Failure analysis of Injection moulded parts using DSC.

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Abstract:
The main purpose of this thesis was to study the use of differential scanning calorimetry (DSC) in the failure analysis of injection moulded plastics parts and focus on correctly interpreting data produced by Pyris software. DSC analysis was used to determine different chemical and physical properties of polymers where heat flows in and out of the samples were measured as a function of time and temperature.
PP and PLA injection moulded tensile test specimens (dogbones) produced in Arcada were chosen as the main subjects of study. Analysis of thermal properties between precise and imprecise PLA dogbone and between raw PP and imprecise PP dogbone were done in order to highlight reasons of failure (imprescise shape formation) in PLA and PP dogbones.
Thermal properties were studied for establishing experimental parameters in the new DSC calorimeter at Arcada, and further analysis was made using most relevant collected data. The information concluded after the experiments suggest that melting temperature is decreased in imprecise PLA dogbone than in precise PLA dogbone. Due to decrease of melting temperature, crystallinity temperature has also decreased in imprecise dogbone. So it suggests that difference in melting temperature in same material can be due to improper heat treatment in the process or imroper timing in injection cycle. Similarly, analysis was made between raw PP and imprecise PP dogbone.

Keywords:	DSC, Injection Moulding, Dog bone, PP, PLA, Glass Transition, Crystallinity, Specific Heat Capacity, Thermal Analysis.
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Abbreviations

C_p : Specific Heat Capacity

DSC : Differential Scanning Calorimetry

mg : milligram

PLA : Polylactic Acid

PP : Polypropylene

T_c : Crystallization Temperature

T_g : Glass Transition

T_m: Melting Temperature

FOREWORD

I would like to express my gratitude to my supervisor Mr. Stewart Makkonen-Craig, Senior professor at Arcada University of Applied Sciences for the guidance throughout this thesis work. Also, I would like to thank Mr. Harri Anukka, Laboratory Engineer and Mr. Silas Gebrehiwot, Senior lecturer at the Department for providing samples and other info for the experiment.

I would like to thank Mr. Shiva Bhandari, my classmate with whom experimental part was done together under supervision of Mr. Stewart Makkonen-Craig. It was more systematic for us to work together, since it helped us to gather variety of sources of information and share our ideas. The final analysis made here can be different than of Shiva`s analysis because analysis was made individually as per our knowledge. I would also like to thank Uyen Nguyen and Lynsey Lius who helped me at the beginning to get familiar with DSC machine, all the teaching members at Department of Energy and Materials Technology and my fellow students at Arcada University of Applied Science.

And finally, I like to dedicate this thesis work to my parents, my family members and my close ones who always motivated me during my studies.

29 May 2020

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1 INTRODUCTION

1.1 Background

Throughout the history, people had been using simple thermal analysis tests to determine the purity of material for different purposes in manufacturing. Since then people tried to find out more efficient and scientific ways for thermal analysis of materials. The first thermometric measurements were carried out in 1887 by French scientist, Henry Le Chatelier. First differential temperature measurement of sample was carried out by British scientist, William Roberts-Austen in 1899. It took time for commercial instruments to appear until 1960. Recently, there are more advanced technology equipped commercial instruments available in market for different purposes. (Mettler-Toledo AG, 2013)

"Different types of products have different polymer composition as a material, so there will be different failure reason of the products." DSC can help to characterize the different properties of polymers, like melting point, crystallinity, and propensity of the polymer to under crystallization at elevated temperatures. By using DSC, thermal analysis of the material composition can be done to choose suitable raw material for successful product design through injection moulding process.(Sichina, 2000)

Injection moulding is the most popular process for producing plastics products. It is famous because it gives a designer the opportunity to create true three-dimensional part shapes and the designer can control all the surfaces of the plastic parts being manufactured. Injection moulding process involves many steps, where every step counts for the successful product production. The selection of the suitable material and ideal operating parameters of injection moulding machine as per requested product are the key important factors to be noted in successful product design. So, DSC can be suited well in order to overcome all the problems related to material selection and for analysing suitable operation parameter of machine.

There are different parameters in injection moulding that need to be considered precisely for successful part production. Like suitable melting temperature, mould temperature, injection pressure, injection speed, and mould cycle. All these parameters are researched and applied throughout the process to obtain high quality end parts. There are certain transitions like glass transition, melting and crystallization that a material goes when

thermal energy is applied to it. All materials possess different thermal properties depending on how they were produced and may shows different properties under different processing parameters like in temperature, pressure, and flow rate. It is difficult to verify that final product meets its quality with just universal experimented data of materials while production. It is very important to study how material behaves under processing condition and how it is compatible at end product. DSC is a powerful tool that provides designer thermal properties of raw materials, their processing parameters in injection moulding and thermal properties associated in final end products.

1.2 Objectives

This thesis is a study of possible failure reasons of imprecise injection moulded PLA and PP dogbone using DSC as analytical tool. Case study for analysing failure reasons of dogbone is done in this thesis. The main objectives of this thesis are as below:

- To correlate injection moulding parameters and DSC curves through literature review and experiments.
- To learn Preparation of samples for DSC and to interpretation of DSC results.

Furthermore, this thesis will describe the literature of injection moulding, DSC, polymers (PLA and PP), common possible defects in injection moulding and DSC as problem solver. The steps of experiment like sample preparation, processing of the samples in the DSC and techniques for interpreting DSC results are also described. Detailed information on results and analysis are also presented in following chapters.

2 LITERATURE REVIEW

This chapter mainly focuses on the overview of existing knowledge about DSC, injection moulding and relevant studies. Explanation of DSC, injection moulding, possible defects on injection moulded parts and use of DSC in thermal analysis are briefly presented. In injection moulding material are heated during the process to their melting point and then injected in the dye of desired shape to attain the final product. DSC gives the information of thermal properties of a material; it can be used as a tool for material study in injection moulding process.

2.1 DSC.

Differential scanning calorimetry is one analytical tool used to study different thermal properties of polymers. Endothermic and exothermic effects, transition and enthalpies reaction, characterize a peak and specific heat capacity can be measured. In DSC sample and reference are heated at same temperature rate and difference in heat flow at same temperature is measured. The relevant transitions involved in DSC are described in the following subsections. The schematic illustration of the DSC process is shown in Figure 1

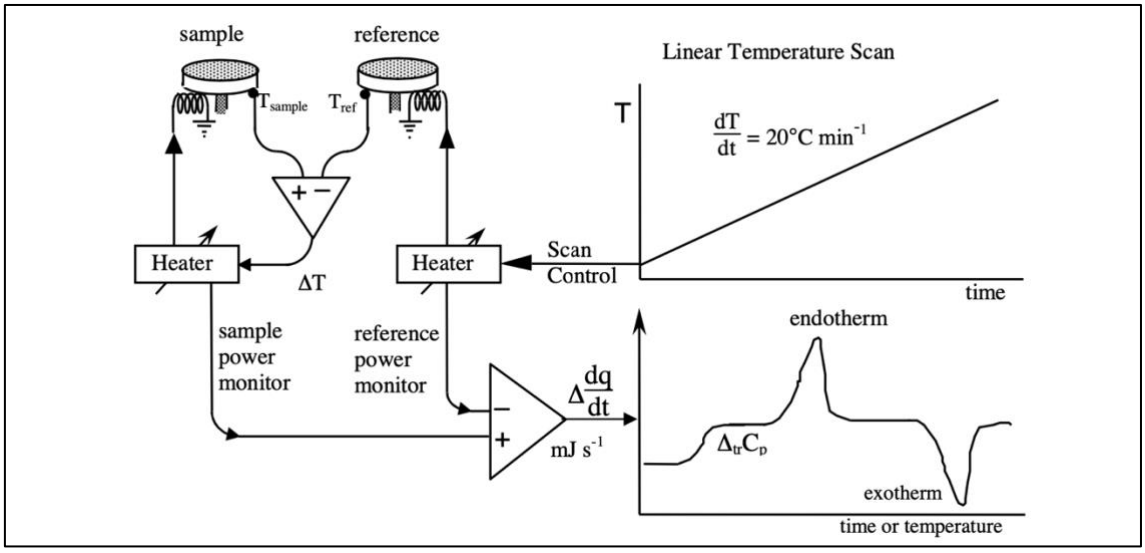

Figure 1: schematic drawing of DSC apparatus with function flowchart. Sample and reference are heated at same rate (dT/dt) and difference in heat flow (Δ dq/dt) at same temperature is determined by amplifier in form of thermograph. (Colby college, ei pvm)

2.1.1 Glass Transition and Glass Transition Temperature (T_g)

In semi crystalline materials (having amorphous and crystalline regions), only amorphous region undergoes glass transition. In amorphous solid, molecules are in disorderly arranged pattern, so melt transition goes gradually when heat is supplied. In this transition, when temperature increases, the solid molecules start to get flexible and moves slowly from initial state, showing elastic property at certain temperature range. This temperature at which solid glassy state of material turn into elastic rubbery state is called glass transition temperature (T_g). whereas in crystalline materials, presence of highly ordered definite molecular patterns and uniform intermolecular force in crystallites they melt all at once when finite amount of heat is applied. So completely crystalline materials do not show T_g.

