Differential scanning calorimetry (DSC) of failed injection molded parts

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This thesis was written about the analysis of failed injection molded polymer parts by using differential scanning calorimetry (DSC). The thermal properties of the selected materials for the experiment were identified by the parameters such as glass transition, endothermic, exothermic peaks and melting points. Polylactic acid (PLA) parts showed glass transition temperatures (around 60-75℃), which influenced the results in DSC. Whereas the glass transition of polypropylene (PP) parts were very weak because of their high crystallinity, brittle and hard nature.

Materials that can be either crystalline or amorphous, liquid, or solid, fibers or polymer that can be tested by DSC to get the thermal behavior of the material. Therefore, DSC is the important technique for the thermal behavior of the materials. The main thing that has to be noticed in this experiment part of the thesis is the failure part of injection molding polymers of PP and PLA were observed non-filled which can be because of problem with the mold, defect with resin or problem with the processing.

The thesis was done with the interest of my field of study. During my study period I studied about the DSC and its application. It was always interesting to learn about the new things. So. The main reason for this thesis is to find out the thermal behavior of the unknown material with the help of DSC technique.

Keywords:	Differential Scanning Calorimetry, Melting point, Glass transition, amorphous, Crystalline, endothermic, exothermic, Polylactic acid (PLA), Polypropylene (PP), semi-crystalline.
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Glossary

DSC: Differential Scanning Calorimetry

Tg℃: Glass transition

T_m℃: Melting Temperature

Tc℃ : Crystallization Temperature

PLA: Polylactic Acid

PP: Polypropylene

PE: Polyethylene

C_p: Specific heat capacity

Cps: Cp of sample

Cpr: Cp of reference

mr : mass of reference

ms: mass of a sample

H: Difference of sample and empty pan

h: Difference of reference and empty pan

Contents

1 INTRODUCTION

1.1 Background

Injection molding is the process in which the molten polymer is pressed under a high pressure into mold cavity through an opening. During injection molding process the polymer in the form of pellets are fed into the injection molding machine through the hopper. The material is then delivered forward by a feeding screw and forced into split mold and filling its cavity through a feeding system with sprue gate and runners. Injection molding it is highly productive for large number manufactured parts in polymer industry. This method is profitable to produce large number of identical parts. Injection molding has numerous applications. Injection molding is used to manufacture different parts such as DVDs, pipefitting, toothbrush, bottles for beverage, car handles, electrical parts, mirror housing and many more from minor parts to major parts in different industries. (Leon Welsh, Yessenia Shade, 2014)

The analytical technique of differential scanning calorimetry (DSC) was first introduced with purpose-built commercial instruments during the early 1960s, it has then been found to provide a convenient and useful method to measure the glass transition, melting and crystallization of uncured prepregs and cure laminates and moreover, and the degree of cure of final product, the heat of reaction during prepreg processing and relative resin reactivity. DSC is the most versatile thermal analysis techniques available. It can also be used with composites and composites processor to study thermodynamics process (glass transition, specific heat capacity) and kinetics events such as cure and enthalpic relaxation associated with physical aging or stress. (Differential Scanning Calorimetry, 2019)

1.2 Scopes and limitation

The DSC results are very important values to be aware of the thermal behavior different polymers associated in the lab. The physical, mechanical and chemical properties of the polymers are influenced by thermal condition and thermal history.

The limitation and scope of the thesis is mainly focused on the analysis of injected molded plastic parts by DSC (Differential Scanning Calorimeter) software. The plastic products produced by injection molding machine can be fail by different reasons and with various respects such as non-filled parts, color difference. It also mainly focused on comparing with non-failure products with respect to correct interpretation of data analysis and correct curves in DSC software.

1.3 Statement of objectives

This project was aimed to find out the calorimeter of failed injected molded parts by using DSC method.

Similarly, the main objective of the thesis was to analyze the facts and reason of the failure injected molded parts of the sample or the products which are manufacture during the injection molding process. The thesis also based on calculate the exact or estimated data of the samples while measuring it during the thermal process by DSC method.

Some aims are listed below:

- During the process we will be able to identify the unknown polymer for processing the material into useful products and predicting its performance during product lifetime.
- The quality of product before and after DSC testing will be compared according to their calorimeter for the fine product.
- The study case about the failure of the injected molded parts will be done by doing the research and find out the reasonable solutions.

2 LITERATURE REVIEW

2.1 Principles of calorimetry

Simply DSC is a technique to study what happens to the polymer when they are heated. So, get to know what happens to the polymer when we heated. So, those steps are followed. Its simple method. Usually there are two pans. in one pan, the sample where we put our polymer sample and the other one is the reference pan which is empty. Each pan sits on the top of the heater. Then we well turn the heat on through computer operator. After turning on the heat it will heat two pans in specific heating rate, usually something like 10℃ per minute. The computer makes sure that the heat rate stays the same throughout the experiment. (Edward L. Charsley, 2001)

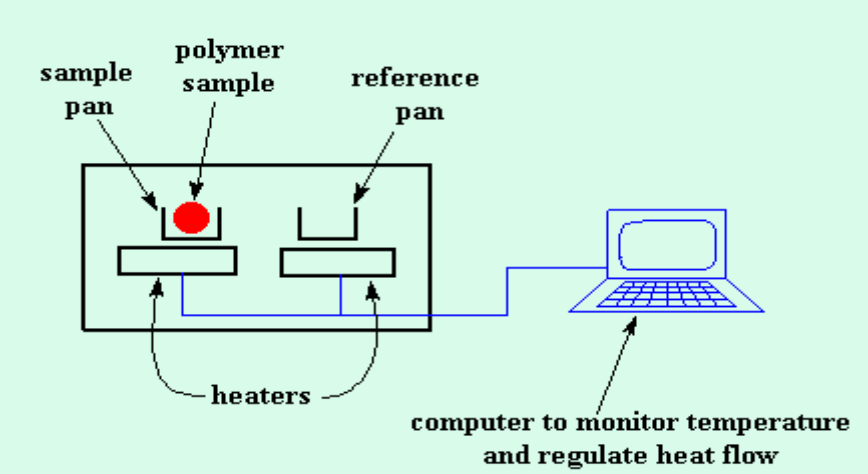

Figure 1 Principle of DSC

But it makes sure that two pans with their separate heater heat at the same rate as each other. They would not heat at the same rate because the reason is simple, and two pans are different where one has polymer within it and another does not have. And the polymer sample means there is another material over it so, it will take more heat to keep the temperature of the sample pan increasing at the same rate as reference pan. (Differential calorimetry, 2003-2020)

2.2 Application of DSC to injection molding

Injection molding is the important method for this thesis. The material we used for DSC testing were manufactured by injection molding method. The polymer produced from the injection molding were the demand of the thesis. The major application of DSC is to characterize the properties of the thermoplastics for injection molding process. During the injection molding process, a molten thermoplastic such as PET, nylon, PPS etc. is quickly forced into a mold which pre-formed to desired shape of the final product. Therefore, the polymer must have properties to flow into the mold. If the mold is comparatively large, then the polymer should have the ability to flow quickly to reach all parts of the mold before it crystallizes or hardened. In other hand if the mold is smaller than the polymer must have higher viscosity.

For the injection molding manufacture process, it is important to have right properties of thermoplastics which run the process in appropriate order and for the desirable products. An ideal thermoplastic should always have Tg, melting temperature and heat of melting, crystallization temperature and time. The polymer should show the isothermal crystallization behavior. The polymer should have different effects on crystallization such as effects of polymer additive, polymer chemistry polymer recyclables and crystallinity of final product. (Sachina, W.J, 2000)

2.3 DSC as a problem-solving tool for the injection molding

DSC measures the heat flow into or from a sample under heating, cooling or isothermal conditions. DSC is very helpful for the injection molding process which provides important information that requires for the injection molding process during its running. It provides the information based on parameters such as melting, crystallinity, and the tendency of the polymer under crystallization at higher temperatures. Through this the molten polymer can be cooled to isothermal conditions and the resulting crystallization of the polymer can be ascertain under the true isothermal conditions. Since the DSC helps to mimic or stimulate the condition that injection molded will meet in everyday life situation.

2.4 Processing-related factors in failure

Injection molding process involved number of factors for the failure of injection molded products. This processing method include the factors and variables common to processing method in general high stress rate and high orientation (frozen in stress), diffusion of formulation ingredients, and other. While injected molded parts have gates and weld line that can provide inherent weak points in the parts. When the shear rate is higher in injection molding than I extrusion and roto molding, giving high frozen-in stress and other potential sources of failure. The most common error in injection molding is to reduce cycle time too much which possibly requiring a colder mold in result it may appear to increase productivity, it often results in high frozen in stress, causing stress-cracking or warpage. (Ezrin, 2013)

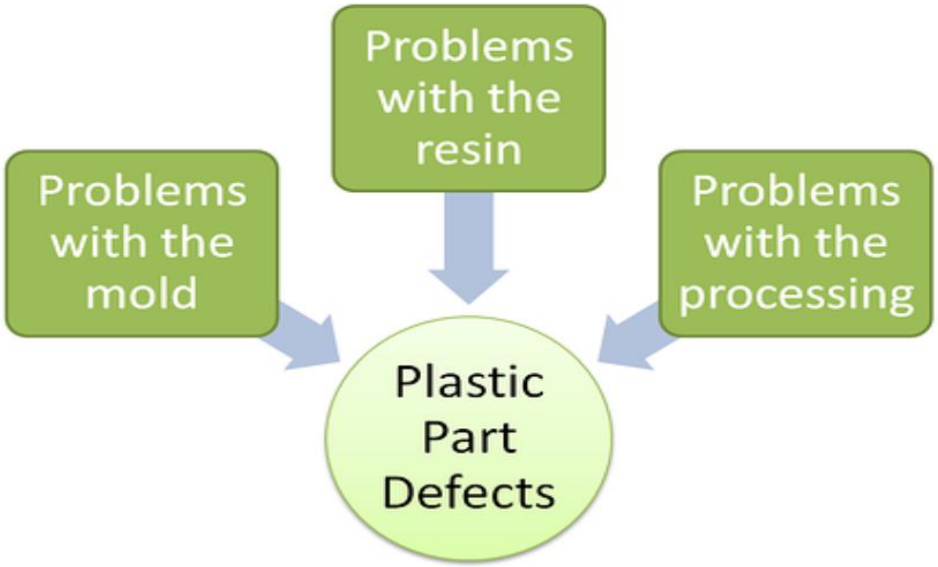

Figure 2 Factors related failure in injection molding

Below (figure 2) injected molded polymer products of (PLA) polylactic acid have one failed as a product during the injection molding process because of different factors such as defects with the mold, it might also be defect with the resins and problems with the processing method. The failure product is not filled well which may get deform and does not look same as optimum product. To know the actual reasons and to find out the reasonable data we used DSC. The non-failure PLA is in a good shape because which is fully filled during injection molding process.

