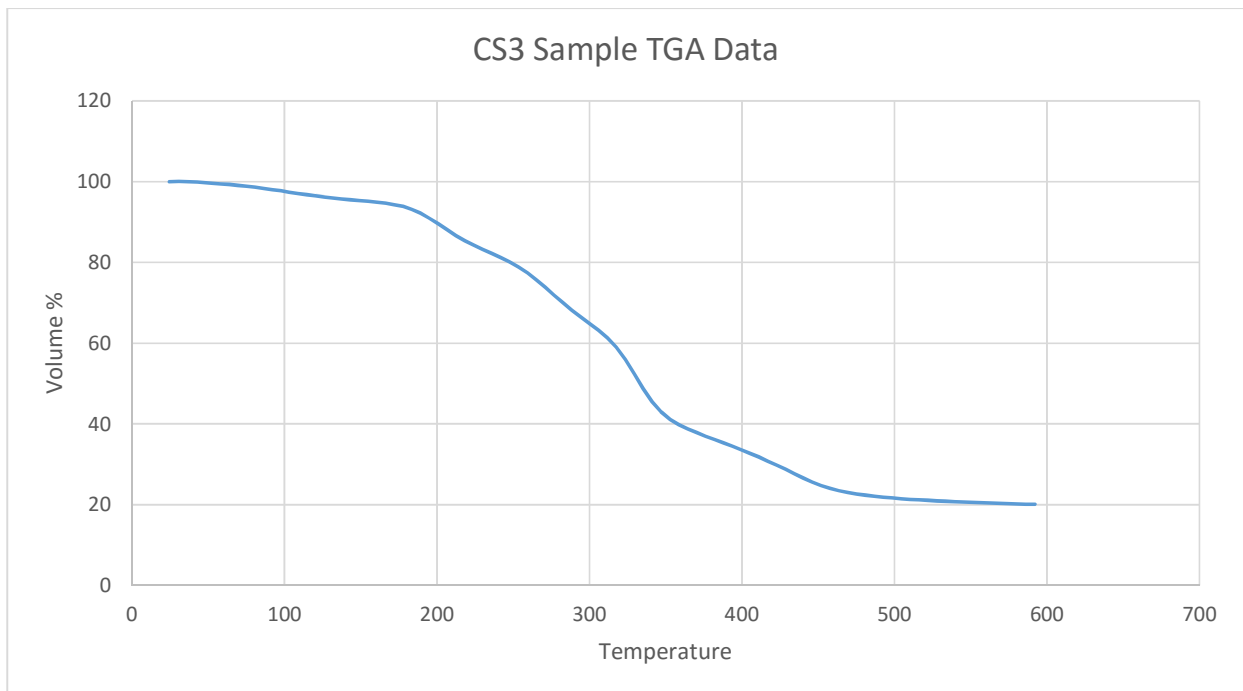


Figure 18 TGA data curve

The X-axis can be displayed as time or temperature and the ordinate Y-axis can be displayed as volume percent (%). A graph is displayed from left to right. The descending TGA thermal curve indicates a weight loss occurred Thermogravimetric test was done after observing the IR spectra of sample. Since the initial degradation was observed in IR spectra there was a doubt of sample having water molecules. In such condition it is considered that sample is not standard enough to be tested in DSC instrument. Again same CS3 sample was tested. In this process the sample is decomposed in presence of nitrogen. The test shows the decomposition temperature of sample material is 175°C. Heat from 0 °C to 175 °C at 10 °C/min in Nitrogen atmosphere with a degradation rate of 10 mg/min