T_g is important because it helps to observe thermal properties and molecular structure of polymers for further processing application field. T_g does not always occur at a distinct temperature but over range of temperatures because the mobility of polymer chains increases significantly with heat treatment. It depends on the molecular weight, thermal history, measurement method and heating or cooling rate of polymer. (University of South Carolina Upstate, 2000)

2.1.2 Melting Temperature (T_m)

It is an important thermodynamic property of crystalline region of semi crystalline polymers, that gives information on the temperature of a polymer that undergoes on heating a change from solid to liquid state. When a solid material is heated, its molecules absorb kinetic energy and the molecules start to move, breaking its structure pattern and melt eventually. The temperature at which its solid molecules change to melt state is melting temperature. It is denoted by T_m.. At this state aligned molecular chains change into viscous liquid where molecules are in highly random state, that is amorphous. So, in melt phase any polymer, crystalline or amorphous, will exist in amorphous state. Solid and liquid phases are in equilibrium state at the melting temperature. Impurities in polymers and imperfection in crystals are top factors for deviation in values than measured of pure samples.

2.1.3 Crystallinity and Amorphousness

A degree of presence of crystallites in a polymer affects its properties: the more crystalline a polymer, the more regularly aligned its chains that leads to increases on its hardness and density. When thermal energy is applied to a crystalline material, it melts all at once. So, crystalline materials have a sharp melting point. But in amorphous material, due to absence of crystallites, the melt transition is slower and has no sharp melting point. It suggests that crystalline material has sharp melting point than of amorphous material. Crystallinity occurs when a polymer is cooled after melting or after solvent evaporation. At this state, molecular energy starts to reduce, and viscosity increases, and crystallites start to reappear. The particular temperature at which crystallites occur is the crystallization temperature and denoted by T_C. The thermal history of material affects the degree of crystallinity present in a material. (Kulkarni, 2007)

2.1.4 Specific Heat Capacity

Specific heat capacity is the most important factor that determines how DSC works. In DSC, material thermal properties are measured by observing how the specific heat capacity of material is changed by temperature. It is the amount of heat energy required to raise the temperature of per unit mass by 1 °C. Its unit is joules/°C and is denoted by C_p. It can be derived from heat flow and heating rate relationship.

Heat flow = $\frac{total\ heat\ supplied}{time} = \frac{q}{t}$ (1)

Heating rate = $\frac{Change\ in\ temperature\ (\Delta T)}{time} = \frac{\Delta T}{t}$ (2)

Now dividing equation 1 by equation 2 gives C_p

$C_p = \frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T}$ (3)

Or, $C_p = \frac{q}{\Delta T}$ (4)

This equation is programmed inside DSC machine and C_p is calculated from the slope against amount of heat and temperature. (HUMBOLDT UNIVERSITÄT ZU BERLIN, ei pvm)

It is the quantitative thermodynamic value that gives information on how a material stores additional energy at the molecular level. It gives information on amount of heat energy needed to raise temperature and amount of heat energy needed to decrease temperature at

certain range. In crystalline materials, molecules can only vibrate so they have low C_P; in an amorphous material, molecules are in irregular arrangement, so they have high C_P. So, by observing C_P, one can get information about molecular structure of materials. (Cassel, ei pvm)

2.2 Injection Moulding process

The manufacturing process, where parts are produced by injecting molten material into mould using varieties of materials. Materials like Plastics (Thermoplastic and Thermosetting plastic), metals, glasses and elastomers are used as raw materials that goes through different stages in processing to obtain desired parts of different shapes and sizes. Raw materials are chosen according to needs, function and sustainability of designed part. Materials for the part are selected, fed into heated barrel, mixed, and injected into mould, where it cools and hardens in the shape of designed mould cavity. All these entire process since designing the parts, choosing material for parts, material for mould, and the properties of moulding machine plays vital role for success of parts designed. (Wikipedia, 2019)

The best thing about injection moulding is, same parts can be created millions of time with success. (Rogers, 2015) For this, injection moulding machine, raw material (Plastic) and mould are needed, here are some steps involved that need to be take in account in for producing efficient final parts

Generally, Raw material are chosen as per the application of final parts and its compatibility in manufacturing process. Mostly polymer is best suited for injection moulding process. There are lots of varieties in grades or blends to choose for different type of parts production.

Polymers like thermosetting plastics; Polyurethanes (PUR), Unsaturated polyesters (UP), Epoxides (EP), Vinyl esters (VE) are used for manufacturing mostly hard parts. Once they are produced, they are difficult to recycle due to adding of hardening liquid resin and another curing agent. They are mostly preferred for producing plastic parts having special characteristics like good heat resistivity and electrical properties. These materials are also used in injection moulding to produce special shaped parts.

Thermoplastic polymers are also known as soft plastic because they get soften when heated. Also, they can be recycling and easy to process, therefore they are highly preferred

to produce parts in large volume through injection moulding. Polymers like, Polyethylene (PE), Polyethylene terephthalate (PET), Polyvinyl chloride (PVC), Polylactide (PLA), Polypropylene (PP)are mostly used according to different function of injected parts. (Leomuovi, 2019)

2.2.1 Injection Moulding machine and its theory

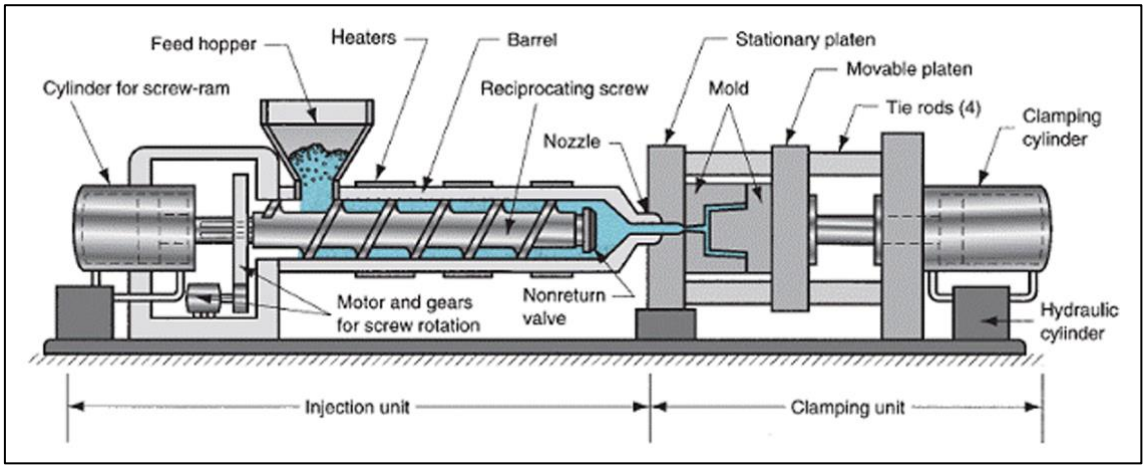

Figure 2: Injection Moulding machine components (Custompart.net, 2019)

This machine uses high pressure to inject molten raw material into mould to produce parts of desired shape and size in high quality and speed. Skilled manpower is required to operate this machine because even small unnoticeable errors like in feeding rate of raw material, changes in temperature, clamping force can lead to malfunction on durability of final parts. So, it is very important in need of skilled manpower to operate it. Schematic view of injection moulding machine with its component is shown in Figure 2Figure 2: Injection Moulding machine components (Custompart.net, 2019) **Error! Reference source not found.**.There are four main steps involved during injection moulding cycle and they are, clamping, injection, cooling and ejection. (Leomuovi, 2019)

- Clamping and Plastification

Two halves of the mould are clamped together with enough force to close the mould airtightly by clamping unit, this force is called Clamping Force. (Custompart.net, 2019) Raw material is melted using heat and ready to be injected into mould in this stage. When raw materials are melted, they turned into molten viscous state having certain melt flow index property. Materials with low viscosity have high melt flow and requires less

clamping force. Changes in property of material may change viscosity of material and hence change in melt flow. Original properties of raw material should not be change and the enough clamping force to close the mould need to be maintained accordingly throughout the process. (Leomuovi, 2019)

- Injection

After suitable temperature is reached, molten material is injected into the closed mould cavity by the injection unit. So, the clamping force for mould must be greater than the injection force. The injection force and injection time depend on the thickness, size and shape of mould. There is enough time to hold the mould closed, so that material is hold packed into the mould cavity in order to minimise the irregularities on the surface of the object. (Leomuovi, 2019)

- Cooling

The cooling process is the longest and an important stage in Injection moulding because in this stage, molten plastic starts to solidify into desired shape inside mould cavity. Cooling process starts as soon as Holding pressure is applied after injection. Holding pressure is released after enough cooling time is reached as per the thermodynamic properties of the material. So, enough cooling time of the material are considered precisely in order to prevent warping. (Custompart.net, 2019)

- Ejection

This is the last stage in the injection moulding process. Final parts are removed from the mould cavity once sufficient cooling is made and the part is hard enough. During cooling, the Part sticks on the wall of mould, so force applied to eject the part from mould by an ejection unit.

