



Materials Analysis of Recycled PLA from 3D Printing

Degree Thesis

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<p>Abstract:</p> <p>Additive is not new term in this plastic industry, additives have been used in polymers to make the product better and to preserve them. Different additives are added to polymers to get the desired results. These chemical substances increase the functionality and properties of polymers. Colourants were used to get different colours on polymers. Reinforcements were used to make the polymer stronger. These additives have both pros and cons on polymers. This made polymers to behave differently. The main objective of this thesis is to study about the polymers on mechanical properties, thermal properties and rheological behaviour. The materials in this case was PLA failed 3D printed parts(supplier unknown). These parts at first were sorted into different colours, red, white and black. These parts were shredded using shredder and were extruded from extrusion making them into filaments. These filaments were then dried up using air dryer and make into pellets using pelletizers. Pellets were examined using Differential Scanning Calorimetry (DSC) Melt Flow Index (MFI), Fourier Transform Infrared Spectroscopy (FTIR). These pellets were used in injection molding to make samples for mechanical testing. During these processes, there a lot of difficult things in extrusion process and testing MFI of pellets. The importance of heating chamber in extrusion were known. The speed of screw during extrusion process was found in effecting the quality of filaments. The results were similar like I expected. These samples containing different colourants behave slightly differently in most of the tests. This thesis was done because of personal interests and to increase the knowledge about mechanical properties of polymers and different additives.</p>	
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Table of Contents

LIST OF FIGURES	5
1 INTRODUCTION.....	1
1.1 BACKGROUND.....	2
1.2 Objectives.....	3
1.3 Literature Sources	3
2 LITERATURE REVIEW	3
2.1 Plastics.....	4
2.2 Different types of Additives.....	5
2.3 PLA.....	7
2.3.1 Applications.....	7
2.3.2 Molecular structure	8
2.4 General Manufacturing Process.....	9
2.5 Extrusion	10
2.6 Injection Molding.....	10
3 MATERIAL TESTING	12
3.1 FTIR.....	12
3.1.1 Attenuated Total Reflectance (ATR)	13
3.1.2 FTIR Spectrophotometer.....	13
3.2 MFI.....	14
3.3 DSC	16
3.4 Tensile Testing.....	17
4 METHODOLOGY.....	21

4.1	Material and Equipment.....	21
4.2	Experimental Part.....	22
4.3	Testing.....	27
5	RESULTS.....	32
5.1	FTIR.....	32
5.2	MFI.....	35
5.3	Tensile Testing.....	36
5.4	DSC	38
6	DISCUSSION.....	40
6.1	FTIR.....	40
6.2	MFI.....	40
6.3	Tensile Testing.....	41
6.4	DSC	41
7	CONCLUSION.....	42
7.1	Improving the Test	42
	REFERENCES	43

LIST OF FIGURES

Figure 1 Molecular structure of Polylactide	8
Figure 2 Molecular structure of D-Lactide	8
Figure 3 Molecular structure of L-Lactide	8
Figure 4 Manufacturing process	9
Figure 5 Schematic diagram of extruder	10
Figure 6 Injection molding machine	11
Figure 7 Annotated picture of Nicolet 6700 FT-IR	14
Figure 8 Annotated picture of capillary viscometer	15
Figure 9 DSC PT1600	17
Figure 10 5 kN Testometric machine	20
Figure 11 3D printed failed parts(red)	23
Figure 12 3D printed failed parts(white)	23
Figure 13 3D printed failed parts(black)	23
Figure 14 Shredded black PLA	24
Figure 15 Shredded white PLA	24
Figure 16 Filaments cooling down with cooling water	25
Figure 17 Pelletizing the filaments	26
Figure 18 FTIR of red sample	28
Figure 19 FTIR of white sample	28
Figure 20 FTIR of black sample	28
Figure 21 Tensile testing of specimen	30
Figure 22 White sample after tensile testing	31
Figure 23 Black sample after tensile testing	31
Figure 24 Sample preparation and placing inside machine	31
Figure 25 Spectra of pure PLA	33
Figure 26 Spectra of Black samples (PLA)	33
Figure 27 Spectra of red samples (PLA)	34
Figure 28 Spectra of white samples (PLA)	34

Figure 29 All PLA Compare	35
Figure 30 Stress-strain curve1	36
Figure 31 Stress-strain curve2	37
Figure 32 Stress-strain curve3	37
Figure 33 DSC curve of virgin PLA	38
Figure 34 DSC curve of white PLA	38
Figure 35 DSC curve of red PLA	39
Figure 36 DSC curve of all samples	39

Abbreviation

PLA: Polylactide or poly (lactic acid)

FTIR: Fourier Transform Infrared Spectroscopy

DSC: Differential Scanning Calorimeter

MFI: Melt Flow Index

Foreword

I am very much thankful and like to express gratitude to my supervisor Harri Anukka for his support, guidance and inspiration throughout my research.

I would also like to thank my examiner Stewart Makkonen Craig for helping me to decide to start my thesis.

I would like to acknowledge the help and support provided by Silas Gebrehiwot while doing injection molding.

Helsinki, March 2020

Resham Tamang

1 INTRODUCTION

Polymers are composition of many molecules or chain of repeated monomers. These monomers have different characteristics and help polymers to have their characteristics. The polymers are influenced by the way they are arranged in the chain. Polymer like rubber are stretchy in nature and glass are hard in nature, as the molecular geometry of rubber is linear network and the molecular geometry of glass is tetrahedral network (UNSW Sydney, 2019). Polymers usually represents the word plastics, meaning synthetic polymers. However, there are natural polymers like wood and rubber, which consists of hydrocarbon isoprene. Likewise, proteins (natural polymer) consist of nucleic acids and amino acids. Similarly, DNA and RNA (found in all living cells) are natural polymers made up of nucleotides (Bradford, 2017).

Polymers have now been included in almost every part of human beings, from household to medical and health sector in modern world. People are being in contact with polymer containing products almost every time and always. Products like mobile phones, clothes, cars, plastic bottles, and packaging all contain polymers. In these polymers, chemicals are added to polymers for better processing of polymers and for increasing lifespan of polymers. The most common types of additives used in synthetic polymers are stabilizers, flame retardants, plasticizers, and lubricants (UNSW Sydney, 2019).

This thesis is mostly focused about the PLA and changes in its mechanical properties. The polymers are never in same condition or perform same after some period or mixing with other additives. The mixing of additives changes the matrix of polymer chain leading to change in properties of PLA, mechanically, structurally and rheological. The main reasons for resulting in these kinds of changes is due to the amount of additives in composition of polymers and other is the degradation of polymers. The amount of additives that are added to polymers may result in the changes of mechanical properties like stress, strain forces, brittleness and other behaviors. The amount of additives can sometimes affect the molecular weight, less molecular weight always influence the degradation of polymers. (Thomas Publishing Company, 2019)

Recycling of plastics means collecting of plastic wastes and reprocessing those into new and useful products. The main goal of plastic recycling is to minimize the plastic waste and plastic pollution, as well as to minimize the extensive use of virgin natural resources required to produce

new products. There has been realization of plastic recycling as the plastic wastes are always dangerous as they end up in water bodies, oceans and landfills. And these plastics are easy to mold into different types of shapes within low budgets with the use of currently available technology. There are many processes in recycling of plastics like collecting, sorting, shredding, washing, melting and pelletizing.

During these processes, the polymers can be contaminated which will affect the properties of recycled polymers. Mixing of two different polymers or plastics can result in unexpected behavior of recycled polymers. Because of this, there is need of doing these processes properly and contaminated free. There is also quite difference in pure and recycled polymers as the polymer chain of recycled ones are broke down during the recycling process. This results the degradation of polymers as suggested by many research and articles.

This thesis is divided into several topics like literature review, aims, methodology, experiments, results and discussions. These topics will describe how thesis was done, all the steps and process. There will be more discussions about the background of PLA additives, preparation of samples, all the test and experiments performed to achieve the results. The parameters for the experiments were taken from scientific research articles and journals. The achieved results were analyzed, and discussion were made.

1.1 BACKGROUND

Plastic additives are chemicals added to polymers to make it better functional as well as changing properties according to our needs. There are various types of polymers additives like colorant additives, reinforcement, fillers, plasticizers and many more. These additives effect the properties of polymers both mechanical and chemical. Recycling of polymers have been advanced because of the new technology and process. The use of additives has made some effects on the recyclability of polymers. There might not be a very huge difference but, we are sure that there is still some minor effects of these chemicals in polymers as well as on their recyclability. (Food Packaging Forum, 2019)

There has been a lot of study about PLA, as it has been viewed as the replacement of many petroleum-based materials. There has been a lot of research regarding the use of PLA in drug delivery in past and several experiments have been performed to increase the mechanical properties of PLA. The experiment to increase the mechanical properties of PLA was conducted. Methyl methacrylate (MMA) and butyl acrylate (BA) were used to blend with PLA in different ratio to get the desired goal. (Sang, et al., 2014)

PLA is supposed to be one of the biodegradable polymers in natural environment, however many tests conducted have shown the other way. PLA are not that environmental degradation, when they are left in environment as they are resistant to microorganisms from soil and water. They need to be hydrolyzed by the elevated temperature of approximately 60°C, which reduced the molecular weight of polymer. The high temperature and high humidity can increase the rate of degradation. (Farah, et al., 2016)

1.2 Objectives

The main aim of this thesis is to perform analysis of PLA using different testing methods, to study about polymers on their mechanical properties, to find out the changes in the properties of Polylactic Acid (waste PLA) because of additives as well as of recycling, to test the (pellets) samples using FTIR, and mechanical properties, to study rheological behaviors of samples and to study about the degradation of samples

1.3 Literature Sources

While collecting information and data for this thesis, both qualitative and quantitative method were used. Different types of research, literature review, photo taking, articles, book, internet and websites were used as qualitative method. For quantitative method, all the numerical data were collected from different types of experiments that were performed in laboratory. Technical data about the materials were taken from internet.

2 LITERATURE REVIEW

In this part, general information about plastics, PLA, application of PLA, additives in PLA, manufacturing process as well as different testing methods will be discussed. Before writing, proper research was done in internet, articles, books and other sources of information.

2.1 Plastics

Plastics have changed our modern life so much and now; we are depended on plastics products. It is very difficult to imagine our daily life without these plastics products, as these products have made our life so much easier. We can't imagine our phones without these plastics as circuit boards, cable insulation and many other internal and external parts are made using plastics. Cars, we used in our daily life have many parts like steering wheels, synthetic bumper and dashboards are made from plastics. Our entertainment industries which are mostly depended on the equipment made from plastics like CDs, video and audio tape. The electronics equipment like televisions, AC, refrigerator and heater are also products from plastics. Indeed, it would not have been possible to read this report without plastics. (Royal Society, 2009)

All the plastics products are made with combining the main polymer and blend of material called additives. Additives are chemical compounds that are added to polymers in small quantities. These additives are added to improve the quality and performance of polymer or plastics. Additives had helped plastics to become more strong, tougher and colorful. Without the presence of additives, the plastics products are very unlikely to do or perform better both mechanically and functionally. Not only these, additives had made production process faster and easier, the production costs have been decreased with the use of additives in plastics products and these products lasting forever helped to save money. (Pritchard, 1998)

Environmentally, this leads to sustainability and helps to save the raw materials for future use or future generation. We must understand that our today's world would be a lot less safe, very expensive without the additives. Even in our car, we would ride in our daily life, has safety belts, which are very strong and made from plastics with additives, and have made cars a lot safer. Mixing additives with pure polymers have reduced the costs of plastics products a lot, otherwise products made out of pure polymer would be very expensive, making them accessible to very few people. (British Platics Federation, 2019)

In the market, there different types of plastics available for consumers as well as the manufacturer of plastics products. The most common plastic used are: Acrylic or Polymethyl Methacrylate (PMMA), Polycarbonate (PC), Polyethylene (PE), Polypropylene (PP), Polyethylene Terephthalate (PET), Polyvinyl Chloride (PVC) and Acrylonitrile-Butadiene-Styrene (ABS). PMMA is best for the use in optical products as it is very transparent and lightweight. It is also

shatter resistant, which makes it perfect for alternatives of glass. It can resist impacts of high amount, almost eighteen times than that of glass and is very easy to handle and process, making it possible to use in different and many applications. (Pawar, 2016)

The main reason of using Polycarbonate (PC) is because of its toughness, stableness and transparent. This plastic is clear as glass and two hundred fifty times stronger than glass. PC are very easy work within molding in both cold-formed as well as in hot-formed. The PC sheets can be cut easily without even forming and fabrication. This is mostly used in greenhouses, sunglasses, police riot gear, DVDs and more. There are four types of Polyethylene (PE) low, medium, high and ultrahigh, density Polyethylene. This PE is most common plastic used in world. Plastics bags, clear food container, disposable packaging, gas pipes, shrink film, screw closers, plastics bottles, pipes, body armor for military, hydraulic seals spine implants, ice skating rinks and more are made from PE. (Tufts University, 2019)

Polypropylene (PP) is second most used plastics after PE. PP is stronger than PE and a lot flexible than PE. It can also absorb a lot of stress, is heat resistant, acid resistant and cheap. PP's sheets are used in making different automotive parts, food containers, laboratory equipment and medical devices. PET is fourth most produced plastics and is thermoplastic resin of polyester family. It is shatterproof, chemical resistance to water and other organic materials. It is used in carbon nanotubes and for clothing. PVCs are mostly used to make construction materials, windows, water bottles, non-food packaging and more. It is also used in clothing, plumbing products, electric cable insulation and more. ABS is used because of its highly processable features, as it can be processed from 200 microns to 5mm thickness, It is mostly used in refrigeration and automotive industries and in other products like gauges, protective headgear, luggage and more. (A&C Plastics, Inc, 2019)

2.2 Different types of Additives

Different additives have different functions and the manufacturer uses them in order to achieve the desired functions and to make the products more functional and to last longer. Some additives are antimicrobials, which helps in preventing deterioration of the plastic materials. This is mainly done to maintain hygiene for food packing as well as to prevent the mechanical properties

of plastics itself. Antistatic additives are those which are used to prevent to build up electric charges (Croda International Plc, 2019).