6.3. DSC Data

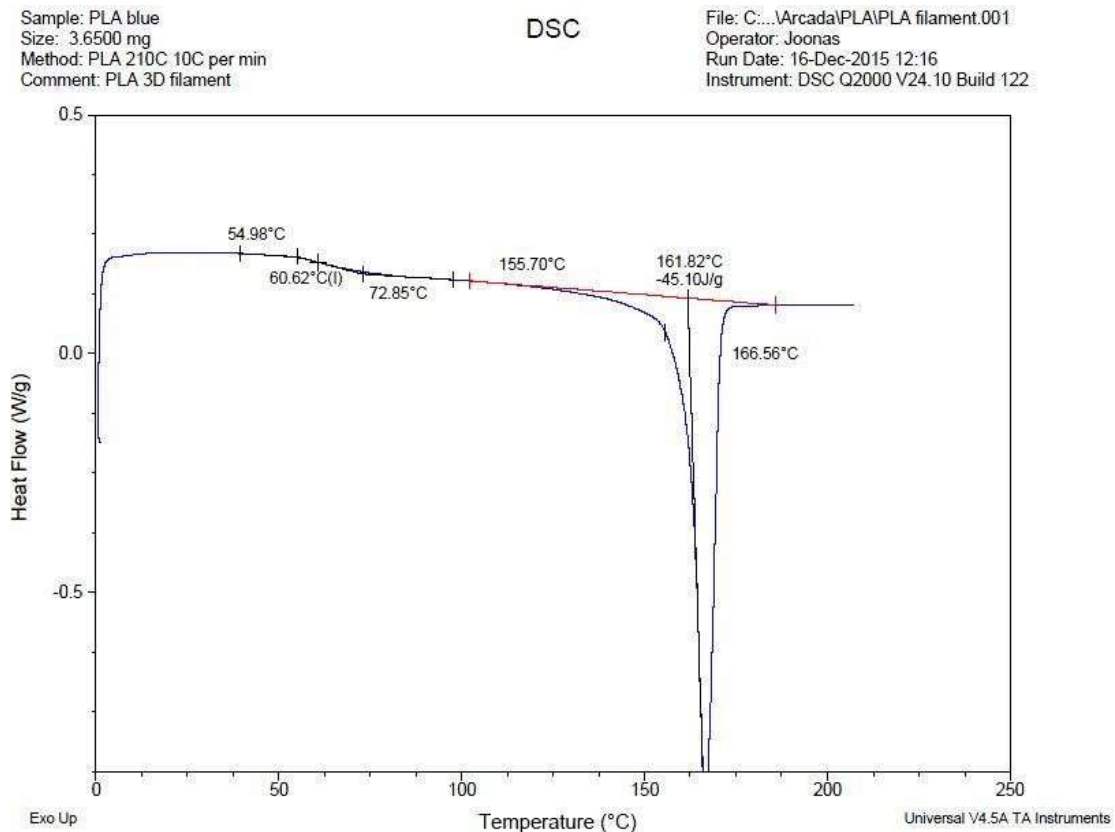


Figure 19 DSC test of PLA (sample references) Showing Glass transition point at 64 and Melting point at 166.56

The above graph shows the DSC test of PLA blue filament, taken as a reference sample from Arcada lab. Here it shows the melting point $T_{(m)}$ and glass transition $T_{(g)}$ point of PLA. Here PLA has glass transition range at 60.62 °C- 72.85, glass transition point showing 64 °C and melting point at 166.56 °C.

Sample: csthree hermetic pan
Size: 2.2500 mg
Method: Fabian_0-200C_10K/min
Comment: Cell constant calibration

DSC

File: C:\...\Arcada\PLA\PLA filament.006
Operator: Joonas
Run Date: 17-Dec-2015 14:25
Instrument: DSC Q2000 V24.10 Build 122

