

**Polypropylene Film Rapid Degradation through
Prodegradant Incorporation**

By

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ABSTRACT

Disposing plastic articles is becoming a major problem in municipal waste management as its degradation process takes quite a long time and contributes to mounting landfill and clogging of the drain. Therefore, this study is conducted on the usage of prodegradant in enhancing the degradation process. The study also determined the optimum level of prodegradant in a polypropylene film. Polypropylene film is widely used in agricultural, medical and household applications. The investigation focused on thermal degradation where the plastic is exposed to heat for a certain period of time. The changes in mechanical and physical properties due to the exposure are monitored. Oxygen-Induction-Time (OIT) test was performed using the Differential Scanning Calorimetry (DSC) to observe the effects on thermal properties. It is concluded that prodegradant incorporation in PP film significantly accelerates PP film thermal degradation. A prodegradant of 0.1wt% is adjudged as the optimum level.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ASTM	American Standard Test Method
-CH ₃	Pendant Group of Methyl
c.o.f	Coefficient of Friction
Control	Sample name for PP without prodegradant
DSC	Differential Scanning Calorimetry
GBR 1	Sample name for PP with 0.1 wt% of prodegradant
GBR 2	Sample name for PP with 0.2w% of prodegradant
GCMS	Gas Chromatography Mass Spectroscopy
HPLC	High Performance Liquid Chromatography
MD	Machine Direction
MFI	Melt Flow Index
MWD	Molecular Weight Distribution
OIT	Oxygen Induction Time
PE	Polyethylene
PIB	Propylene-I-Butene
PP	Polypropylene
PP 604I	Polypropylene pellet of grade 604I
PPMSB	Polypropylene (M) Sdn Bhd
PRSS	PETRONAS Research and Scientific Studies
TD	Transverse Direction
T _c	Crystallization Temperature
T _g	Glass Transition Temperature
T _m	Melting Temperature

UV

Ultraviolet

wt%

Percentage in weight of prodegradant incorporated

CHAPTER 1

INTRODUCTION

1.1 Background

Throughout the history of science and technology, a lot of engineering achievements have occurred and improvements of the construction material are developing continuously. Today, various competitions are occurring which induced the desire to develop more cost-effective but quality materials.

In plastic engineering, materials that come into most concern to scientists and engineers are polyolefin such as the polyethylene and polypropylene. The efforts to produce more cost-effective goods with wide applications are directed towards the efficient use of these materials as film, fiber and moldings. This remarkable development is due to the ease of polyolefin fabrication with effective production, improvement on catalyst and well-controlled polymerization process.

Thus, the strong market demand for good performance and cost-effective plastic materials is becoming more realizable.

1.1.1 Polypropylene Film

Polypropylene was initially produced commercially about 45 years ago after the successful development of a suitable stereo-catalyst, which enabled the polymer to have the kind of structural characteristics useful of rigid items [1]. Earlier, the

existence of polypropylene is considered only as the intermediate to polyethylene and polystyrene. Later, the market is becoming more competent with the use of polypropylene as the base resin.

The study is based on the polypropylene as film in plastic industry. Polypropylene (PP) film has excellent moisture barrier characteristics, good clarity, high gloss and good tensile strength [2]. The resin also has a high melting point, which makes it desirable in packaging that requires sterilization at high temperatures. PP film is widely used in food, agricultural and medical industries as packaging materials.

However, the usage of PP film is found in applications where degradation is a problem [3].

1.1.2 Degradation Process

Degradation is a process that involves the changes in physical properties and effects the chemical properties of the particular macromolecules. For polymer, it causes a reduction of molecular weight and diminution of the chain length [4].

The handling of PP film waste is becoming a problem to the municipal board as the degradation process takes a long time and contributes to clogged drain and mounting landfill. For a successful disposal PP film on outdoor exposure or soil burial must become brittle, rapidly enough to disappear visually, and the degraded material must be susceptible to biological attack giving complete conversion to biomass without release of toxic products [5].

1.1.3 Prodegradant

To ensure the PP film fits those requirements, a prodegradant is introduced. Prodegradant is an additive that is mixed in PP process, making it undergo rapid degradation process. It is also expected that the degradation of PP film will be faster without sacrificing other mechanical properties.

1.2 Problem Statement

The usage of prodegradant in PP film is expected to accelerate the degradation process. Care must be taken in order to incorporate an acceptable level of prodegradant so as not to deteriorate the PP mechanical properties.

Thus, this study is very significant in finding the best level of prodegradant in the film degradation process so that it would not change the mechanical properties. Moreover the incorporation of prodegradant should be economical and environmentally-friendly.

1.3 Objectives

The objectives of this investigation are:-

1.3.1 To prove the usefulness of prodegradant as an additive in PP film to accelerate the degradation process.

1.3.2 To find the best level of prodegradant in film rapid degradation that would not give drastic changes to PP film mechanical and physical properties

1.4 Scope of Work

PP film is incorporated with 0.1wt% and 0.2wt% of the prodegradant. The behavior of the PP film was compared to PP film without prodegradant incorporation.

Thermal studies and oven ageing investigation was carried out to determine the extent of thermal degradation of the three PP samples. The investigation is done at different time and degree of exposure to the heat.

Mechanical and physical properties were also monitored to ensure that prodegradant incorporation does not cause excessive physical and mechanical properties deterioration. Properties that are investigated include haze, clarity, coefficient of friction (c.o.f), blocking force and melt flow index (MFI).

The susceptibility of oxygen uptake in the PP film was also determined and the relationship between level of prodegradant incorporation and Oxygen Induction Time (OIT) was established. This is to observe the thermal stability of the three PP samples.

CHAPTER 2

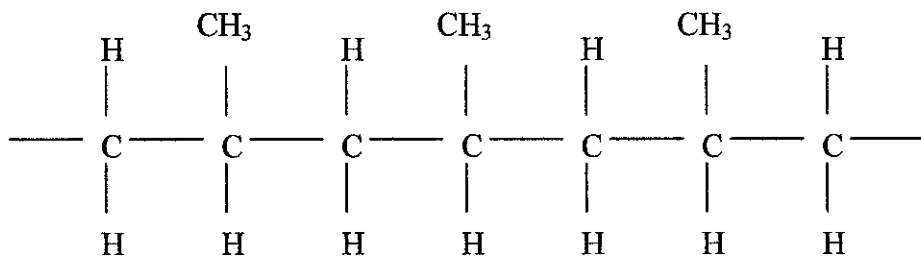
THEORY/ LITERATURE REVIEW

2.1 Properties of Polypropylene

Polypropylene (PP) is a thermoplastic material that is produced by polymerizing propylene into very long polymer molecules or chains. The significant growth of PP usage is attributed to a combination of many factors other than physical and chemical properties. It has appropriate rheology and thermal behavior that makes it processable in a variety of different equipment.

2.1.1 Chemical Structure

The structure of polypropylene is as shown below.



The small pendent group (-CH₃) is readily accommodated and fit well into a crystal matrix that gives PP a high level of crystallinity. If the pendent groups get larger and bulkier, the polymer is amorphous. The degree of crystallinity and amorphous is very much related to the PP properties that will be explained later in the rest of the chapter.

Crystallinity in some resins is a state of molecular structure denoted by uniformity and compactness of the molecular chains. This characteristic is attributable to the existence of solid crystals with definite geometric form. Amorphous region is where there is no definite structure of the regular crystalline chains.

Polypropylene is a semicrystalline polymer; it varies in degree of crystallinity and thus different types of crystal structures are possible. However, it depends on the stereochemical structures, the processing conditions and the presence of additives [6].

2.1.2 Mechanical Properties

Mechanical properties are associated with elastic or inelastic reaction when a force is applied to PP. The mechanical properties that are chosen for data gathering are coefficient of friction (c.o.f), blocking force, tensile strength and elongation.

Coefficient of friction (c.o.f) represents the ratio of frictional force. Friction is usually the gravitational force that acts perpendicular to the two surfaces in contact. It has two types. The first is static c.o.f which is related to the force measured to begin movement of the surfaces relative to each other. The other is kinetic c.o.f which is related to the force measured in sustaining the movement.

Blocking force is defined as the degrees of blocking (undesirable adhesion) existing between layers of film that may be developed under pressure during storage or use. It is undesired in product as it gives a stickiness condition between the film layers. Thus it affects the film quality as it prevents film surface separation.

Both c.o.f and blocking force are related to the existence of additives known as slip agent and anti-block respectively [6]. Slip agent is used in PP film making to promote slippery effect of the film surface. Anti-block is used to avoid the blocking in PP film. Thus, c.o.f and blocking force are important to control the affect of these additives.

However, involvement of prodegradant in PP film might give some changes to the film surface. It is expected that there will be slight increment in c.o.f and blocking force measurement due to change in surface condition of PP film with prodegradant.

Tensile strength refers to the maximum tensile load sustained by a specimen during a tension test, divided by its cross-sectional area. It can be used to indicate the amount of stress needed to elongate a certain material.

Elongation is the increase in length of a specimen at the instant before rupture occurs. Percentage elongation is expressed as the ratio between the increases in distance between two gauge marks at rupture to the original distance between the marks; the quotient is multiplied by 100.

The relationship between tensile strength and elongation is represented in Figure 1 and Figure 2 below.

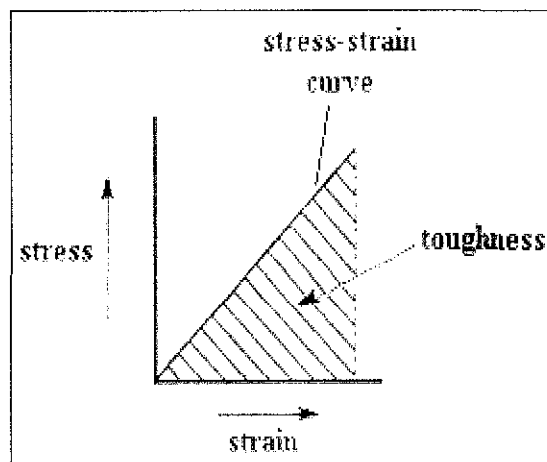


Figure 1: The relationship between stress and strain; showing the toughness region

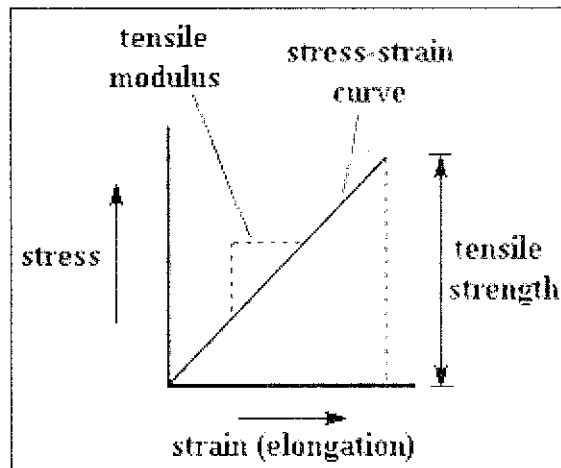


Figure 2: The relationship between stress and strain; showing the tensile modulus region

From both figures, we can see that when tensile strength (stress) increases with decreases elongation, the material is not tough. And the material gets tougher when the condition is reversed. Toughness is indicated by the area under the graph of stress-strain curve.

Tensile and elongation also are related with the level of crystallinity. The degree of crystallinity can be shown from the material's toughness. Generally, toughness decreases as the crystallinity decreases. In other words, the material gets brittle when the structures become more amorphous. Crystallinity is related with the length and arrangement of the molecular chain [7]. It is expected that, when PP is mixed with prodegradant, the chain will be shorter and arranged in a more random crystalline and thus impart an amorphous state to the PP film.

The strength of PP is also affected by the exposure to heat, shear force and other physical exposure. When the material is exposed to excessive heat, the molecular structure will change. At high temperature, the molecules have less strength. Thus it is expected that as PP material is exposed to heat (ageing) for long periods, the material will become brittle and gives a lower value of tensile properties.

The direction at which the material is elongating is also a factor of its tensile properties. In the film properties, there are two directions taken into consideration

namely transverse and machine directions. This is as shown by the figure below. For machine direction (MD), there is strong covalent bond between carbon atoms and need more energy to break, where as it is much weaker for transverse direction (TD) due to weak intermolecular forces. Therefore, in this study, results for TD are expected to be lower than MD.

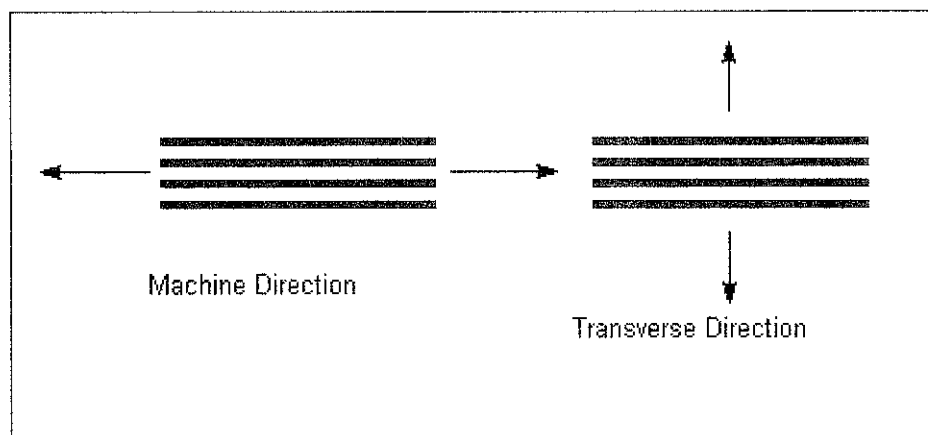


Figure 3: Basic structure of molecular chain when being tested at machine or transverse directions.

2.1.3 Rheology Properties

Rheology is defined as the study of flow. It is important in PP because of the broad range of processing techniques to which PP is subjected.

The important definition in rheology properties is Melt Flow Index (MFI). It is the amount in grams per 10 min, of a thermoplastics resin which can be forced through an extrusion rheometer orifice of a 0.0825 inch diameter when subjected to a force of certain grams at a specific temperature. MFI is used to indicate the uniformity of the flow rate of the polymer and also as indicator to other properties.

Even it is not a fundamental properties of the polymer, MFI is an empirically defined parameter that is influenced by the physical properties, molecular structure and the condition during measurement. As the molecular weight distribution of PP gets broader, it will be more viscous and thus have a lower melt flow rate [7].

Molecular Weight Distribution, MWD is the ratio of weight average molecular weight to number average molecular weight. This term is used to denote the chain length of any polymer as those polymers are having very large number of actual molecular weight.

MFI is directly linked to MWD. It will be affected when prodegradant is added in the PP samples. Prodegradant is used to shorten the length of the molecular chain, thus it is expected to give lower MWD or in higher MFI.

2.1.4 *Optical Properties*

Optical properties are related to the properties of material when exposed to light. It is related to the specimen's crystallinity and surface properties. The chosen properties for the study are haze and clarity. Both haze and clarity are affected by the degree of crystallinity and also the processing conditions.

By definition in ASTM D1003, haze is the percentage of transmitted light that, in passing through a specimen deviates from the incident beam by forward scattering. Only light flux deviating more than 2.5° on the average is considered to be haze. In other terms, it is known as cloudy or turbid appearance of a transparent specimen caused by the light scattering. For clarity, as defined in ASTM D1746, it is the ability to transmit image-forming light. It depends on linearity of the passage of light rays through the material. Clarity is determined by small-angle scattering.

These optical properties are important in this study as it shows the affect of prodegradant on the film surface. As haze and clarity are also related to the slip agent additive, it also can be a parameter in monitoring the prodegradant incorporation with PP film.

2.2 Application of Polypropylene Film

The combination of these excellent properties gives a wide application of PP in industries. Its resin can be converted into final product as film, fibers and moldings.

For PP film, the usage can be found in food industries such as for snack-food packaging and bakery products [7]. Because of its excellent clarity and gloss, it is printable through the use of some additional surface treatment technology. In the snack-food packaging it is used as a multilayer bag construction. This is because it is able to provide resistance to moisture vapor to keep the snack crisp and fresh. It also is providing a heat sealable layer. Thus it is suitable to package freshly baked bread.

In the medical area, it is used for medical product storage and disposable bags. As it has the ability to resist heat and moisture vapor, it is suitable in packaging the medicine and medical material to keep them clean and in proper condition before being applied to the patient. PP film is also suitable for sterilizing at high temperature by some special techniques and thus allows it to be used in the medical industries.

It is also used in agricultural industries as the wrapping material and others. Its great clarity makes it able for flexible packaging. Thus for agricultural used, it can be used to pack the agricultural product such as the vegetables from farm so that the vegetables will be protected from the insects and sunlight directly. It keeps the vegetables fresh before being sent to the customers.