Antioxidants are mainly used to prevent the polymers from reacting with oxygens. This helps polymers to discoloration and to make polymers strong for longer time. Biodegradable additives help to biodegrade the polymers easily as it makes the polymers softer and more flexible. Heat stabilizers are those additives which are added to polymers during manufacturing process to prevent polymers from decomposition as the manufacturing processes as, polymers are processed in very high temperature. Internal lubricants are used or mixed with polymers to increase the melt flow of polymers as they make processing the polymers make easier((Zweifel, et al., 2009)

Light stabilizers are additives used in polymers to make safe from UV light. UV light can degrade the chemical properties of polymers and with the use of light stabilizers can help them in preventing chemical degradation of polymers. Colorants or pigments are used to add or create a color of polymers. The tiny particles are added in virgin or colorless polymers in order to get the desired color in polymers. Reinforcements in polymers are added to make the polymers to increase the strength and to improve stiffness as well as tensile strength of materials((Zweifel, et al., 2009).

Glass fibers are one of the additives that have been used in PLA. The main aim of adding glass fibers in PLA is to increase the strength and stiffness almost 10-40% compare to PLA without additives. The proprietary nucleation packages helps to keep the cost in control as they are easily available in standard and fast-cycle version which increased the crystallinity of polymers resulting high heat resistance. (NatureWorks, 2007)

Thermoplastic starch (TPS) after blending with PLA, helped to improved it's properties. Addition of 4% to 8% of Terraloy MB-90001A, (which is water clear melt strength), helped to increase pull force in extrusion process by nearly three to five times. Blending PLA with Polyhydroxy butyrate valerate (PHBV), helps to increase heat resistance of PLA, making possible it to process in higher heat. It also makes PLA to become durable for renewable. Bioloy002(is semi-crystalline alloy), additives used in PLA, contains 35% biobased carbon, helps to boosts the mechanical properties of PLA. (Plastics Technology, 2019)

2.3 PLA

Polylactic acid or polylactide commonly known as PLA is thermoplastic polymers which is mostly derived from plant starch like corn, sugar cane, or sugar cane beet, pulp and cassava. These are all raw materials for PLA and these raw materials are renewable biomass or resources. That is why PLA is also known as bioplastics as PLA are made out of renewable resources. The PLA has similar characteristics to other polymers like Polypropylene (PP), Polyethylene (PE) or Polystyrene (PS). There are mainly two ways of production of PLA. However, to make the cost efficient in production, PLA can be produced with the existing equipment that are originally designed to produce the plastics from petrochemical industry plastics (Nagarjan, et al., 2016).

2.3.1 Applications

PLA is also second most produced thermosetting bioplastics in the world. PLA has been used in many areas, mostly they are used to make plastic films, bottles, biodegradable medical devices like rods, plates and rods as they are expected to be biodegradable with in short period of time. PLA has special features of constricting in contact of heat, which makes them suitable for the use in shrink wrapping material. PLA is also used in 3D printing as PLA melt easily because of the low glass transition temperature. But they aren't suitable for holding hot drinks or liquids. There are many types of Polylactic acid like PLLA (Poly-L-Lactic Acid), PDLA (Poly-D-Lactic Acid) and PDLLA (Poly-DL-Lactic Acid). However, they have similar features as they are produced from in similar way and similar raw materials. (Creative Mechanism, 2019)

PLA is one of the polymers that is used in 3D printing. There are several reasons for PLA being used like PLA are inexpensive, PLA have low melting point (190-210) compare to other. The PLA is easy to work with, the quality of products printed using PLA are very good, while printing using PLA there is also not bad odor, and there is no warping in products. Getting many PLA blend in cheap price is also considered to be one of the advantages of using PLA as printing materials. Blends like matte white to wooded-filled spools cost around 20 to 40 euro each. PLA can also be found in different and many colors, making printed products vibrant and looking attractive. Nowadays, PLA blends have got a lot better in terms of durability. (ALL3DP, 2019)

2.3.2 Molecular structure

The molecular formula of Polylactic acid is $C_5H_8O_5$. The molecular formula of D and L-Lactide compound is $C_6H_8O_4$. The molecular weight of polylactic acid is 148.11g/mol and L-lactide is 144.12g/mol. These poly (D, L-lactic acid) is special copolymer which is composed of 2- hydroxypropanoyl and 2-hydroxycetyl units. This is actually copolymer macromolecule and also a polyester macromolecule. (PubChem, 2019)

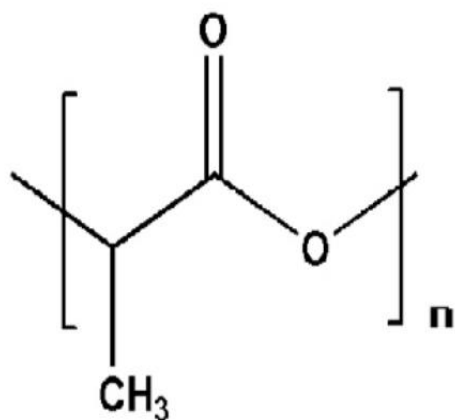


Figure 1 Molecular structure of Polylactide

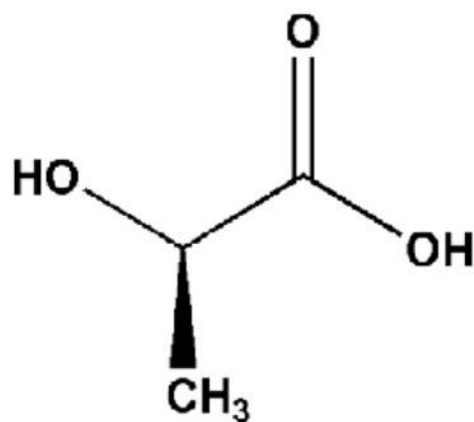


Figure 2 Molecular structure of D-Lactide

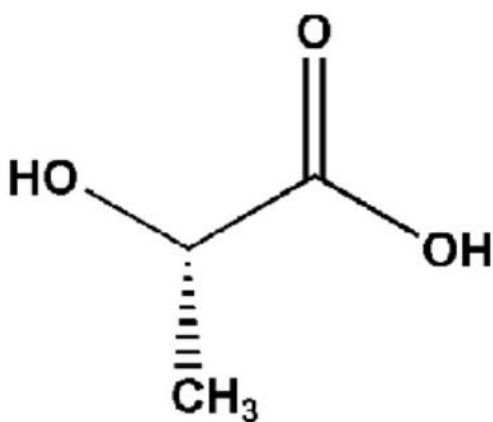


Figure 3 Molecular structure of L-Lactide (Cinelli et al., (2019)

2.4 General Manufacturing Process

Before manufacturing PLA, raw materials like corn starch, sugar beets are fermented to make lactide acid. As shown in figure 4, there are two ways of producing PLA. One way of producing PLA, which is also most common method, is to ring-opening of polymerization of lactide acid using catalyst as tin octoate in the solution or melt form or suspension form is also possible. This is also known as polymerization of lactide. Another method is the direct condensation of lactide acid, also known as condensation process of lactide. This method is like polymerization process. Condensation process is done with in temperature of 200°C because above this temperature the lactide become entropically enfavored. After this, the reaction produced one equivalent water for every condensation also known as esterification step. These waters are removed by using vacuum or by azeotropic distillation to drive the reaction during polycondensation process. Polymerization of racemic mixture of L- and D- lactide leads to the synthesis of d-lactide and l-lactide. Another method of manufacturing is to by making contact of lactide acid with a zeolite but the condensation reaction in this process in just one step and the temperature in this process is just under 100°C . (Hitachi Limited, 2019)

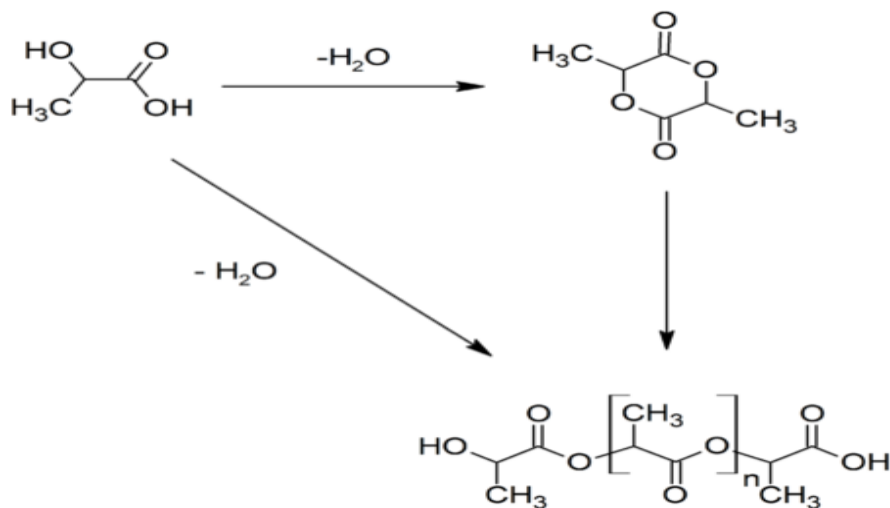


Figure 4 Manufacturing process (Phite Technology, 2020)

2.5 Extrusion

Plastic extrusion means to change the solid plastic into the desired shape for better production of usable products. In this process, the material is pushed through required die. There are different kinds of die used in extrusion process according to the needs and demands of industries like solid dies, hollow dies, monodies, semi-hollow dies etc. The extrusion machine used in industries are very big and difficult to handle, then those are in laboratory of school. Extruder has many important components like heater, water cooling, water bath, puller, feed, motor, screw, etc. In extrusion process, the extruder is turned on and desired temperature for heating zone is set and need to wait until the set temperature is reached. Then, raw materials that needs to be extrude are put in feed, these materials pass through the screw speed (rpm round per minute) and melted in heating zone. Then, these melted materials come out from die and reach into the cooling water. Then, the puller that pulls the filament is also set in specific speed according to speed of extruder. (Milacron, 2019)

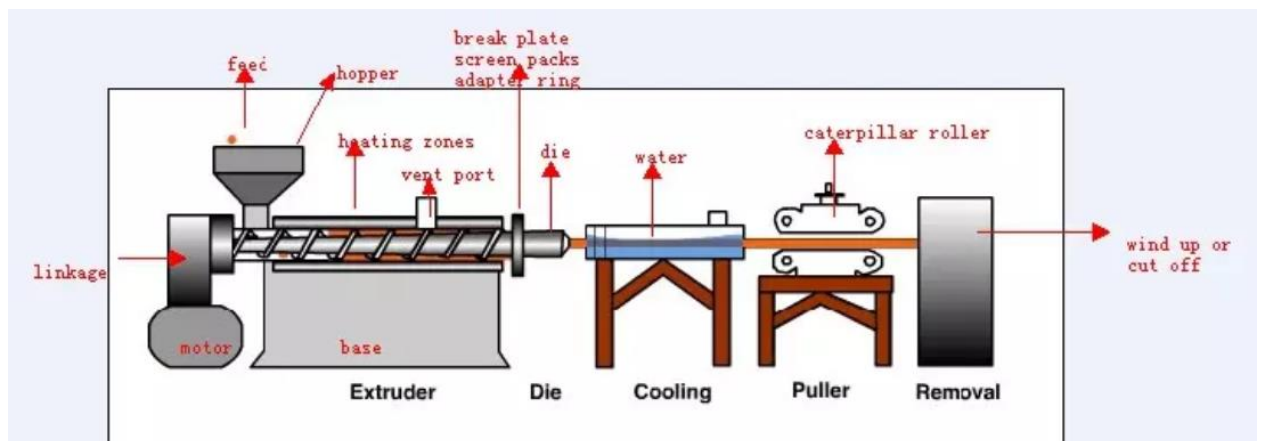


Figure 5 Schematic diagram of extruder

2.6 Injection Molding

Injection molding is the process of melting thermoplastic pellets and polymers, that are injected using certain pressure into a mold cavity, later mold is filled and solidifies into solid final product, which might not even need final finishing. The melting temperature in heaters in injection unit is always higher than that of the materials. The molds are usually made from using aluminum metal, giving advantage of saving valuable time while doing injection molding process in compare

to the molds made from steel, which takes longer time to cool down. Nowadays, the injection molding machine are mostly universal. This means, the molds can be changed according to the needs of producers. In the market, there are different types of molds and different types of injection molding process are used. Injection Blow molding is one of the most used process. Extrusion blow molding, injection stretch blow molding are also widely used.