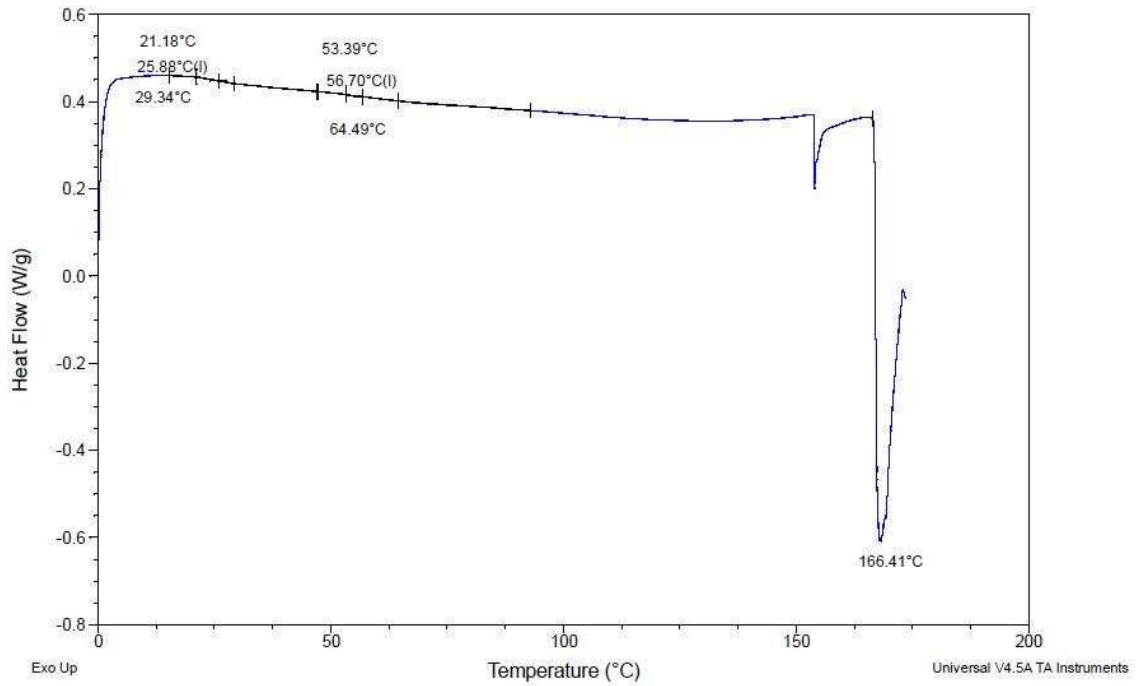


Figure 20 DSC test of CS3, Showing Glass transition point at 64.49 and Melting point at 166.41

The above graph shows the DSC test result of corn sample 3 (CS3). It shows the glass transition point and melting point of a sample material, here glass transition range shows T_g at 56.70 °C- 70.00 °C and T_g point at 64.49 and glass transition point at T_m at 166.41 °C temperature.

Sample: csthree hermetic pan
Size: 2.2500 mg
Method: Fabian_0-200C_10K/min
Comment: Cell constant calibration

DSC

File: C:\...\Arcada\PLA\PLA filament.006
Operator: Joonas
Run Date: 17-Dec-2015 14:25
Instrument: DSC Q2000 V24.10 Build 122