For such advantages in its crystallinity; that results in high optical and rheology properties, it is also being used in the clothing articles such as the men's shirt, pocket pages for photographs, sheet protectors, and as the outer-nonporous sheet on disposable diapers.

These wide applications of PP in various industries are becoming an opportunity for the scientists and engineers to generate their ideas and provide benefits to society.

2.3 Principles of Degradation

The degradation of polymers involves several physical and chemical processes. Those processes accompanied by structural changes will lead to deterioration of quality of polymeric material. Generally, degradation can be divided to four modes of operation [8]. Those modes of degradation depend on the agent or driving force that makes them possible. The modes are:

2.3.1 Chemical Degradation

Chemical degradation is induced by chemicals that are brought into contact with the polymer. Most chemical reagents such as alkalis, basic salts, and acids will cause deterioration of PP mechanical properties. Even for liquid, they can weaken the surface layer of the PP film and inducing environmental stress cracking through salvation or swelling [9].

2.3.2 Thermal Degradation

Thermal degradation occurs at certain temperature that causes the chain length or molecular size to change. The properties and composition of a polymer within certain limits is studied upon increasing temperature in inert or oxidative atmosphere. Thermal stability of the material can be investigated. Thermal stability is limited by the strength of the bond and does not necessarily reflect the strength of the dominant bond type. The comparison between PP and other polymer are in increasing order as follows: PIB < branched PE < PP < Linear PE [9].

There are some criteria for evaluating thermal stability that have been used by the researchers to study on thermal degradation [9]. Among there are the temperatures at which the polymer molecular weight decreases; initial change rate of a property at a given temperature; and the temperature at which the oxygen consumption reaches a certain value.

2.3.3 Biological Degradation

This mode of degradation is induced by microorganism that produces a variety of enzymes. Living organisms such rodents, insects, bacteria and germs can attack synthetic polymer chemically or mechanically. However, the activities of organism are affected by other agents such as heat, stress, oxygen content and water [10]. Organisms' survival is dependent on those factors. Biological degradation is generally studied by growth test of microorganism on a solid media.

2.3.4 Mechanical Degradation

Mechanical degradation manifests itself when a polymer experiences shear force that produces macroscopic effect to the polymer. This mode of degradation generally occurs at the beginning of a staged process in the presence of oxygen and heat. It is difficult to differentiate between mechanical or thermo-oxidative degradation. However, from many studies done, mechanical degradation is found to be the source of alkyl radicals' formation that is involved in the initial step of thermal oxidation.

2.3.5 Light Induced Degradation

This degradation occurs by irradiating the polymer with ultraviolet or visible light. When the polymer is irradiated with the light source, it will change its molecular structures and cause deterioration of its properties.

2.4 Prodegradant

Prodegradant is an additive to promote faster degradation process. It is developed to overcome the problems of recycling and enhance municipal waste management. A few characteristics of an additive should be taken into consideration before it is used in the production process.

As an additive in the process, the prodegradant should be permanent, having low volatility under processing and service conditions. It should have good heat, light, hydrolytic, processing and chemical stability. To be more effective, it should have sufficient retention time in the polymer substrate and able to disperse evenly during polymer processing. During its service lifetime, prodegradant must have sufficient mobility and compatible in complex compound. This is to ease the handling of prodegradant. Moreover, it must be nonflammable and nontoxic to the environment as it will effect the surrounding.

2.5 Sample Preparation

The PP pellets utilized is the 604I grade produced by Polypropylene (M) Sdn.Bhd. (PPMSB). The pellets mixed with certain amount of prodegradant using tumbler mixer for 30 to 60 minutes of time. Then, the mixture of prodegradant and pellets is compounded using a twin-screw extruder. The samples will be: PP without prodegradant (control); PP with 100ppm of prodegradant (GBR1) and PP with 200ppm of prodegradant (GBR2).

2.5.1 Mixing and Compounding

Mixing is done using a tumbler mixer and twin-screw extruder. Tumbler mixer (Figure 4) is used to mix raw pellets and prodegradant. The mixing process took 30minutes to 1 hour. Twin-screw extruder (Figure 5) is used to compound the mixture

of pellets and prodegradant to produce a homogeneous sample.

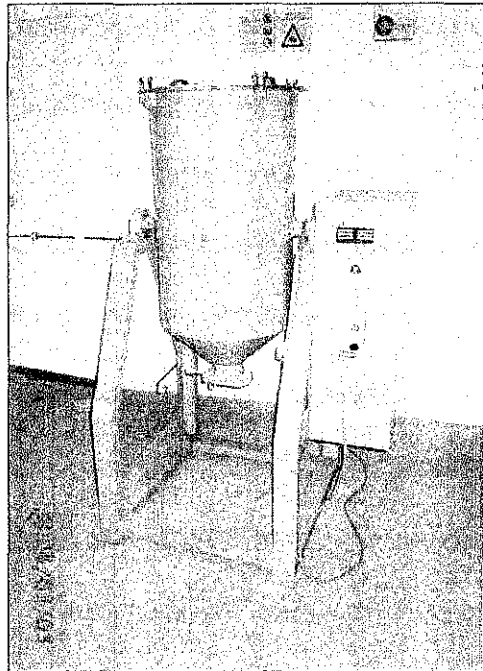


Figure 4: Tumbler Mixer to mix pellet with raw prodegradant

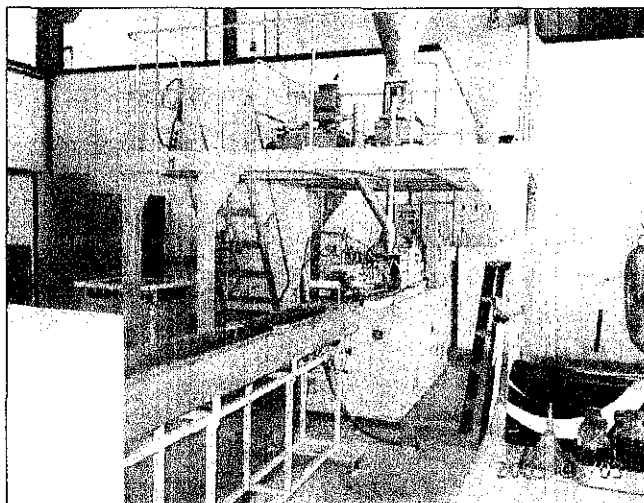


Figure 5: Twin-Screw Extruder to compound mixture of Pellet with prodegradant

2.5.2 Film Making

The film is made using a blown film machine as shown in Figure 6 below. The homogenized samples from twin extruder is fed to feeding hopper and compressed at

200°C. The melting sample is fed through a die at 210°C to be formed as film. Lastly, the film is cooled down and rolled by the rollers of the machine.

Blown film has pros and cons compared to cast film [10]. It is generally more crystalline and has higher haze level than cast film. It is also having greater stiffness and ability to improve the barrier to moisture and gases. However, due to higher level of melting in the process, the uniformity of film thickness and sheet flatness is affected. This might affect the testing' results especially for tensile property tests as those tests require the thickness of the film to be uniform.

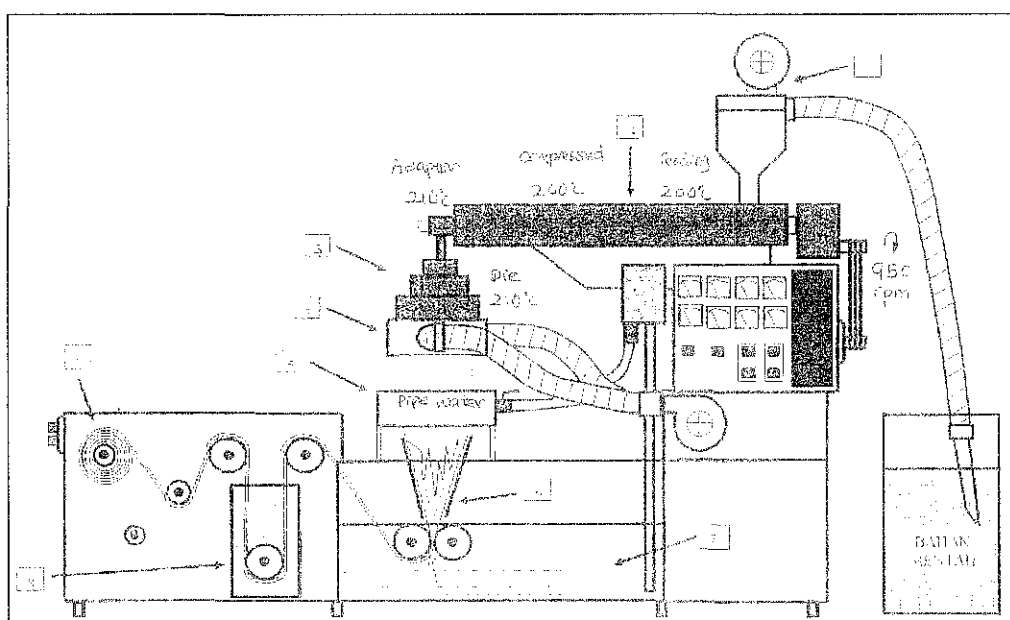


Figure 6: Step of Making Blown Film

2.6 Thermal Analysis by Differential Scanning Calorimetry (DSC)

DSC is used to study the changes in PP when it is exposed to heat. It is able to determine the glass transition (T_g), crystallization (T_c) and melting point (T_m) of a polymer. It is also applicable for determining the thermal stability and reversibility and chemical half life. The basic structure of DSC is in Figure 7 as shown below:

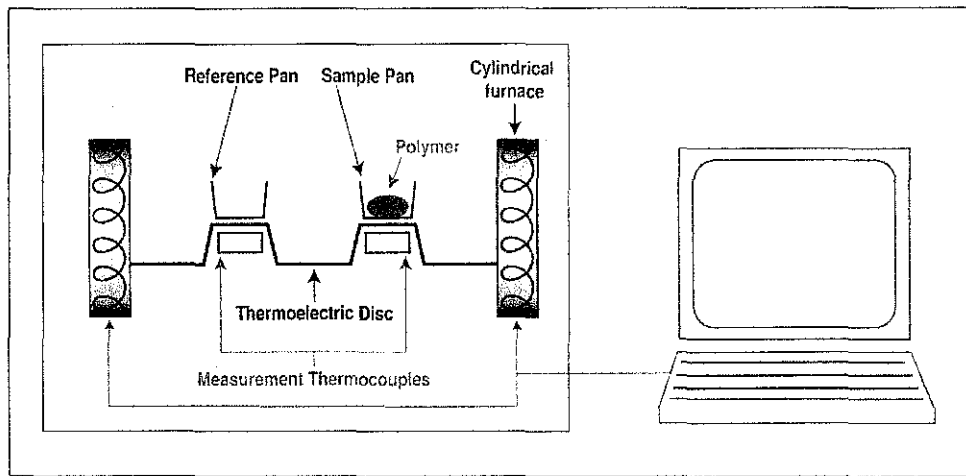


Figure 7: Basic structure of Differential Scanning Calorimetry

By referring to Figure 7; 5 to 10mg of PP samples is placed on the sample pan, then it is heated starting from 25°C. The reference pan is let to be empty during the process. The cylindrical furnace heat up the sample till it reached 220°C and the process is automatically stopped. The results from DSC are plotted in a graph and the determination of melting point and OIT is computed by the computer. Below is a general plot from a DSC:

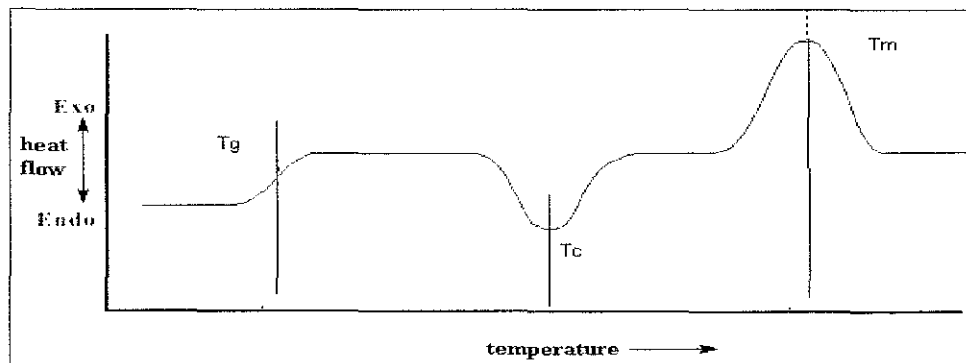


Figure 8: Typical structure of graph plotted from DSC

Melting point (T_m) is the highest peak of the graph. From the melting point, the percentage of crystallization can be determined. It is expected that there is not so much difference between samples with and without prodegradant. If there is no difference, it shows that the mechanical properties of PP are maintained even when prodegradant is incorporated.

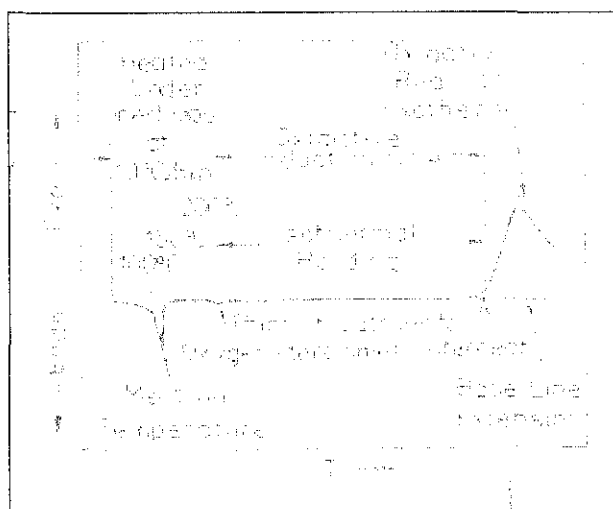


Figure 9: Determination of OIT

As shown in Figure 9, Oxygen Induction Time (OIT) is the time interval from when oxygen flow is first initiated to the oxidative reaction. In DSC it is determined from the data recorded during the isothermal test. OIT results are often used to select optimum resin formulations. Volatile antioxidant may generate poor OIT results even though they may perform adequately at the intended use temperature of the finished product. It is very important as it shows the stability of material. Thus, OIT for samples with more prodegradant is expected to be lower as they have less resistance to oxidative reaction.

CHAPTER 3

METHODOLOGY

A lot of studies have been done to improve the degradation process of polymer using various kinds of method [10]. Basically, the study is focused on thermal degradation modes. The procedures or methods that will be involved in the project are:

3.1 Mixing and Compounding of Pellets

A bag of 25kg PP 604I was mixed with 0.1wt % of prodegradant and another bag with 0.2 wt %. One control sample was prepared; the PP 604I is not mixed with any prodegradant. Each sample is mixed using tumbler mixer for 30 minutes. The bag of pellet is put into a hopper and extruded in a twin-screw extruder to be compounded. The compounded mixture i.e. PP604I with 0.1 wt % then is being pelletized by a pelletizer.

3.2 Film Making by Blown Film Machine

The films samples are prepared using Blown Film Machine. Pellets that have been compounded are fed into the hopper. The machine is checked to be in good condition first. The processing condition is set up so that the blown film made is having good quality. The process is started and the film that is being extruded through the die will be in the form of blown film when get through the rollers of the machine.

3.3 Conditioning Samples

All the samples are conditioned at $23\pm 2^{\circ}\text{C}$ and $50\pm 5\%$ relative humidity for not less than 40 hours. The test to be done is also conducted at the same condition as the samples. This step is to ensure the structures of PP film are stable and not subjected to any changes during the test. The changing in molecular structure of PP film will give deviation in results.

3.4 Melt Flow Index (MFI) Measurement

MFI is the degree of flow of PP when subjected to 2.16kg of weight at 230°C for 10 minutes. In this study, the test is done on PP film after the blown film making. The sample can be in any form for this test.

In this investigation, specimens are strips of film. 5g of each sample is prepared. The temperature is set at 230°C and the load is 2.16kg. The specimen is put into the bore of the cylinder. After the temperature reaches its stable condition, the measurement is started. The measuring flow rate is recorded. The result of each sample is compared.

3.5 Haze and Clarity Determination

Haze and clarity is the optical behavior of PP film. Haze represents the cloudiness and clarity represents the clearness of PP film. The test was done after the film was conditioned at $23\pm 2^{\circ}\text{C}$ and $50\pm 5\%$ for more than 40hours. The surface of film is kept clean and smooth during the test to avoid results deviation.

Five specimens from each sample are prepared with 50mm diameter each. The thickness of each sample is measured. The specimen is placed against the entrance port of the integrating sphere (part at which haze meter and clarity meter measured

the light). A beam of light is directed to the specimen. The measurable light will be calculated by the instrument. Other specimens are repeated for the same method and average of results is taken.

Figure 10 and 11 is showing typical structure of haze and clarity meter. Also shown is the calculation of the measurement.