Polymer pellets are loaded onto the barrel, where these pellets are melted down by the heaters, the temperature are always set up higher than the melting point of polymers. Then, molten polymers are compressed and are injected into the mold's runner system or nozzle with the help of screw, speed of screw is usually set in round per minute. The ejector pins or movable platens help to remove the ready parts and are collected in loading bin. These samples or products are collected and shipped thereafter. (ProtoLabs Ltd, 2019)

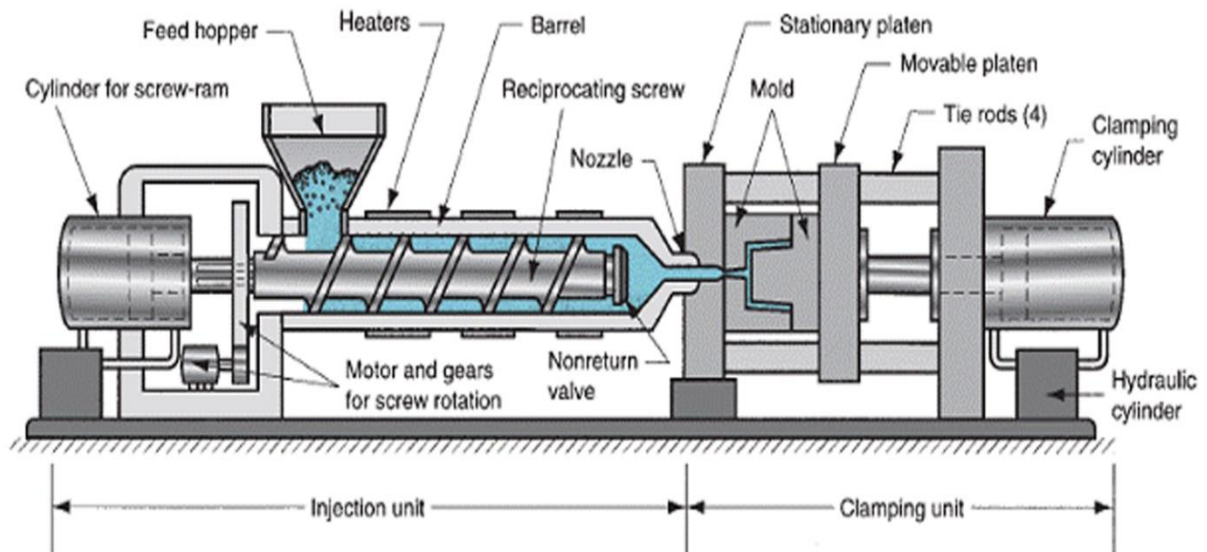


Figure 6 Injection molding machine

3 MATERIAL TESTING

Different types of material testing methods were used to test the samples. Here, literature review of those testing method is discussed. Research were done about these methods in advance to get the enough knowledge and proper way to perform the testing successfully. The methods like Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC, Melt Flow Index (MFI) and tensile testing are discussed below.

3.1 FTIR

Fourier Transform Infrared Spectroscopy also known as FTIR, or mostly known as infrared spectroscopy, is being developed as one of the most used and important techniques to find out about the chemical groups of materials. Infrared spectroscopy can be performed in all solid, liquid or gas materials. Because of this ability, FTIR has provided a lot of opportunities in the field for different polymers and additive characterization. With the help of this, different materials can be analyzed in both quantitative analysis and qualitative analysis very fast, with relatively very low instrument cost.

Table 1 Interactions of matter with electromagnetic radiation

Electromagnetic Radiation	Types of Interactions
Near IR($0.7\text{-}2\mu\text{m}$ or $13300\text{-}4000\text{ cm}^{-1}$)	Molecular vibrations
Mid IR($2\text{-}25\text{ }\mu\text{m}$ or $4000\text{-}400\text{ cm}^{-1}$)	Molecular rotations
Far IR($25\text{-}1000\text{ }\mu\text{m}$ or $400\text{-}20\text{ cm}^{-1}$)	Molecular rotations

In the beginning of 1950s, the first infrared spectroscopy instrument or a dispersive infrared spectrophotometer was successfully introduced. However, the first Fourier transform Infrared Spectrophotometer was introduced only towards the end of 1960s and at that time there were some limitations and the production costs were very high. It was only possible during mid-1980s to introduce a high technology spectrophotometer in good price and this time, there were more advantages over the disadvantages of the instruments like, reduction in the time to process the spectrum, increase in the resolution and sensitivity(higher signal, noise ratio). This leads to

development of ATR known as Attenuated Total Reflectance, Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), and PAS (Photoacoustic Spectroscopy). (Naranjo, et al., 2008)

3.1.1 Attenuated Total Reflectance (ATR)

In this technique, the IR infrared radiation is emitted internally by the sources, this IR radiation is reflected in a very high refractive index crystal. Some of these evanescent waves or IR radiation interacts with the sample which is in direct contact of crystals. After this, the surface spectrum of sample is collected. The wavelength of incident radiation also known as penetration depth, the angle of incident radiation, the refractive index of crystal as well as sample can be measured with the help of equation. However, the penetration depth is affected by the wavelength and refractive index of crystal. Higher the wavelength and refractive index of crystal, higher the penetration depth and vice-versa. For ATR, the penetration depth is always below one micrometer for refractive index of ATR crystal at mid-IR wavelength. (Naranjo, et al., 2008)

3.1.2 FTIR Spectrophotometer

Infrared Spectrometer or Infrared Spectrophotometer or simply FTIR spectrophotometer, is a device that measures the absorption spectrum of a sample as shown in Fig. 4.1.1. In this device, the main parts are as follows: source (Infrared), mirrors (fixed or movable), beam splitter, sample compartment (where sample is placed), detector, and processing unit. IR source is that component, which produces wide spectra of infrared radiation, which interacts with the sample. Usually, the IR source is the refractory material, which produces IR radiation, when heated in a very high temperature. For heating purpose, metallic filament are used, a nickel chromium is mostly used in this device. The IR radiation is result of high temperature. While using this device, the temperature must be carefully controlled. Sudden decrease in the temperature cause decaying of IR energy (Naranjo, et al., 2008).

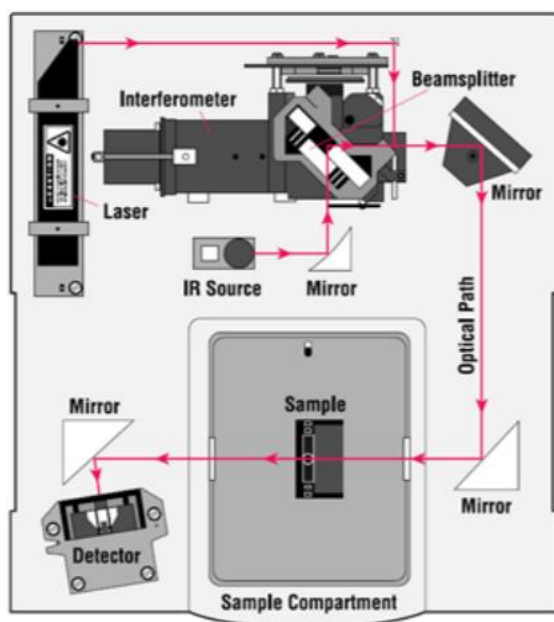


Figure 7 Annotated picture of Nicolet 6700 FT-IR

Different IR sources are used like: GLOBAR, NERNST, EVER Glo, Tungsten filament etc. Beam splitters are almost similar like mirrors, but they are semitransparent mirror. Here, interference phenomenon take place. Fourier Transform calculate and keep record of all wavelength of IR radiation in interferogram. After the radiation interacts with the sample, the interferogram is decoded into a absorption spectrum by Fourier Transform.

There are many beam splitters used like: Quartz, CaF₂, KBr, Ge on KBr, Ge on Csl and MYLR. The detector is very important component of spectrophotometer, which notes the absorption of IR spectra of sample after the interaction of IR radiation. The most used detectors are: DTGS/Csl, DTGS Polyethylene, MCT, and DTGS/KBr. FTIR can be used for testing both solid and liquid samples. For solid samples, they are grounded finely into powder using transparent powder however, liquid samples can be test by direct transmission of IR radiation. (Newport Corporation, 2019)

3.2 MFI

Melt flow Index also known as MFI is a measure of the resistance to viscosity of the molten polymer or sample in a specific temperature when a given force is applied for certain period or

fixed time. Usually, MFI means measuring melt flow of thermoplastic material or sample for the period of ten minutes and temperature of 210°C. To measure melt flow, melt flow indexer is used. MFI helps us to find out the rheological properties of sample which means flow properties and deformation of sample when certain amount of force is applied for specific time periods.

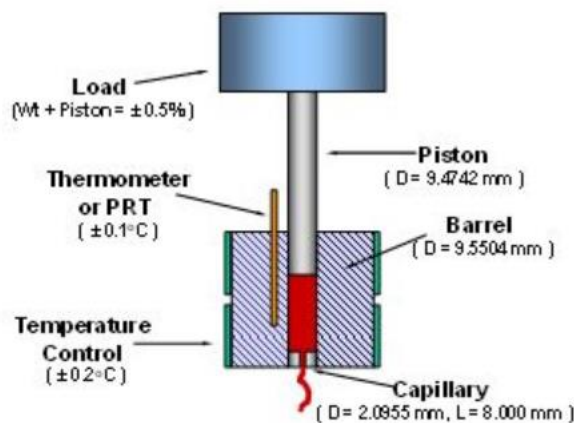


Figure 8 Annotated picture of capillary viscometer

The Melt Flow Indexer is a device used to measure the melt flow. There are different devices used in the market like extrusion plastometer, capillary viscometer, rotational rheometry and extensional or elongational rheometry. Capillary viscometer is most of the simplest and common device to measure viscosity of sample, that's why this device had been used in my experiment. This device had components like capillary or straight tube, pressure driven piston (which helps to flow sample), thermometer to measure temperature and temperature controller. As the piston is driven using load and pressure, there is maximum shear rate, strain rate or velocity gradient at the wall or barrel of this device, but zero in center of the flow, which helps to get homogeneous flow of sample. The main reason of being widely used of capillary viscometer is that it is very easy to operate and relatively low cost for production and provides the best rheological values of samples. (ScienceDirect, 2019)

3.3 DSC

Differential Scanning Calorimetry is also known as DSC, is a thermal technique that measures the amount of heat required to increase the temperature of sample in a specified time. It measures the actual difference of heat required to increase the temperature of sample from one point to higher point. During this process, DSC helps to find out whether the sample absorbs or emits heat. DSC is mostly used to find out melting temperature, glass transition temperature of sample, and crystallization temperature of sample. Glass transition temperature (T_g) is the temperature where the sample turns into gas if heated and turns into solid if cooled down. Melting temperature (T_m) is thermodynamic transition of sample in which the sample starts to melt and flow. Crystallization temperature (T_c) is the temperature of sample in which the semi crystalline sample starts to form crystalline. It is always between glass transition temperature and melting temperature.