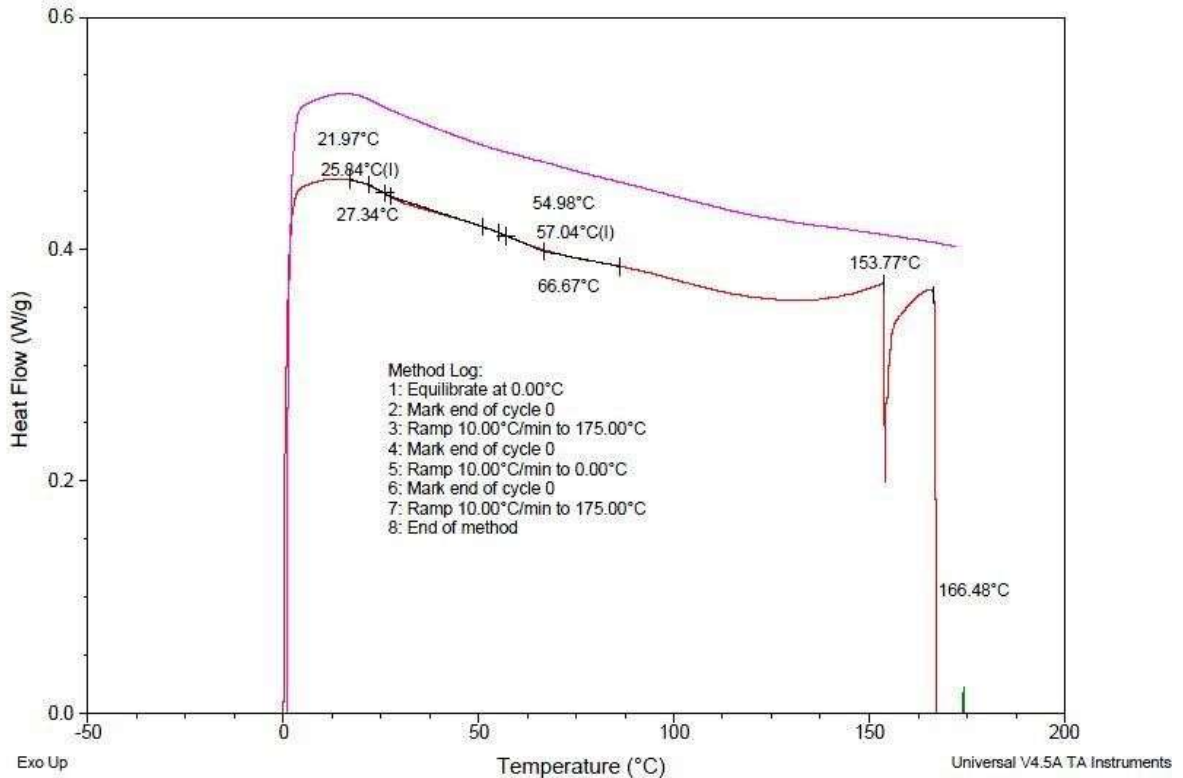


Figure 21 DSC test of CS3, in slow heating cycle, showing glass transition point at 57.04 and Melting point at 166.48

The above graph shows the DSC test result of CS3 in slow heating process, the maximum temperature taken was 175 °C. In the above result the glass transition T_g range is at 54.98 °C - 66.67 °C and T_g point at 57.04. Melting point T_m is at 166.48 °C temperature.

Sample: csthree hermetic pan
Size: 2.4000 mg
Method: 0-180C_20K/min
Comment: Cell constant calibration

DSC

File: C:\...Arcada\PLA\PLA filament.008
Operator: Joonas
Run Date: 17-Dec-2015 16:00
Instrument: DSC Q2000 V24.10 Build 122