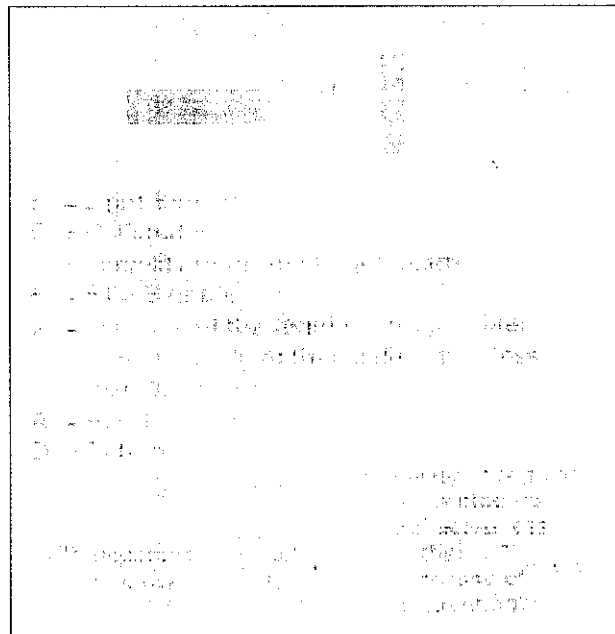


Figure 10: Basic Structure and Calculation Involved in Determining the Haze Percentage.

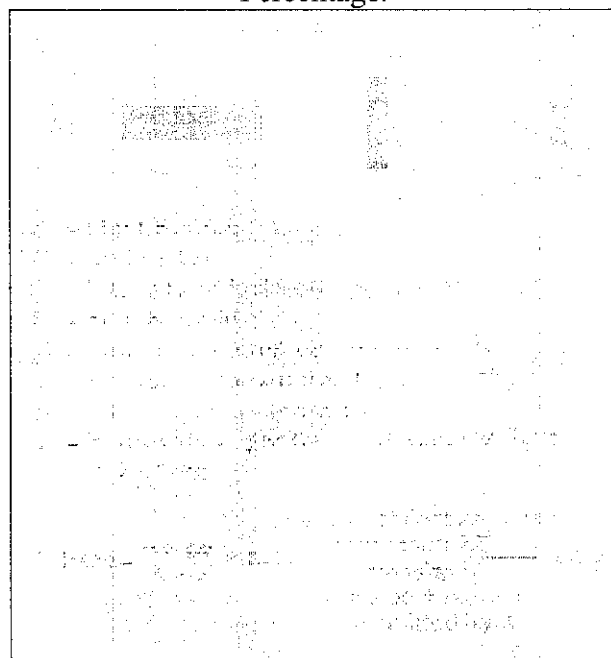


Figure 11: Basic Structure and Calculation Involved in Determining the Clarity Percentage.

3.6 Blocking Force

Similar as haze and clarity tests, blocking force is also done after the conditioning step. Blocking force is the unwanted adhesion between two layers of film that give difficulties in film separation. The head or load used in measuring blocking force is shown in Figure 12.

In this test, five specimens were prepared with 150mm x 250mm dimensions. The thickness of each specimen are measured and set in the program used. The two ends of the double layer of film are taped on the upper and lower block. After all the settings have been set, the experiment is started and the measuring data is recorded. The graph of the results is plotted automatically. The steps are repeated for another four specimens.

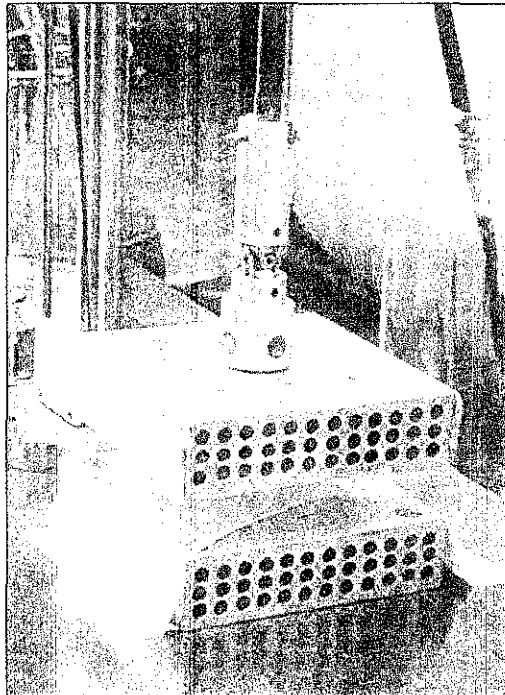


Figure 12: Load used in Blocking Force Measurement

3.7 Coefficient of Friction (c.o.f)

Coefficient of friction represents the ratio of friction for PP film. It is important to observe PP film surface. The test for c.o.f was done after the conditioning step. The load used is 1kN.

Five specimens with 130mm x 250mm are prepared and the thickness of each specimen is measured. The specimen is taped on the measuring plane and a sled is located on it. After all data has been set in the program, the experiment is started. The measured friction will be for static and kinetic friction. Both are recorded. The steps are repeated for another four samples.

3.8 Tensile Properties

Tensile properties are related with the behavior of PP film when elongated and exposed to stress. Two directions, transverse and machine directions were tested to relate with the theory. The test was done on samples that have been exposed at different thermal duration and temperature which are at 50 and 70°C for 50, 100, 150, 200 and 250hours. The load used to measure the tensile properties is 5kN. The results of those samples then were compared with samples at room temperature.

Five specimens from each sample are prepared using the cutting blade. The specimens are 25.4mm in width and about 50mm in length. Thickness for each specimen are measured and recorded before the experiment. The details of the specimens are recorded in the program used for the testing. For this study, the initial grip is set at 50mm with rate of grip separation is 500mm/min. A specimen is placed at the specimen clip and the START button is pushed to start the testing. The graph for the elongation trend is automatically shown by the program used. The measurement will stop automatically when the grip separation reaches 500mm. For

any break occurring during the measurement, the process must be stopped manually. All data are printed.

As can be seen in Figure 13, a sample is under the tensile measurement.

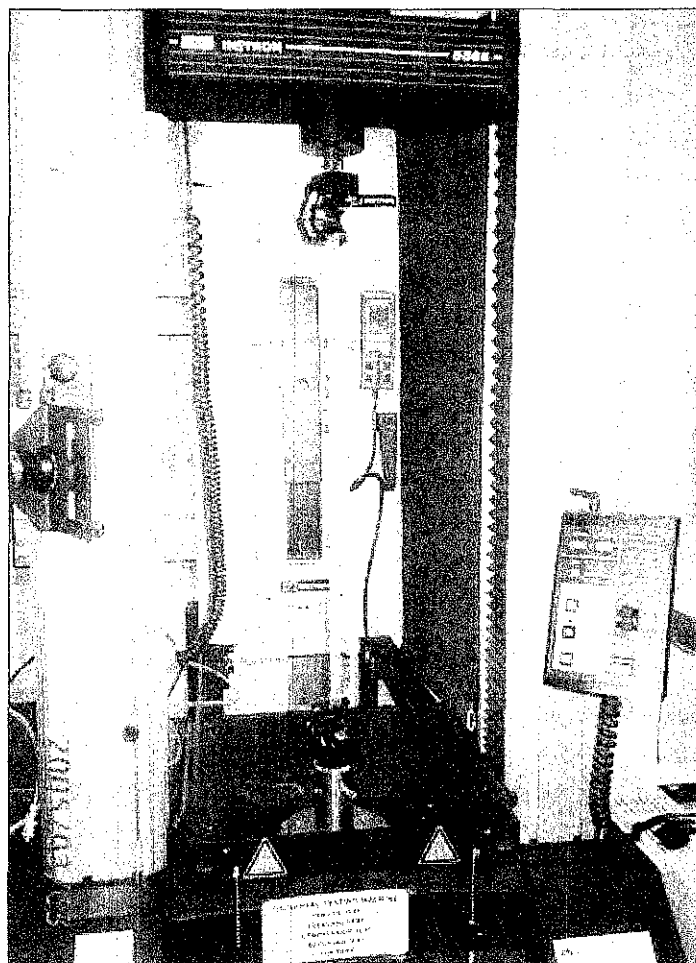


Figure 13: Tensile Test Unit

3.9 Ageing

Ageing is a process of exposing material to certain temperature at certain duration. In this investigation, PP film with or without prodegradant are aged in an oven so they will experience controlled heat. The oven used in the investigation is represented in Figure 14 below.

Five specimens for each sample are prepared by cutting the samples with 25.4mm x 100mm dimensions. The oven is set at the desired temperature i.e. 70°C. All samples

is placed in the oven and conditioned in the oven for desired hours i.e. 100hrs. All samples are taken out when the desired ageing time is reached.

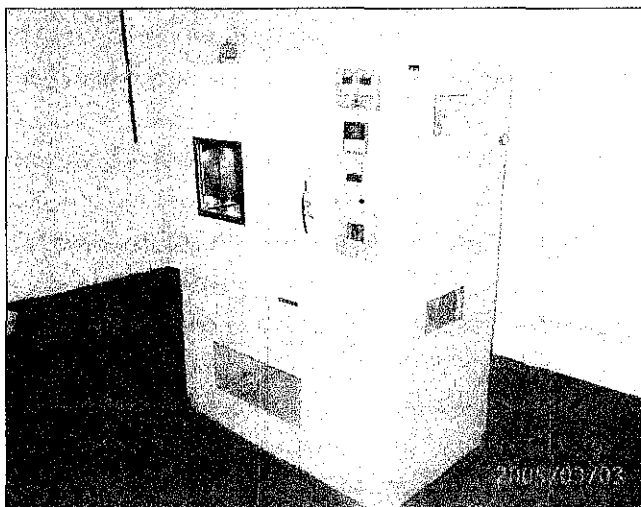


Figure 14: Oven Ageing used to Age all Samples

3.10 Determination of Melting Point and Oxygen Induction Time (OIT) Using Differential Scanning Calorimetry (DSC)

DSC is designed purposely for thermal studies. In this study, melting point is determined to verify that prodegradant will not deteriorate PP physical and mechanical properties. OIT is the duration of PP film reacts with oxygen in an oxidative condition. The determination of OIT is used to monitor the thermal stability of PP film and thus finding the best level of prodegradant incorporation.

The specimen is put on the sample pan and heated together with reference pan in the oven. The heating process is happened at certain rate as per set in the program. The trend of changes in temperature and heat flow will be automatically plotted by the program. The point of melting will be detected from the graph. All the data obtained from DSC will be used to determine the Oxygen-Induction-Time of the samples.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Comparison of Rheology and Optical Properties

The comparison is based on MFI, percentage of haze and clarity, c.o.f and blocking force.

4.1.1 Melt Flow Index (MFI)

Below is the graph of MFI for the three different samples.

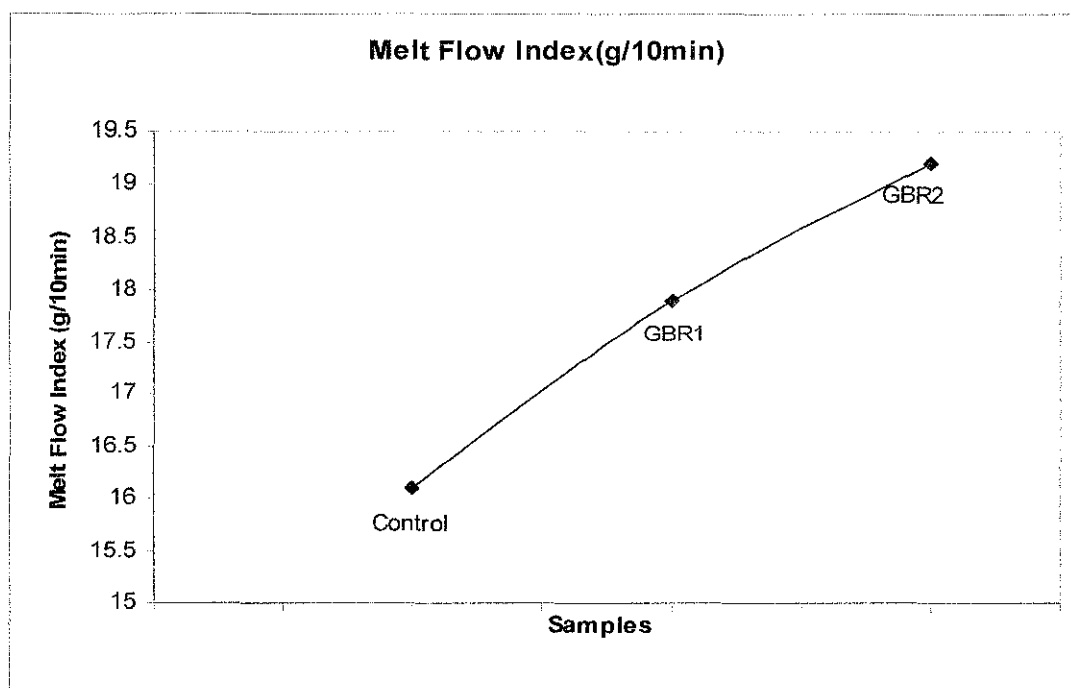


Figure 15: Result of Melt Flow Index for Each Sample

The graph shows the MFI values increase with increasing prodegradant level. The increment in MFI corresponds to the degree of flow for PP with an increased GBR

loading. It agrees with the theory that with existence of prodegradant, the molecular chain is shortened. Thus, the MWD of material gets narrower and resulted in PP having a higher MFI. Prodegradant causes the melt flow index to increase associated with formation of shorter molecular chains.

4.1.2 Percentage of Haze and Clarity

The comparison of haze and clarity percentage can be seen from the Figure 16 and Figure 17. Figure 16 shows that with prodegradant in PP samples, the haze level is reduced. Figure 17 shows there is slight increase in clarity percentage for GBR1 and from level off or dipped for GBR2. The results show that there was improvement in optical properties of PP when prodegradant is added. This is due to the changes in crystalline structure of PP with prodegradant.

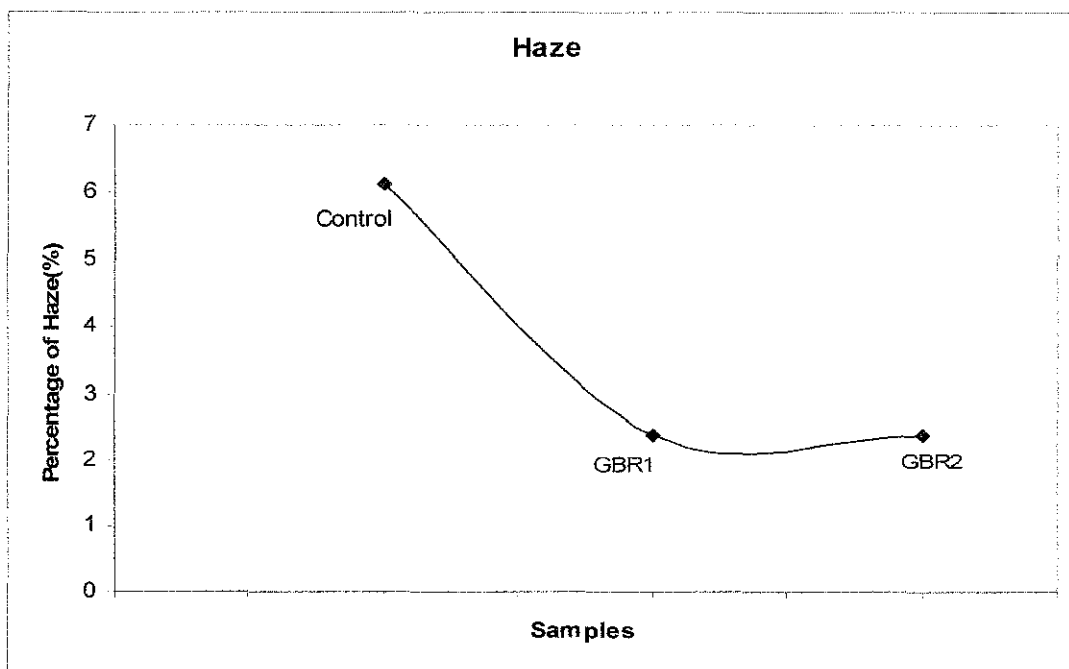


Figure 16: Result for Percentage of Haze for Each Sample

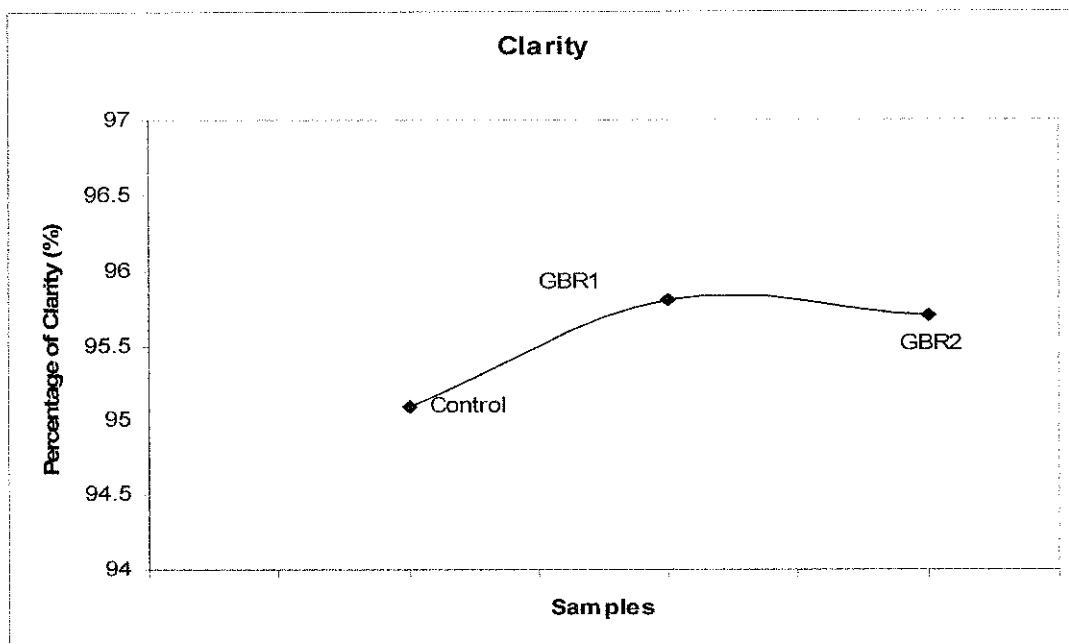


Figure 17: Results for Percentage of Clarity

Prodegradant disrupts crystallinity and causes amorphous content to increase. Hence it improves the clarity and haze properties compared to control samples.