Table 2 Thermal properties(Nature Works)

Thermal	Nominal ValueUnit	Test Method
Deflection Temperature Under Load		
66 psi, Unannealed	111 to 208°F	ASTM D648
66 psi, Unannealed	122 to 248°F	ISO 75-2/B
Glass Transition Temperature	134 to 136°F	ASTM E1356, DSC
Vicat Softening Temperature	130 to 141°F	ISO 306
Melting Temperature	309 to 340°F	
Peak Crystallization Temperature (DSC)	266 to 345°F	ASTM D3418

From the above table, the thermal properties and thermal data of virgin PLA is known. The melting temperature is 309 to 240⁰ F (154 to 171⁰C), glass transition temperature is 134 to 136⁰ F (57 to 58⁰ C) whereas the peak crystallization temperature is 266 to 345⁰F(130 to 174⁰ C). Vicat softening temperature is 130 to 141⁰F (54.5 to 60.5⁰C).

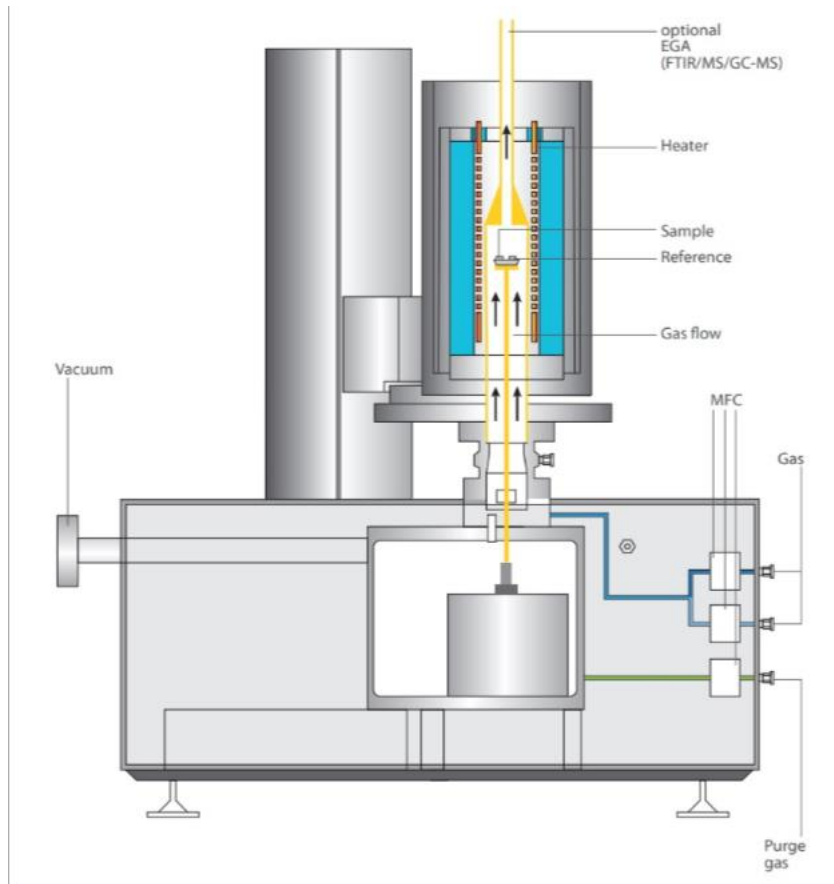


Figure 9 DSC PT1600

Differential Scanning Calorimeters are devices used for DSC. In the market, there are many calorimeters used. In the figure no.3, schematic diagram of DSC PT 1600 is shown. There are many important components of this devices like heater (to provide heating), reference, gas flow, vacuum and purge gas (Naranjo, et al., 2008).

3.4 Tensile Testing

Tensile testing is the test that is performed on the materials to find out their mechanical properties. For this, stress and strain test is performed on the samples. Stress is the material property of a material that exhibits the amount of force exerted by a particle of the material to its adjacent particle of the same material. The stress can also be simply defined as the ratio of force applied over cross – sectional area of the material. Mathematically,

$$\text{Stress} = \text{Force applied} \div \text{Cross – sectional area} \quad (1)$$

The SI unit of stress is Pascal (Pa) but it is generally expressed in MegaPascal (MPa).

Strain is the deformation of the material on application of external force on it. Simply, Strain is the ratio of change in length over original length. Mathematically,

$$\text{Strain} = \frac{\text{Change in length } (x)}{\text{Original Length } (L)} \quad (2)$$

As strain is the ratio of lengths, it is unitless.

Hooke's law holds true for some materials under certain loading condition and is not a universal law for all the materials. It states that the strain generated in a material is directly proportional to the stress applied along the direction of cross – sectional area.

$$\text{Stress applied} \propto \text{Strain Generated} \quad (3)$$

$$\text{Stress applied} = E \times \text{Strain generated} \quad (4)$$

Where E is the proportional constant and is the material property known as modulus of elasticity. Simply, it is the ratio of stress over strain. As strain is unitless, the unit of E is same as the unit of stress (MPa, or more popularly GPa).

From equations (3), (4), and (5), we obtain a new equation for modulus of elasticity

$$E = \frac{\text{Force applied} \times \text{Original Length}}{\text{Cross – Sectional area} \times \text{Change in length}} \quad (5)$$

$$\text{or, } \frac{F \times L}{A \times x} \quad (6)$$

Bending modulus is the rigidity of the material or the tendency to resist bending in the presence of external as well as internal loading conditions. It is simply the ratio of stress over strain but can be calculated in many ways. Some of them are listed below:

$$E_{\text{bend}} = E = \frac{F \times L}{A \times x} \quad (7)$$

$$E_{\text{bend}} = \frac{12}{d_{11} \times t^3} \quad (8)$$

Where, d_{11} = Laminate Compliance Matrix

t = thickness of the lamina

$$E_{\text{bend}} = \frac{\Delta \delta}{\Delta x} \quad (9)$$

$$\text{Where, } \Delta \delta = \text{Stress} \quad (10)$$

$$\Delta x = \text{Strain} \quad (11)$$

Table 3 Mechanical data

Mechanical	Nominal ValueUnit	Test Method
Tensile Modulus		
73°F	129000 to 529000psi	ASTM D638
73°F	416000 to 519000psi	ISO 527-2
Tensile Strength		
Yield, 73°F	8990 to 9040psi	ASTM D638
Yield, 73°F	2250 to 10400psi	ISO 527-2
Break, 73°F	5550 to 8420psi	ASTM D638
Break, 73°F	2000 to 10200psi	ISO 527-2
73°F	2560 to 9310psi	ASTM D638
73°F	6530 to 9430psi	ISO 527-2
Tensile Elongation		
Yield, 73°F	9,8 to 10%	ASTM D638
Break, 73°F	0,50 to 19%	ASTM D638
Break, 73°F	1,0 to 12%	ISO 527-2
Flexural Modulus		
73°F	330000 to 652000psi	ASTM D790
73°F	44200 to 1,38E+6psi	ISO 178
Flexural Strength		
73°F	8360 to 15800psi	ASTM D790
73°F	1310 to 16000psi	ISO 178

From the above table, the mechanical data and information of virgin PLA in normal temperature can be known. There are several types of testing methods and data are given in two standard testing methods. ISO and ASTM are most common standard testing methods. Tensile modulus is 129000 to 529000 psi (8894 to 36473 Pa) according to ASTM D638 and according to ISO 527-2, tensile modulus is 416000 to 519000 psi (28682 to 35783 Pa). According to ASTM D638, tensile strength yield is 8990 to 9040 psi (619.8 to 623 Pa) and tensile strength break is 5550 to 8420 psi (382 to 580Pa). According to ISO 527-2, tensile strength yield is 2250 to 10400 psi (155 to 717 Pa) and tensile strength break is 2000 to 10200 psi (138 to 703 Pa).



Figure 10 5 kN Testometric machine

Testometric machine is used to find out mechanical properties of samples. This machine finds out the stress and strain of materials. After the samples are placed, force is applied in specific rate of time, after that stress and strain curve can be seen on the screen of computer with the help of special software that comes with this testometric machine. (Testometric Co. Ltd, 2019)

4 METHODOLOGY



4.1 Material and Equipment

The materials (3D printed failed parts) supplier unknown were used as our main materials. Because of this, it was unable to identify what additives and other material were added in our samples (PLA). Pure(virgin) PLA (supplier Prenta) were also used in testing. These pure PLA was used in injection molding, FTIR, MFI an DSC.

For this thesis, all the equipment used, were from Arcada's chemistry lab and Arcada's production lab.

- Single Screw Extruder, Eco Ex model extruder made by KFM
- Rapid Granulator series 15
- Pelletizer, made by KFM
- Melt Flow Indexer by Noselab ATS SM
- AVR3 G Drying machine by Labotek
- Testometric M350-5CT
- DSC 4000 by PerkinElmer
- Spectrophotometer V-670 by Jasco

4.2 Experimental Part

At first all the materials (3D printed failed parts), were separated according to their respective colors. These failed parts were collected in long time, almost with in the time frame of two years. These failed parts were separated into three different colors, white, black and red. Enough materials of white and black colors were collected but red colors parts were collected in less amount, which might not be enough to make a sample for mechanical testing.



Figure 11 3d printed failed parts(red)



Figure 12 3D printed failed parts(white)



Figure 13 3D printed failed parts(black)

All these parts were collected in separated boxes and measured carefully. After, taking measurement of the weight of these parts, the following information were known:

Table 4 Failed parts and their weight

3D printed failed parts(colors)	Weight(g)
Red	780
White	7,418
Black	6,841

These collected parts were then carefully shredded using shredder. Shredding process was done separately for the each of the different colors. Before doing shredding, collected materials were broken down into smaller pieces so, it would easily pass down through the feeder zone and reached to shaft and blades where there are rotatory cutter and stationary cutter. Frequent opening of the shredder was needed during the process and cleaning were done as the materials got stuck while performing shredding. The screening net were cleaned as well. The shredded materials were collected later in dryer bags as shown in figure 8 and 9.



Figure 14 Shredded black PLA



Figure 15 Shredded white PLA

Table 5 Shredded materials

Shredded materials	Weight(g)
Red	768
White	6811
Black	6449

After shredded materials were carefully measured, it was found out that some materials were lost in the shredding process as shown in the table above. The main reason behind this was cleaning of shredder machine when it got stuck. Some materials were lost while collecting the shredded materials.

All these shredded materials were dried up using dryer in the lab using temperature of 60°C for 6 hours as given parameters for the PLA by the manufacturer (NatureWorks, 2005). These PLA materials always absorbs the moisture in it so it's better to dry the materials before performing

extrusion process. If the materials are not dried up properly, it effects the quality of the filament. While performing extrusion process of white filaments there was some sound coming from the feeder as this material was not properly dried up and then shredded white PLA were put again to dryer and extrusion was performed next day and this time filaments were of good quality then previous ones and the sound was a lot less.

Table 6 Temperature parameters used in extrusion

Zones	1	2	3	4	5	6
Temperature	190	190	190	190	190	

The temperature parameters as shown in above figure and the screw speed of 50 rpm(rotation per minute) were used in the extrusion process for all the different PLA materials. The temperature of zone six was not important in this experiment as single screw was being used in extrusion. It was known that the screw speed is a most important part of this extrusion process. If the speed is too low, then materials will stay in heating chamber for long time resulting in degradation if filaments. If it's too fast, then materials won't have enough time to melt down properly in heating chambers resulting in quality of filaments.