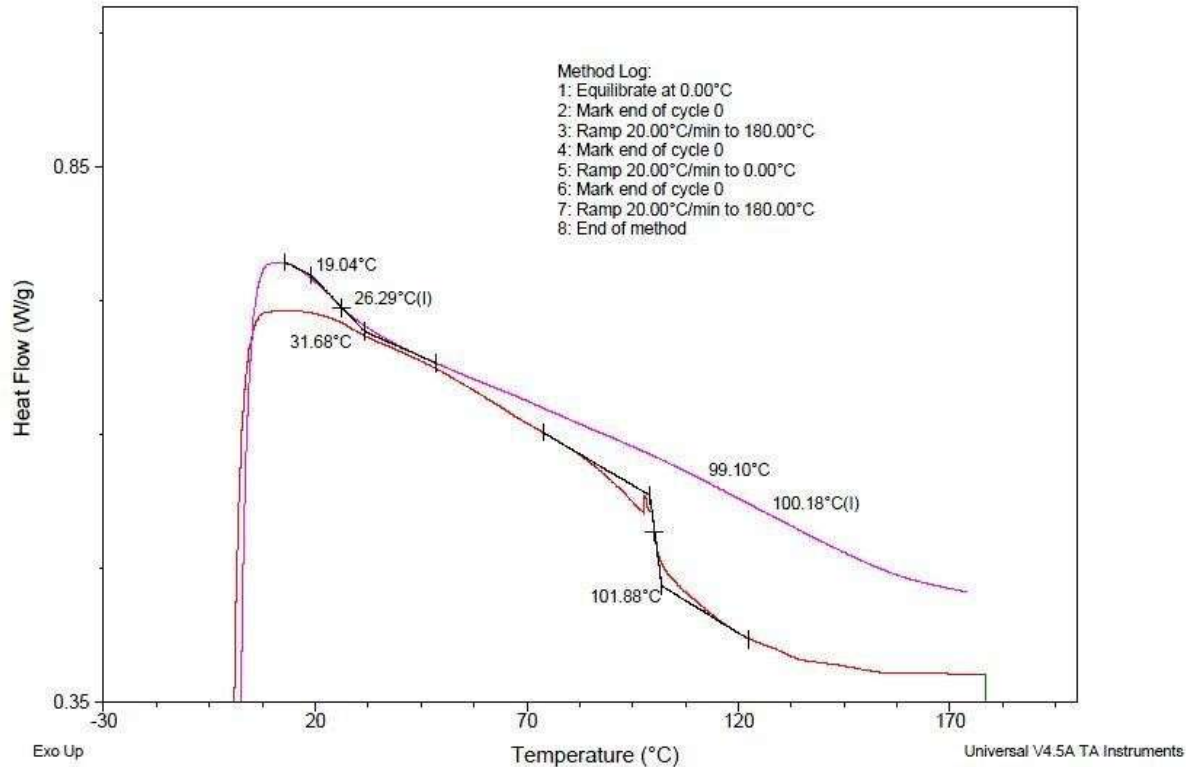


Figure 21 DSC test of sample with fast heating

7. Data Analysis

The various properties like melting point, glass transition, temperature characteristics, acidity, and other properties of Bio-degradable plastic material are discovered from this research. The following table shows the collected data result.

Table 3. Showing DSC test results of i. PLA (sample reference), ii. CS3 (Corn Sample 3), iii. CS3 slow heating

DSC test (sample)		T _g Glass transition range Degree Celsius (°C)	Glass Transition point T _g Degree Celsius (°C)	T _(m) melting point temp Degree Celsius (°C)
i.	PLA	60.62- 72.85	64	166.56
ii.	CS3	53.39 - 64.49	64.49	166.41
iii.	CS3 slow heating	54.98 – 66.67	57.04	166.48

Analysing the data from the table, the material properties of starch based plastic PLA and CS3 sample shows quite similar temperature properties. With glass transition temperature, T_g around 58°C the sample behaves as rubber on temperature above glass transition. The curve in DSC is found to be obtained high because during this time there is no crystalline structure is formed and the DSC instrument can easily analyse the material during the endothermic process. The exothermic is obtained when the cold crystallization occurs above T_g. When it is exothermic the curve of the DSC instrument is absent during this process because the ray of the DSC refracts during the exothermic activities.

8. Conclusion

Since, direct food was used for starch extraction and hand filtration was done while processing, there lies many impurities that may be seen or not in sample. The initial stage in DSC test too shows that something must have absorbed the heat and evaporated. However the material properties of Corn sample are very much similar to the sample reference PLA. The variation in temperature point could be due to impurities or due to heating rate while testing. The material properties shows that the sample that has been created is not exactly PLA but similar to PLA. Therefore CS3 also can be more physically or chemically modified in order to use it in several field where PLA is being used. As a result it can be also use in Injection molding, extruding or 3Dprinting manufacturing process too. While analysing we should be very careful on the shrinkage Percent of the bioplastic so that we could manipulate objects within the given tolerance to make the product.

9. Discussion

The bioplastic can be obtained from corn based starch .The extraction of bioplastic can be more simple with other tools like non-stick foil could have been helped a lot better. The sample was hard to pull out and took longer time to do manually. This thin sheets took longer time to be dry because of the sugar present in them. The produced bioplastic shows similar properties compared to PLA. Thus, it can be used as biodegradable plastic in smaller scale to larger scale. The process can be more simplified with as per demand. Environmentally and socially it is wise option to use bioplastic with the everyday food and it is safer compared to oil based plastic. The residue can be used to extract sugar and or can be digested in bio digester to produce gas for cooking purposes. This makes us to help reduce carbon footprints in the world and can delivers us greener and fresher living.