4.1.3 Coefficient of Friction and Blocking Force

Figure 18 and 19 show the results of the three samples. Both graphs clearly show the different of results between the samples.

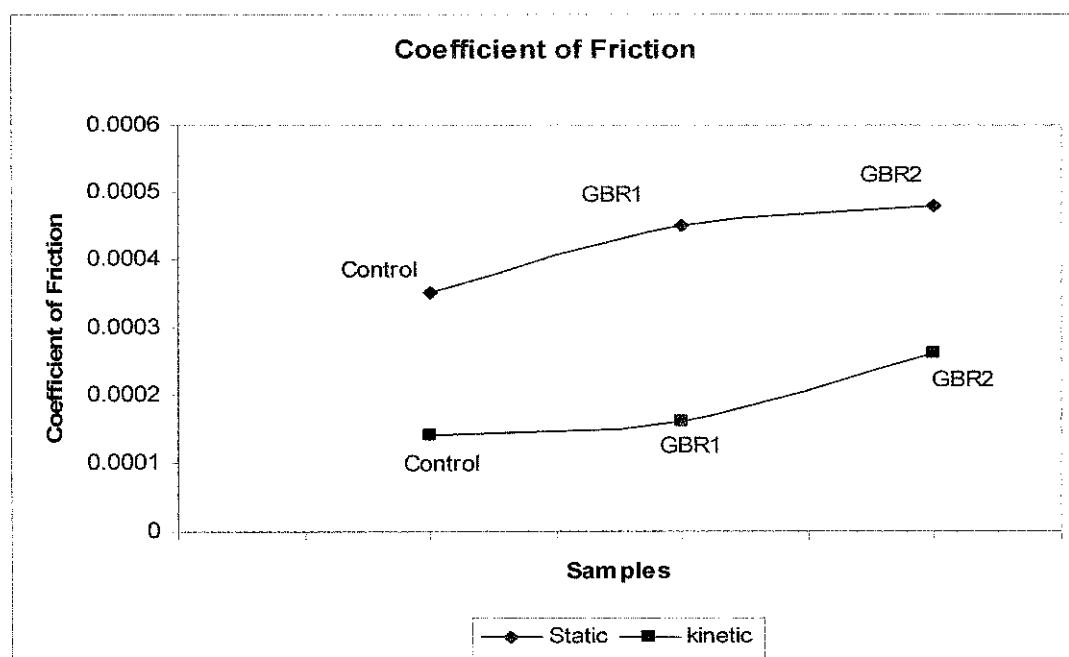


Figure 18: Result for Coefficient of Friction (COF) for Each Sample

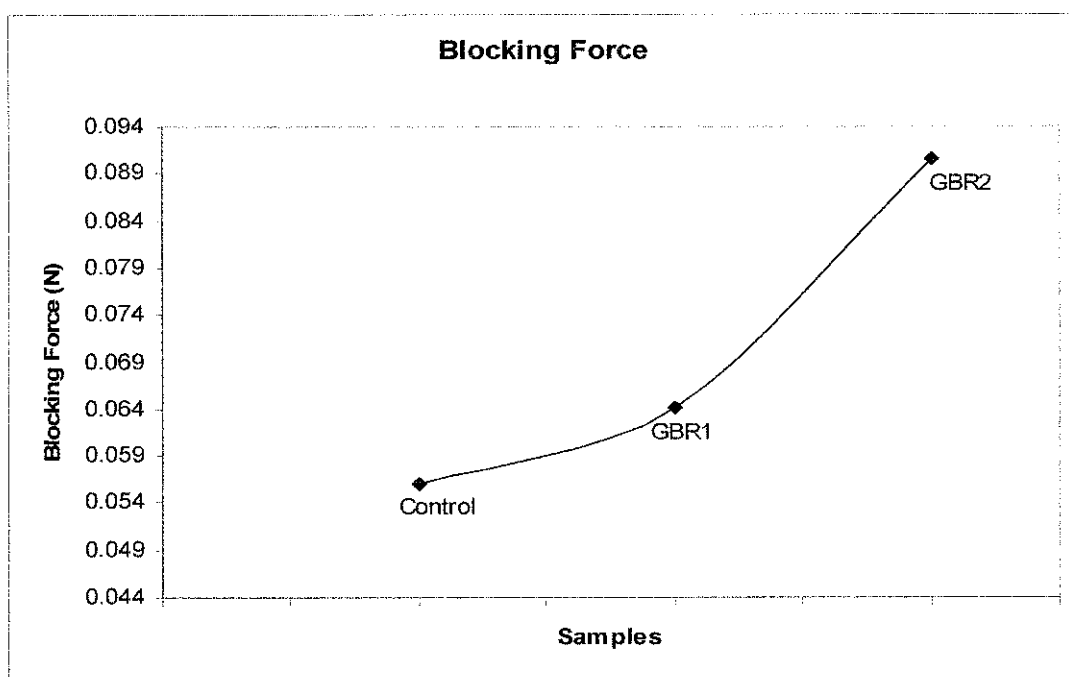


Figure 19: Result for Blocking Force of Each Sample

For c.o.f and blocking force results, both shows increasing results when more prodegradant in PP samples. The c.o.f increased is related to samples having a rougher surface and cause the friction ratio to increase with the increasing level of GBR. Blocking force increased also shows the film's layer is more adhesive and more difficult to be separated.

4.2 Comparison of Mechanical Properties

The comparison of mechanical properties is done by comparing the results of tensile strength and elongation of each sample. The results are different for different direction of samples tested.

4.2.1 Machine Direction

Figure 20 is the trend for machine direction of all samples. For samples without ageing, they have high stress and strain; which shows they are very tough samples. It is similar for control sample exposed to heat at 50°C.

However, for control at 70 °C, GBR1 and GBR2 at 50 °C, they are having less strain but still high stress. Thus it shows they are strong but becoming brittle as they cannot elongate further.

As the samples were exposed at higher temperature as shown by GBR1 and GBR2 at 70 °C, they are becoming weaker and more brittle. This is shown by lower stress and strain values.

Hence, the existence of prodegradant and exposure to heat caused the PP to be brittle and weak. It promotes the degradation of PP chains break at a faster rate. Result shows that tensile properties decreased with increasing duration of exposure to heat and amount of prodegradant incorporation.

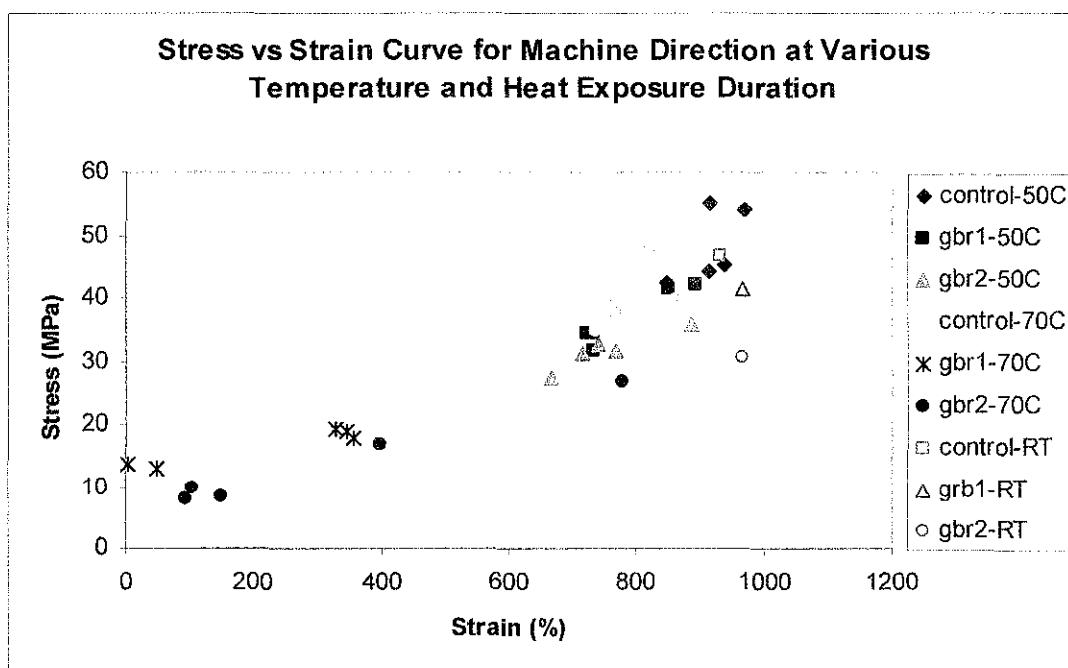


Figure 20: Stress vs Strain Relationship for all Samples at Different Conditions at Machine Direction

4.2.2 Transverse Direction

As with the machine direction, all samples of the transverse direction possess high stress and strain properties (Figure 21). As the samples are exposed to heat at higher temperature and longer time, they become weaker and more brittle.

Comparing the transverse with machine direction results, it can be seen that, for TD the values are accumulated at lower region of stress-strain relationship. But, for MD, the values are accumulated at higher region of the relationship. It shows that the machine direction is tougher than the transverse direction. At transverse direction the molecular chain need less energy to break. Therefore, the process of breaking the chain will be easier for transverse direction and promote faster degradation as the degree of molecular chain orientation becomes more pronounced for samples pulled in the machine direction.

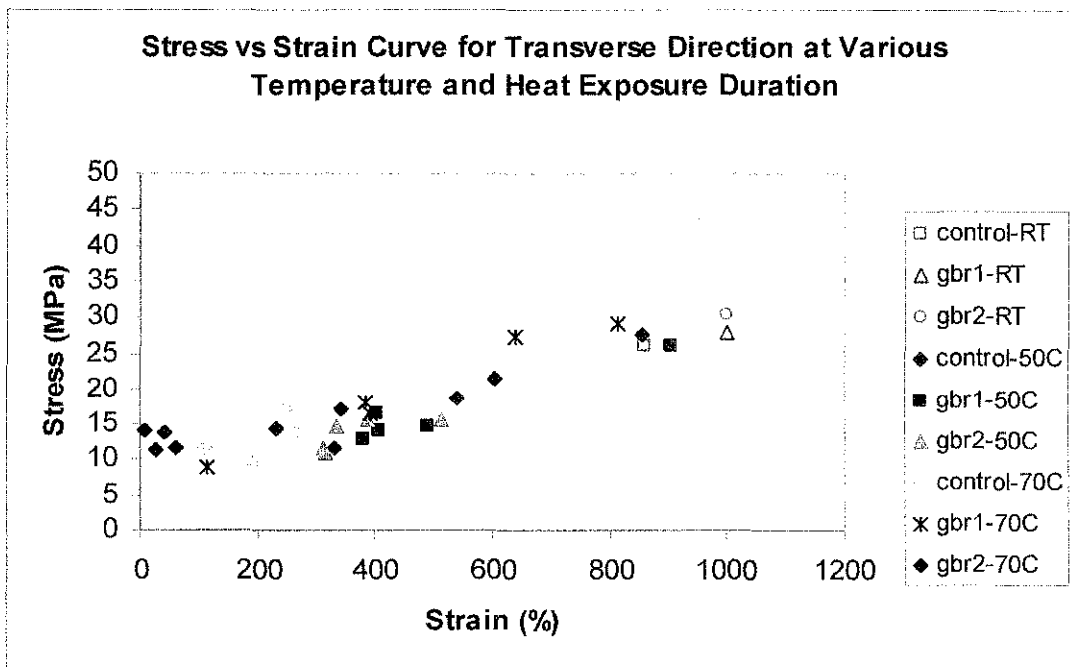


Figure 21: Stress vs Strain Relationship for all Samples at Different Conditions at Transverse Direction

All results of tensile properties are significant in comparing with the results from DSC. As the values of tensile properties decrease, the degradation process is expected

to be accelerated. This is due to the activities of degradation agents namely prodegradant and heat. Both agents help in accelerating the degradation of PP material.

4.3 Comparison of results from DSC

The comparison is done based on results from melting point and OIT. All results show significant use of prodegradant and heat in thermal degradation process.

4.3.1 Melting Temperature

For melting point, the comparison is done with the average melting point between control, GBR1 and GBR2 samples. Figure 22, 23 and 24 are representing the results of melting point for control, GBR1 and GBR2 respectively.

As for control samples, at any temperature and duration of heat exposure, an average melting point of 162.33°C is obtained. From theories, the melting point of PP is generally between 160 to 165 °C. Thus, the result is within the acceptable properties for PP.

The average melting point for GBR1 is 162.90 °C. It is similar with GBR2 where the average melting point is 162.89°C. From both melting points, it shows that incorporation of prodegradant in PP film will not significantly alter the thermal properties of PP.

The preservation of thermal properties suggests that there are significant changes to bond strength of control PP and additivated PP. This is favorable as prodegradant is expected to alter or accelerate UV and thermo-oxidative degradation without sacrificing physical and mechanical properties of PP.