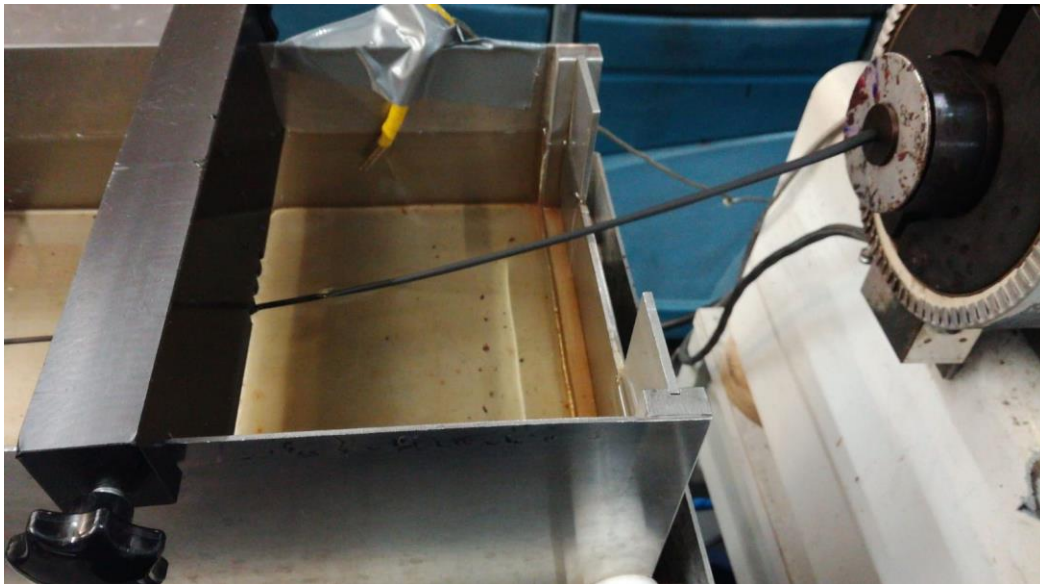


Figure 16 Filaments cooling down with cooling water

While doing this, cooling bath water was used as well, as it makes to control the overheating of heating chambers. Cooling water temperature of 30°C was used to cool down the filament and puller to pull the filaments. The temperature of this cooling water was constantly monitored by using laser thermometer gun and sensor as well.

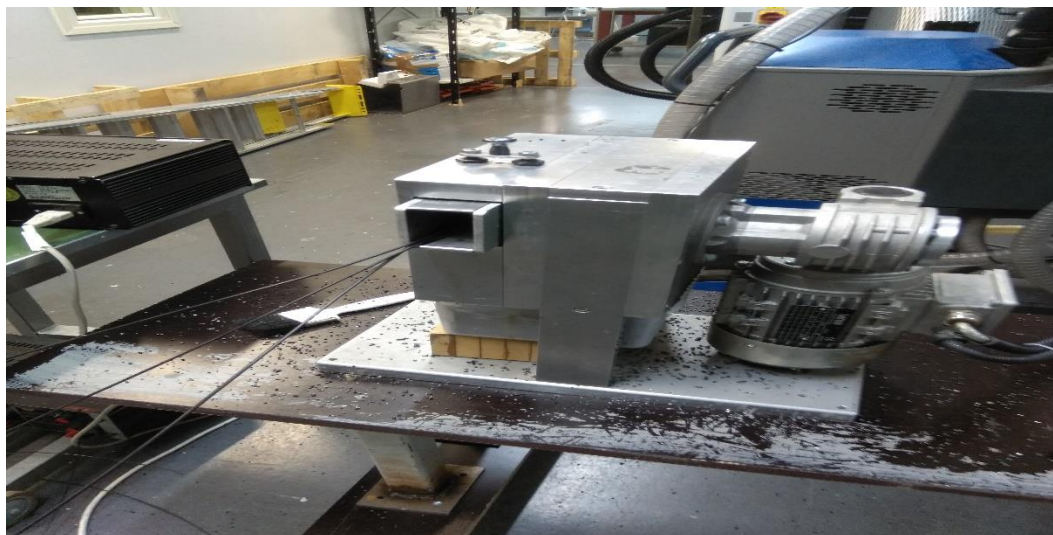


Figure 17 Pelletizing the filaments

The filaments produced from extrusion were pelletized using pelletizer. The speed for the blade was set 10 rpm using same extrusion machine. Pelletizing filaments was difficult to perform as the filaments were frequently stuck and stopping of pelletizer was needed to open and clean the pelletizer. Pellets were collected in bag.

Table 7 Pellets and their respective weight

Pellets	Weight(g)
Red	296.3g
White	1 st bag(697g) 2 nd bag(1403g)
Black	1 st bag(723g) 2 nd bag(1478g)

The weight of the pellets was measured and found out be as mentioned in the table above. As the first extrusion was not successful of the white materials, they were done two times and

filaments were collected differently and separately pelletized. The first bag contained the pellets that were collected first time and the second bag contained the pellets of successful extrusions. Black filaments were pelletized in two different days and collected separately.

4.3 Testing

After preparing samples successfully, they were tested using different testing methods like FTIR, DSC, MFI and tensile testing.



Figure 18 FTIR of red

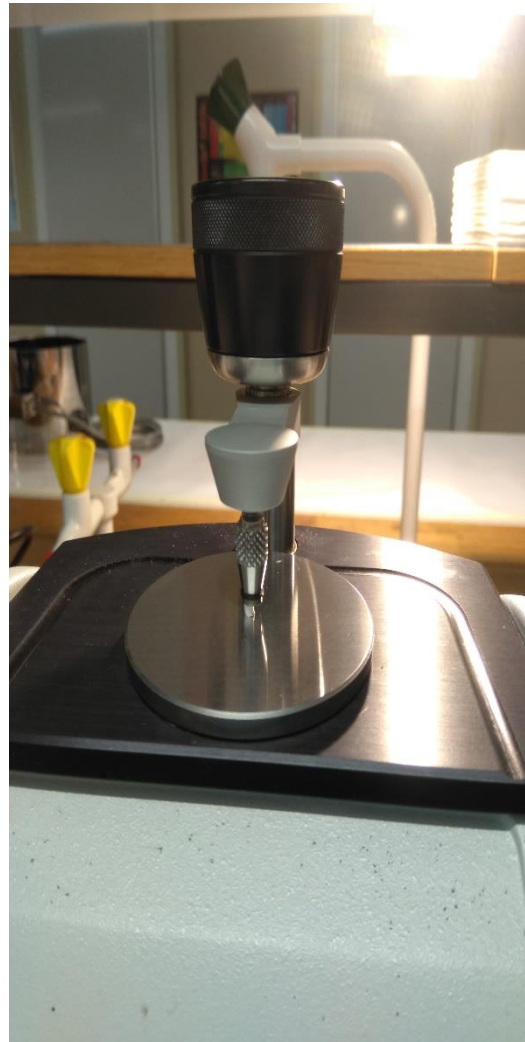


Figure 19 FTIR of white sample



Figure 20 FTIR of black sample

Attenuated Total Reflection FTIR spectroscopy was performed on all three colored samples and virgin PLA sample as well. Several samples were tested and the three spectra that were similar were taken for further analysis. Proper cleaning of device was done with iso propanol. The crystal was cleaned properly, and the forceps used to handle sample was cleaned as well. Proper gloves were used while handling samples as the device can detect very small contaminants. The results can be affected by the human breathe and air that's why before collecting spectra of sample, data were collected of background as well.

MFI (Melt Flow Index) of all different color samples were performed using ISO standard 1133. The standard die of normal length 8 mm and nominal bore diameter of 2.095mm was used. The temperature of 210⁰C was set up during these tests. The external load of 2.16 kg was added on piston. The extrudate cut off time interval was determined using guidelines for experimental parameters however, the cut off interval time for some samples were adjusted. To achieve this, the test on same colored sample was conducted repeatedly and several times to improve the accuracy as well to get the correct sizes samples. The cut off interval were 8sec, 9sec, 6sec, and 5 sec for

virgin(pure) PLA, black, red and white pellets respectively. The samples were dried up before conducting tests to remove air bubbles or moisture, which increases the accuracy of the test.

The extrudates were carefully measured using Vernier caliper(scale) and making sure that extrudates were of length from 10mm to 20 mm. Three best samples were collected, and their mass were weighted, and their average mass was calculated. While performing the tests proper cleaning of cylinder and die were done using cotton cloth. This is important because remaining melted pellets in cylinder of previous test can affects the next test. During these tests, proper standard guidelines and experimental were followed. Proper heat resistance gloves were used to handle the hot die and rod.

Injection Molding was used to prepare the samples for tensile testing. This process was very difficult to perform as the technical data sheet for recycled PLA pellets were unable to find. However, technical data sheet for virgin PLA was available from suppliers (Naturework is biggest supplier of PLA) and in internet as well. To find out the correct parameters was difficult and injection molding was performed several times, adjusting parameters each time. After several attempts, enough samples were molded that were good to perform tensile testing. Only virgin PLA, white and black pellets were injection molded to make samples for tensile testing, this was done as there were not enough red pellets to make samples using injection molding.

Table 8 Temperature profile and parameters for Injection molding

Melt temperature	210 ⁰ C
Feed throat	24 ⁰ C
Zone 1(Feed Temperature)	205 ⁰ C
Zone 2(Compression Section)	215 ⁰ C
Zone 3(Metering Section)	220 ⁰ C

Nozzle	225 ⁰ C
Mold	55 ⁰ C
Screw speed(rpm)	30
Back pressure(bar)	10
Mold Shrinkage	0.004in/in

Tensile Testing of five samples of each color, white and black were done. The maximum stroke used was 100 mm and 5kN force cell. 100 mm is the speed for moving upper clamps of the machine. The samples were carefully measured and had dimensions of 3.31mm thickness, width of 13.24mm and length of 400mm. Specimens for tensile test were obtained from injection molding.



Figure 21 Tensile testing of specimen

The specimens were placed in between lower and upper clamps. The machine is controlled by Win software connected to the computer and as the test is started, the upper clamp slowly starts to move upward with the set speed and force. While moving upward, the specimen broke as it could not bear force. Then, the stress and strain curve is obtained with the help of software in computer.

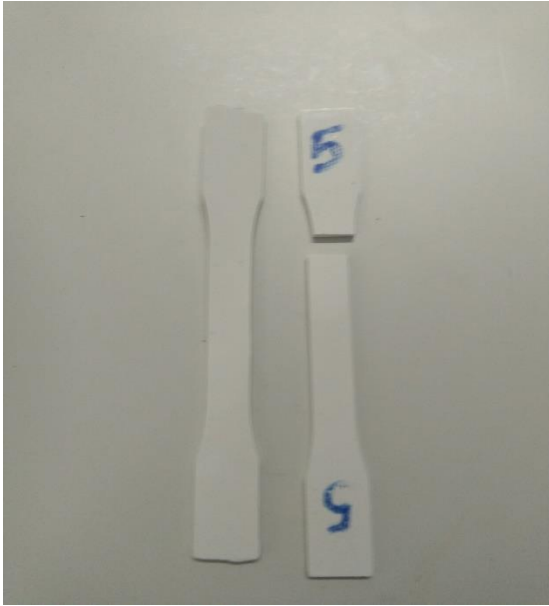


Figure 22 White sample after tensile testing



Figure 23 Black sample after tensile testing

Fig 13 and fig 14 shows the broken samples after injection molding. PLA is non elastic, so it tends to break down after certain force is applied and after reaching its breaking point from ultimate tensile strength point.

DSC tests were performed on all red, black, white and virgin(pure) samples and the results were saved properly.

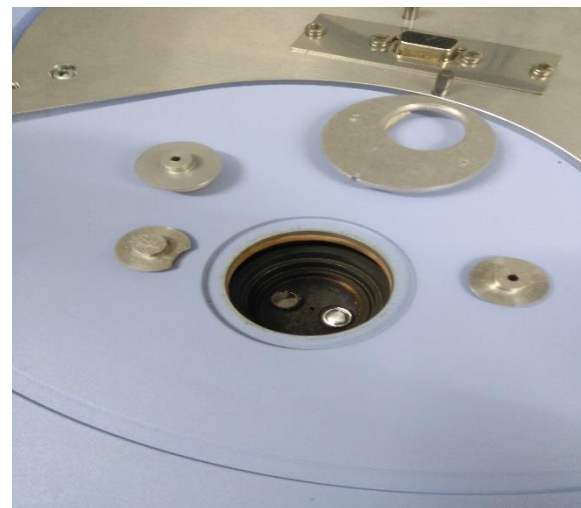
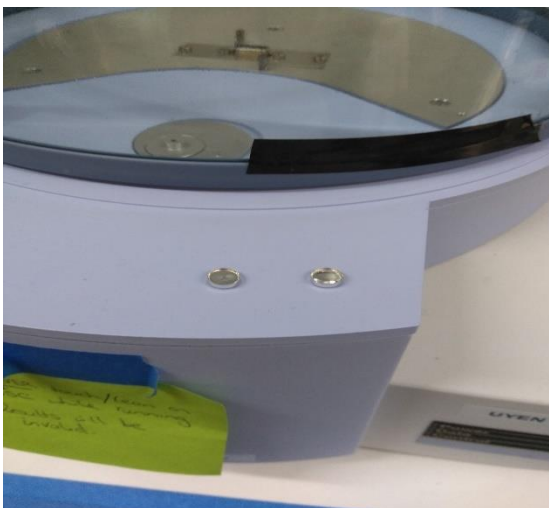


Figure 24 Sample preparation and placing inside machine

DSC tests were performed using Perkin-Elmer DSC machine. The samples were cut down into very small pieces, weighing 6-9 mg. The samples were first heated to 200⁰C, to remove all the thermal history of samples, which would help to get right results. After, that temperature was decreased to 12⁰C and again heated up to 200⁰C at the rate of 10⁰C per minute. While conducting the test, the nitrogen gas flow was set to 20 mL/min. During the test, the glass transition temperature (t_g), crystallinity of sample and melting point were calculated from endothermic curve that were got from Pyris software.