In the ejection cycle, once a part is ejected, the mould is clamped close for the next cycle to be injected and this cyclic process continues until the required quantity and quality are reached. For most of the parts produced, some post processing is required like trimming of extra material attached in parts due to cooling of material in the channel inside mould cavity. This excess scrap material can be recycled. There is some degradation in the

property of recycled materials, so a suitable ratio of the composition of recycled material to raw material can overcome the failure in parts in recycling. (Custompart.net, 2019)

2.2.2 Mould design

The mould is a core part of the injection moulding process. The final part is formed inside the mould cavity when molten material is injected inside it and allowed to cool. The mould is designed as per the function of final part. In order to achieve the precision and efficiency of final mould, it requires highly technical and complex process due to various components that need to be taken care during mould design. For example, by reducing maximum thickness of wall of part designed help to reduce cycle time; or by applying corners where possible, enhances durability and applying drafts carefully help for easy removal of parts from mould. (Dienamics , 2019)

2.3 Possible Defects and their causes in injection moulding process

Stress plays important role in the injection moulding process. Applied temperature and pressure in injection moulding creates stress in the parts. This stress is transformed into potential energy, stored in atoms that binds the molecules in an oriented shape, so the product performs as designed. Polymer molecules at normal state are random coils with no particular shape. When heat is applied their molecules are oriented like stretched rubber band and when rapid cooling during processing is done it does not allow enough time for relaxation resulting in the frozen-in stress in parts. This frozen-in stress can be relieved with time and temperature, allowing molecules to gain original relaxed orientation. So, applying suitable heating/cooling rate and appropriate moulding condition helps to eliminate the formation of frozen-in stress or residual stress in the parts that would otherwise lead to mechanical failure of injected parts. Some of the possible common physical defects that can be observed with eyes, with their causes is presented below in Table 1Table 1. (Ezrin, ei pvm)

Table 1: Possible Defects and their causes in Injection moulding parts (Custompart.net, 2019)

Possible Defects	**Causes**
Bubbles	Presence of moisture in raw material Non uniform cooling rate High injection temperature
Sink marks	Non uniform cooling rate. Low pressure while injection
Ejector marks	Cooling time too short.
Unfilled sections	Not enough shot volume. Flow rate too low
Flash	High injection pressure. Low clamping force.
Warping	Varying cooling rate

2.4 DSC as a problem solver for injection moulding

All the polymer processed in injection moulding goes through several thermodynamic phase transitions. It means all the polymer possesses some kind of thermal properties that are required for favorable manufacturing processing. Polymer are chosen according to function of final parts and their processing parameter. To ensure the quality and sustainability of designed parts, post analysing of raw material is required because while manufacturing, thermal and mechanical properties of material is affected by various step involved in manufacturing. Therefore, it is important to assure constant quality of material from post processing to final end parts. DSC can be very suitable for analysing thermal properties of polymer. (AZoNetwork, 2020)

Raw material arrives from different supplier in processing unit. Sometimes there may be small variation in chemistry and additives can lead to malfunction of part designed. DSC can resolve this problem by identifying suitable thermal properties and processing

parameter of injection moulding machine. For example, simple isothermal crystallization tests perform in DSC can help to identify crystallization properties of polymer that undergoes injection moulding process, and can help to determine the ideal injection moulding process parameter for this specific polymer. (Sichina, 2000)

There are various inbuilt thermodynamic calculations in the DSC instrument that help to provide quick results on thermomechanical property of polymers. Although there may need few calibrations by operator. Beside quick result DSC can be run using small samples, less control and easy method development. So, DSC can be termed as powerful thermal analytical tool for injection moulding. Below are some specific needs addressed by DSC in polymer processing.

- Determine suitable processing temperature (injection, moulding, extrusion)
- Identify Unknown polymer samples. (Martin Doedt, ei pvm)
- Analysing quality (Failure analysis, evaluation of new material)
- Measure specific heat capacity, crystallinity, Glass Transition.
- Finds degree of cure and effects of aging.
- Determine effects of additives, and phase separation (polymer blend and copolymer)
- Evaluating performance of designed parts under operating temperature and choosing raw material for specific functions. (EAG lNC, 2017)

Application of DSC in the measurement of effect of heat treatment on polymer crystallinity was performed by (Hitachi High Technologies, Tokyo, 2008) is presented here. In their experiment PP was used as sample of investigation. Four pieces of PP weighing 0.5 mg were heated from room temperature to 200 °C at 10°C/min. They were heat treated up to 110°C, 115°C and 120°C and one without heat treatment. In this case PP melting was around 160°C for all samples with additional minute endothermic peak for heat treated samples and smooth curve for no heat treatment sample as shown in Figure 3. They suggested that each heat treatment temperature produces different crystal structure formation. So, this experiment illustrates use of DSC to find thermal property of polymer about crystallization and its heat treatment. (Hitachi High Technologies, Tokyo, 2008)

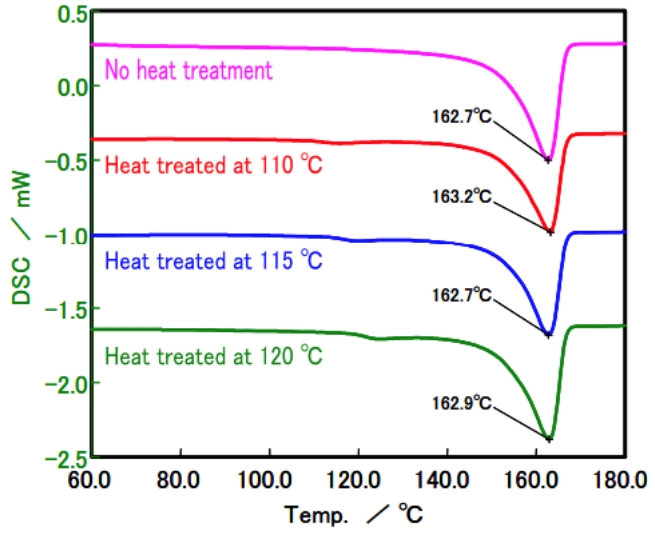

Figure 1 DSC curves for Measurement Condition 1

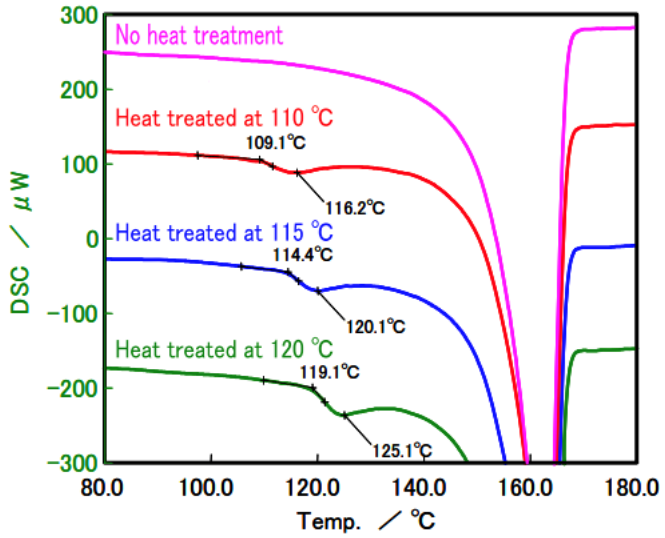

Figure 2 Enlarged views of the DSC curves for Figure 1

Figure 3: DSC graphs of PP measured by (Hitachi High Technologies, Tokyo, 2008)

3 EXPERIMENT AND METHODOLOGY

This chapter is about the experiments carried out, the methods and materials used during the research. PP and PLA were chosen because they have similar melting points thus easier samples to carry out a study and also because their availability at the production lab at Arcada University of Applied Sciences. The experimental part was done in the chemistry laboratory at Arcada University of Applied Sciences. Lots of literature review were done to find suitable processing parameters for DSC experiment of PP and PLA, interpreting DSC curves and analysing results.

3.1 Materials

3.1.1 Polylactic Acid (PLA)

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 disadvantage of PLA is it has slow crystallization rate, obtaining sufficiently high crystallinity within reasonable manufacturing time is difficult. (J. Coulter, P. Gao, A. Duhduh. A. Kandu, 2019)

During this experiment mainly two types of PLA products were chosen for the study. The first dogbone is precise dogbone and another dogbone sample with irregularities in shape, imprecise produced from injection moulding process were chosen. The DSC test samples were taken from same area of each dog bone, i.e. from the cavity of imprecise (fail PLA)

dogbone and the cavity of the precise dogbone (optimum PLA) as marked black circle in Figure 4.

Figure 4: PLA injected dogbones used as sample, black circle mark is the area where main sample for experiment were taken

3.1.2 Polypropylene (PP)

PP is most used thermoplastics in everyday objects like in packaging, household appliances, automotive and so on. Heat treatment used for producing PP plays important role in the final properties of PP by changing its crystal formation behavior. There are different grades of PP which leads to different thermal properties of PP. Different grades can be used for variety of purposes. They can be identified using different thermal analysis methods like DSC. While processing PP in injection moulding, holding time pressure, holding time, melt temperature and types of additive used make changes in the quality of final products. So good knowledge of thermal analysis and correctly interpreting result could help to minimize the production of failure parts.

PP was chosen as the subject of study in second part of experiment. Here, raw PP (Figure 5) and imprecise PP dog bones (Figure 6)were examined as samples in DSC and analysed to determine the failure reason. A tiny piece of dogbone sample was cut through failure surface of PP dogbone using scalpel, marked black in Figure 6.

Figure 5: Raw PP used as sample in experiment.