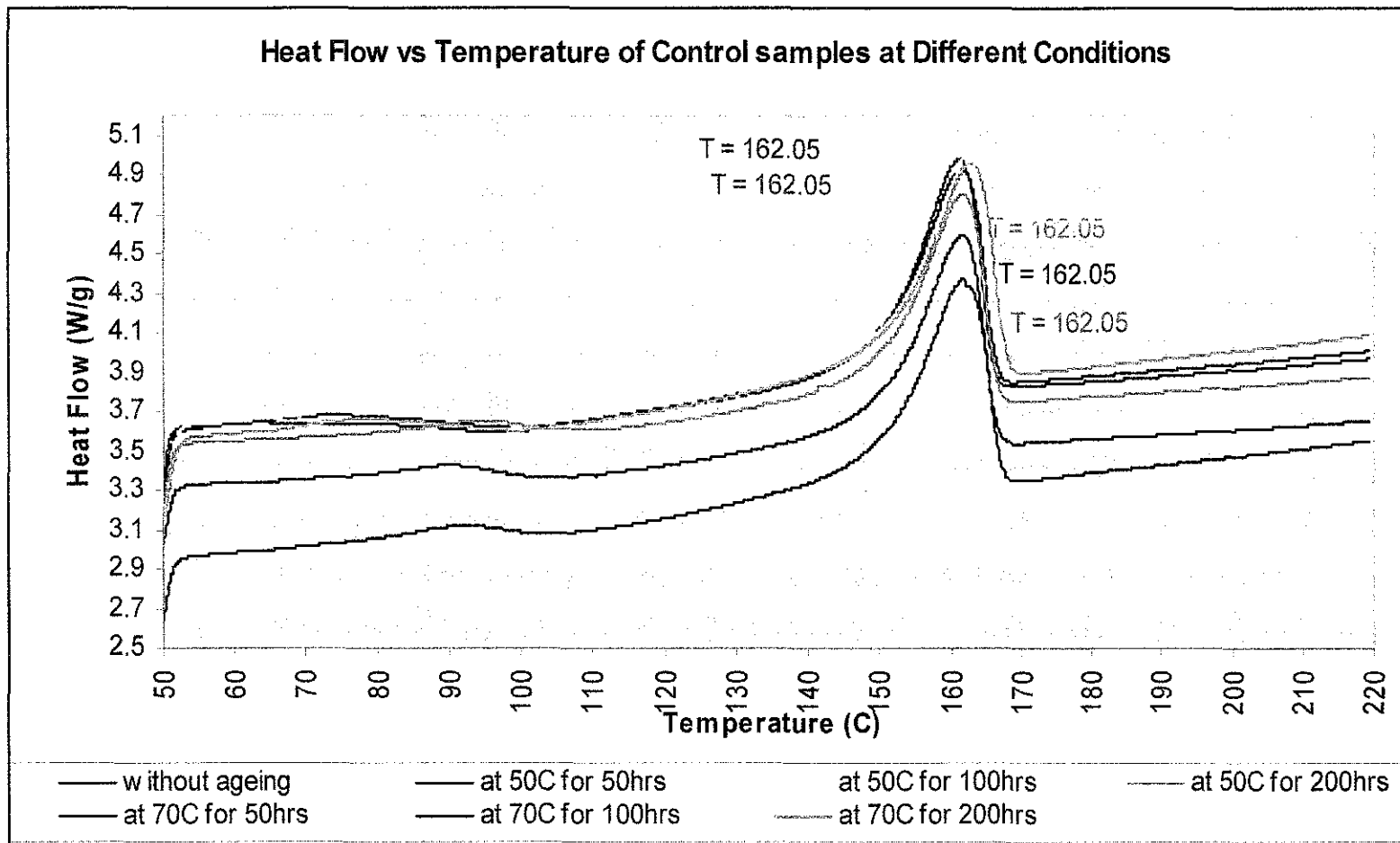


Figure 22: Melting Point Determination Using DSC; Control Sample at Various Conditions

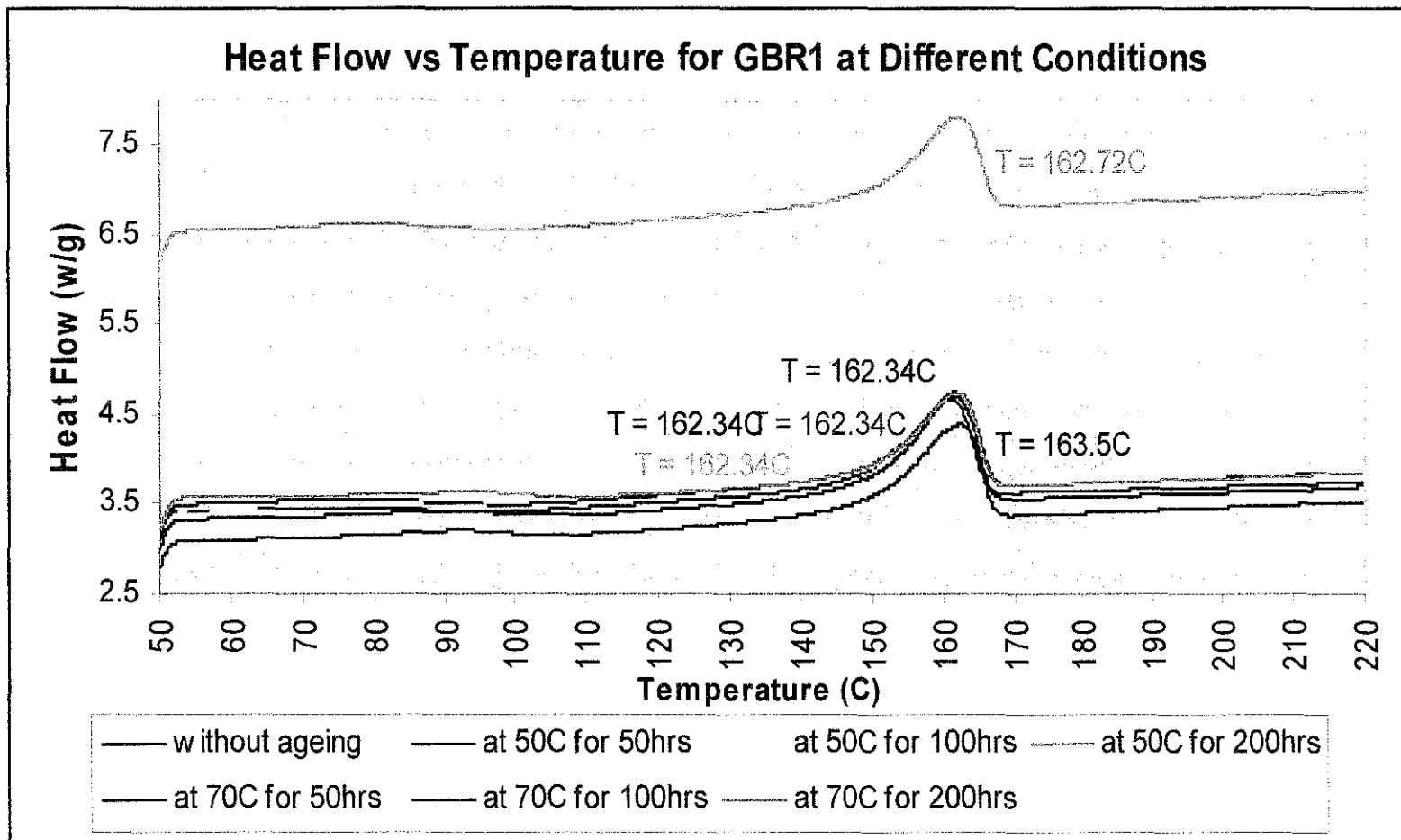


Figure 23: Melting Point Determination Using DSC; GBR1 at Various Conditions

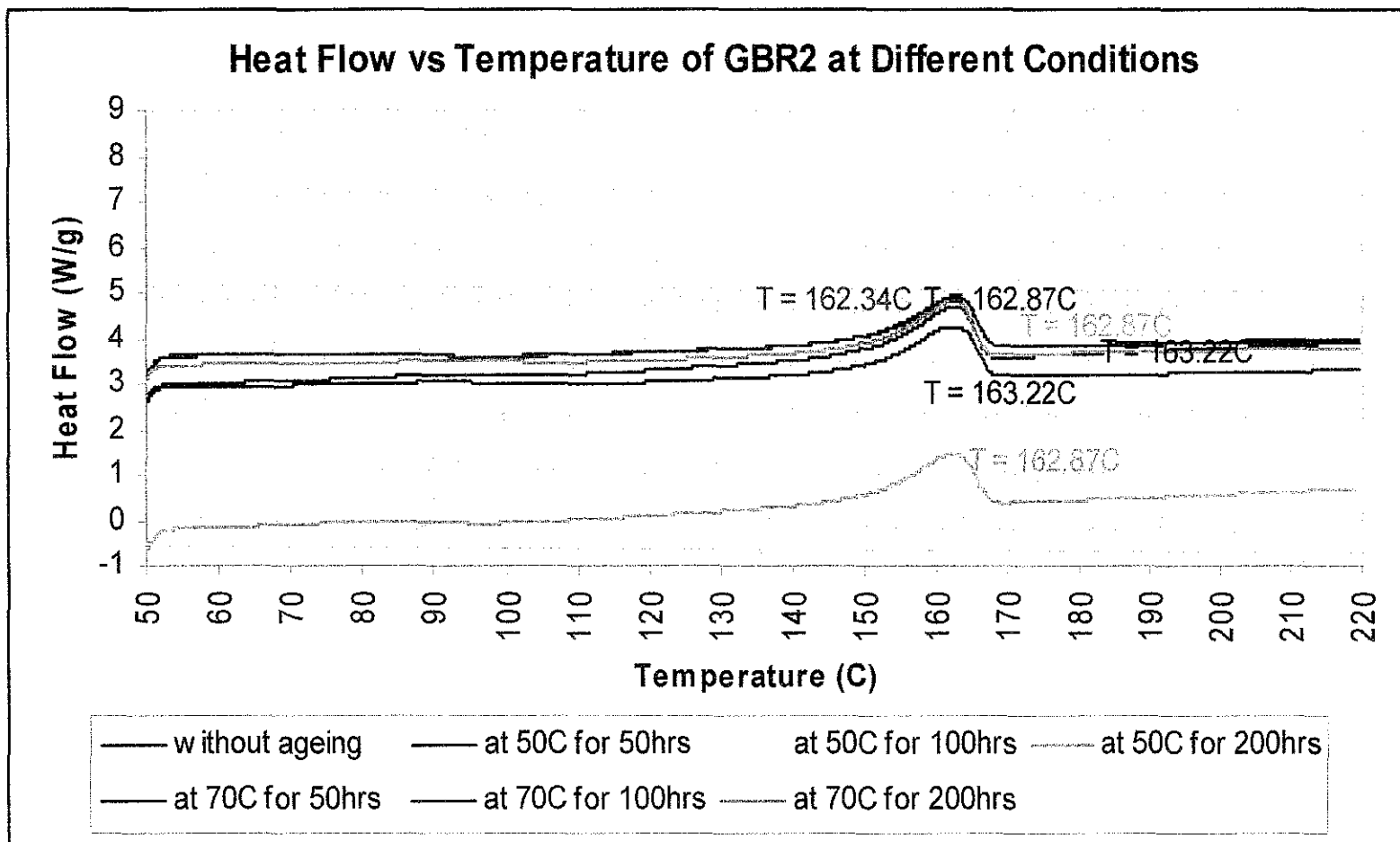


Figure 24: Melting Point Determination Using DSC; GBR2 at Various Conditions

4.3.2 Oxygen Induction Time

OIT is determined from the point at which the heat is held constant until it increased and reached the polymer's melting point.

Figure 25 shows the results of OIT from DCS. The trend of OIT is decreasing as time and temperature increased. At room temperature, GBR1 and GBR2 both have much lower OIT than control sample. This is similar for condition when ageing at 50°C for 50hours till 200hours. However, at higher temperature of 70 °C, the difference in OIT is getting smaller. Of overall, the prodegradant gives significant results in thermal degradation of PP film.

The average of control samples' induction time is much higher than those incorporated with prodegradant. Higher OIT indicates high resistance to oxidation reactions; only a few PP molecules react with oxygen in the air. This is due to longer molecular chain of PP.

For both GBR1 and GBR2, the results are at lower average of OIT than control sample. Thus it indicates that both GBR1 and GBR2 are having less resistance to oxidation rate than control sample. GBR2 is having lower OIT than GBR1. This is expected as GBR2 is incorporated with more prodegradant. The incorporation of PP with prodegradant produces shorter molecular chain. These chains are easier to be broken down by the oxidative reaction and shorten the time to degrade.

Based on all results, it proves that incorporation of prodegradant in PP film has accelerated the degree of degradation. A higher temperature and longer time of exposure to heat give further enhancement in degradation process. This is showed by result of control sample at 70°C where it has started to reach similar condition as samples with prodegradant. Samples with lower OIT show that they are less stable

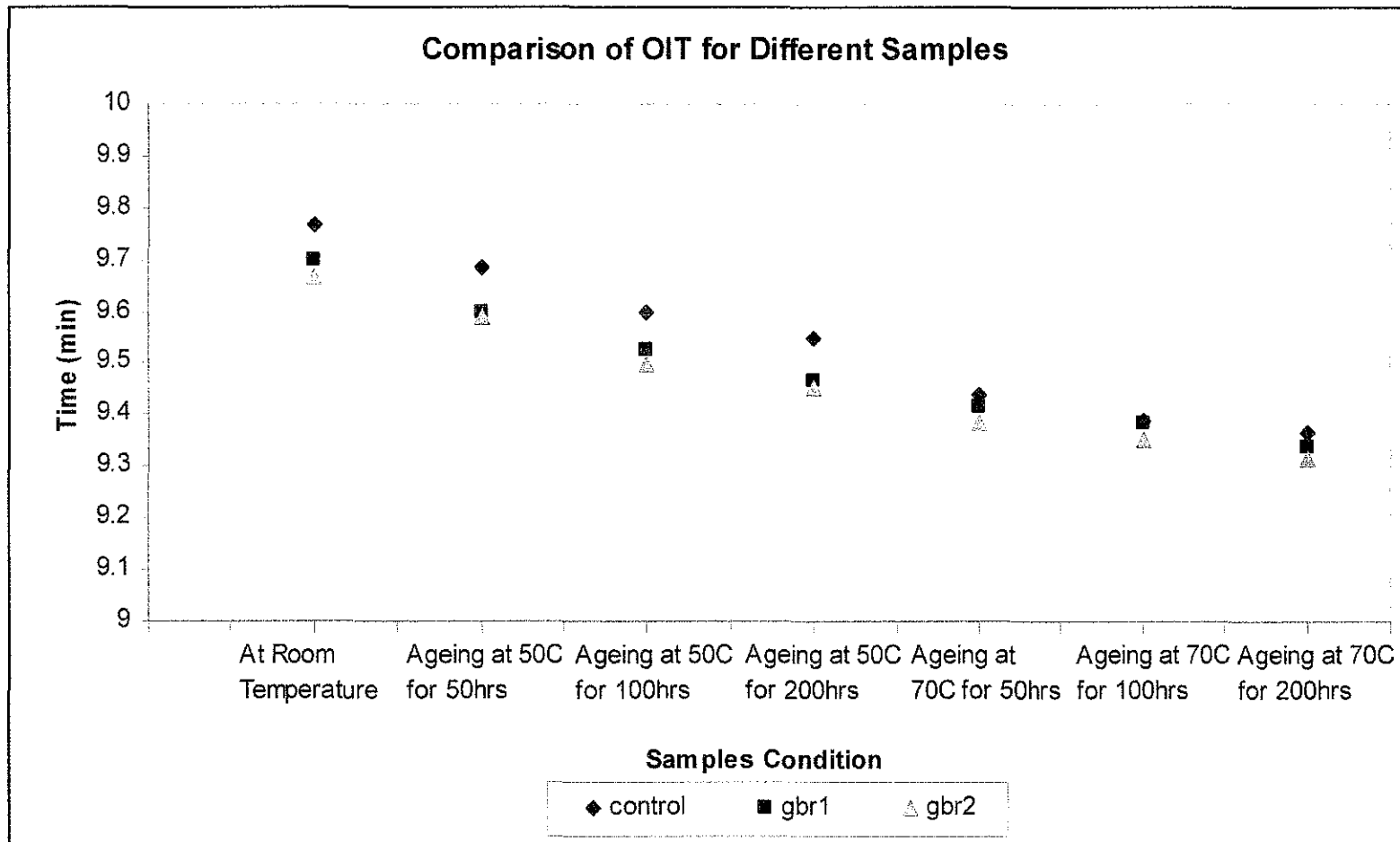


Figure 25: Comparison of Oxygen Induction Time between samples

and easier to degrade.

However, for result of GBR1 and GBR2, they are not so much differ compared to each other. Thus, 0.1wt% of prodegradant is considered to be the best amount for incorporation in PP film. With less prodegradant incorporated, it will have lower economical cost. There is also better justification in GBR1 mechanical and physical properties as shown in all results than for GBR2.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

5.1.1 The prodegradant is proved to be useful in incorporating with PP film as it accelerates the degradation process that is proved from the OIT results.

5.1.2 The best level to incorporate prodegradant in PP film making is 0.1 wt% as it does not give drastic changes to its mechanical and physical properties as can be seen from the comparison between control and GBR2 samples. .

5.1.3 Prodegradant preserves or not alter the physical and mechanical properties of PP film as the results are in acceptable range. Moreover, it improves the optical properties of PP film.

5.2 Recommendations

5.2.1 Identify prodegradant properties by using Gas Chromatography Mass Spectroscopy (GCMS), High Performance Liquid Chromatography (HPLC) and Atomic Absorption Spectrometer (AAS) for better understanding on how it works in degrading materials

5.2.2 Residual identification of prodegradant after a Thermal Gravity Analysis (TGA) study. The residual can be in the form of organic or non-polymeric additives.

5.2.3 Determine the mechanism of UV degradation of the prodegradant whether it is UV absorption, radical scavenger or energy transfer with the help of Ultraviolet Spectroscopy.