Samples were broken down or cut into smaller pieces and measured properly. These small pellets were stored in plate covered with lid and put inside the machine. During the test, continuous nitrogen gas flow was checked. The temperatures at both 200⁰C and 12⁰C were hold for one minute for more stabilized temperature because sudden change in temperature can provide a false curve.

5 RESULTS

The results were obtained from different testing methods. The results are discussed below. The results achieved were almost similar as hoped.

5.1 FTIR

The FTIR spectra of samples were obtained with the help of OMNIC software installed in computer which was connected to the ATR Spectrophotometer. Before performing test, samples were dried for 6 hours with temperature of 60⁰C using dryer. More than four and five samples of each color PLA were examined, and spectra were collected. Infrared spectra between 4000 to 500

cm were scanned, in total of 12 scans were performed for one sample.

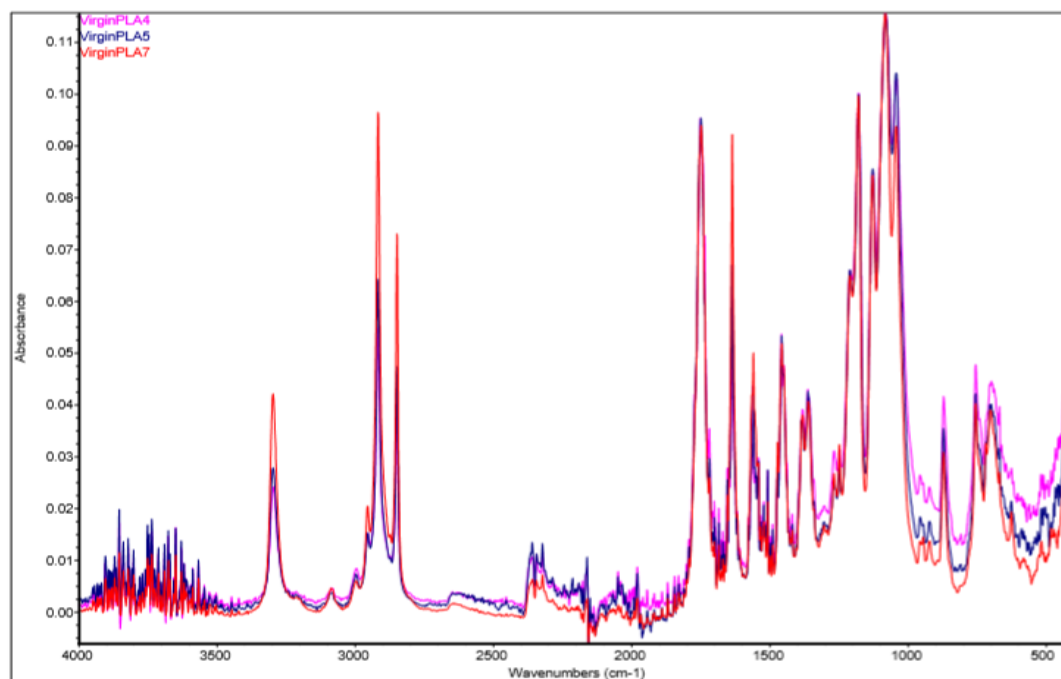


Figure 25 Spectra of pure PLA

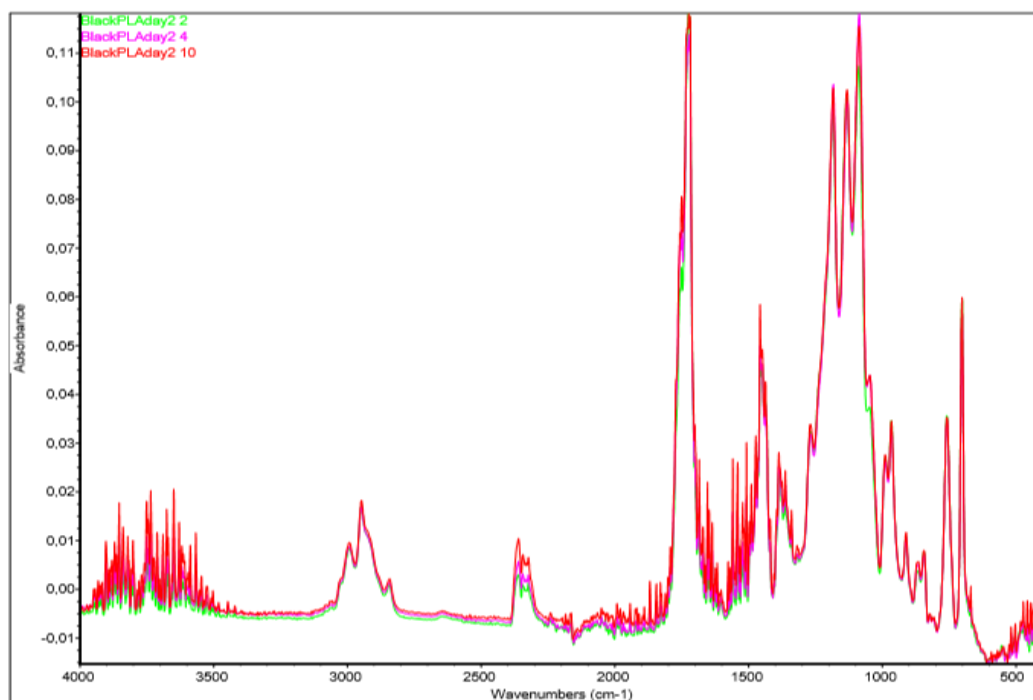


Figure 26 Spectra of Black samples (PLA)

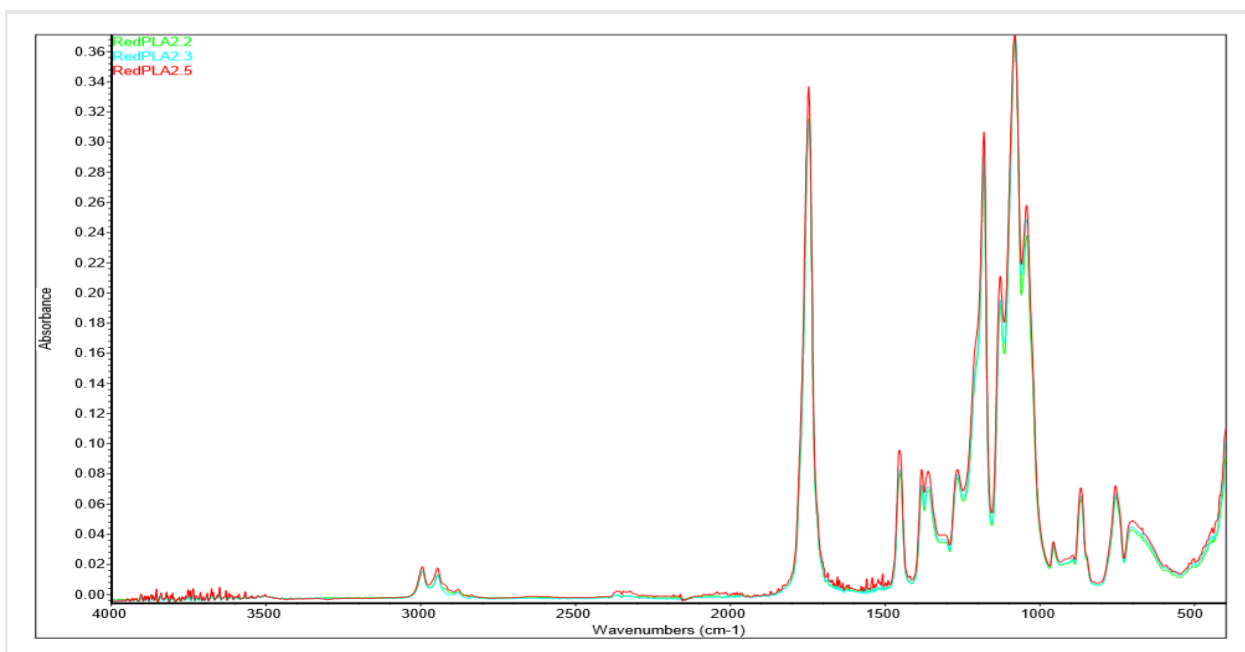


Figure 27 Spectra of red samples (PLA)

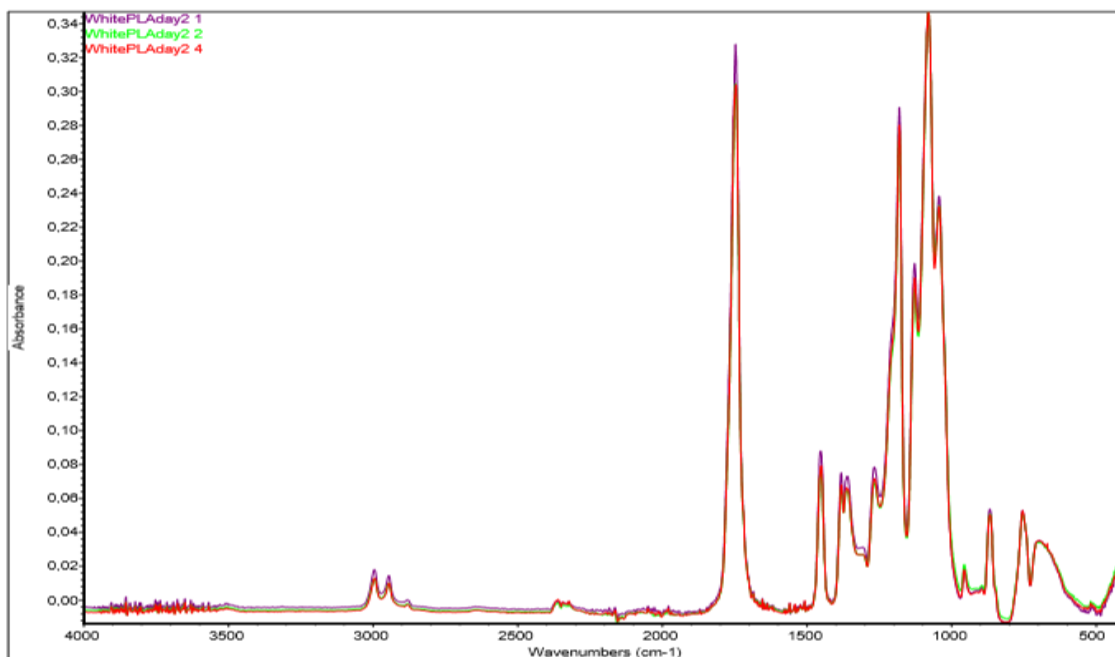


Figure 28 Spectra of white samples (PLA)