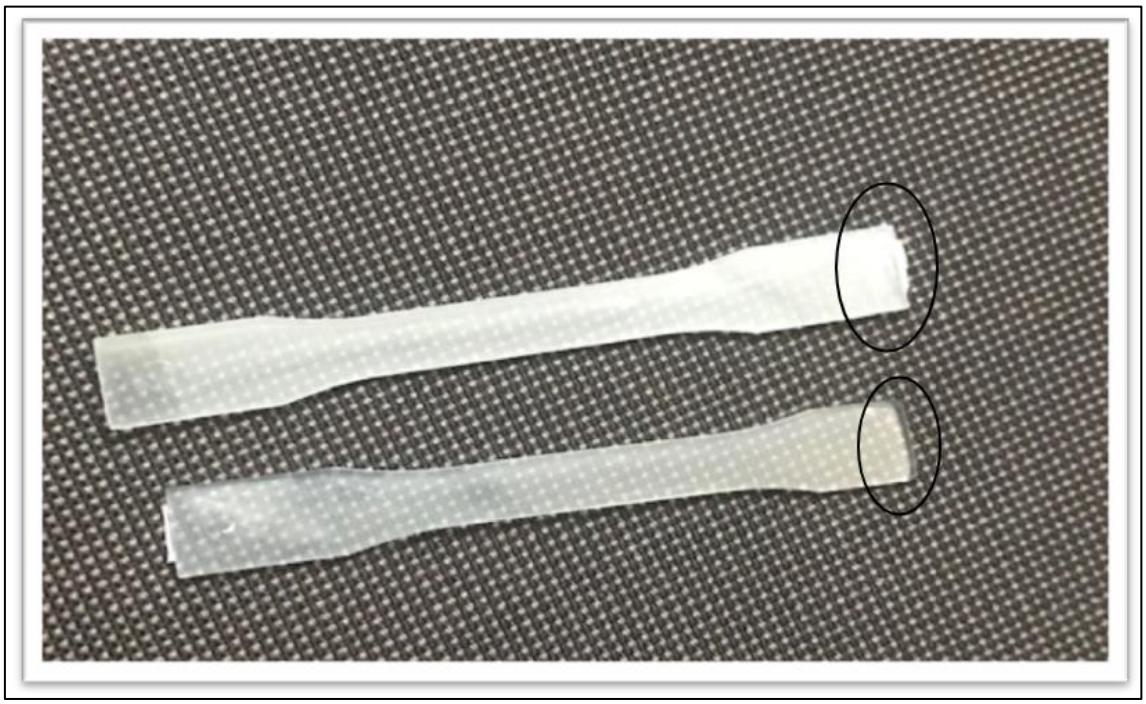

Figure 6: Imprecise PP dogbones used as sample for experiment, black circle mark is the imprecise area from where main samples were examined

3.2 Equipments

The following equipment were used throughout the experiment

- Calorimeter

DSC 4000, by Perkin Elmer was used as calorimeter in this experiment. It is single furnace DSC where sample are proceeded as programmed and real time thermograph can be viewed in Pyrsis software

Figure 7: DSC 4000 by Perkin Elmer

- Nitrogen gas cylinder

Nitrogen gas was used to create inert, dry atmosphere at the heating chamber of DSC. It was supplied through gas cylinder. It was connected via pipes to inlet chamber of DSC 4000.

Figure 8: Nitrogen gas cylinder

- Microbalance

It was used to measure the mass of sample. Mass should be noted precisely as much, since mass of sample is directly proportional in obtaining C_p of material

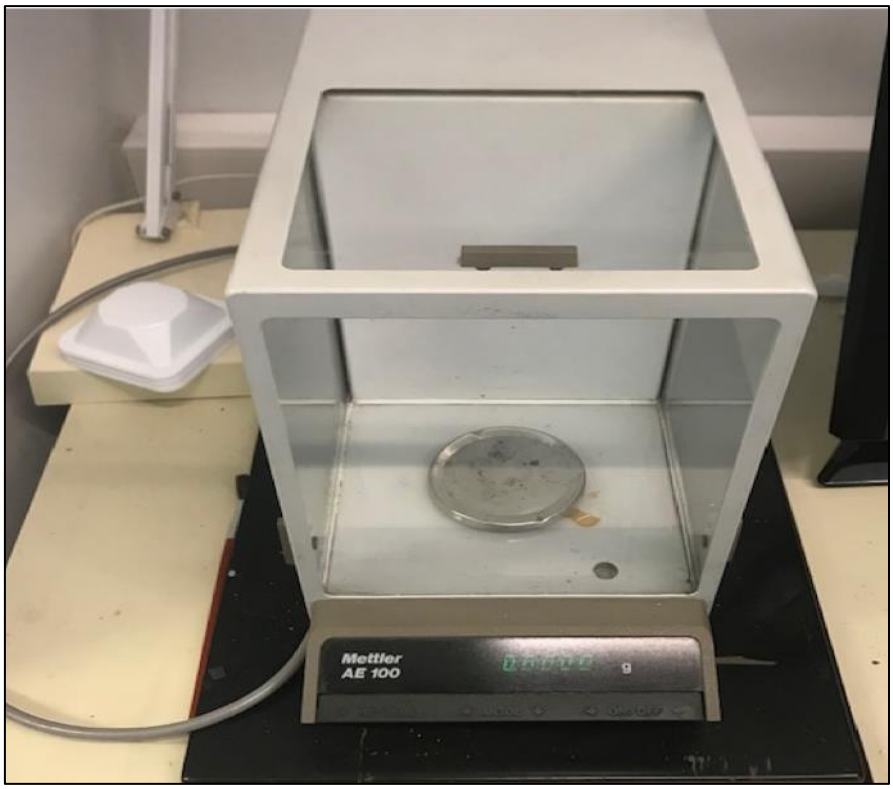

Figure 9: Microbalance to weigh the samples.

- Capsule press

It was used to seal a sample inside pan covered by lid, and to crimp the excessive edge part of pans.

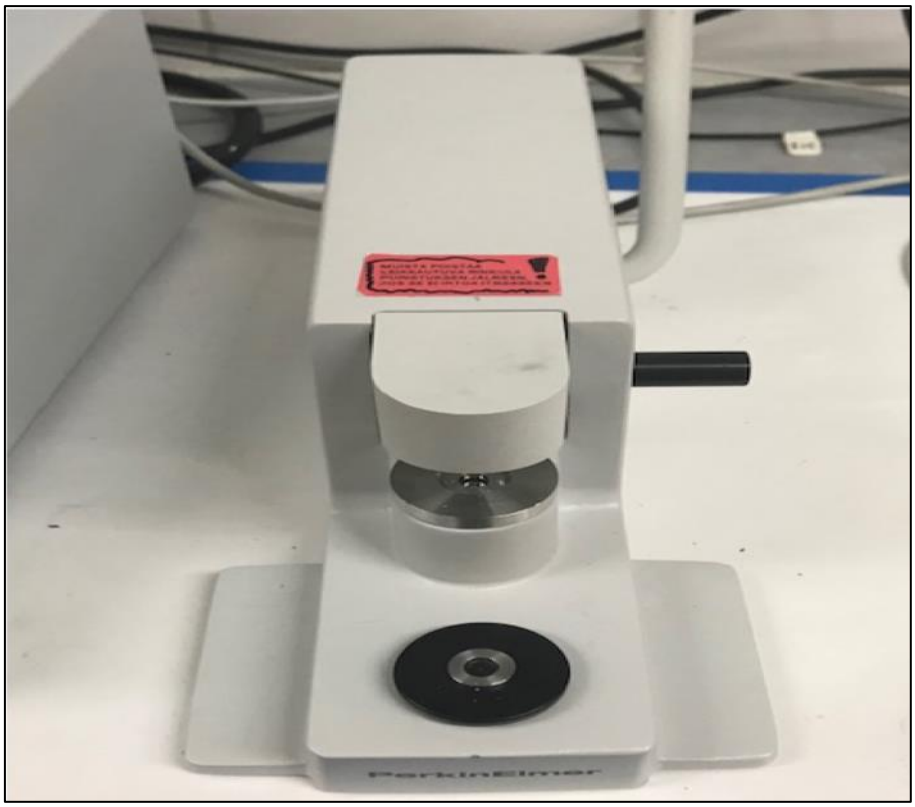

Figure 10: Capsule press to seal sample inside aluminum pan and lid.

- Standard aluminum pans and lids

Standard aluminium pans and lids were used to seal sample inside them. 40 μL pans were used and can be used for temperature range of -140°C to 600 °C

Figure 11: Aluminum pans and lids for sample sealing.

- Glycol cooling unit

It is a fluid bath composing of 50% ethylene glycol and 50% deionized water. It was connected directly to the inlet and outlet ports of DSC analyser. It was used to set initial temperature and for further cooling in experiment.

3.3 Sample preparation for experiment

One piece of precise dogbone and one imprecise dog bone (having irregular shape on the edge) made of PLA were chosen for sample, which had been injection moulded in Arcada`s injection moulding machine. Precise dogbone is the tensile test specimens produced for research in Arcada`s production lab and imprecise dogbone is from same production lot. Both of these sample were prepared and examined individually. Likewise, for PP, raw PP used to make tensile test specimen (dogbone) and imprecise dogbone (having irregular shape on the edge) was produced from same raw PP used here. Both samples were prepared and examined individually.