10. Future of Starch

The study of starch and PLA has a very long history from 19th century in plants science and technology. Starch has high demand and considered as a good diet of food source. However keeping balance in food demand and considering the starch based industrialization can motivate many to make starch as a multibillion industry. Different starch based bioplastic can be treated and modified. Treatment like Plasma treatment, in order to apply bioplastic as an inner coating in food packaging industries. Green in environment will be added if maximum use of bioplastic is in use. It can also help in reducing the global warming situation and gives safe food packing with organic material.

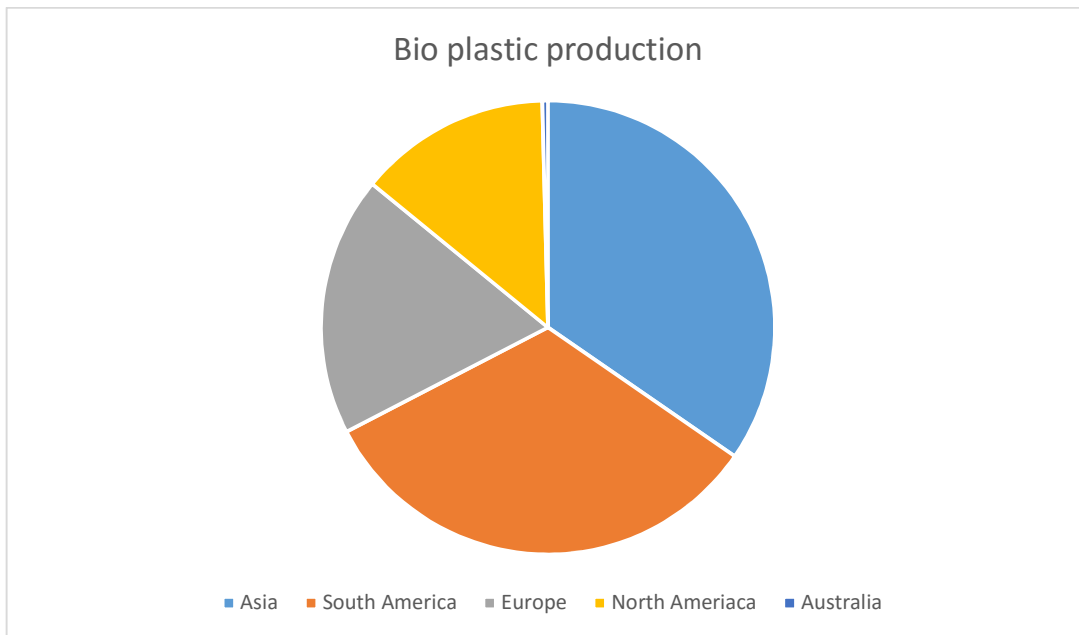


Figure 22 Showing Global Bioplastic production

The global bioplastic production capacity is supposed to increase in 2016 by 500% .Which makes this research forward. According to survey done in 2011 it was manufactured 1.2 million tonnes and made turnover of 2 trillion euros creating 22 million jobs .In 2012 there was huge increase in the production reaching up to 1.4 million tons. It is expected that the production capacity will rise to 6.2 million tons in 2017 (European bioplastics, 2015).This activities includes the bioplastic production in Asia, South America, Europe, North America, Australia and Japan which is 34.6%, 32.8%, 18.5%, 13.7, 0.4% and japan has highly dependency on naphtha imports. Asia is expected to produce 46.3% of world's bioplastic production. Japan also produce strong bioplastic material using traditional alternatives (S.N. Jogdand, 2014).