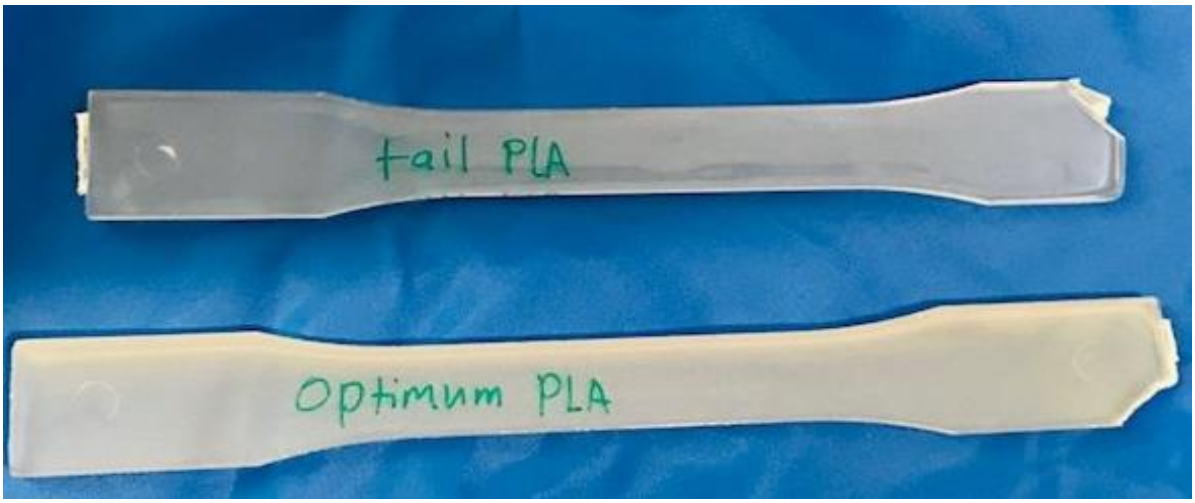

Figure 3 Different shape on failure PLA and Non-failure PLA from injection molding

2.5 Definition of terms

The glass transition, melting point, crystallinity, and specific heat capacity are the important parameters which determine the result and appear in the DSC curve. The thermal properties of the selected materials for the experiment were identified by the parameters such as glass transition, endothermic, exothermic peaks and melting points.

2.5.1 Glass transition

When the irregular shaped polymer is heated, at which the temperature the polymer turns to viscous and glassy liquid or glassy is called glass transition temperature Tg. Below this temperature, the amorphous polymer takes characteristic of glassy-state properties like brittleness, stiffness, and rigidity while cooling. To exhibit Tg the polymer should be amorphous or semi-crystalline. On the other hand, the fully crystalline polymer does not exhibit Tg instead the only it exhibits Tm (melting temperature).

While polymer turns to rubber from glassy state, this transition is most important character of polymer behavior marking the region of dramatic changes of physical properties such as stiffness, rigidity, hardness, and elasticity. (omnexus, 2020)

2.5.2 Melting point

The crystalline regular shaped polymer is heated under certain temperature in which the polymer changes from solid to liquid state that point is called the melting point and the temperature at which the polymer changes from solid to liquid is a melting temperature. While heat may allow to form in polymer but over heating of it can be their undoing. so, While the polymer keeps heating past its Tc eventually the temperature reaches another thermal transition which is called melting. When we reach the its melting temperature, or Tm, those polymer crystals began to fall apart, this case they melt. the chains split out of their arrangements and begin to move freely. and in case we are wondering we can see this happening on a DSC plot. We should consider one thing here is, when the heated polymer gave off when it crystallized, we know that when we reach the Tm, it is payback time. there is latent heat of melting as well as latent heat of crystallization. when the polymer crystals melt, they must absorb heat in order to do so. and melting is the first order transition, and this mean that mean when we reach the melting temperature, the polymer will not rise until all the crystals have melted. This means that little heater under the sample pan is going to have to put a lot of heat into the polymer in order to both melt the crystals and keep the temperature rising as that heat of the reference pan. the extra heat flow shows figure 3during melting on DSC. (Centre, 2003-2020).

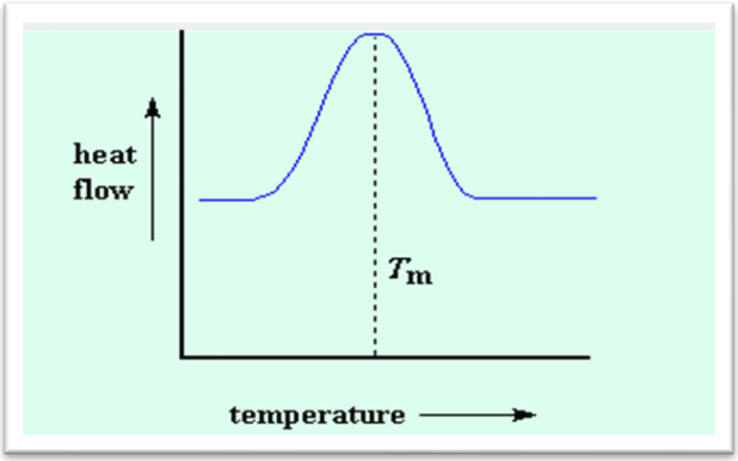

Figure 4. Heat flow going up during melting

2.5.3 Crystallinity and amorphous

When the polymer is cooled from certain temperature and the molecules gives the shape and arranged in an order and give regular shape then this process of thermal property is called the crystallization of polymer.

Crystallinity defines of long-range order in a material, and strongly affects its properties. The more crystalline in a polymer, the more regularly aligned its chains. When the degree of crystallinity increases, and hardness and density of polymer also increased. So, therefore the degree of crystallinity has a high influence on hardness, density, transparency, and diffusion. (Oxford dictionary of science, 1999)

We might be confused to determine whether the polymer is crystalline or amorphous. But Some of the polymer are crystalline where some are amorphous polymer. But crystalline polymers are not entirely crystalline. Basically, most polymers are not mostly crystalline. Those polymers in which their chains or part of the chains, that are not in crystal have no order to the arrangement of their chains are said to be amorphous polymer. Simply they are in irregular shape polymer. DSC can tell us about how much the amorphous and crystallinity consists in a polymer. If we know the latent heat of melting, we can figure out how much crystallinity and amorphous within the polymer sample by DSC. First, we must measure the area of big peak we have for melting of polymer.

Then, we divide area by heating rate in DSC experiment. Heating rate is unit of K/s. So, the expression become simpler.

The degree of crystallinity can be calculated with the following equation.

$$x_C = \frac{\Delta Hm - \Delta H_{C,C}}{\Delta H_m^0} \times 100\% \qquad \textit{Equation.....(1)}$$

Where,

ΔH_m is the exothermic enthalpy of melting, $\Delta Hc,c$ is the enthalpy of cold crystallization and ΔH^0_m is the exothermic enthalpy of melting of the same polymer with 100% crystallinity. (Thermal method)

2.5.4 Specific heat capacity

Specific heat capacity is a fundamental thermodynamic property. It is the important factor to change the structure by measuring with DSC. To raise the temperature of the material the amount of heat must be supplied. So, basically, it is the amount of heat energy that is necessary to heat one gram of the material one degree Celsius. Cp is the characteristic thermal property of a material. So, it is a measure of how the material stores additional energy at the molecular level as it is heated. For instance, when the material is heated through the glass transition region, the molecules gain mobility, the material softens, and Cp increases. So, Cp shows the changes in the structure.

The conditions for the measurement of the sample, the reference (a sample with known specific heat capacity) and the empty pan are same. The specific heat capacity of the sample can be calculated with Figure 4 required components. (R. Bruce Cassel)

Figure 5 shows an example of measuring specific heat capacity by using DSC. The sample is measured under different conditions such as the reference (a sample with a known specific heat capacity) and the empty pan were the same. The specific heat capacity of the sample can be calculated by (equation 1) from the DSC data obtained (a, b, and c in Figure 5).