A sample was first cut from irregular surface of imprecise dogbone with the scalpel and a tiny amount of observed sample was weighed by microbalance and noted. Then the weighed sample was put into the aluminum pan and was sealed by the capsule 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.

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 was set to 12℃, and so initially cooled down from room temperature. This initial temperature was set using cooling unit.

Before preparing the sample capsules, the nitrogen gas flow had to turned on, so that it removed moisture in the DSC chamber until the sample is loaded and started. Samples were handled carefully to avoid additive contamination during preparation.

3.4 Experiment

3.4.1 For precise PLA dogbone

A piece of sample weighting 9 mg was taken from the same area of dog bone where sample for failure PLA dog bone was taken. It was sealed inside aluminum pan using capsule press and similarly empty pan was prepared as reference pan. Both were placed inside DSC calorimeter in sample dish and reference dish respectively and the programme was run in Pyris software. Since the melting temperature range of PLA is 150$_o$C to 160$_o$C (Rogers, 2015) , it was held for 1 min at 12 $_o$C and then heated to 200 $_o$C at the heating rate of 20 $_o$C/min

3.4.2 For imprecise PLA dogbone

A piece of sample weighting 7.6 mg was taken from irregularity area of failure PLA dog bone. It was sealed inside aluminium pan using capsule press and similarly empty pan was prepared as reference pan. Both were placed inside DSC calorimeter in sample dish and reference dish respectively and the program was run in Pyris software. It was heated from initial set temperature 12 $_o$C to 170 $_o$C at the rate of 20 $_o$C/min and then it was held for 1 min at 170 $_o$C and again cooled to 12 $_o$ C at the rate of 10 $_o$C/min.

3.4.3 For raw PP

A piece of raw PP was used as sample weighting 7.50 mg. It was sealed inside aluminium pan using capsule press and similarly an empty aluminium pan was sealed as reference pan. Both were placed inside DSC calorimeter in sample dish and reference dish respectively and the program was run in Pyris software. Since the melting temperature range of PP is 165$_o$ to 175$_o$ (Anon., n.d.), it was hold for 1 min at 12$_o$C and was heated from initial set temperature 12$_o$C to 200 $_o$C at the rate of 20 $_o$C/min. It was hold for 1 min at 200 $_o$C and then cool to 12 $_o$C at the rate of 20 $_o$C/min.

3.4.4 For failure PP dogbone

A piece of sample weighting 8 mg was taken from irregularity area of PP dog bone. It was sealed inside aluminium pan using capsule press and similarly empty pan was prepared as reference pan. Both were placed inside DSC calorimeter in sample dish and reference dish respectively and the programme was run in Pyris software. It was hold for 1 min at 12 $_o$C heated from 12 $_o$C to 200 $_o$C at the rate of 20 $_o$C/min and then it was hold for 1 min at 200 $_o$C and again cooled to 12 $_o$C at the rate of 20 $_o$C/min.

3.5 Techniques for interpreting DSC graphs

Important transitions like glass transition temperature, melting temperature and crystallinity were observed from the DSC thermograph obtained from Pyris software. First, thermal properties of PP and PLA were studied, and relevant parameters were applied to their specific temperature ranges. For example, the melting temperature of PP is around 160 °C, so PP was heated up to 200° C at the rate of 20 $_o$C/min in both cases and for PLA, imprecise dogbone was further cooled to 12° C at the rate of 10 °C/min, so that all the possible transitions within this range could be observed. Multiple samples were run from both PP and PLA dogbones using different heating range and sample mass. The best results are presented and analysed here. Differences in thermal properties of the same material helped to find possible causes of material failure.

Generally, there is not any ready-made computer software for analysing DSC curves in single run. Having lots of experience in thermal analysis and good knowledge of transitions that occurred in experiment is the scientific way for interpreting curves as

much as correctly. In this experiment following techniques were examined for interpreting DSC curves. Some of the possible ways to analysis curves are described below.

3.5.1 Identifying Artifacts

Artifacts are external causes that leads to misinterpretation of data in curves. They can be defined as technical term rather than sample itself in experiment. Some of the artifacts that may occur in experiment are:

- Sudden change in heat flow between sample and the pan, this may be caused due to sample of irregular shapes that make uneven contact with base of pan.
- Sudden change in heat flow between the pan and DSC sensor, this may be caused due to small movement of pan around the sensor.
- Temperature Fluctuation: due to passing of cool air into measuring cell which leads to noisy signals in curves.
- Transition at 0◦; It indicates presence of moisture or inert gas in sample.

Quality of data improves on possible avoiding of artefacts from the process. Often it is difficult to identify artefacts in single run. So, it requires multiple run until the most relevant data is obtained. (UserCom, 2000)

3.5.2 Baseline Subtraction

Baseline is the curve obtained when the empty pan without the sample is run. It is always good to perform baseline run before performing experiment with sample. So, real heat flow into sample can be obtained by subtracting baseline curve from measured curve with sample under same circumstances.

3.5.3 Measurement specification

Certain measurement specification like temperature range, temperature rate and sample weight play important role in obtaining high quality data. This are specified on the basis of the physical and chemical properties of the sample. For example, if cooling rate is low,

sample molecules has more time to rearrange the structure leading to a higher crystallinity degree than usual. So, adjusting the cooling rate, allow molecules to settle in its original state properly can give closeness to actual result. Also, setting appropriate temperature range at which thermal transition occurs in particular sample can give result close to true value. Likewise choosing appropriate sample weight as per the sample nature is very necessary for quality data. Large sample are used for detecting weak effects at low heating rates and small sample are used when high measurements rates are needed. (UserCom, 2000)

4 RESULT AND ANALYSIS

The results presented here are the thermal properties of sample PP and PLA obtained from Pyris software. Glass transitions temperature, melting temperature and crystallinity were noted directly by identifying transition peaks from DSC graph in Pyris software. Like, crystallization occurs at exothermic peaks and melting occurs at endothermic peaks, T_g can be observed at starting baseline shift transition in DSC graphs. This chapter describe the thermal properties of samples used and analyse their transitions based on their results for failure reasons.

4.1 Precise and imprecise PLA dogbones results

Figure 12, shows the result obtained from DSC data analyser software, Pyris when precise PLA dogbone was used as sample. The following are its main transition noted.

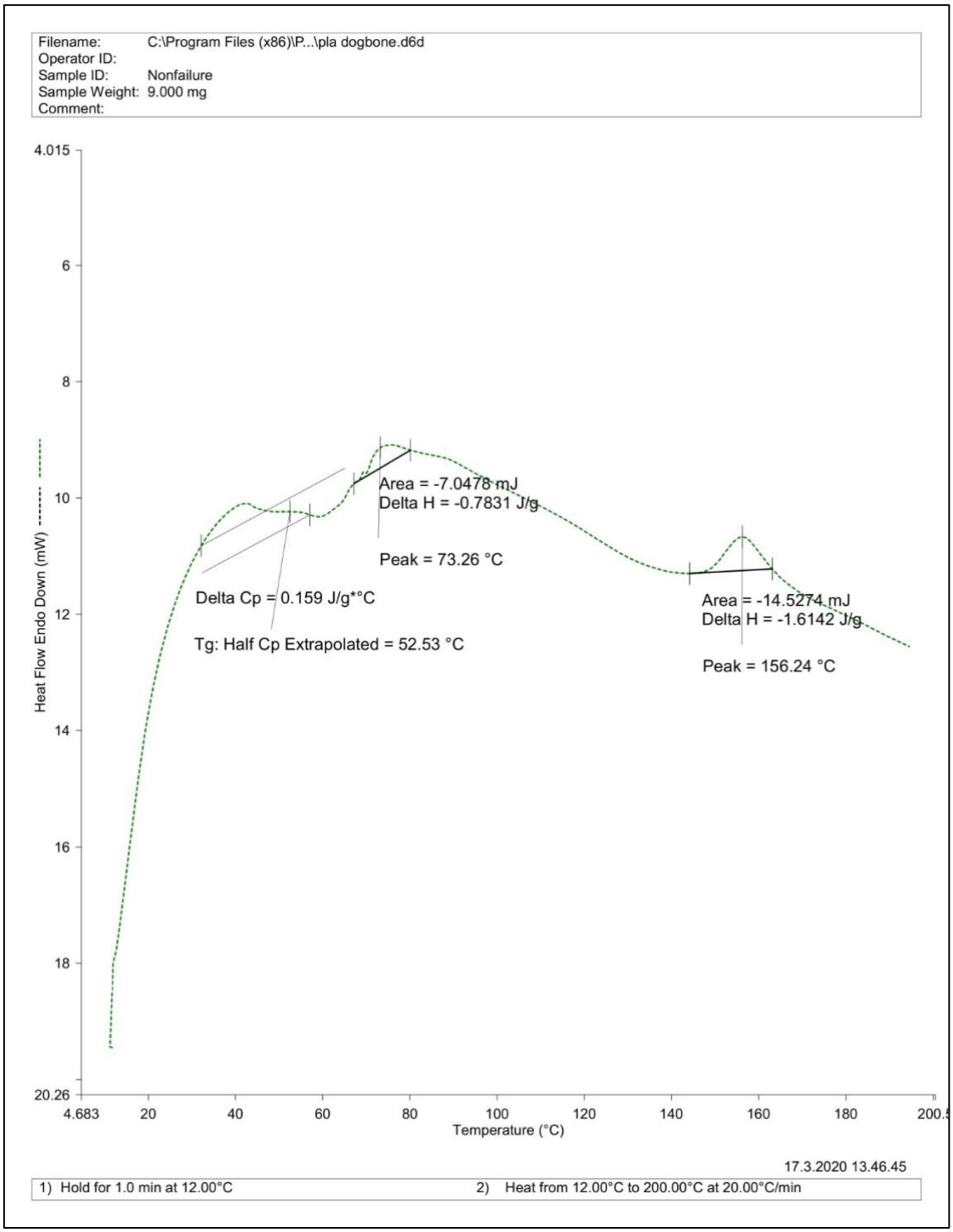

Figure 12: DSC graph of optimum PLA dogbone sample from Pyris software.