The rise in the global bioplastic is growing in the present context. The company are more interested towards the research done in laboratory to move towards the sustainable future. Soon it is expected to have huge demand in the field of sustainable bioplastics. The field of bioplastic is sooner to be applied in various fields like electronics automobiles and consumer goods manufacturing. Some of the plastic have been traditionally created by expanding their use towards the modern application like polybutylene terephthalate (PBT) and acrylonitrile-butadiene styrene (ABS) (European bioplastics, 2015). These kind of application and use of bioplastic may become the solution for the sustainable future and provide us more freedom in choosing or growing materials around own farming fields.

Lots of fruit and vegetable in nature contains starch from which, Banana starch is certain to join the group of global industries of starches.

References

- European bioplastic, 2015. *FACT SHEET European bioplastic*, Berlin: s.n.
- AINI, N. N. B. M., Dec 2010. *BIODEGRADABLE BIOCOSMPOSITE STARCH BASED FILMS BLENDED WITH CHITOSAN AND GELATIN*, Faculty of Chemical & Natural Resources Engineering Universiti malaysia: s.n.
- Chaplin, M., 2001. *Water structure and science*. [Online] [Accessed 28 03 2016].
- Corn Refiners Association, 2009. *The corn refining process*, s.l.: s.n.
- David E. Henton, P. G. J. L. a. J. R., 2005. Polylactic Acid Technology. In: *Natural Fibers, Biopolymers, and Biocomposites*. s.l.:s.n.
- Eastman polymers, Eastman Chemical Company, 2011. *Processing and mold design guidelines*. [Online] Available at: http://www.eastman.com/Literature_Center/P/PP7.pdf
- Encyclopedia Britannica, 2010. *corn: corn products*, s.l.: Britannica Online for Kids.
- Eur-Lex Access to European Union law, 2013. *Europa*. [Online] Available at: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52013DC0123#document1> [Accessed 28 03 2016].
- European bioplastics, 2015. *Global bioplastics production*. [Online] Available at: http://www.european-bioplastics.org/2015/11/04/pr_151104/ [Accessed 11 04 2016].
- Europe, S., 2012. The european starch industry.
- Hitachi hightech corporation, 2007. *Thermal analysis of polylacvtic acid*. Tokyo: Hitachi hightech corporation.
- James LUnt, A. L. S., n.d. *polylactic acid polymer from corn, application in textile industry*, s.l.: Cargill dow polymers LLC.
- Jamshidian, M., September 2010. *polylactic acid, production, application*, s.l.: Comprehensive Reviews in Food Science and Food Safety.
- Lawrence S. Lerner, 1996. *Physics: for scientists and engineers*. s.l.:Jones & Bartlett Learning.

- Lievendag, N., 2014. <http://nicklievendag.com/>. [Online]
Available at: <http://nicklievendag.com/filament-guide/>
[Accessed 2015].
- National Center for Biotechnology Information, 2008. *PubChem Compound Database*. [Online]
Available at: <https://pubchem.ncbi.nlm.nih.gov/compound/2483692>
[Accessed 07 September 2015].
- Otulugbu, 2012. *production of ethanol from cellulose sawdust*, Helsinki: thesus.fi.
- P. Atkins, J. d. P., 2002. *Physical Chemistry*. New York: Oxford University Press.
- peek, N., 2008. *rapid prototyping of green composites*, s.l.: s.n.
- S.N. Jogdand, 2014. *Bioplastics*. [Online]
Available at: <http://www.slideshare.net/induniva/bioplastics-38041666>
[Accessed 11 04 2016].
- Scanlon, J. S. a. M. J., 2016. Emerging Model Organisms. *Maize (Zea mays): A Model Organism for Basic and Applied Research in Plant Biology*.
- Singh, R. P., August 2003. *compatibilization on the inherent biodegradability of the host polymer*. s.l.:s.n.
- Smooth-On, Inc, 2015. *Smooth-On, Inc , make it now*. [Online]
Available at: <http://www.smooth-on.com/images/XTC-Skull.jpg>
- T. Tábi1, I. E. S. F. S. A. S. L. J. G. K., 2010. *Crystalline structure of annealed polylactic acid and its*. s.l.:eXPRESS Polymer Letters.