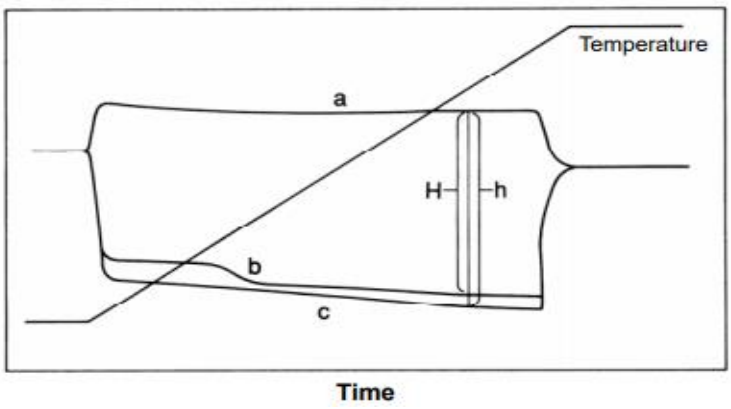

Figure 5 Principle of Specific heat capacity temperature vs Cp

a: stand for empty pan

b: stand for sample

c: stand for reference

$$C_{PS} = \frac{H}{h} \cdot \frac{mr}{ms} \cdot C_{Pr}$$ Equation.....(2)

Where, Cps: Cp of sample

Cpr: Cp of reference

mr : mass of reference

ms: mass of a sample

H: Difference of sample and empty pan

h: Difference of reference and empty pan

(Hitchi Hightech Science corporation, 1981)

3 EXPERIMENTAL METHOD

3.1 Sample information

The samples were taken from Arcada`s laboratory department of energy and material technology. The raw materials of polymers which are important application for the injection molding process were manufactured in different prestigious companies within the Finland. Those material were supplied to Arcada as the raw material for the small-scale business or for the laboratory testing or experiment for the students of Arcada. Since I was working as a lab assistant in the lab last year, I was given the work to check the polymer material list that has arrived Arcada lab for the injection molding process. So, through this I was able to know the information about the raw materials and where they were manufactured. However, the work was closely related with my thesis work. Those were the exact polymer materials that were required for the experimental part of my thesis. Among them I chose Polylactic acid (PLA) and Polypropylene (PP) to perform the DSC experiment because the polymer which I use were easily available and which makes the work more effective and these are the regular polymer which often used as a sample material for DSC purpose. Besides, PLA and PP gives the effective data and have fine thermal properties for the experimental task. The information of the polymers that I have used for the DSC experiment are in the tables 1-5.

Material	PLA
Manufacturer	Natureworks
Application	Injection molding
Grade	High heat film, general purpose film. etc

Table 1 Information of PLA sample material (Borealis, 2007)

Physical properties	PLA
Specific Gravity	1.24
MFR, g/10 min (210℃, 2.16kg)	7

Melt Density (g/cc)	1.08 at 230℃
Mechanical properties	PLA
Tensile strength @ Break, psi (MPA)	7,700 (53)
Tensile Yield Strength, psi (MPa)	8,700 (60)
Tensile Modulus, kpsi (GPa)	5000 (3,5)
Tensile Elongation, %	6,0
Noticed Izod impact, ft-ib/in (J/m)	0,3 (16)
Melting point (℃)	(155-170)

Table 2 Typical material and application properties (Borealis, 2007)

Material	PP cellulose fiber reinforced
Manufacturer	UPM
Grade	ForMi GP 40
Application	Injection moulding applications instead of PP, filled PP or several other plasti

Table 3 Information of PP material (Borealis, 2007)

Property	Tested method	GP 30	GP 40	GP 50
Density, g/cm^3	ISO 1183	1.02	1.07	1.12
Tensile strength, N/mm^2	ISO 527-2	41	50	58
Tensile modulus N/mm^2	ISO 527-2	2900	3800	4700
Strain (tensile), %	ISO 527-2	4.8	4	3
Charpy impact strength, notched, kJ/m^2	ISO 179/1eA	4.2	5.5	3.7
Cellulose content, weight %		30	40	50

Table 4 Physical and mechanical properties of Propylene (PP) (Borealis, 2007)

Parameter	
Melt temperature	210-260℃
Injection pressure	<1200 bar
Temperature profile from nozzle	195/190/185/180℃
Mould temperature	+60 - +80℃
Injection speed	As high as possible

Table 5 Parameters for typical molding machine (Borealis, 2007)

3.2 Sample preparation

The injection molded dog bone is first cut through certain parts with the tiny knife and tiny amount of observed sample was weighted by milligram scale. Then the weighed sample was put into the aluminum pan and was sealed by sample press. Then the sample was placed on a sample dish where there remained one empty dish which is called reference dish. For this empty dish another empty capsule was also prepared to measure the blank curve and then placed in reference dish.

Things to be noted: before preparing the sample capsules, the liquid nitrogen tank had to be filled to make sure that there was enough liquid nitrogen during the whole measurement.

Then the samples capsules were put into a furnace carefully by tiny fork. So, the measurement was started when the initial temperature had been reached. Usually, the initial temperature es set to be near room temperature around 12℃.
The important thing is that the temperature is an essential parameter which may influences the DSC results. To save the experimental time the heating rate could be differ from cooling rate during this experiment.

3.3 Material selection

3.3.1 PLA (Polylatic Acid)

During this experiment mainly two type of PLA products were chosen for the investigation. As we have the main theme of this study is DSC of injected molded failure parts, we had to choose both failure or nonfailure parts of PLA from failure dogbone and nonfailure dog bone produced through injection molding method. The failure polymer is the polymer product or design which comes out as something deform in either with physical properties or thermal properties within during injection molding process. The reason for failure can be vary which is explained in section 2.2.3.

Polylactide acid (PLA) is a thermoplastic polymer obtained from renewable resources. This contrasts with common commercial grade thermoplastics, such as those from polyethylene family, and isotactic polypropylene, which are derived from nonrenewable resources. In this, way PLA can be produced with different properties from primarily amorphous to largely crystalline. PLA are available in different forms. PLA has two isomers namely the L-Latic and the D-Latic acid. The three forms of PLA are available commercially such as L-lactide, pure D-lactide and a mix of L and D-lactide.

Injection molding is the primary fabrication method for producing PLA parts. PLA could be semi crystalline polymer. The physical properties including crystallinity of these material can vary with the processing conditions. The certain additives available such as nucleants, and accelerants, impact modifiers, and mold flow agents can affect the crystallinity and the properties as well. The disadvantages of PLA are as it has Tg (approximately 60℃-75℃) resulting in inferior thermal resistance to other industrial polymers. However, the thermal resistance can be improved by increasing the crystallinity in these materials. Therefore, high crystallinity is desirable for the stiffness, strength, and other properties of the fabricated parts. However, the crystallization rate of PLA is slow, so, obtaining sufficiently high crystallinity within reasonable manufacturing is difficult.
(J. Coulter, P. Gao, A. Duhduh. A. Kandu, 2019)

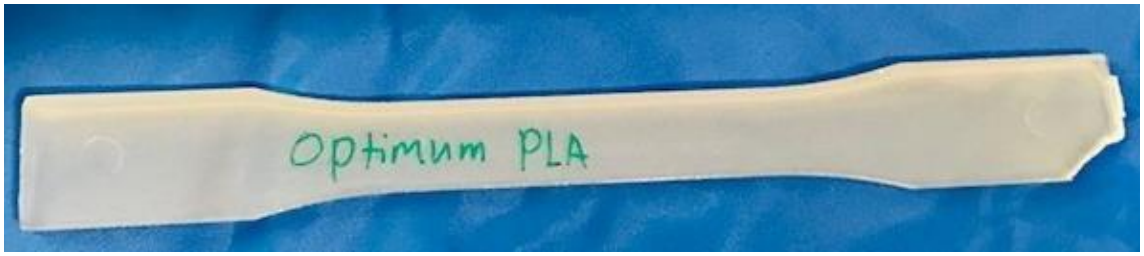

Figure 6 Injection molded PLA dog-bone for DSC

3.3.2 PP (Polypropylene)

PP is one of the most used thermoplastic polymers because of its unique features and versatility. This polymer shows the excellent chemical resistance, low density, high tensile strength and comparatively high melting point. Especially in comparison to the

similar polymer, polyethylene. Polypropylene is used in different sectors for variety of applications including fibers packaging and capacitor films, food containers, home appliances, automotive components, telecommunications cables and injection molded products.

Among all thermoplastics, it is important to characterize the thermal properties of the polypropylene, including melting temperature, percent of crystallinity, crystallization when cooling from the melt and the glass transition, Tg. Besides, variation levels of the polypropylene will show the results in different physical properties and for the process control and optimization, and it is essential to characterize the polypropylene material.

The thermal analysis provides an ideal means of the characterizing the properties of polymers, including polypropylene. So, differential scanning calorimetry (DSC) is the useful method for the characterization of the polypropylene. The measurement of the glass transition Tg of the polypropylene is basically considered difficult by DSC which gives the weak transition. Yet, a DSC having high sensitivity and flat and reproducible baseline can identify weak Tg related with polypropylene. The latest high performance Pyris DSC from PerkinElmer can easily detect the Tg of polypropylene. (Hitchi Hightech Science corporation, 1981)

In this experiment the injection molded polypropylene of virgin PP and non-nonvirgin PP dog bone was tested in DSC. So, there could be some difference in their physical or thermal behavior. The virgin PP was the polypropylene material that has not processed through the injection molding method and which the raw material for the injection molding applications. Whereas, the PP dogbone is the product that was manufacture from injection molding process. The PP used in the experiment was not a pure PP it a composite PP and composite of glass fiber and rest pp polymer, but the glass fiber was very less in comparison to PP polymer. But the exact number was not identified.

Figure 7 Virgin PP

3.4 Blank curve subtraction

In fact, it is not possible to get perfect zero-line heat flux curve between empty sample system and empty reference system. Over entire temperature range. So, in order to obtain the real heat flow rate into the sample, the blank curve must subtract from the actual measured curve. First, the blank curve is detected by two empty capsules at the reference and sample positions. Besides, each experimental technique has a temperature range, cycle, rate that is make the blank curve become different. Likewise, while changing to another experimental method, blank curve must be always determined.

3.5 Temperature rate

The rate of temperature of in DSC surely influences the experiment and the obtained curves. If the temperature rate is set low the sample material has more time to re-

arrange the structure link which may change the initial state of the substance which may give high crystallization degree in result. So high temperature provides the actual results and reasonable curves even though if the conducting thermal coefficient of the sample material is high, unequal temperature at different layers could affect the result.

3.6 Sample weight

The size and weight of the sample also influences the thermal process and DSC results. So, therefore, the sample should be prepared in appropriate size and weight. The sample should be neither too long and heavy nor too tiny and light. The given instructions by the lab should be followed in order to get nice result. Usually the sample weight are depend upon the nature of sample material. Some material requires larger size, or some need smaller in size and weight.