- Glass transition temperature (T_g): 52.53◦ C
- Specific Heat capacity (Cp): 0.159 J/g ◦C
- Crystanality peak: 73.26 ◦C
- Melting peak (T_M): 156.24 ◦C

Figure 13, shows the result obtained from DSC data analyser software, Pyris when imprecise PLA was used as sample. The following are its main transition noted.

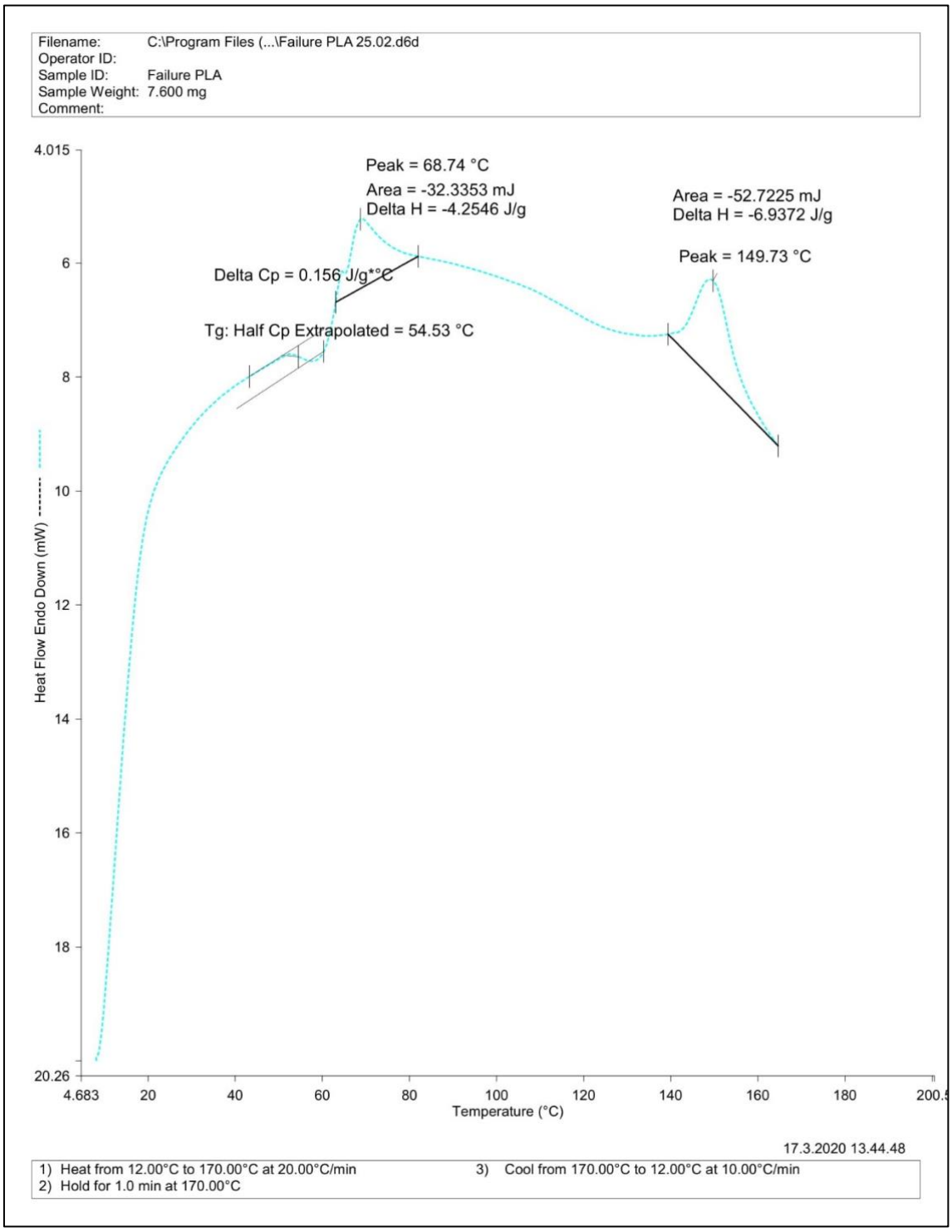

Figure 13: DSC graph of failure PLA dogbone sample from Pyris software

- Glass transition temperature (T_g): 54.53◦ C
- Specific Heat capacity (C_p): 0.156 J/g ◦C

- Crystallinity peak: 68.74 ◦C
- Melting peak (T_M): 149.73 ◦C

4.2 Data analysis for optimum and failure PLA dogbone samples

Figure 14, obtained from Pyris software, combine the graphs of Figure 12 and Figure 13 in one figure so that it is easier to analyse their differences.

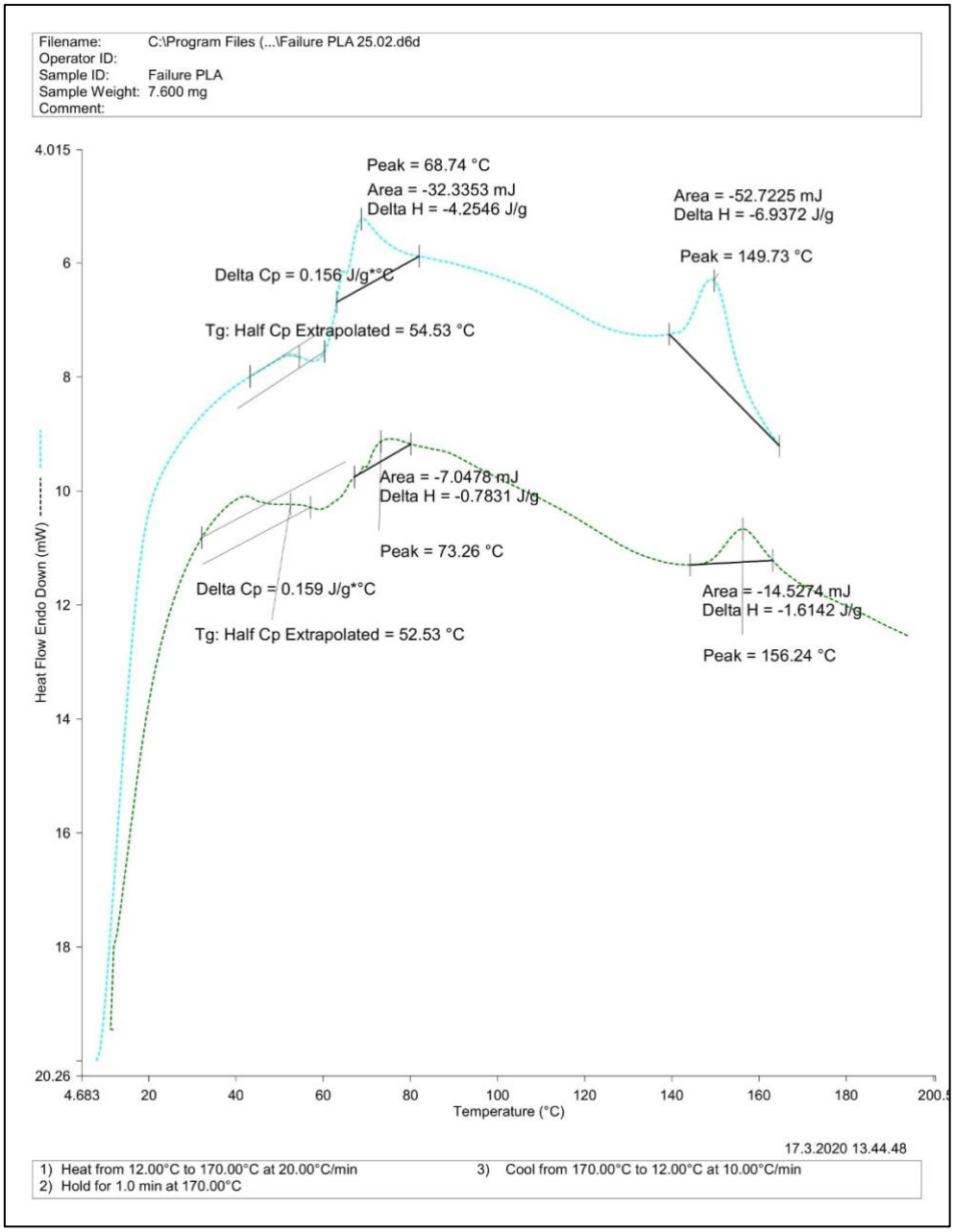

Figure 14: Combined DSC graphs of precise and imprecise PLA dogbone samples from Pyris software, Blue graph is for imprecise PLA and green for precise PLA dogbone.