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15. Article from <<[http:// www.deh.gov.au/](http://www.deh.gov.au/)>> on waste management
16. Article from <<[http:// www.reifenhauser.com/](http://www.reifenhauser.com/)>> on blown film machine structure
17. Article from <<<http://faculty.uscs.edu/>>> on the molecular structure of polymer
18. Article from <<[http:// www.doitpoms.ac.uk/](http://www.doitpoms.ac.uk/)>> on the polymer structure
19. Article on oven ageing at << [http:// www.hwwallace.co.uk/](http://www.hwwallace.co.uk/)>>
20. Article from <<[http:// www.blachford.ca/](http://www.blachford.ca/)>> on prodegradant additive

APPENDICES

APPENDIX A
LIST OF FIGURES

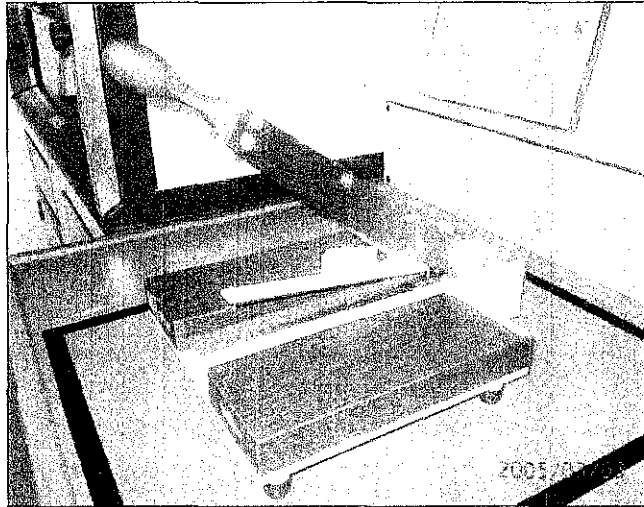


Figure 26: Cutting Tools to cut PP Film into uniform width and length



Figure 27: Samples prepared under conditioning; from left- control, GBR1 and GBR2

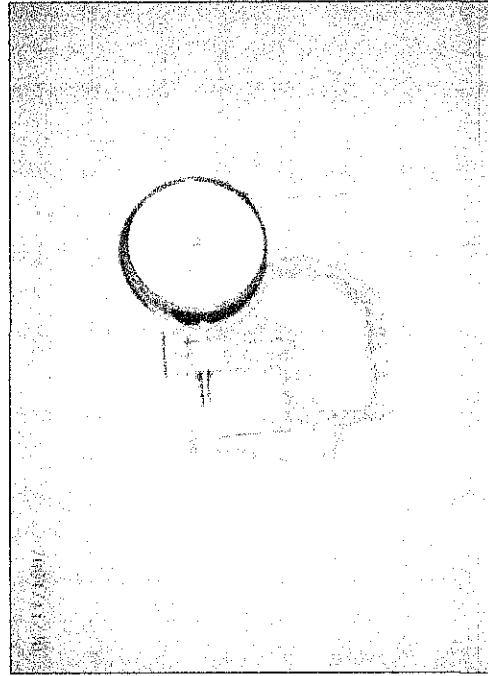


Figure 28: Thickness Gauge to accurately Measure the Thickness of Each Film

APPENDIX B

LIST OF TABLES AND GRAPHS

Table 1: Schedule of Work Plan

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Date	24/1-30/1	31/1-6/2	7/2-13/2	14/2-20/2	21/2-27/2	28/2-6/3	7/3-13/3	14/3-20/3	21/3-27/3	28/3-3/4	4/4-10/4	11/4-17/4	18/4-24/4	25/4-1/5	2/5-8/5	9/5-15/5	16/5-22/5	23/5-29/5
1	Research from books and internet	x	x		x	x	x												
2	Proposal preparation	x	x	x															
3	Preparing of PP film with prodegradant at PRSS				x														
4	Experimental works at PP(M)SB								x										
5	Experimental Works at UTP									x	x								
6	Comparison of results from all experiments				x	x	x	x	x	x	x	x							
7	Preparing reports based on the data obtained					x	x	x	x	x	x	x	x	x					
8	Submission of progress report to supervisor							x											
10	Submission of dissertation draft to supervisor											x							
11	EDX												x						

12	Submission of dissertation final draft to supervisor and coordinator														x				
13	Presentation to external examiners																		x
14	Submission of hardbound copy of project dissertation to coordinator	Week 1 of Semester July 2005																	

Table 2: Results of Properties for Each Sample

Samples	MI	Haze	Clarity	C.O.F		Blocking
	g/10min	%	%	static	kinetic	N
Control	16.1	6.13	95.1	0.00035	0.00014	0.05606
GBR 0.1%	17.9	2.37	95.8	0.00045	0.00016	0.06424
GBR 0.2%	19.21	2.39	95.7	0.00048	0.00026	0.09049

Table 3: Results of OIT Determination

conditions	control	gbr1	gbr2
	time, min	time, min	time, min
RT	9.6	9.634	9.834
50C at 50hrs	9.62	9.837	9.805
50C at 100hrs	9.67	9.857	9.667
50C at 200hrs	9.7	9.797	9.7
70C at 50hrs	9.65	9.834	9.767
70C at 100hrs	9.444	9.867	9.734
70C at 200hrs	9.684	9.837	9.917