Usually if we use large sample mounts it helps to detect weak effects, help to measure filled or diluted samples and it is also for the measurements at low heating rates. But the use of smaller sample size is for the measurements at high rates. The recommended sample amounts for the DSC measurements are given below.

Sample materials	Weigh of the samples
Organic samples	2 to 10 mg
Inorganic samples	5 to 50 mg
Samples with strong exothermic effects	0.5 to 1 mg
Unknown samples	0.5 to 1 mg

Table 6 The weights of samples materials

3.7 Component

In my experiment I used the DSC device from Perkin Elmer. Perkin Elmer compensated Pyris 1 DSC is ideally suitable for the characterization of injection molding

thermoplastics. The device we used for this experiment was DSC 4000 version by Perkin Elmer. Usually this device includes liquid nitrogen tanks, automatic furnace, and sample robot. The device is controlled by an installed program called Pyris manager. The device used for in the experiment is very simple and effective to use and which gives accurate information about the polymer that were used in the experiment.

The DSC experiment is the sequence of heating and cooling process in which the electrical resistors respond to heating and nitrogen gas which keeps the sample dry. In order to keep the temperature precise, we must follow the set temperature rate, and cooling work is separated by two nitrogen liquid tanks. However, one main nitrogen tank may be refilled after several experiments runs. And other one just provides a small amount of nitrogen liquid when temperature almost reaches to ending point. This must be refilled by only authorized or experienced person only.

DSC 4000 does not include sample robot but it would be great to have it because it is easier to move the capsule from a sample dish to disk to the furnace with required force in order to avoid over force applying that may deform the capsule.

Another essential component for the DSC is capsule press. The capsules include an aluminum pan and a cap which must be sealed together by capsule press.

There are numbers of importance features of Perkin Elmer which are useful to the injection molders which are listed below.

- Perkin Elmer DSC has high sensitivity for the detection of the weak transition.
- It separates the overlapping transition, mainly for blended polymer resins, which is often useful for the injection molding.
- It has ability to heat quickly (up to 500 C/min) in order to better simulate real life injection molding conditions. (Sachina, W.J, 2000)
- It brings an outstanding result for the isothermal crystallization measurements which is important for the injection molding process.
- Pyris window software is easy to use which makes convenient for the injection molded polymer.

(Sachina, W.J, 2000)

Figure 8 Nitrogen gas tank

Figure 9 Closed DSC furnace

Figure 10 Sample dish

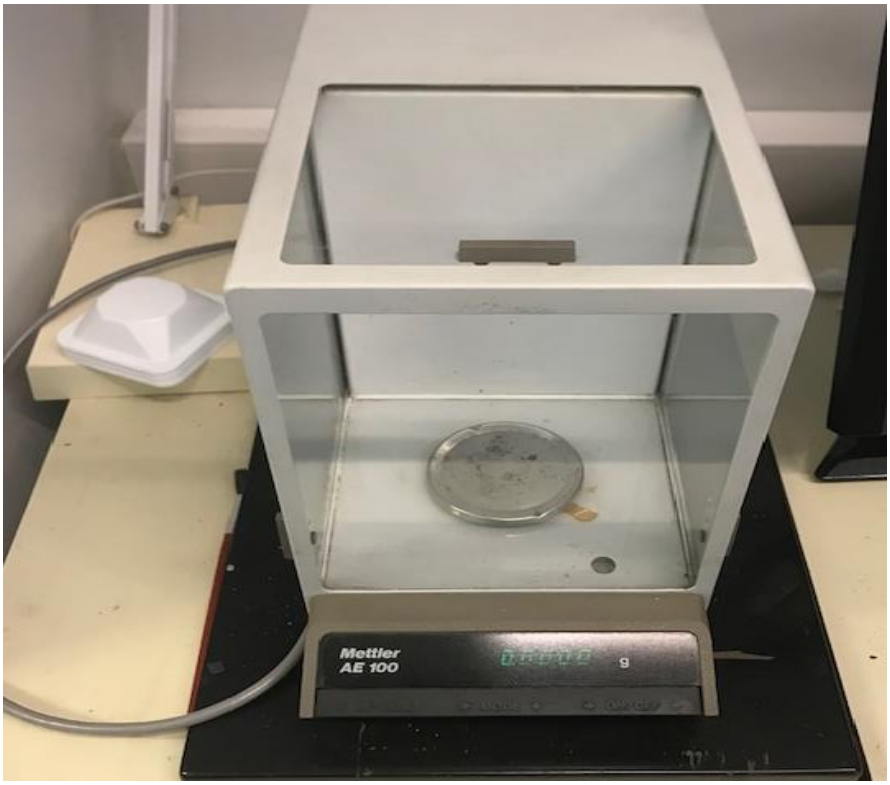

Figure 11 Milligram scale

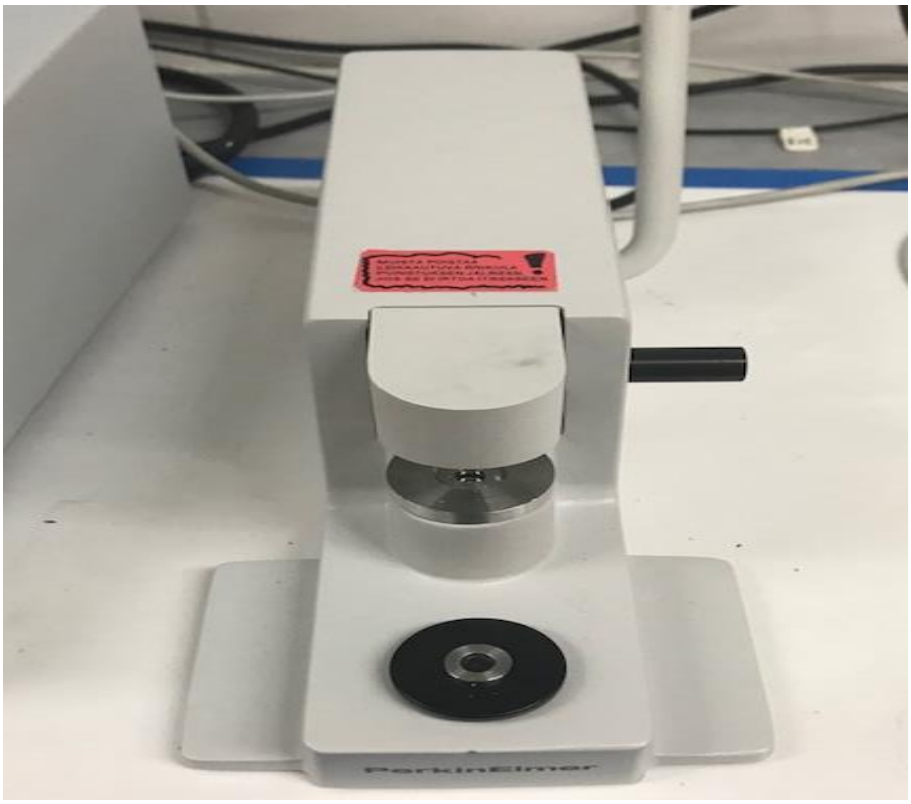

Figure 12 Capsule press

Figure 13 Aluminum sample pans

3.8 Calibration

Calibration is one of the most essential things for every thermal analytical study. Calibration is the formation of a defined relationship between a value of a quantity indicated by measuring instrument and the true value ((E. Gmelin, St. M. Sarge).

Figure 14 PP dogbone from injection molding

4 EXPERIMENTAL RESULTS

4.1 For nonfailure PLA (optimum PLA)

Figure 15 represents the DSC graph along with the curves which represents the experimental data shown as a curve in the graphs. The peaks in the curves identify the thermal value of the PLA.

The data obtained in Figure 15 were done in the laboratory The piece of nonfailure PLA dogbone observed sample were measured 9 mg and then put into the sample pan where the capsule and reference capsule were sealed by the sample press and placed in sample dish and reference dish, respectively. The initial temperature was set at temperature around 12℃. The sample was held for 1 min then it was heated from 12℃ to 200℃ at the heating rated of 20℃/min. The obtained parameter from Figure 15 were chose because the parameters obtained in the graph shows the thermal behavior of the PLA polymer.

The two samples of same material PLA failure and non-failure PLA are heated to different final temperature 200℃ and 170℃ because the sample are tested in two different dates. However, it did not affect the result because the required parameters lie in between 0 to 160℃.