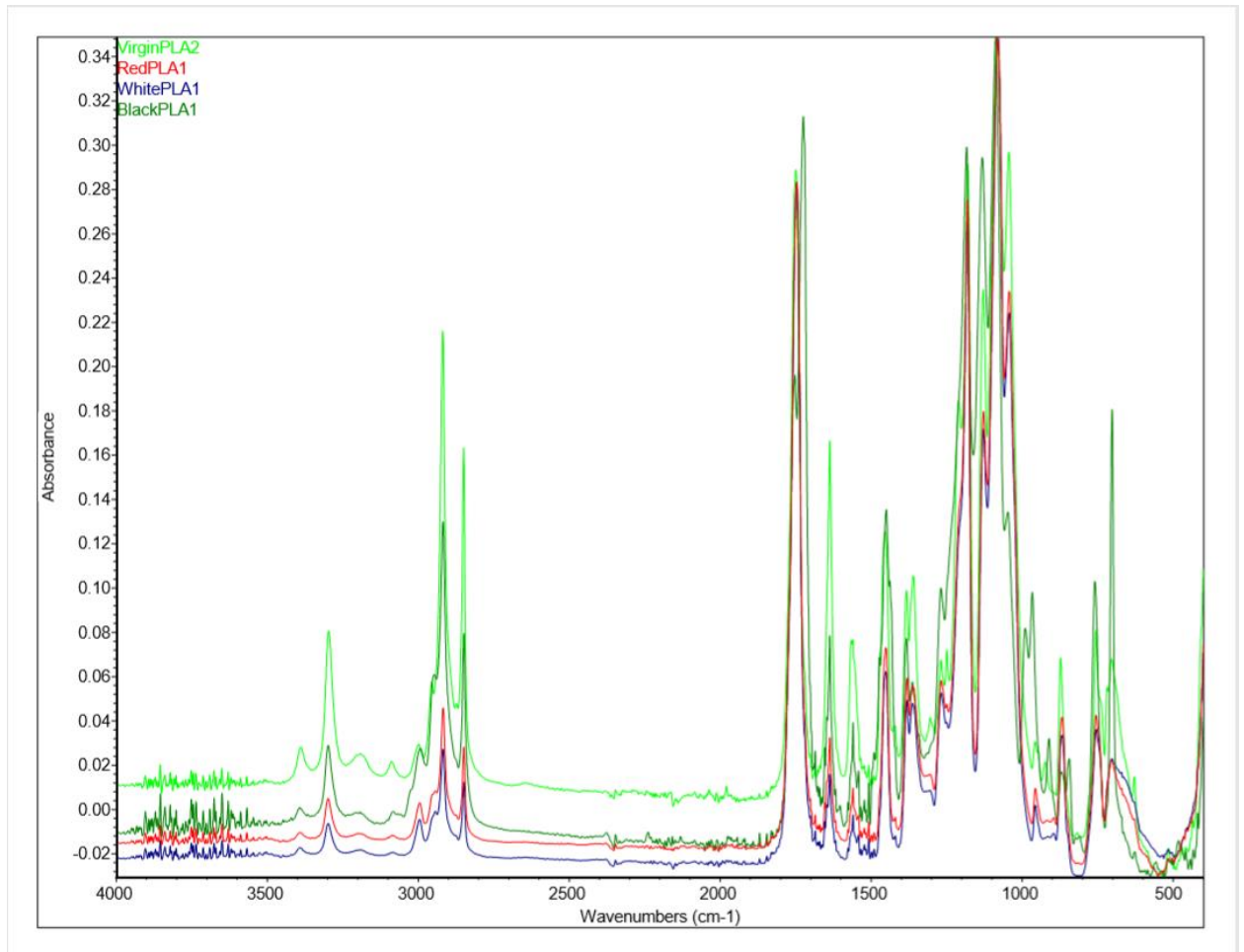


Figure 29 All PLA Compare

5.2 MFI

The melt flow rate for all the samples were done and got the results as expected except for virgin PLA. The formula used to calculate the Melt flow rate is given below:

$$\text{Melt Flow Rate(MFR)} = (600 * m) \div t$$

12

Where

600 is the factor used to convert grams per second into grams per min(600s);

M is the average mass of the cut-offs in grams;

t is the cut-off interval time in seconds;

Samples	Average mass(g)	Cut-off interval
Virgin(Pure) PLA	0.13	8
Black	0.1	9
Red	0.1	6
White	0.1	5

Calculation of MFR was done according to the given formula, as mentioned above;

MFR of virgin(pure) PLA sample=9.75g/10 min

MFR of black PLA sample=6.6g/10 min

MFR of red PLA sample=10g/10 min

MFR of white PLA sample= 12g/10 min

5.3 Tensile Testing

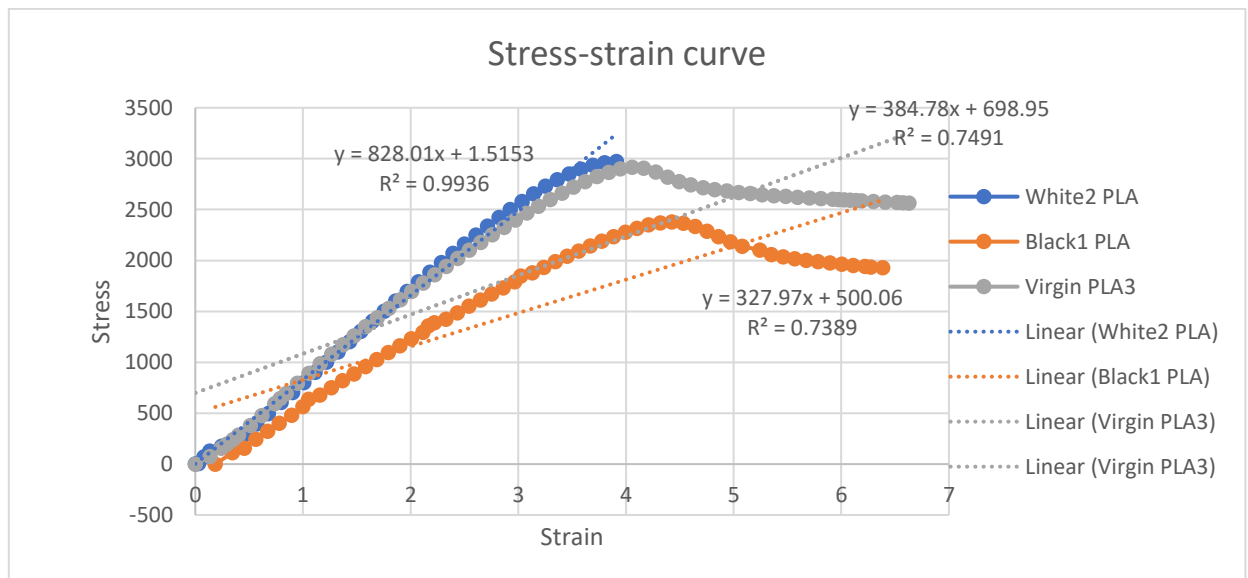


Figure 30 Stress-strain curve1

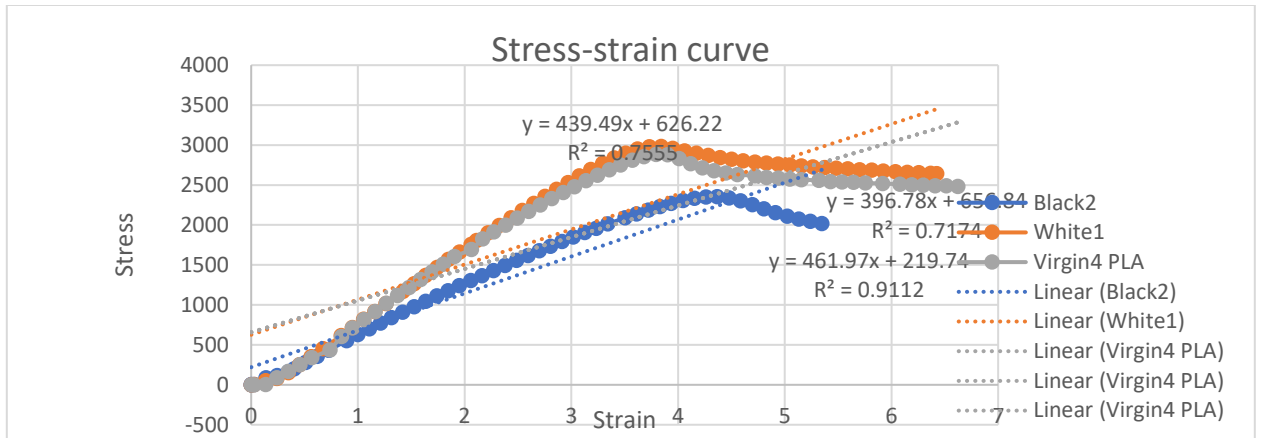


Figure 31 Stress-strain curve2

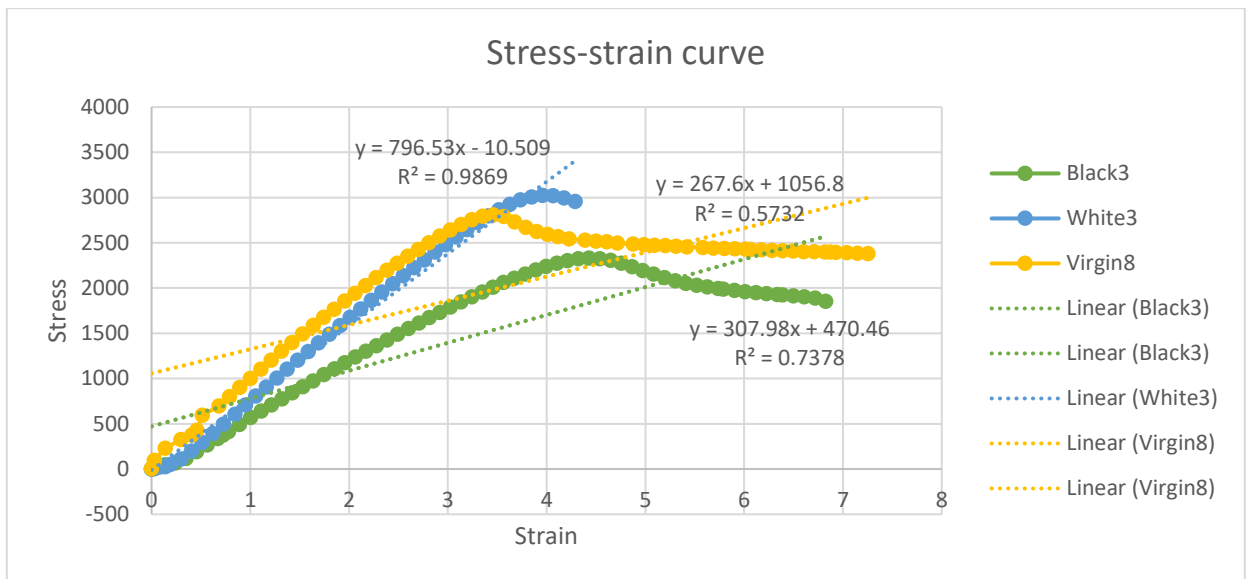


Figure 32 Stress-strain curve3

The tensile tests were performed, and the data of these test were collected in excel format and later on developed into curve in excel file. The stress-strain curve of all samples were compared as shown in figure 23.