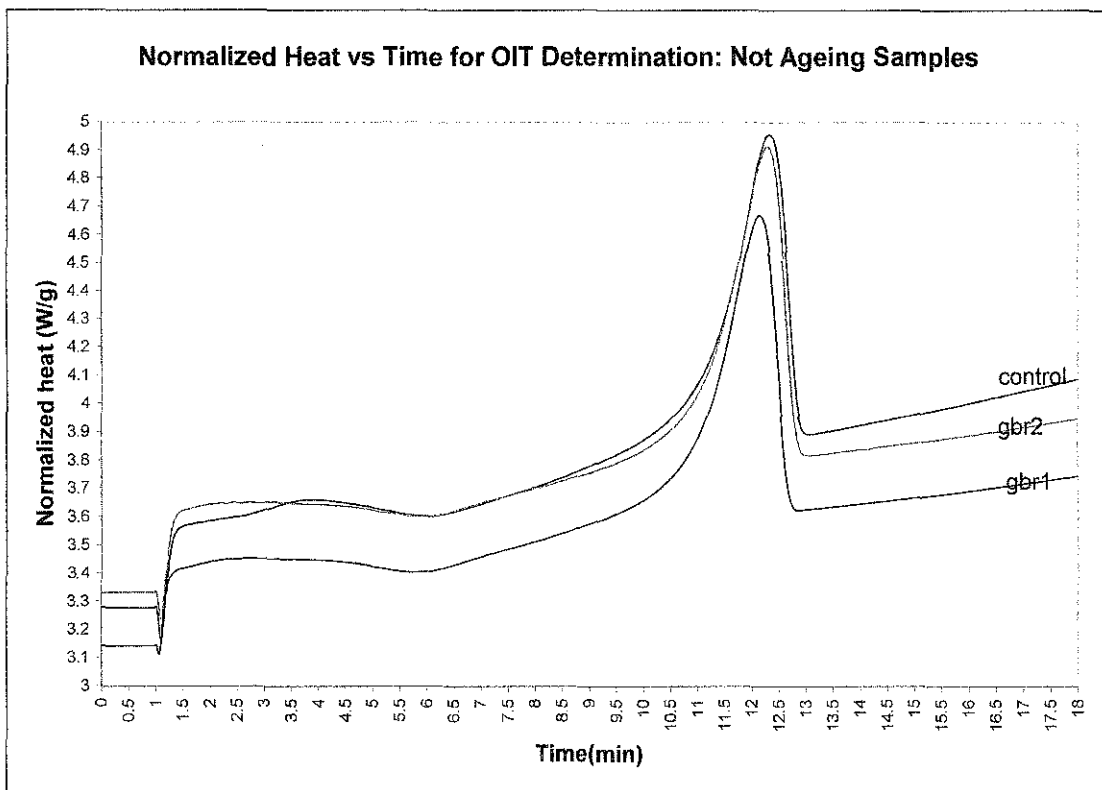


Figure 29: Trend of Normalized Heat vs Time from DSC- without Ageing Samples

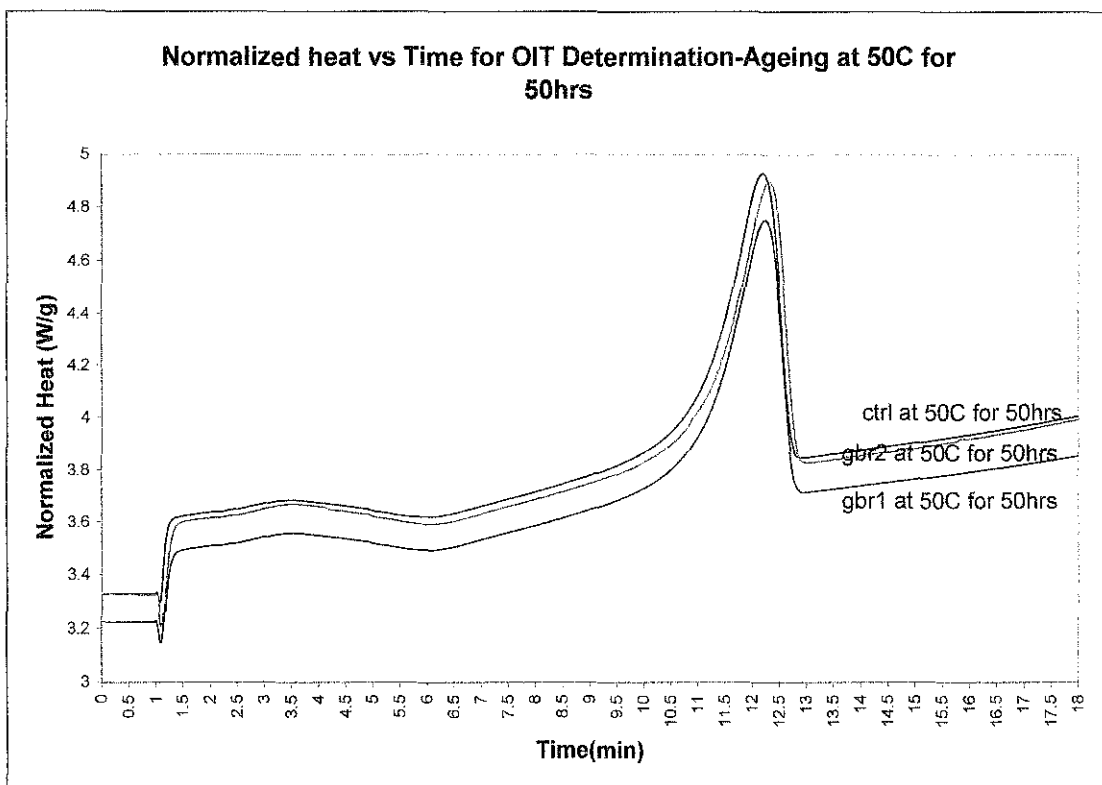


Figure 30: Trend of Normalized Heat vs Time from DSC- Ageing at 50°C for 50hrs

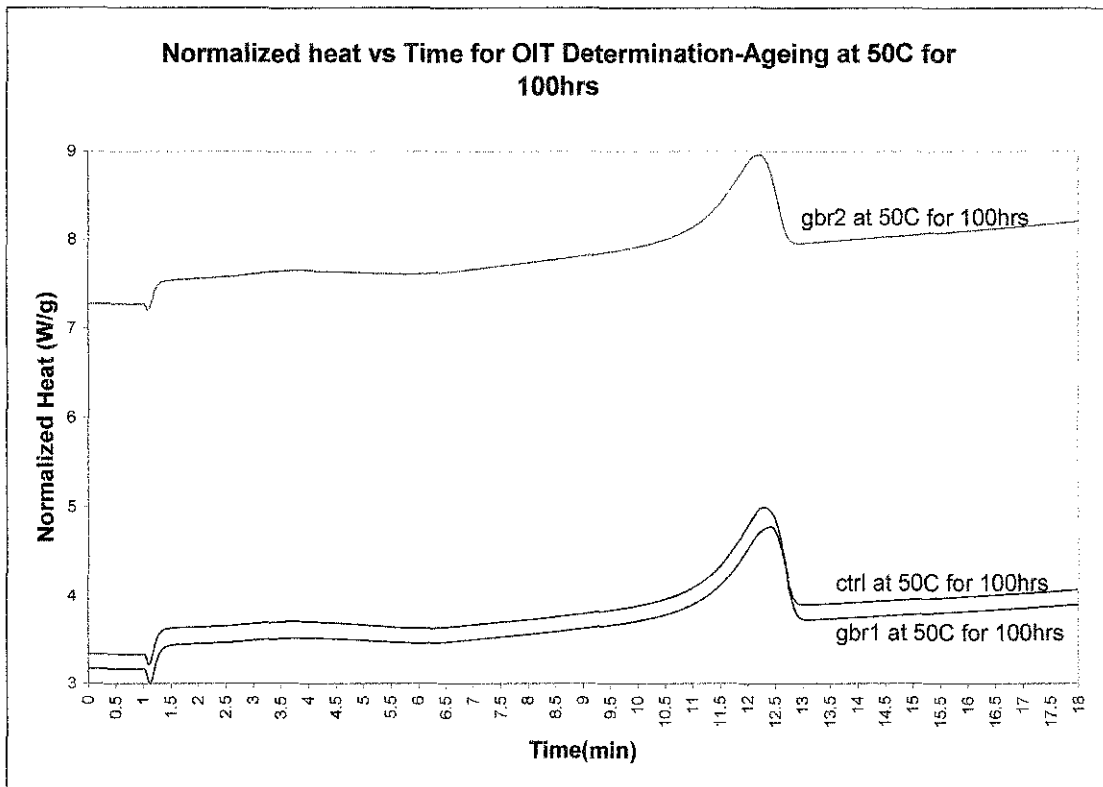


Figure 31: Trend of Normalized Heat vs Time from DSC- Ageing at 50°C for 100hrs

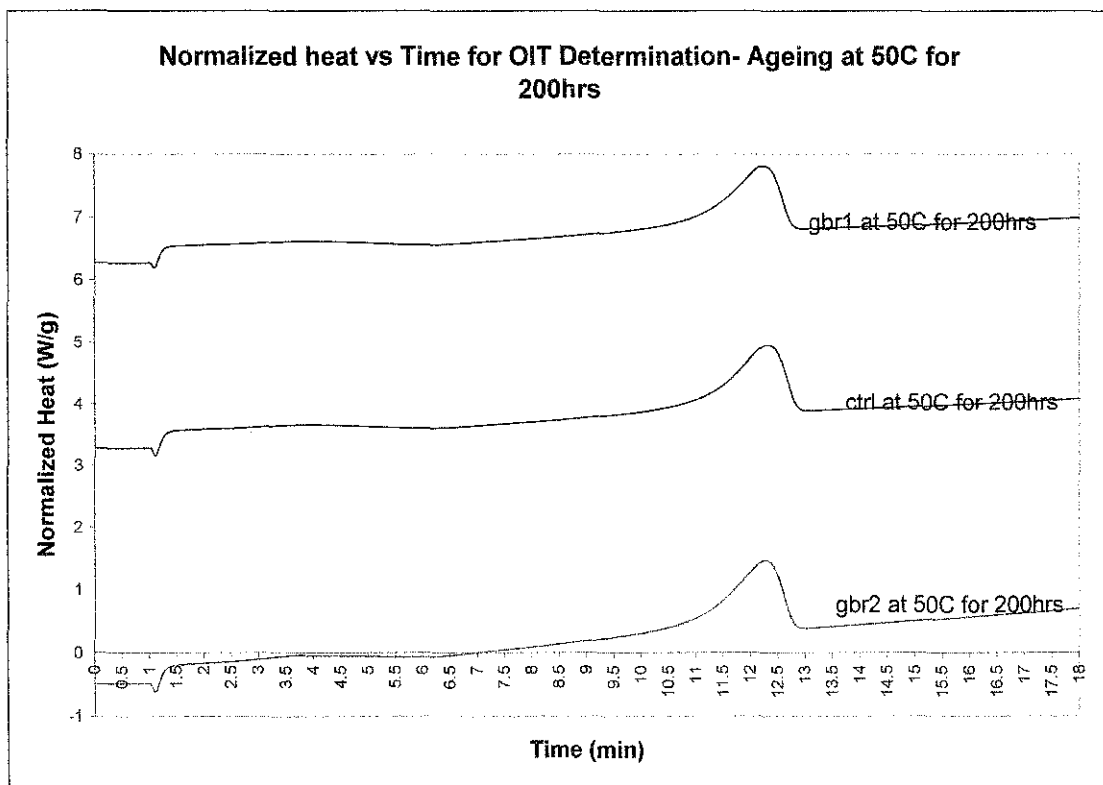


Figure 32: Trend of Normalized Heat vs Time from DSC- Ageing at 50°C for 200hrs

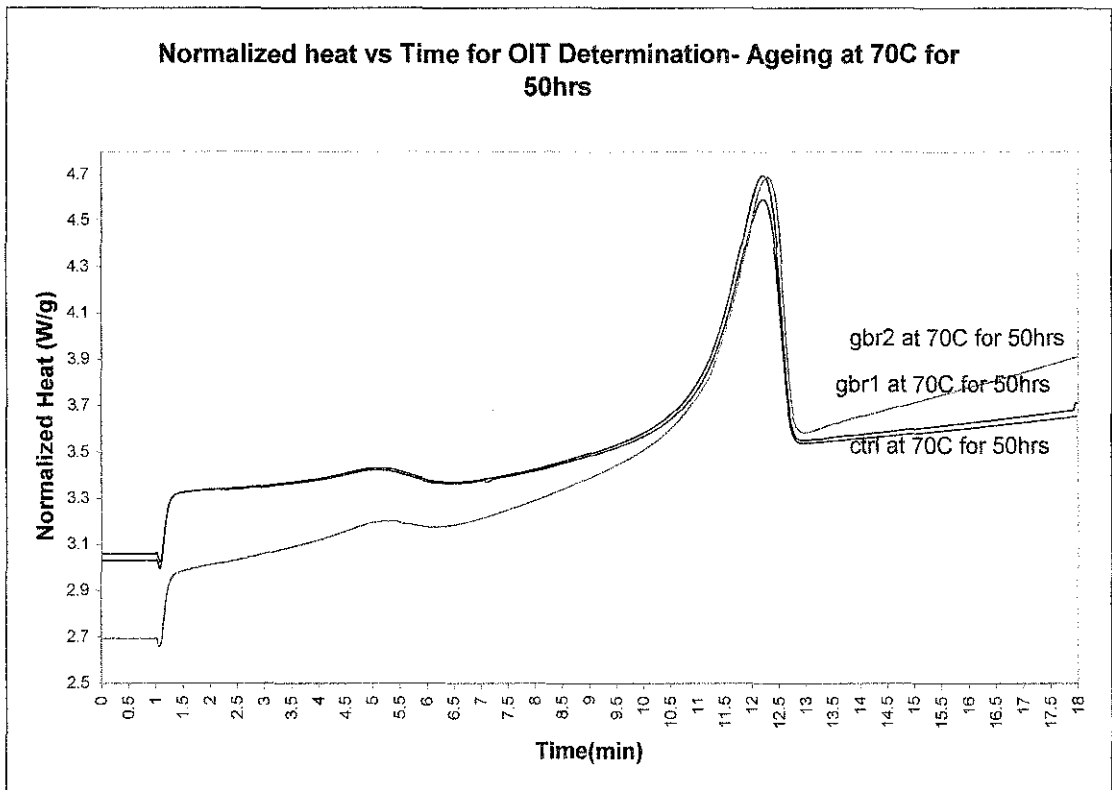


Figure 33: Trend of Normalized Heat vs Time from DSC- Ageing at 70°C for 50hrs

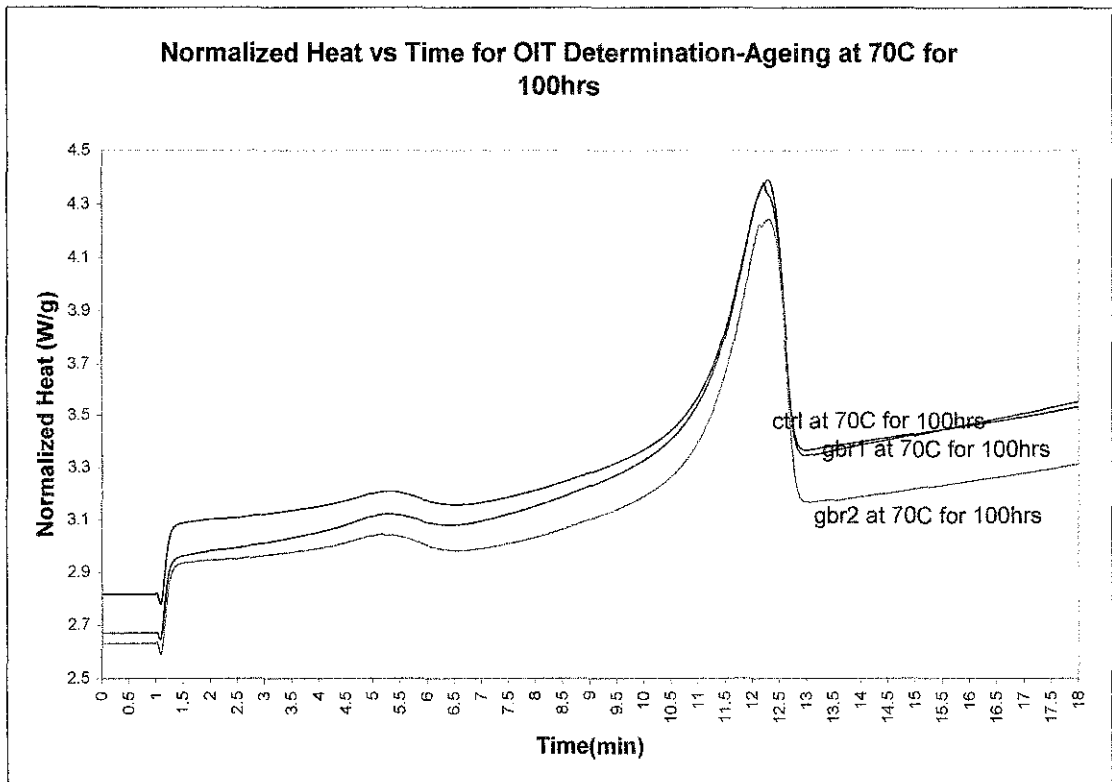


Figure 34: Trend of Normalized Heat vs Time from DSC- Ageing at 70°C for 100hrs

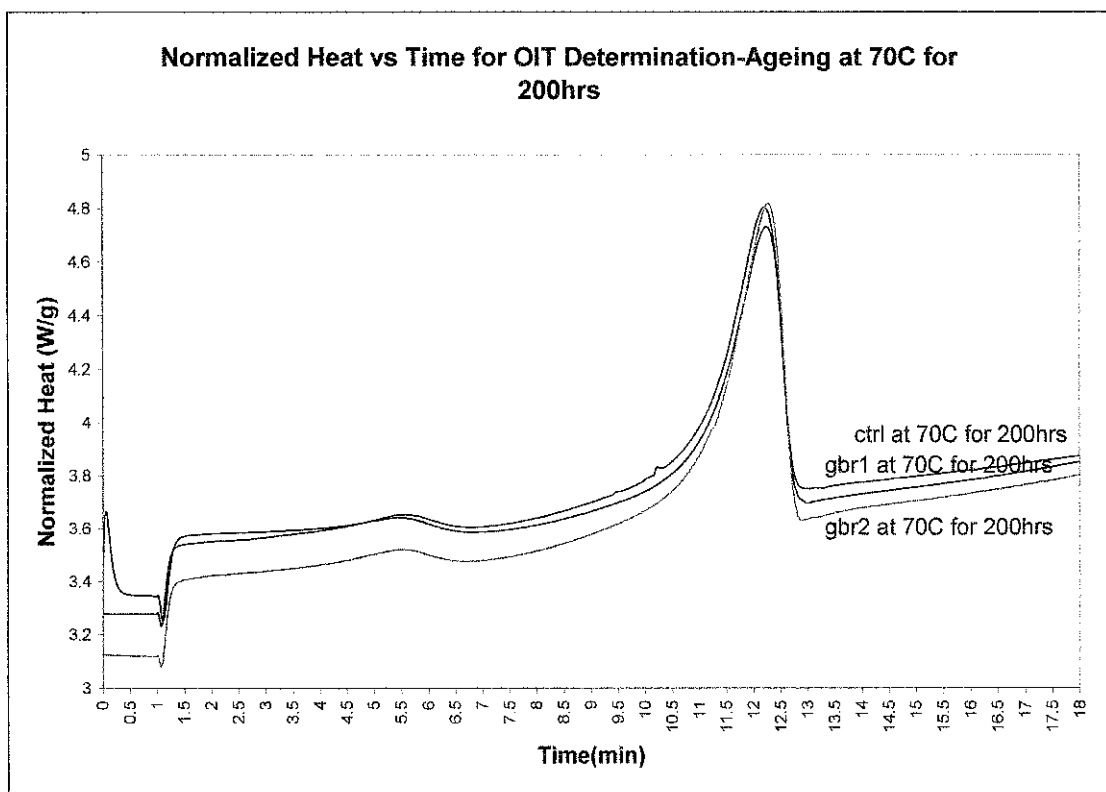


Figure 35: Trend of Normalized Heat vs Time from DSC- Ageing at 70°C for 200hrs

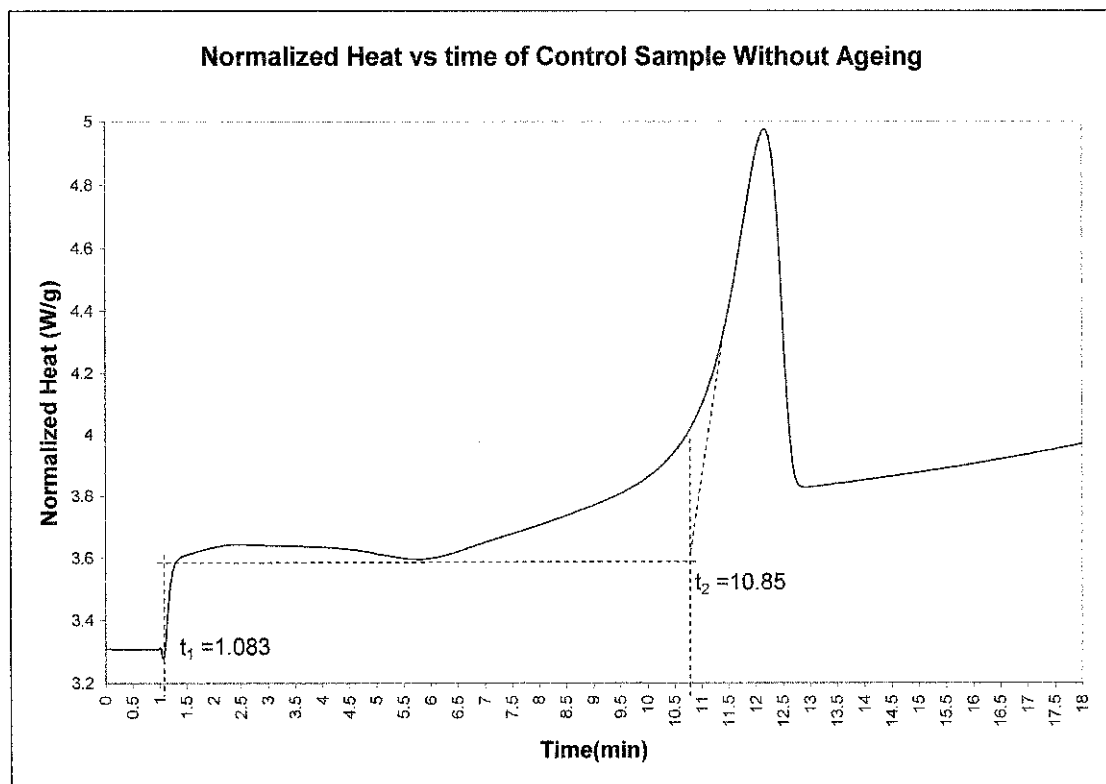


Figure 36: Determination of OIT for without Ageing Control Samples