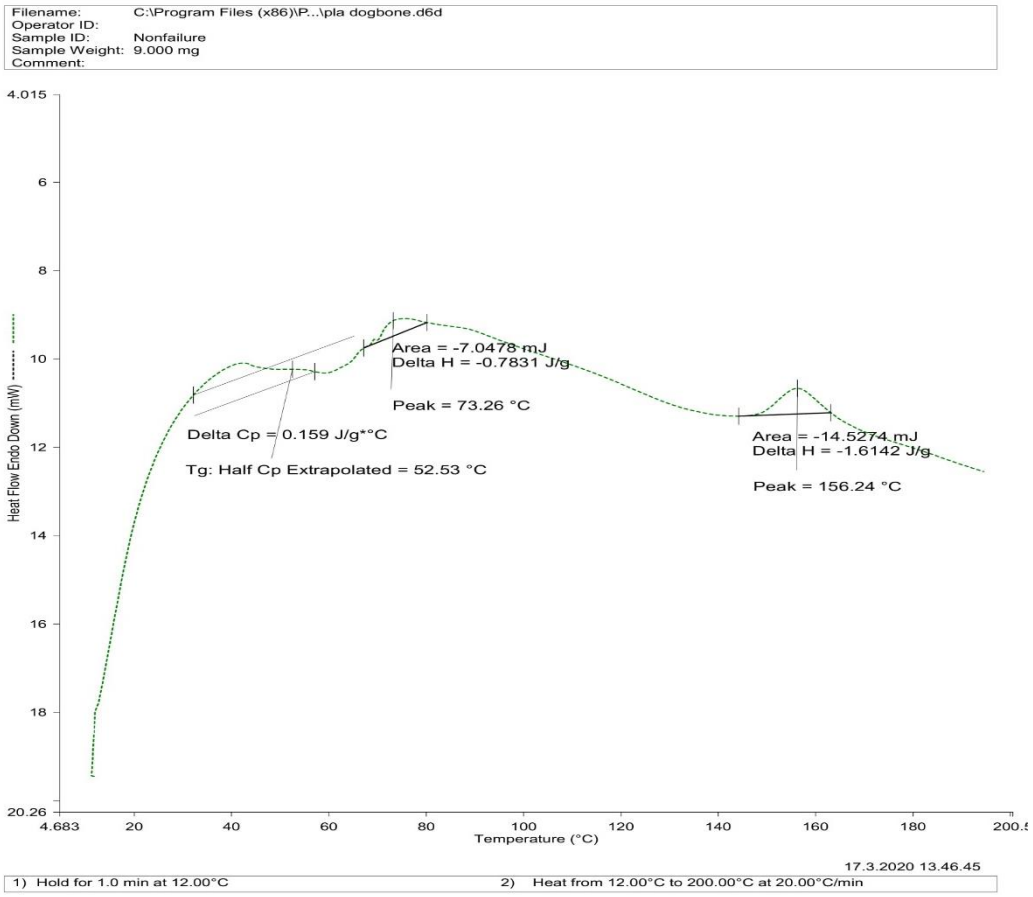

Figure 15 Nonfailure PLA DSC curve obtained

4.2 For failure PLA

Figure 16 represents the DSC graph along with the curves which represents the experimental data shown as a curve in the graphs. The peaks in the curves identify the thermal value of the PLA

The Figure Similarly, the data obtained in Figure 16 were done in the laboratory by the piece of failure PLA dogbone observed sample were measured 7.6 mg and then put into the sample pan where the capsule and reference capsule were sealed by the sample press and placed in sample dish and reference dish respectively. The initial temperature was set at room temperature around 12℃. The sample was first heated from 12℃ to 170℃ at the heating rate 20℃/min. Then it was held for 1 min at 170℃ and again cooled from 170℃ to 12℃ at 10℃/min.

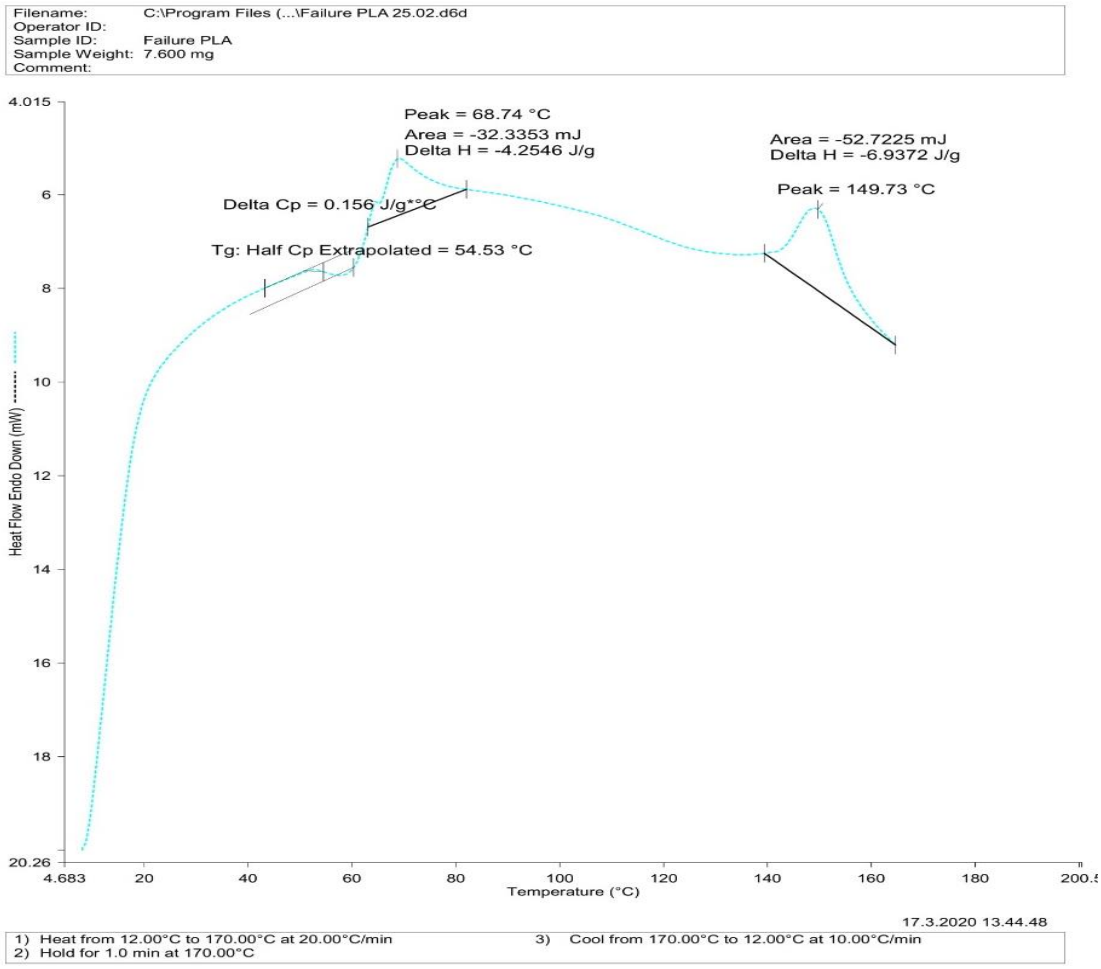

Figure 16 Failure PLA DSC curve

4.3 Experimental part for polypropylene (PP)

In this experiment the virgin polypropylene and the injection molded failure parts of the polypropylene were tested in Differential Scanning calorimetry method. The experimental procedure was stated below.

4.3.1 For virgin polypropylene (PP)

The piece of virgin PP dogbone observed sample were measured 7.500 mg and then put into the sample pan where the capsule and reference capsule were sealed by the sample press and placed in sample dish and reference dish respectively. The initial temperature was set at room temperature around 12℃. The sample was first heated from 12℃ *to* 200℃ at the heating rate 20℃/min. Then it was hold for 1 min at 200℃ and again cooled from 2000℃ to 12℃ at 20℃/min.

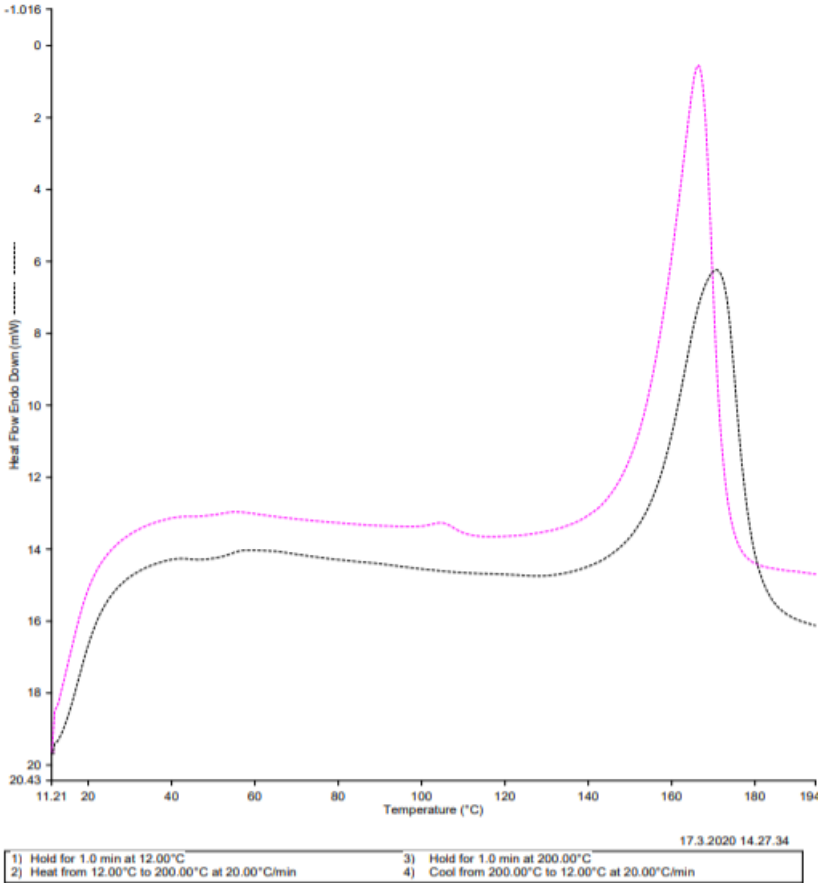

Figure 17 DSC of virgin polypropylene above black curve represents the virgin PP

4.3.2 For injection molded polypropylene (PP) dogbone

Similarly, the piece of virgin PP dogbone observed sample were measured 8 mg and then put into the sample pan where the capsule and reference capsule were sealed by the sample press and placed in sample dish and reference dish respectively. The initial

temperature was set at room temperature around 12℃. The sample was first heated from 12℃ to 200℃ at the heating rate 20℃/min. Then it was hold for 1 min at 200℃ and again cooled from 2000℃ to 12℃ at 20℃/min.