5.4 DSC

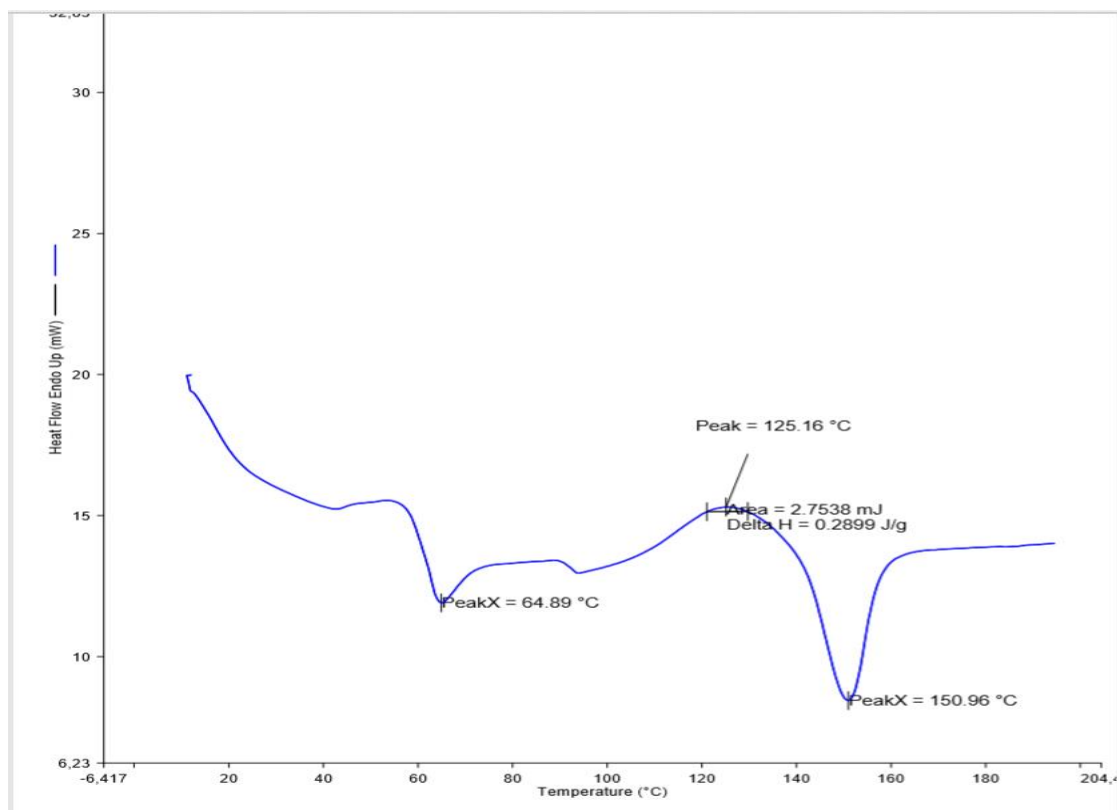


Figure 33 DSC curve of virgin(pure) PLA

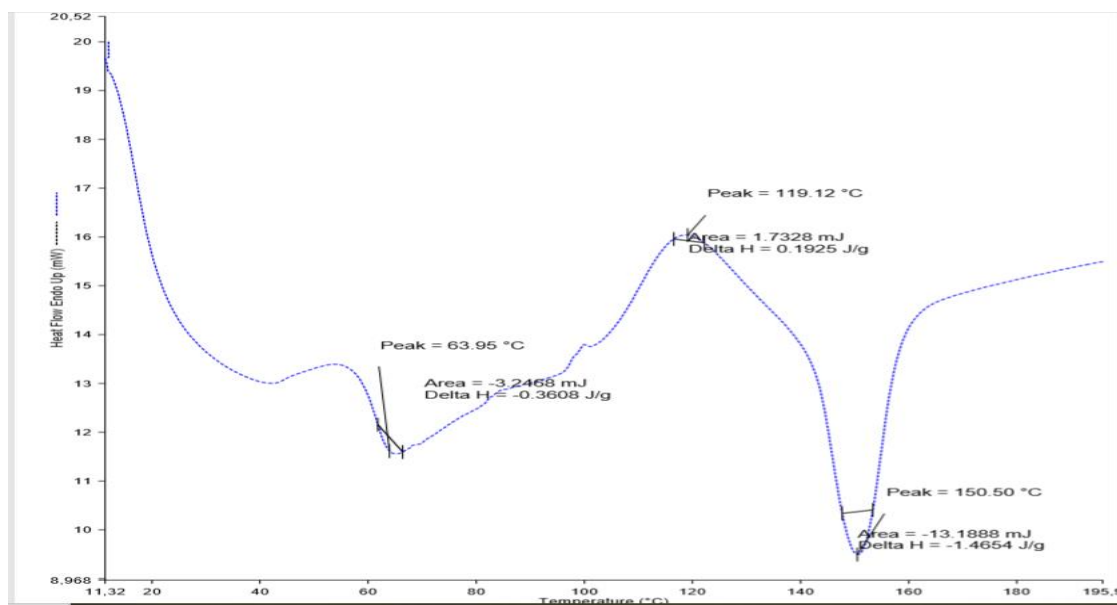


Figure 34 DSC curve of white PLA

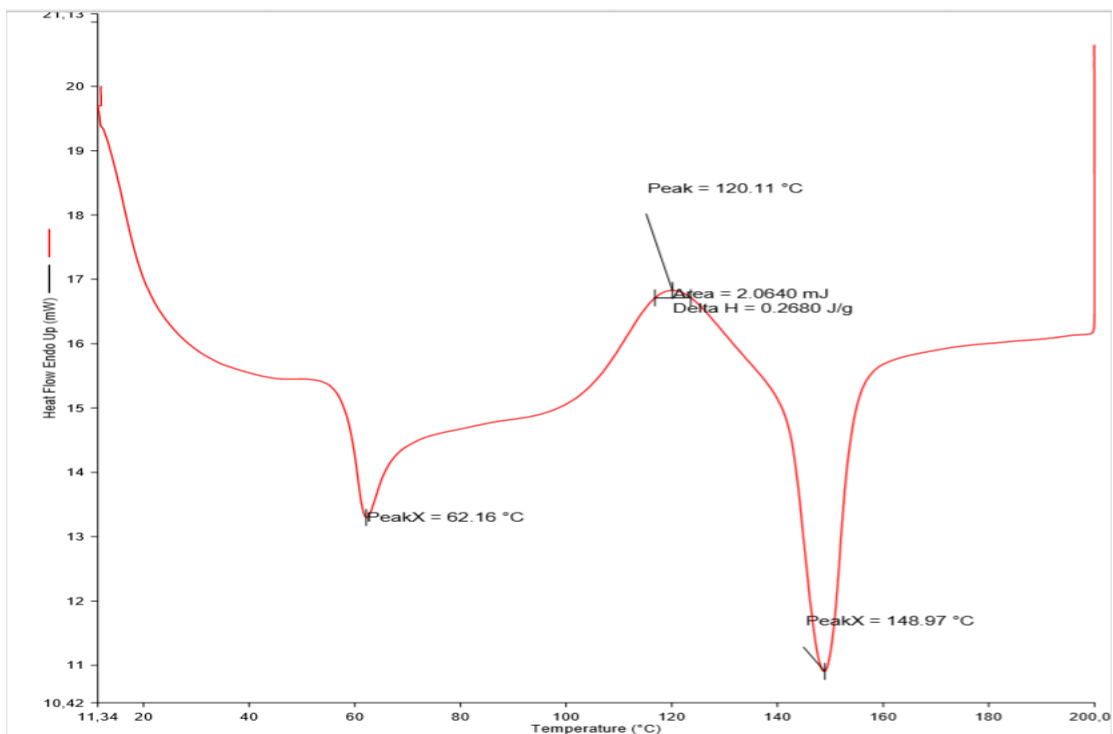


Figure 35 DSC curve of red PLA

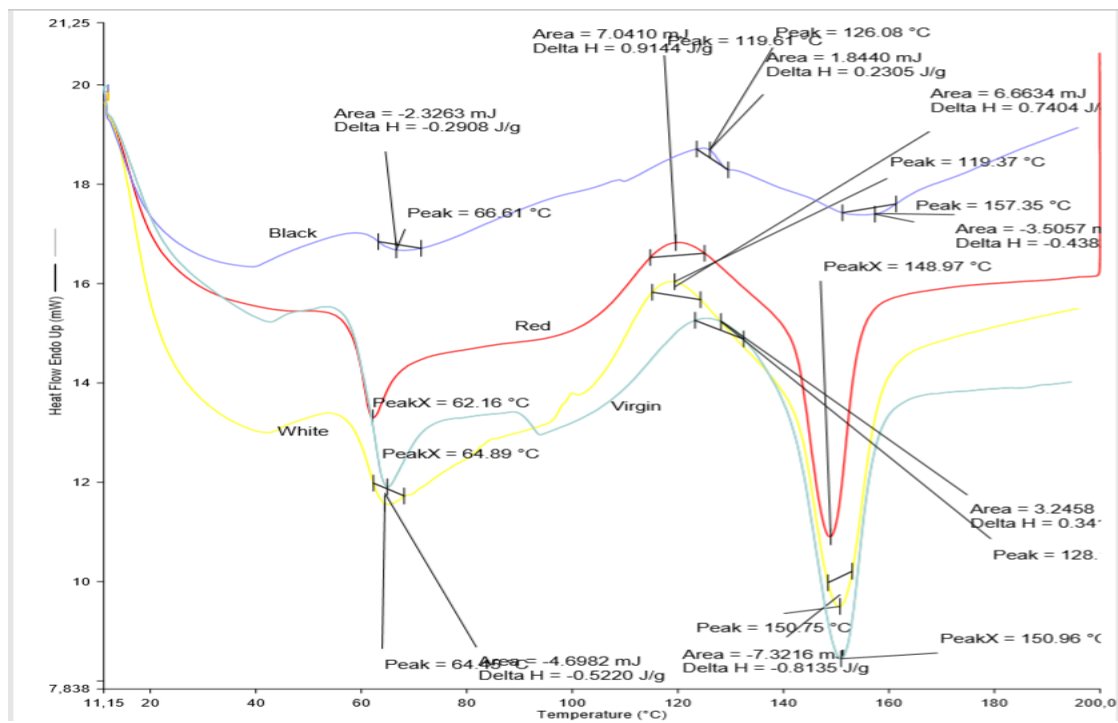


Figure 36 DSC curve of all samples

The DSC curves were got from Pyris software connected to the DSC machine. These curves were converted into pdf format and compared. For easiness to study, all the curves were compared in one screen as shown in figure 31.

6 DISCUSSION

The testing parameters on different samples were kept same and unchanged as this helps to create uniformity and easier to compare all the results after tests. The FTIR spectra of all samples were almost similar, however, the intensity of peaks were different and stretching of certain bonds were also seen in colorant samples. The stress-strain curve shows the different behavior of black and red samples despite being same parameters for MFI test. This test shows that white and black PLA was not good in bearing stress level as pure PLA. The thermal behavior was also seen slightly changed as the glass transition, crystallinity and melting point of these PLA samples were slightly decreased comparison to pure PLA. These results might be the affects of presence of additives like colorant and fillers in samples but cannot be trust since, the chemical compounds or additives used in these samples were from unknown suppliers. These results clearly support that samples from failed 3D parts were degraded mechanically, thermally and chemically and after a certain period of time. The virgin sample outstand all the other samples in most of the tests. The errors in some tests might be because of human error or contamination of sample like that of MFI testing.

6.1 FTIR

Figure 17(spectra of virgin pure PLA) clearly shows that, there is -CH- stretch from 2997to 2985 cm. There is a stretch of -C=O ester at 1759 cm. The -CH-deformation (including sym and asym bend) is seen in 1456, 1383, 1368 cm of spectra. The -C-O- band stretch can be seen in 1269,1186,1134,1091, 1045 cm. The -C-C- band stretch can be seen around 878 cm. In figure 31, spectra of all samples were put together, it was seen that virgin PLA has greater rate of absorbance than those of other colored PLA. However, there is not that remarkable difference in the spectra of these samples. The stretches of other samples occurred at same region, but the peaks were higher and better of Virgin PLA.

6.2 MFI

The melt flow index was calculated for all the samples. The tests were quite unexpected for all the samples, the MFI for virgin PLA was much higher than expected. The MFI for black PLA

was higher than other samples. This shows that viscosity of these samples was different from each other. The red and white samples had higher MFR value than virgin and black PLA, which means that these materials might be degraded more than virgin and black PLA, they were showing resistance to deformation and more uniform flow. The difference in result might be due to human error and contamination of samples.

6.3 Tensile Testing

The details of tensile testing are mentioned in figure 25, figure 26 and figure 27. From these figures mentioned above, virgin PLA is a lot stronger and other colored blended samples were stiff in compare with virgin PLA. However, the black colored samples were better in performance than compared to white ones. Black colored samples were able to bear a lot of strain and did not intend to break down easily like of white samples. Black samples and virgin PLA performed almost similar however, virgin PLA outcast black samples in this test. One of the reasons for this, might be because of the blend mixed in these samples. The virgin PLA did not contain any blend, so they performed very nicely, but other samples contained some colorants, which eventually decreases their mechanical performances. Other reason might be because of degradation of samples. Both black samples and white samples were collected from 3D printed failure parts so, they already had gone through recycling process resulting them in decrease of mechanical performances. The main reason of white samples being stiff might be because of more degradation period as, I came to know that the collecting time period for 3D printed failure white parts (PLA) was unknown, as these parts might were collected within the two years' time, resulting in natural degradation.

6.4 DSC

DSC curve of samples were collected and studied. All the samples tested, show the similar thermal behavior however, slight difference was since among, red, white and virgin samples. The glass transition temperature, crystallinity and melting temperature of these three samples were seen almost at the same temperature including of black PLA. The glass transition temperature was seen between 64-67⁰C, crystallinity was seen between 119-126 ⁰C, whereas melting point was between 148-157 ⁰C. But the curve of black PLA was not that good compared to other PLA samples, however, the glass transition, crystallinity and melting point were successfully seen. Peak of glass transition, crystallinity and melting point in the curve of black PLA sample was not big, like that of other samples. The DSC test for black PLA sample was performed several times and the curves

were similar repeatedly, this might be because black colorant PLA is difficult to perform test and to get the result.

7 CONCLUSION

The results of these samples were achieved as it was thought to be. The results of melt flow index and tensile testing were dependent to each other. Lower the melt flow index lower the tensile strength of these samples were seen after the evaluation of the results. The white samples get the lowest melt flow value and these samples performance on tensile testing were lowest value. The other tests performed on samples also show similar results, the mechanical properties of white samples were poor. FTIR and DSC also show the degradation of these samples.

7.1 Improving the Test

This test can be improved by investing more time, research and technical support. Samples could have been properly stored and it would have been easy, if it was possible to know from when these samples were stored and collected. It would have helped in testing and for analysis of results.

More research could be done to find out the changes in mechanical, thermal and chemical properties of polymers. One example could be focusing more on chemical research and find out about the additives in polymers.

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