Here the green graph indicates the thermal properties of precise PLA sample and blue graph indicates imprecise PLA sample. Since both were produced using same material PLA but difference in their thermal properties can be due to defects while processing. Endothermic melting peak was observed at 156.24° for precise PLA whereas there is decrease in melting peak of imprecise PLA at. 149.73°. This can be due to presence of more crystalline structure in imprecise PLA so that it shows sharp melting point as described in section 2.1.3.

Changes in melt temperature change crystal formation temperature in polymers. Here, difference in melting temperature of same polymer changes their crystalline temperature also. The crystallinity peak was found to be 73.26° for precise PLA and 68.74 ° for imprecise PLA. This suggests that the perfect crystallinity temperature to obtain precise dogbone is 73.26° but slow crystallization occurred in imprecise dogbone at 68.74°. The cooling time to obtain perfect crystalline for any parts being injected is pre-set in the production cycle. Slow crystallization in imprecise PLA means polymer could not flow properly inside all corners of mould and form crystalline at preadjusted cooling time that may deform the shape of dogbone than as expected.

Here the difference in thermal properties of same material throughout same manufacturing lot can be the sign of some unexpected defects in processing. Raw material may be contaminated by unnoticed additives during handling and processing, this also can deform the original properties of raw material which may lead to failure of the parts being injected.

The data obtained from the precise sample highlights the thermal properties required to maintain low rate of failure parts. This data can be used to reduced fail part during production by maintaining optimum temperature during the process in accordance to the raw product used. Although there was small amount of parts failure in one lot of production of PLA dogbones in Arcada's injection moulding machine.

4.3 Raw PP and failure PP dogbone results

Figure 15, shows the result obtained from DSC data analyser software, Pyris when raw PP was used as sample. The following are its main transition noted.

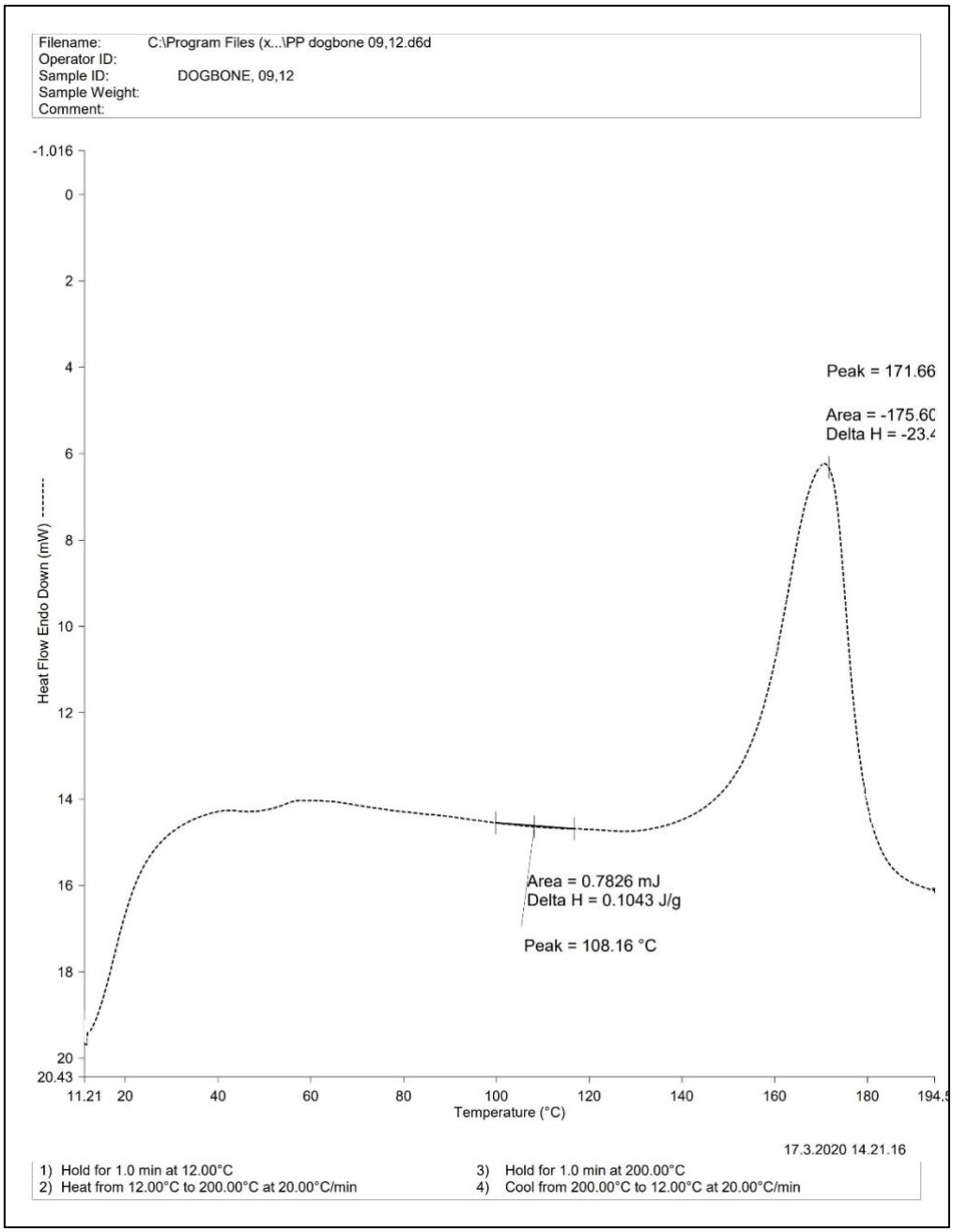

Figure 15: DSC graph of raw PP from Pyris software.

- Glass transition temperature (T_g): Not observed
- Crystanality peak: 108.16 ◦C
- Melting peak (T_m): 171.66 ◦C

Figure 16, shows the result obtained from DSC data analyser software, Pyris when failure PP dogbone was used as sample. The following are its main transition noted.

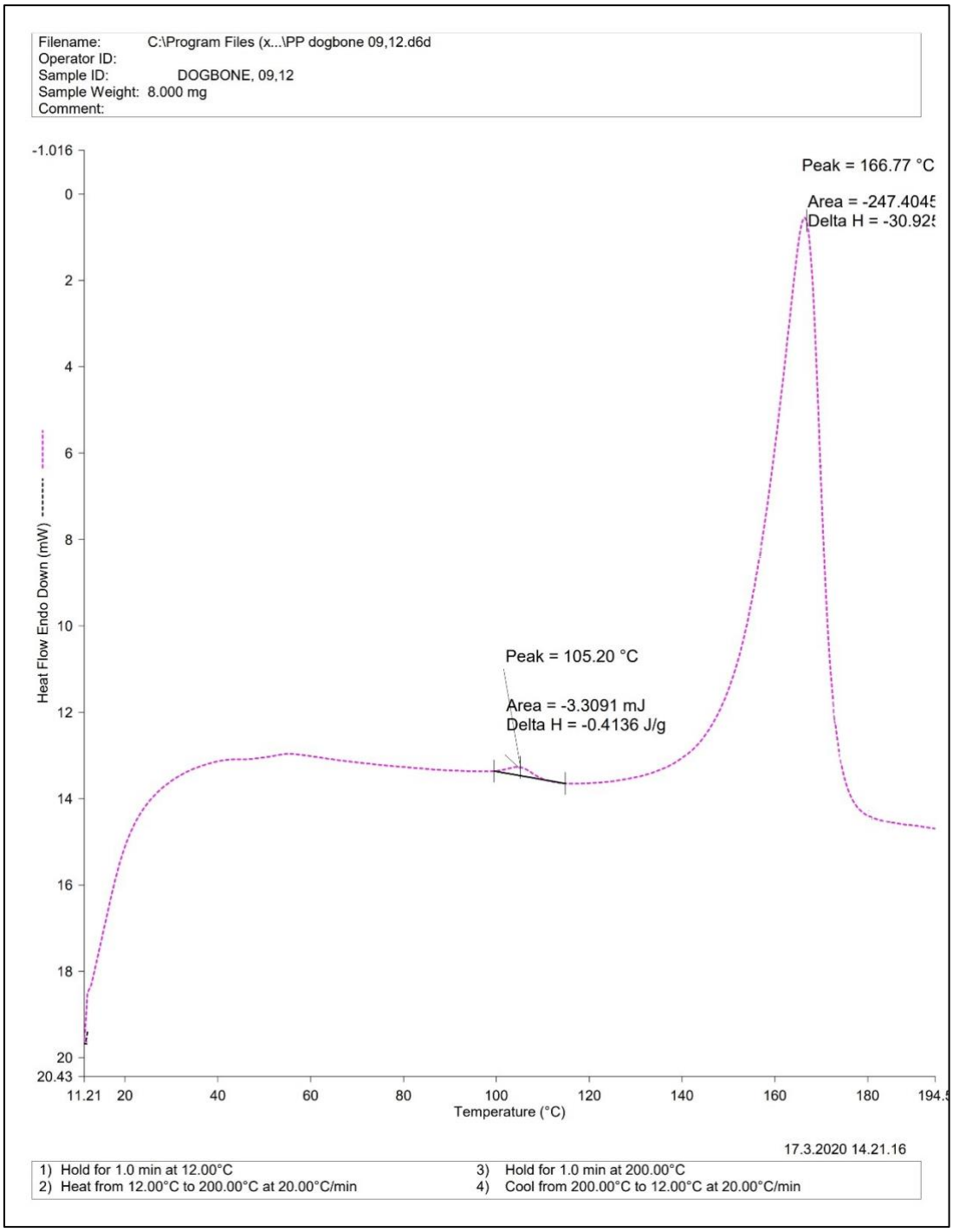

Figure 16: DSC graph of failure PP dogbone from Pyris software

- Glass transition temperature (T_g): Not observed
- Crystanility peak: 105.20 ◦C
- Melting peak (T_m): 166.77 ◦C

4.4 Data analysis for failure PP dogbone and raw PP

Figure 17, obtained from Pyris software, combine the graphs of Figure 15 and Figure 16 in one figure so that it is easier to analyse their differences.