The two sample were

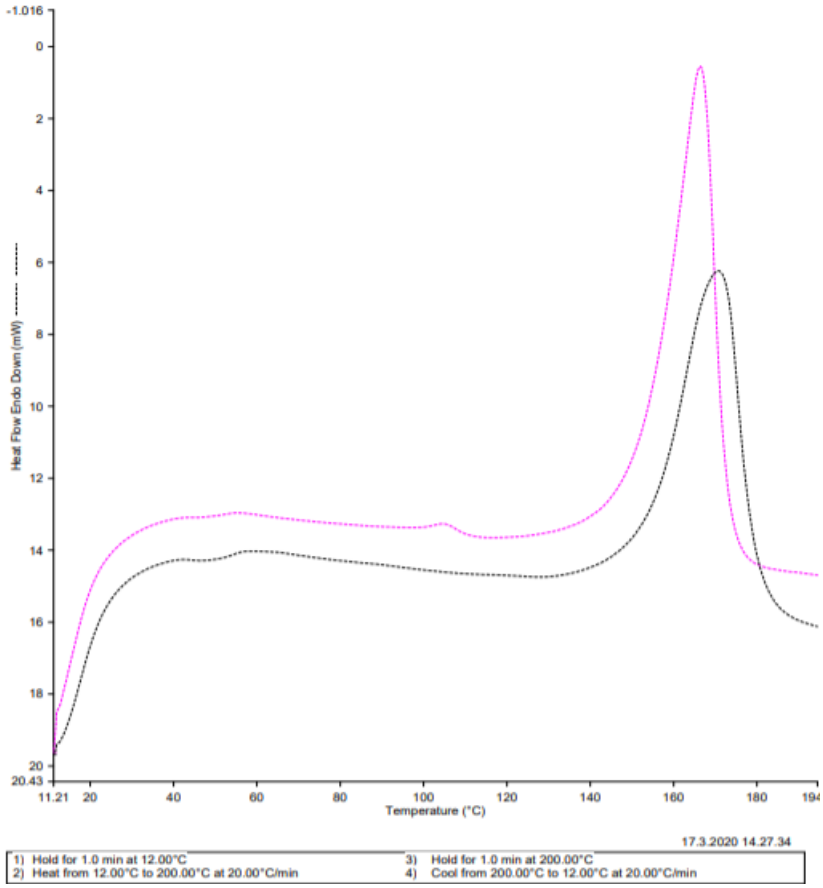

Figure 18 DSC of injection molded dogbone above pink curves represents the PP injection molded dogbone.

5 DATA ANALYSIS OF EXPERIMENTAL RESULTS

5.1 Before analysis while comparing the curves

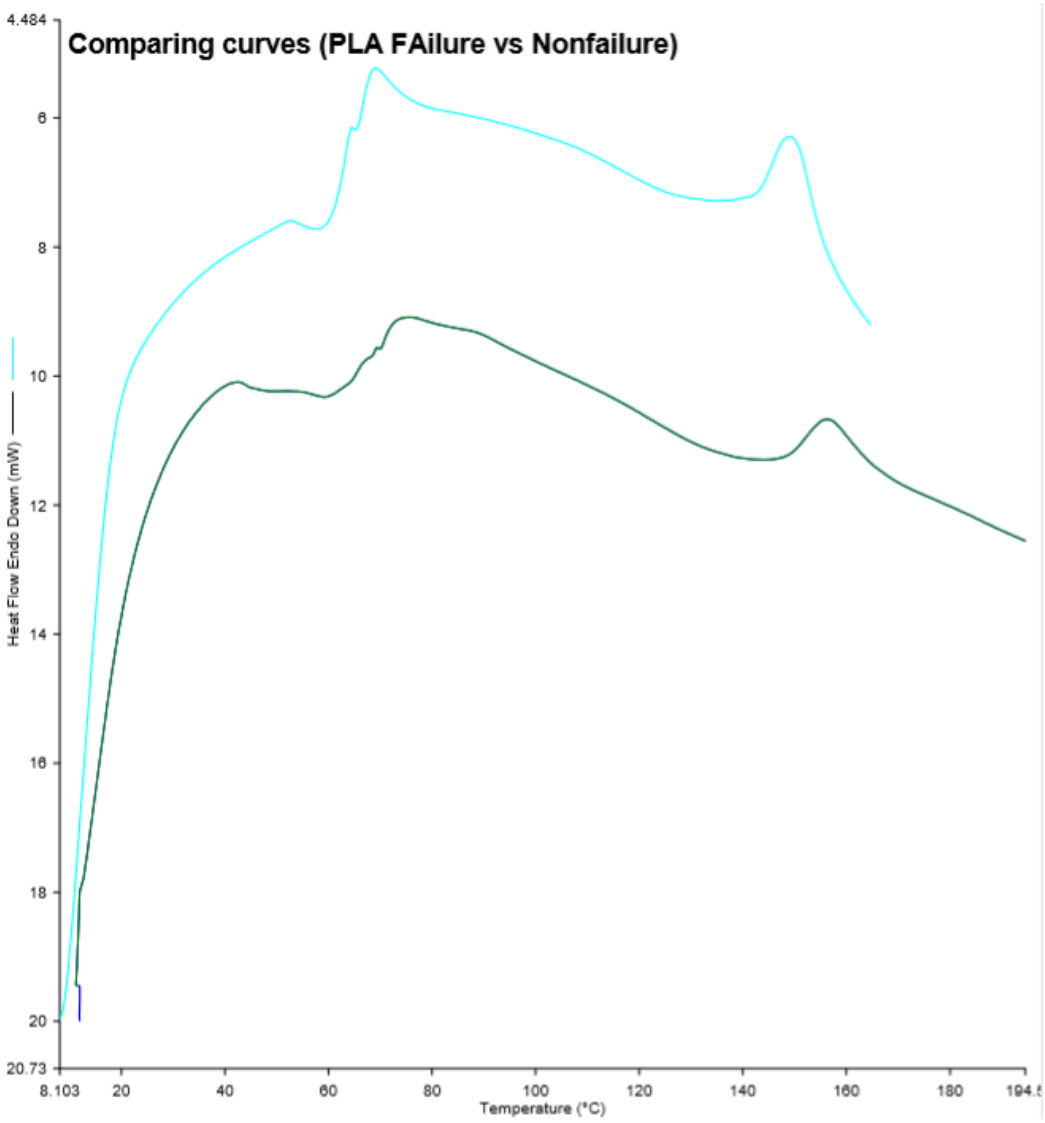

Figure 19 Curves before the data analyzing

From the above Figure18. Those curves represent both the failure polymer and non-failure PLA. The light green curves represent the non-failure PLA from the injection molded while the blue curve represents the failure product of PLA dogbone from the same method injection molding.

5.1.1 Data analysis of PLA (Polylactic acid)

The analysis of parameter through the curves obtained on the graph. The analyzing of thermal properties such as glass transition Tg, crystallinity and melting point are very essential.

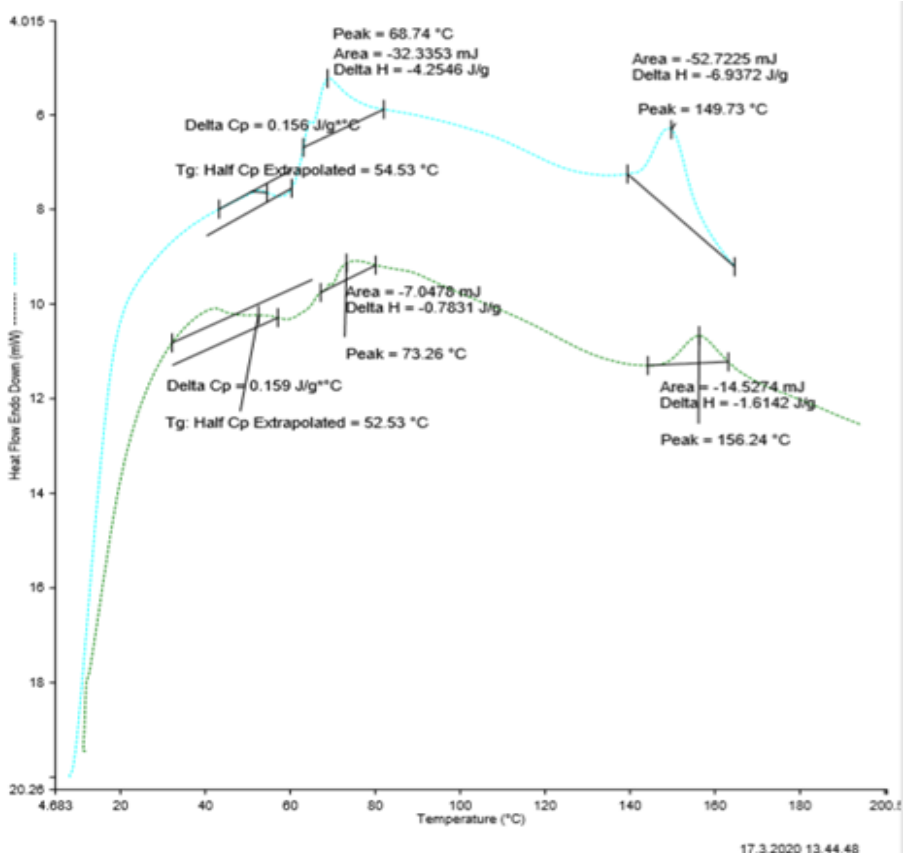

Figure 20 Comparison of DSC curves of PLA

The above graph or curves are the comparison of failure and non-failure PLA polymers. The green indicated curves are the curves of failure PLA whereas the curves indicated with blue is the curves of nonfailure PLA. Although the material is same but manufactured differently in term of deformation in manufacture. The failure PLA dog-bone where manufactured with deform while manufacturing through injection molding method. The failure PLA dogbone in Fig. 1 illustrated that the dogbone product is not filled completely and which is not perfect. The failure can be different reasons such as excessive temperature drop, and pressure drop during the injection process from the gate to the completion of filling. The reason for the deformation poor curing condition and the

poor injection pressure conditions provided during the injection molding process. (Alberto Naranjo, 2007)

In the above analysis from DSC, it illustrated that the glass transition of nonfailure PLA indicated with light green has 52.53℃ with specific-heat capacity 0.159J/g*c while the crystallization temperature was 73.26℃ and the melting temperature is 156.24℃ with the heating rate 20℃/min.

Similarly, the data analyzing for the failure PLA dogbone indicated above with blue curve illustrated that the glass transition temperature is calculated as 54.53 with specific heat capacity of 0.156J/g*c while the crystallization temperature was 68.74℃ and melting temperature temperature was 149.73℃ with the heating rate of 20℃/min.

Thermal properties	Delta H J/g	Glass-transition T_g℃	Crystallization temperature T_c℃	Melting temperature T_m℃
Nonfailure PLA ***(light green curve from fig .11)***	-0.7831	52.53	73.26	156.24
Failure PLA (blue curve from figure.11)	-4.2546	54.53	68.74	149.73

Table 7 Characterization and thermal properties of PLA

5.2 Data analysis of polypropylene (PP)

The data obtained from the graph were analyzed with the Pyris software which is available at Arcada lab in the chemistry laboratory. The data were analyzed very carefully to get the precise result.

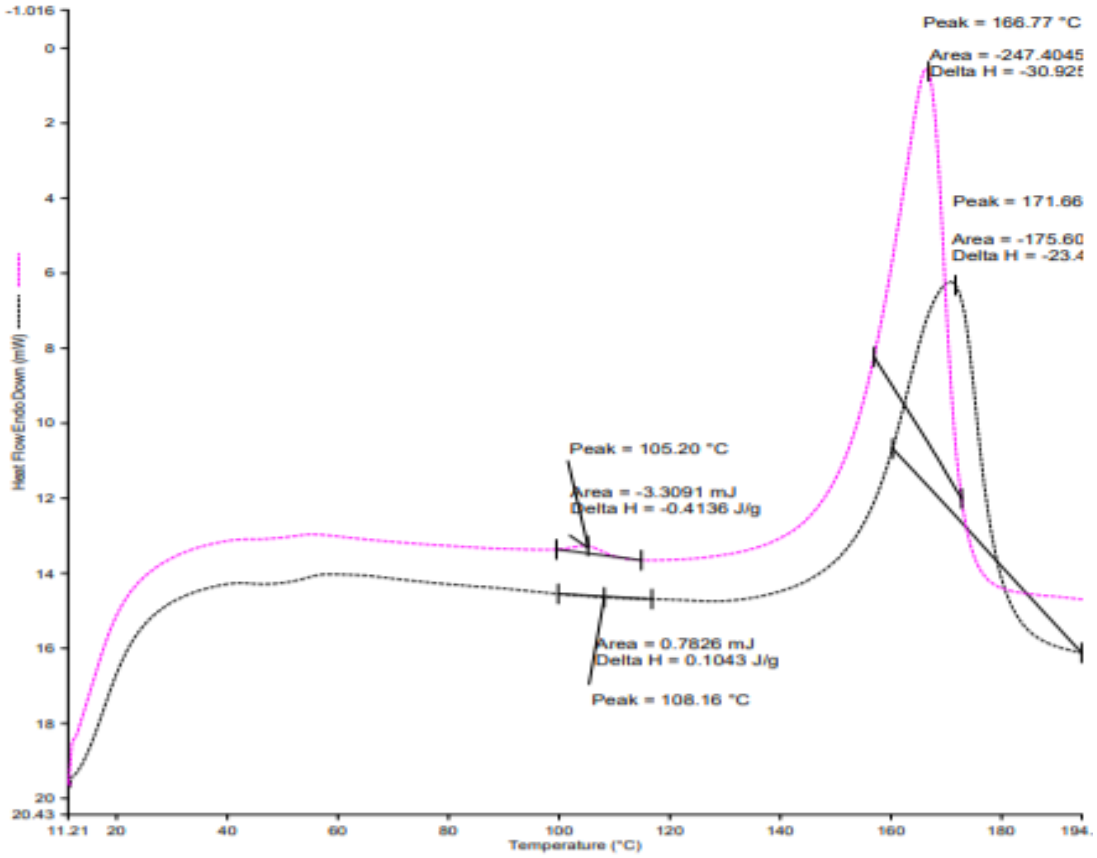

Figure 21 Data analysis of polypropylene polymers

The above overlapped (figure 21) curves represented the virgin polypropylene (PP) and injection molded polypropylene (PP) polymer. While the pink curve has indicated injection molded polypropylene (PP) dogbone whereas, the black curve has indicated the curve of virgin polypropylene (PP) polymer. In addition, the injection molded polypropylene sample was prepared by taking the injection molded failure tiny failure part of the dogbone.

The data obtained above were by heating and cooling of the polymer sample from 12℃ to 200℃ and cooled from 200-12℃. The experiment could not obtain the glass transition Tg because the PP was more of thermosetting plastic and the machine could not go the temperature below -1℃. However, the glass transition Tg of an ideal polypropylene should be around -10℃ to -0℃. But the crystallization temperature and melting temperature was obtained precisely.

The above pink curve which is injection molded PP has the crystallization temperature 105.20℃ and the endothermal peak of 166.77℃ represents the melting temperature. Whereas, the black curve which is virgin PP has obtained the crystallization temperature 108.16℃ and the endothermal peak of 171℃ represents the melting temperature of the virgin PP.

Thermal properties	Glass-transition T_g℃	Delta H J/g	Crystallization temperature T_c℃	Delta H J/g	Melting temperature T_m℃
Virgin PP (Black curve)	-	0.1043	108.16	-23.4	171.66
Injection molded PP (Pink curve)	-	-0.4136	105.20	-30.925	166.77

Table 8 Thermal properties and data obtained from PP polymer

6 RESULTS

6.1 For PLA polymer

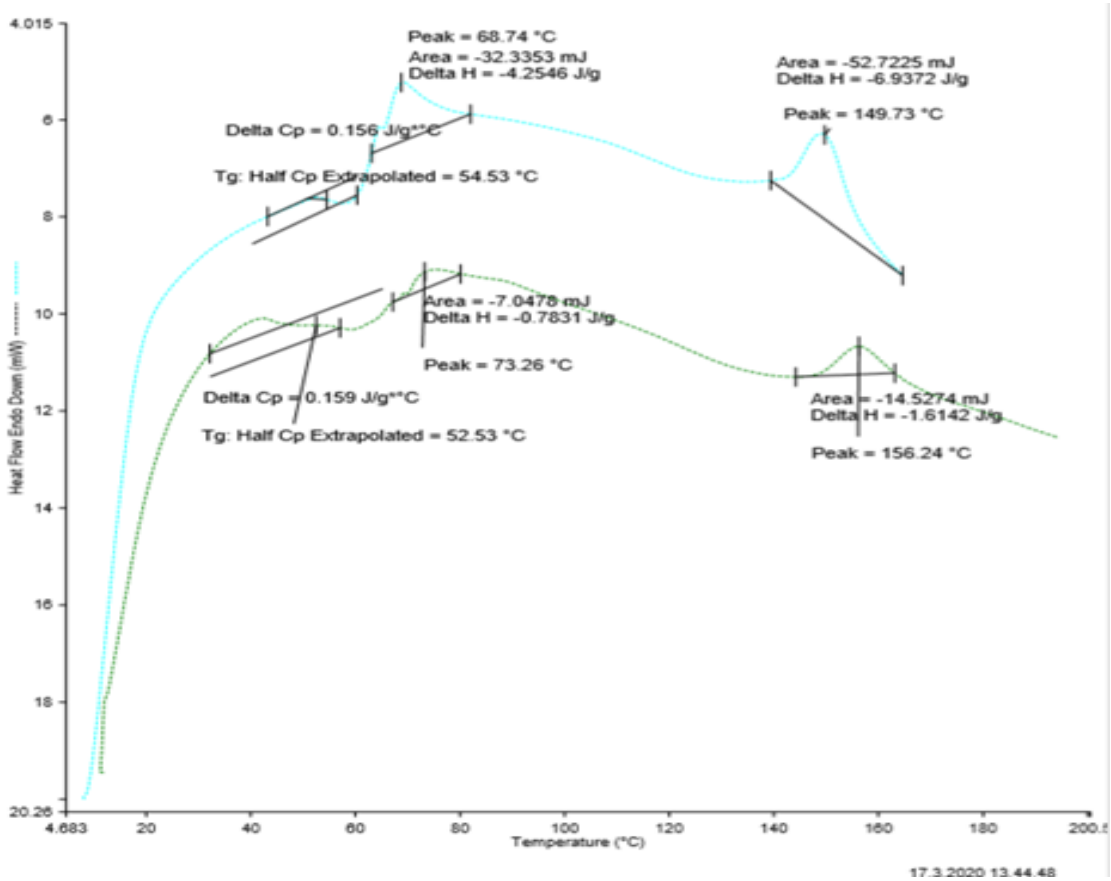

Figure 22 DSC results of PLA polymer where green curves represents nonfailure and blue curve represents failure PLA

The DSC analysis is one of the reliable techniques for the measurement of the melting temperature, crystallization temperature and the glass transition temperature of the semi-crystalline polymer. From the (figure 2) shows the DSC diagrams for the failure and non-failure PLA of injection molding method products. The first peak shows the temperature of 52.53℃ which is the glass transition temperature of nonfailure PLA while the glass transition temperature peak of the failure has shown 54.53℃. while comparing the data

from two different PLA the glass transition of failure PLA is higher than the nonfailure PLA. This is because the decreased in T_g that the nonfailure PLA plays the role of a plasticizer on the PLA by the segmental mobility of the PLA chains while the increasing amount of the failure PLA does not the shows the relevant action of the plasticizer or filler. It means the decreasing in the glass transition temperature the better filler for the injection molding products. The

Similarly, from the compared curves from the figure 15. The crystallization temperature of failure and nonfailure PLA shows the peak temperature of 68.74℃ and 73.26℃ respectively. It can be indicated which might be tiny cause either from the failure or non-failure PLA. However, the PLA was failed to due to the lack of complete filler because of something default during the process which was explained in the section of thesis
(2.2.3) processing-related factors in failures.