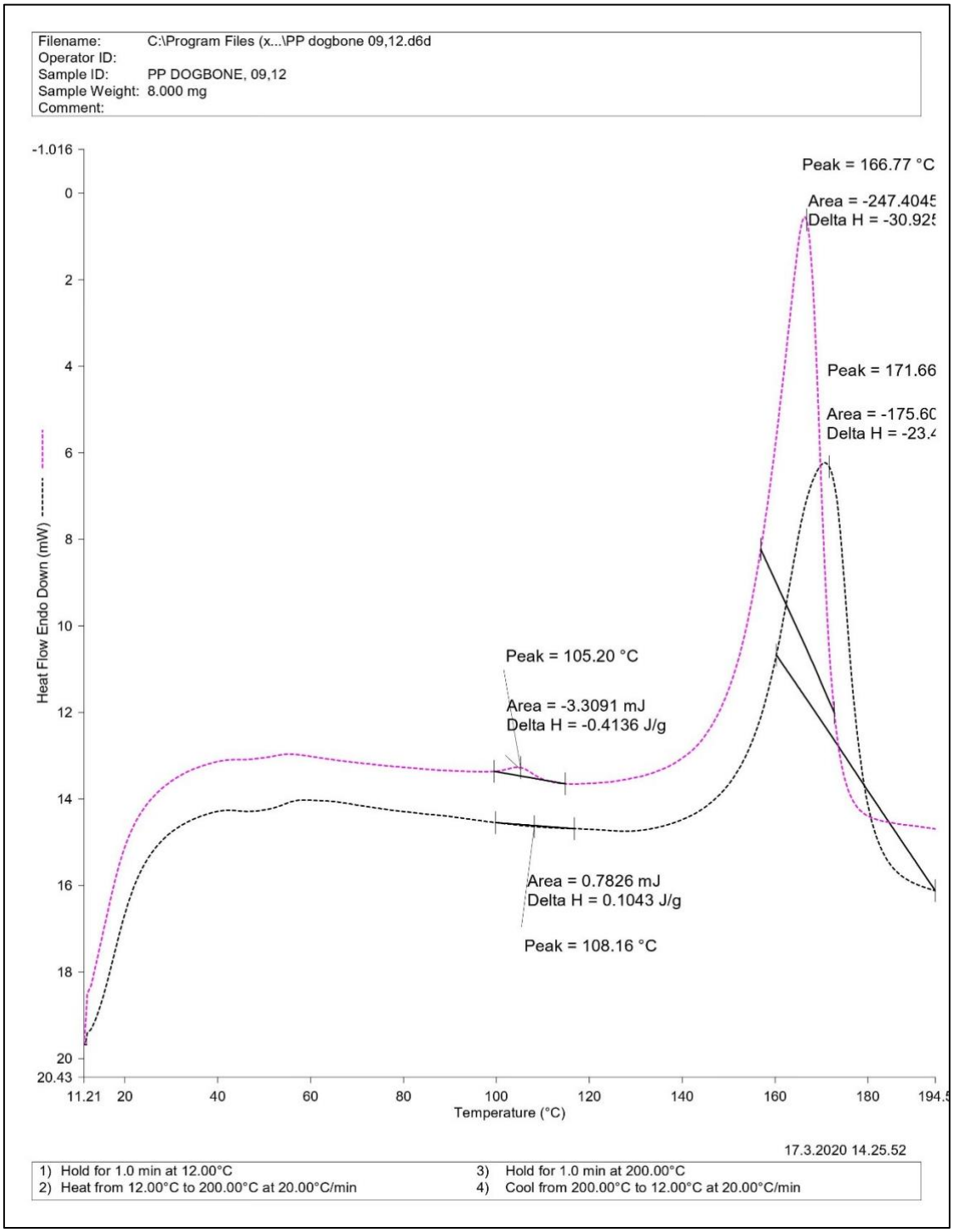

Figure 17: DSC graphs of raw PP and failure PP dogbone from Pyris sostware, pink graph is failure PP dogbone and black graph is raw PP.

Comparison of thermal properties associated with raw PP sample and imprecise PP dogbone is shown in Figure 17. Black graph is raw PP having endothermic melting peak at 171.66°C following by crystallinity peak at 108.16°C, whereas pink graph represents graph of imprecise PP dogbone used. Melting endothermic peak was observed at 166.77°C following by crystallinity peak at 105.20°C in imprecise PP sample. Sharp melting point of imprecise sample suggests that it was more crystalline than raw PP sample.

Heating rate (20 ^{o}C/min) and melting range 200°C are same for both cases, although there is difference in Crystallinity peak and in melting peak. Change in thermal properties of same material is indication of defects in processing parameter of imprecise dogbone.

Changes in melt temperature change crystal formation temperature in polymers. Here, different melting temperature of same polymer changes their crystalline temperature also. The crystallinity peak was found to be 108.16°C for raw PP and 105.20°C for imprecise PP. This suggests that the perfect crystallinity temperature to obtain precise dogbone is 108.16°C but slow crystallization occurred in imprecise dogbone at 105.20°C. The cooling time to obtain perfect crystalline for any parts being injected is pre-set in the production cycle and slow crystallization in imprecise PP means polymer could not flow inside all corners of mould and form crystalline at preadjusted cooling time that may deform the shape of dogbone than as expected.Sometimes nucleating additive are used in moulds to enhance crystallization process. so uneven heat treatment effects the formation of crystal grows due to presence of crystal nucleus after melting also. (Hitachi High Technologies, Tokyo, 2008)

Here the data obtained from raw PP curves reveals the actual property of PP used to make the dog bone and the data from imprecise PP dogbone graph shows the property of the same raw PP after it is proceeded in injection moulding machine. Differences in DSC data can be a clue for failure analysis and data from raw PP can be taken as reference for producing optimum dogbone and other products.

5 CONCLUSION AND DISCUSSION

The main objective of this thesis was to analyse failure reasons of injection moulded PP and PLA dogbones with the help of DSC. Thermal analysis of precise and imprecise PLA dogbone were done and possible reasons of failure were analysed. Likewise, thermal properties of raw PP and imprecise PP dogbone were observed and compared for failure reasons. Possible reasons of failure of PLA dogbone and PP dogbone are described briefly in section 4.2 and section 4.4 respectively. The experiment carried out here was successful in proposing reasons of failure. Thermographs were generated as expected that helped in analysing.

From the analysis of DSC graphs, thermal properties of imprecise PLA and PP dogbone are found to be different than precise PLA dogbone and raw PP which are the main clues for failure analysis. There is decrease in endothermic melting peak in both imprecise PLA and PP dogbone compared to precise PLA dogbone and raw PP. This changes in melting peaks also effect their crystallinity that occurred in different temperature. Different crystallinity value of same material can be variation in cooling time applied. This variation in cooling time effects proper crystallization temperature, that leads improper flow of molten polymer inside all corners of mould cavity and hence deformed shape is formed.

The overall aim of this thesis was to highlight the use of DSC in failure analysis of injection moulded parts. Injection moulded PP and PLA were the subject of study. Samples were prepared and experimented individually, and the final results were analysed using Pyris software generated DSC curves. The steps of the experiment such as sample preparation, processing of the samples in the DSC and techniques for interpreting DSC results are also described above in respective chapters.

The analysis presented in this thesis may not be fully accurate because they were concluded only with literature reviews presented here. The experiments conducted here were done using the limited resources available at Arcada University of Applied Sciences. The main challenges were to choose a particular material as sample and to try experiments using different parameters. Also, we ran out of sample pans and lids in the middle of the experiments and minor problem with the capsule press and nitrogen gas cylinder further delayed our experiments. Due to limited time, experiments with equal mass of sample, could not be done. The best results of PP and PLA, while we were learning to use DSC

and interpreting curves (done in different days) are presented here. So, there are variation in experiment procedure than as described in literatures.

One more case study to identify unknown polymers using DSC was proposed initially for the research but due to the Covid-19 lockdown situation experiments could not be continued as planned hence one case for failure reasons is analysed and presented here. Also, Injection moulding parameter of the samples could not be obtained, so corelating DSC graphs with Injection moulding parameters for analysing failure reasons could not be succeed. The calorimeter (DSC 4000 by Perkin Elmer) used here was quite old model, so it was difficult to perform at a low temperature range. Therefore, the T_g of PP could not be observed. A more modern apparatus, e.g. DSC 8500 by Perkin Elmer, could be used for further studies to attain more precise and a wider range of results.

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