Thus, it has shown the heat flow of endo shows the downward direction because it might be the reason that the heat flow of sample is lower than that of reference.
It was difficult to cut the cut the sample equally. However, the sample weight must be between 5 mg to 10 mg. And about the heat for PLA the heat must be 0 to 170 or above so, I applied this.

6.2 For polypropylene (PP) polymer

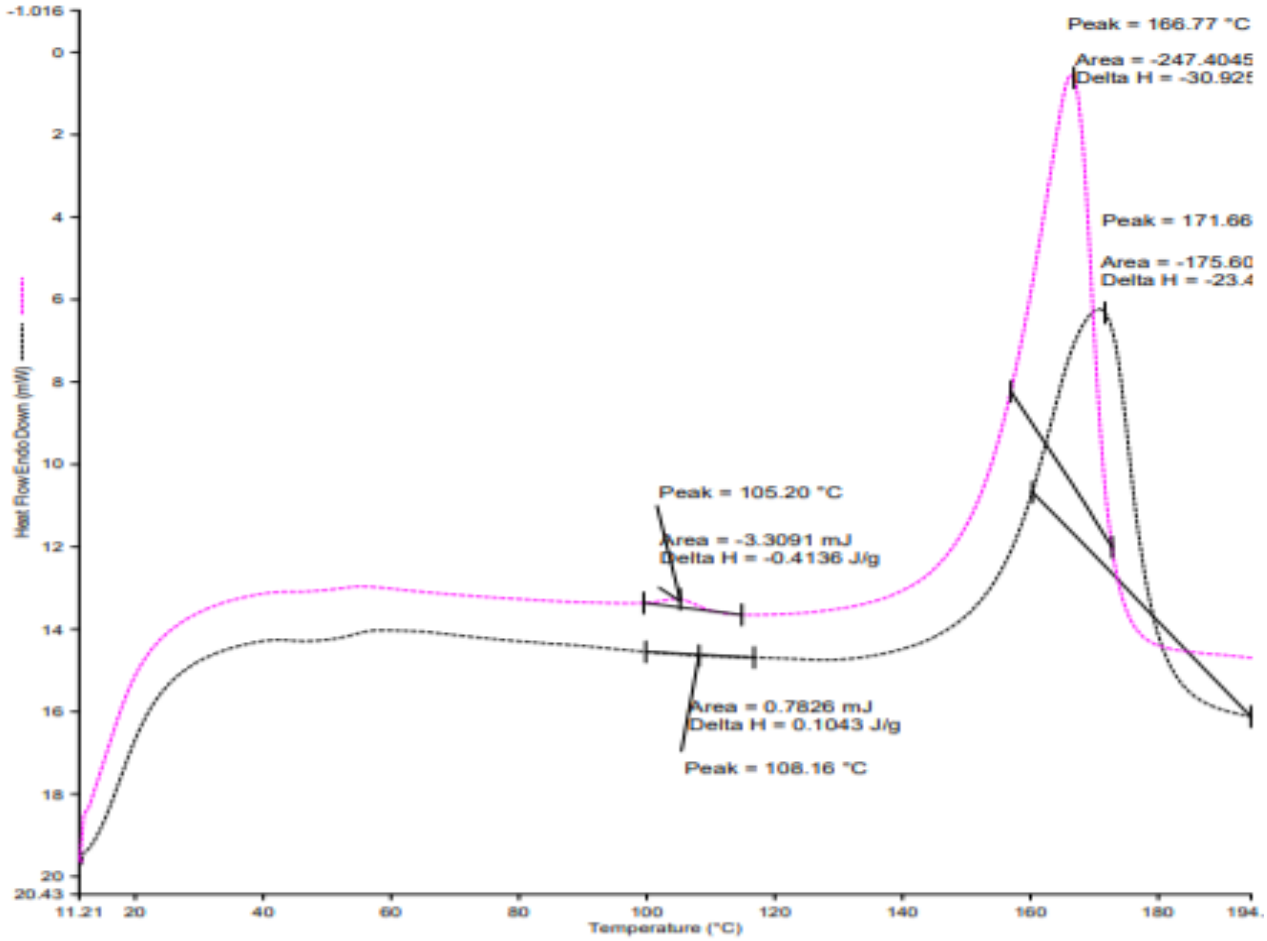

Figure 23 The comparison curves shows the result of virgin and injection molded PP polymer by DSC

The data obtained from fig. 19 which represents the data of the polypropylene. The two different samples with the same materials were experimented. The virgin PP and the injection molded PP. From the Fig. 19 are the DSC results obtained on the as received polypropylene film sample. The polymer exhibits the number of melting transitions and crystallization transition. The crystallization peaks of virgin and injection molded PP are observed at 108.16℃ and 105.20℃ respectively. Similarly, the melting peak of Virgin and injection molded PP peaks observed at 171.66℃ and 166.77℃ respectively. The heat of melting found to be -23.4 J/g and -30.920J/g.

The polymer could not exhibit the glass transition because the material was glass fiber Which is more crystalline, hard and brittle nature of the film sample. Although the Pyris Power Compensation has the high degree of sensitivity to be able to detect the Tg. The glass transition temperature of the polymer was supposed to -5℃ to 10℃ but the temperature could not go below 0℃ which is the polymer is thermoset glass fiber polypropylene.

Thus, it has shown the heat flow of endo shows the downward direction because it might be the reason that the heat flow of sample is lower than that of reference.

7 DISCUSSION AND CONCLUSIONS

The experiment was carried out to relate the thesis topic. So, the results however were generated as we have thought. Each of the research samples gave different thermal behavior after they were carried out by the DSC method.

The injection molding failure parts of the polymer were used as the material for the experiment which met the aim of the thesis. Then, the thermal properties like glass transition temperature, melting temperature and crystallization of the polymer were analyzed with the help of DSC 4000 Pyris manager software. Basically, the thermoset polymer did not exhibit the glass transition, but rest melting temperature and crystallization temperature were measured precisely. To be concluded the reason for the failed of the injection molding products are because of the excessive temperature drop, and pressure drop during the injection molding process which may lead non-fill surface of the products which are explained before.

This experiment was done at Arcada University of Applied Sciences in chemistry laboratory. The experiment was aimed to find the thermal properties of the failure parts injection molding polymer which were available at Arcada. The experiment was done with the co-operation of my fellow Umesh Bashyal. The experiment has carried satisfied result at the end. During the experiment we had to face different challenges and lack. The main challenges were the sample materials were not found easily within the campus lab. And some time the DSC software and machine were not working properly because of its ageing. Anyway, the best part of the experiment was always fun to learn more things about the DSC technique. I was completely new to this field I mean about DSC, but this experiment gave an incredible experience and skills that I could use in the future also.

However, the experiment detail of the polymer is described in Figures. 21 and 22. The experiments were done properly despite some challenges occurred during the experiment time. The experiment took much long time because of lack of some apparatus such as aluminum pan for the sample. Besides, it was quite difficult to collect the required sample for the experiment part.

We can see that the performance of two polymers from injection molding method. The results of Polylactic acid were obtained precise than the results of polypropylene. In fact, the Polypropylene (PP) was a glass fiber thermoset which is brittle and hard in nature which because of this the glass transition cannot be obtained. Besides, the Pyris software also could not read the temperature below 0℃. Otherwise the task was done with the research based of each material that has used in this lab experiment which meet the objectives of the thesis.

To understand entire experiment and the material behavior in depth, further experiments should be conducted. And one should use materials well suited to gives the relevant information. All the materials used in this experimental project were researched on the recommendations of the laboratory members.

8 BIBLIOGRAPHY

Alberto Naranjo, M. d.-A. (2007). *Plastics testing and Characterization* .

Borealis. (2007, 10 25). List of Plastic. [Online] available at: https://famnen.arcada.fi/lab/info/materials/tds/plastic/Borealis_HE%20365%20FB_PP.pdf [Accessed 24.4.2020].

Centre, P. S. (2003-2020). Differential Scanning Calorimetry. [Online] available at: https://pslc.ws/~pslcws/macrog/dsc.htm [Accessed 24.4.2020].

Differential Scanning Calorimetry. (2019, December 2). [Online] available at: https://en.wikipedia.org/wiki/Differential_scanning_calorimetry [Accessed 24.4.2020].

Differential Scanning Calorimetry. (2019, December 2). [Online] available at: https://en.wikipedia.org [Accessed 24.4.2020].

Edward L. Charsley, P. J. (2001). *Principles of Thermal Analysis and Calorimetry.* The Royal Society of Chemistry 2016.

Ezrin. (2013). Plastics failure guide. 245-251.

Hitchi Hightech Science corporation. (1981, June). Scepic heat capacity measurements by DSC I. *Scepic heat capacity measurements by DSC I*, 4. [Online] available at: https://www.hitachihightech.com/file/global/pdf/products/science [Accessed 24.4.2020].

J. Coulter, P. Gao, A. Duhduh. A. Kandu. (2019). Manufacturing Science Laboratory Lehigh University, Bethlehem, PA, 18015. *VIBRATION ASSISTED INJECTION MOLDING FOR PLA WITH ENHANCED MECHANICAL PROPERTIES AND REDUCED CYCLE TIME*.

Joseph D. Menczel, R. B. (2014). *Thermal Analysis of polymer.* Wiley.

Leon Welsh, Yessenia Shade. (2014). *Handbook of Polymer and Plastics Engineering.* Delhi: Academic Studio. [Online] available at: https://ereader.perlego.com/1/book/1238650/1 [Accessed 24.4.2020].

omnexus. (2020). The material selection platform. *The glass transition temperature*. [Online] available at: https://omnexus.specialchem.com/polymer-properties/properties/glass-transition-temperature [Accessed 24.4.2020].

Sachina, W.J. (2000). Application of DSC to Injection Molding. 2000.

Sichina, W. .. (n.d.). Application of DSC to Injection Molding. 4.

Thermal method. (n.d.). 46. [Online] available at: https://teams.microsoft.com/_ [Accessed 24.4.2020].