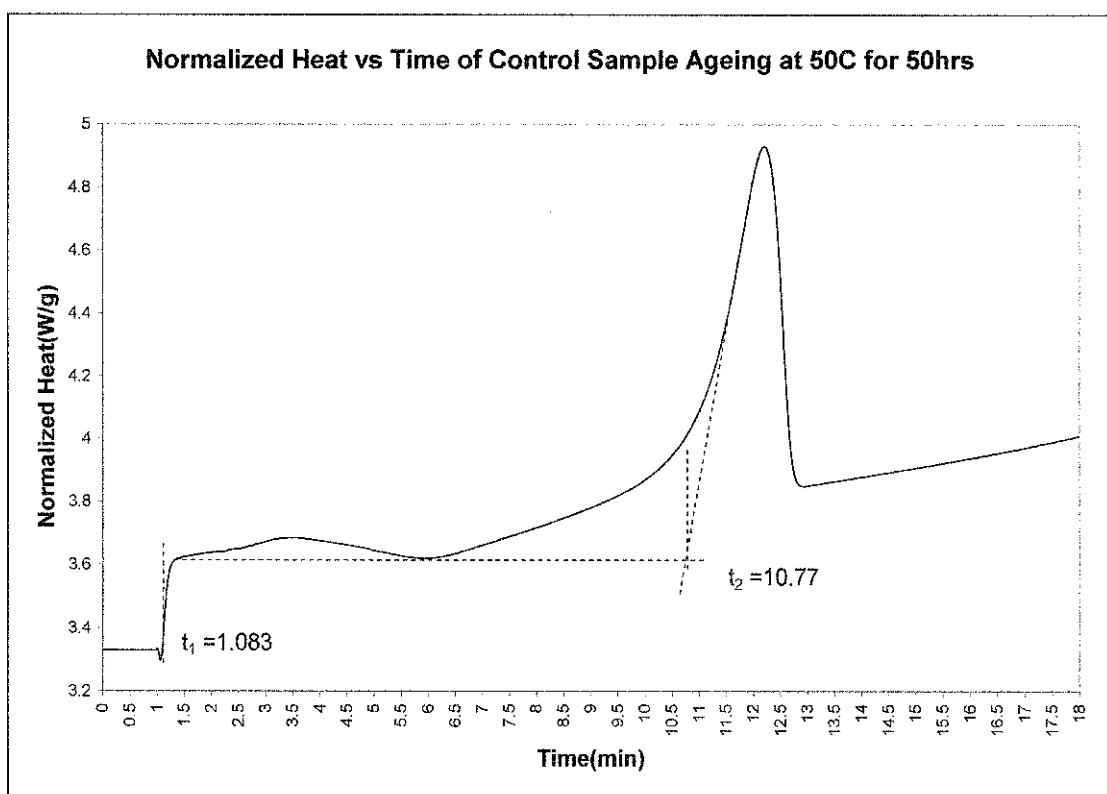


Figure 37: Determination of OIT for Ageing Control samples at 50°C for 50hrs

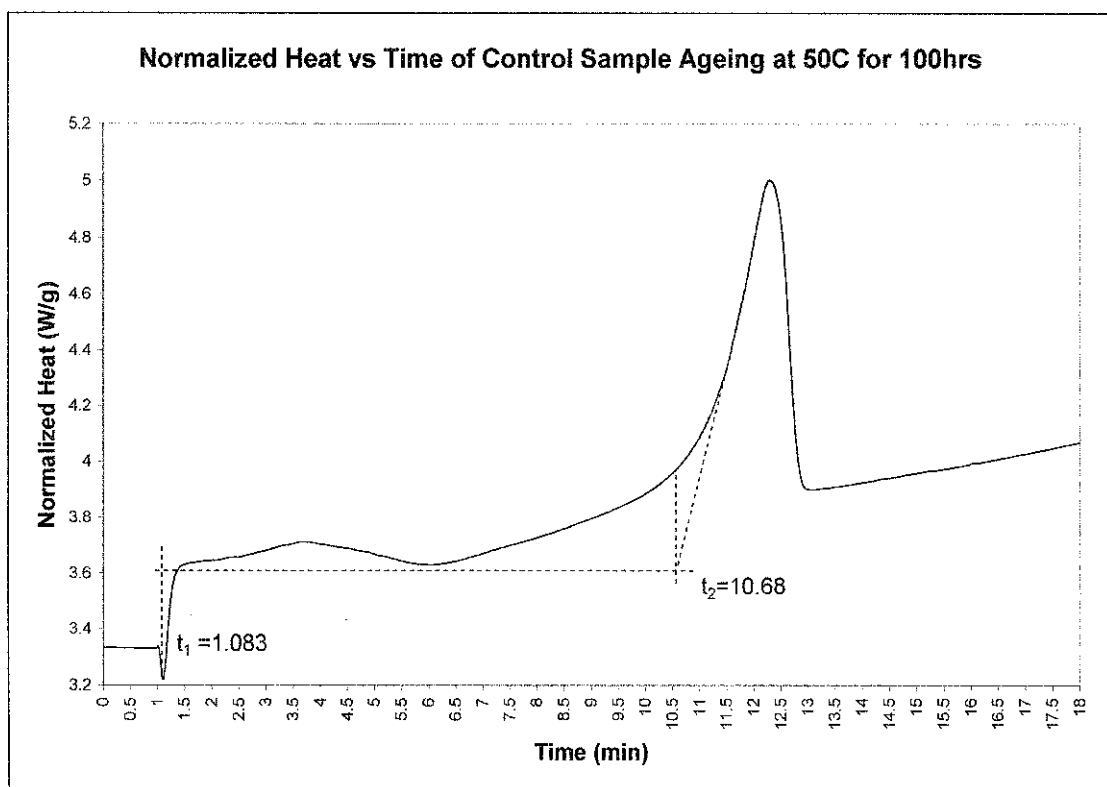


Figure 38: Determination of OIT for Ageing Control samples at 50°C for 100hrs

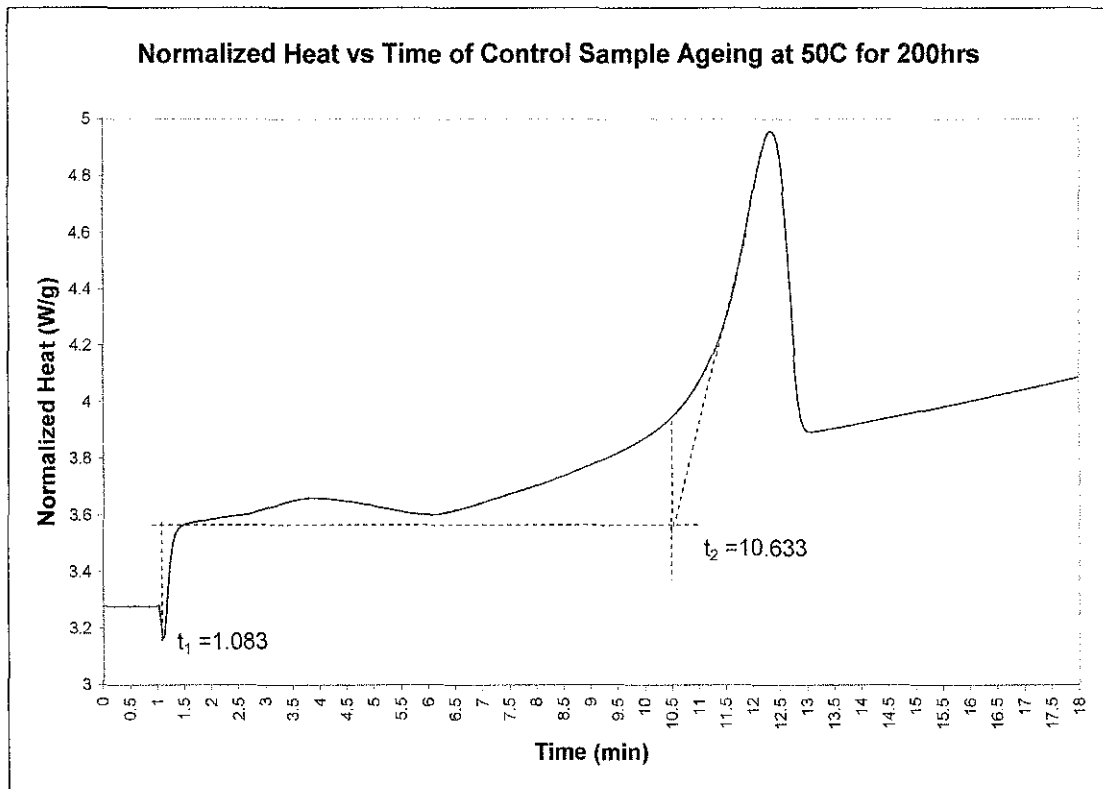


Figure 39: Determination of OIT for Ageing Control samples at 50°C for 200hrs

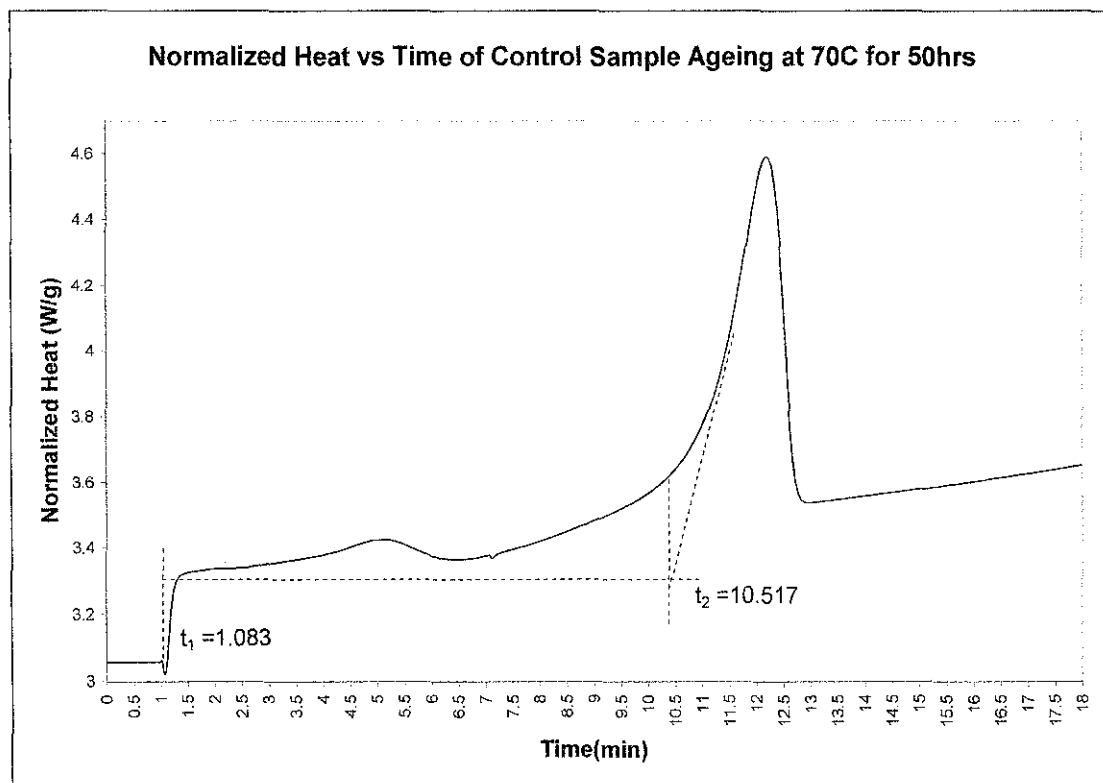


Figure 40: Determination of OIT for Ageing Control samples at 70°C for 50hrs

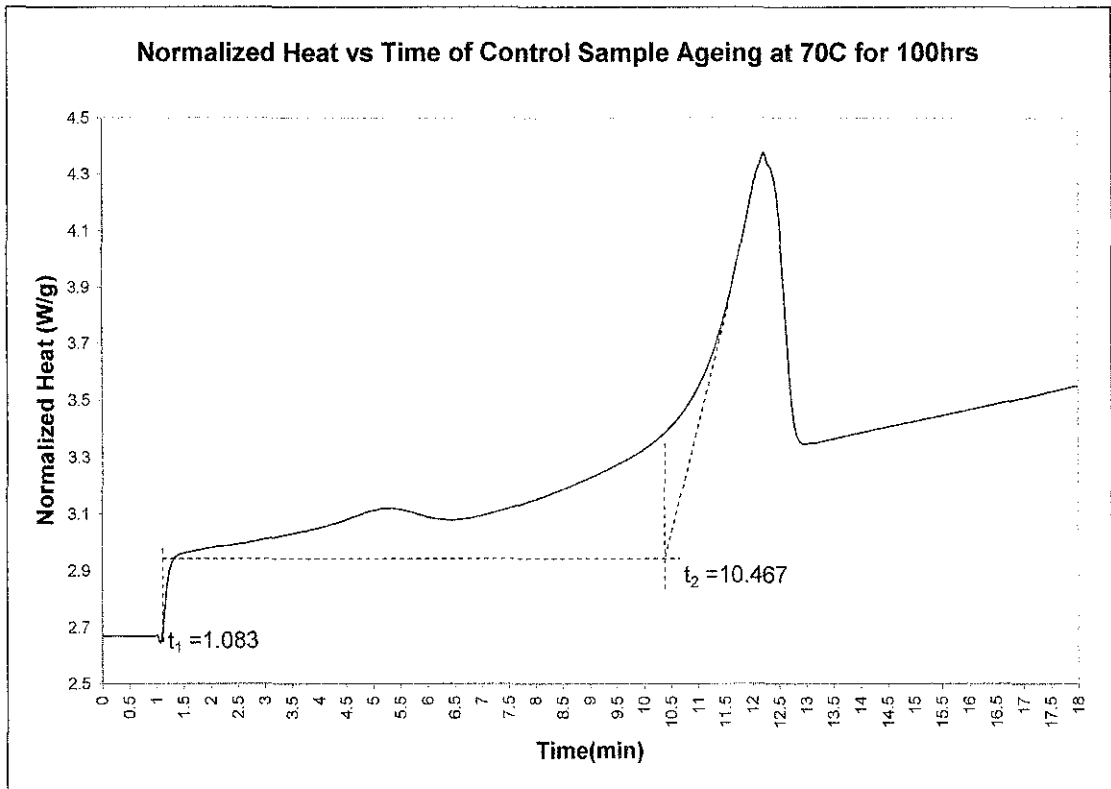


Figure 41: Determination of OIT for Ageing Control samples at 70°C for 100hrs

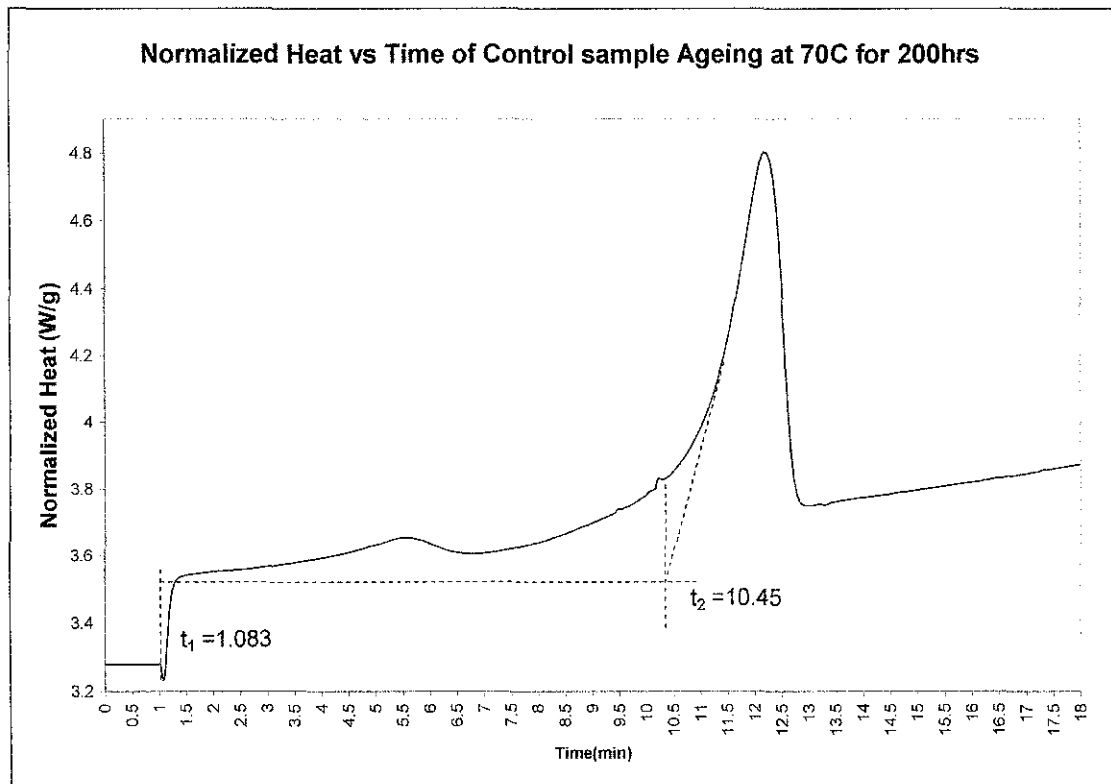


Figure 42: Determination of OIT for Ageing Control samples at 70°C for 200hrs

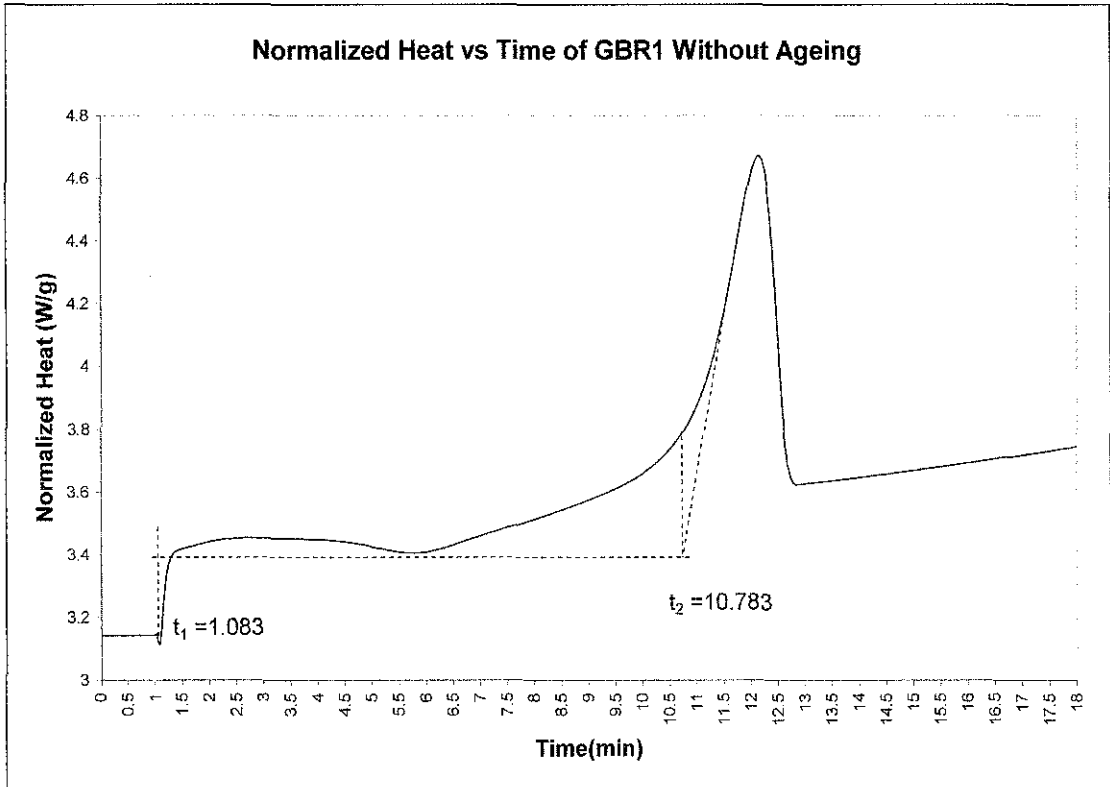


Figure 43: Determination of OIT for Without Ageing GBR1 samples

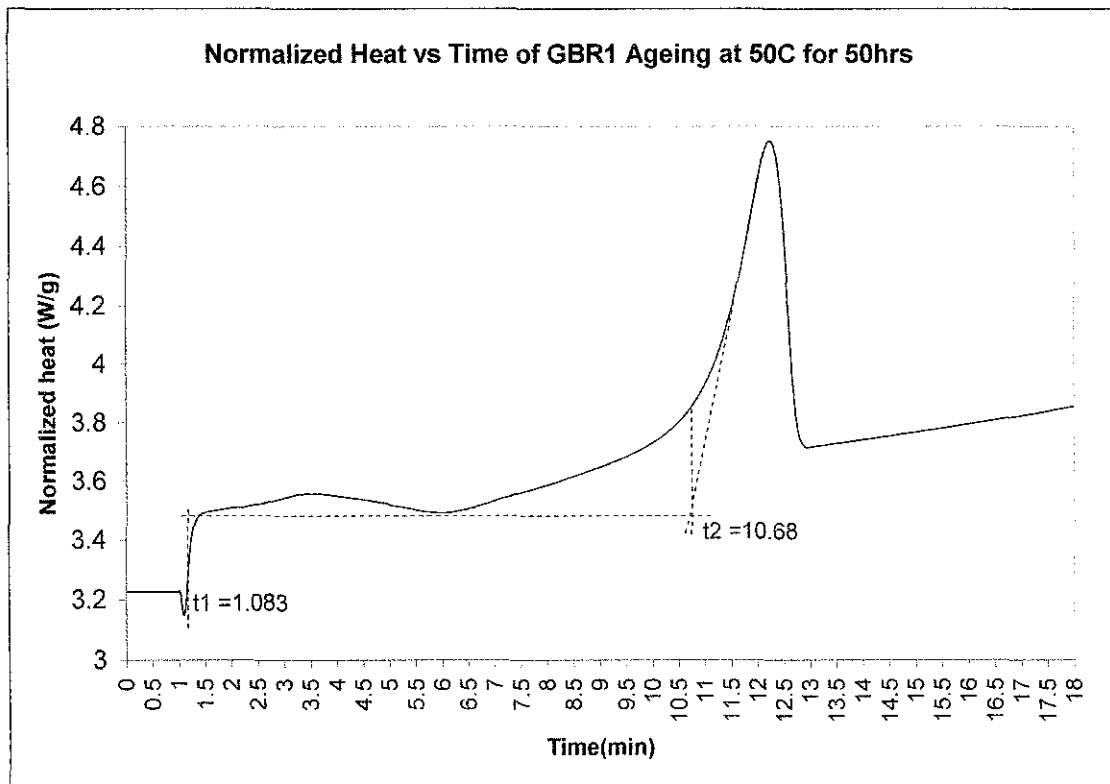


Figure 44: Determination of OIT for Ageing GBR1 samples at 50°C for 50hrs

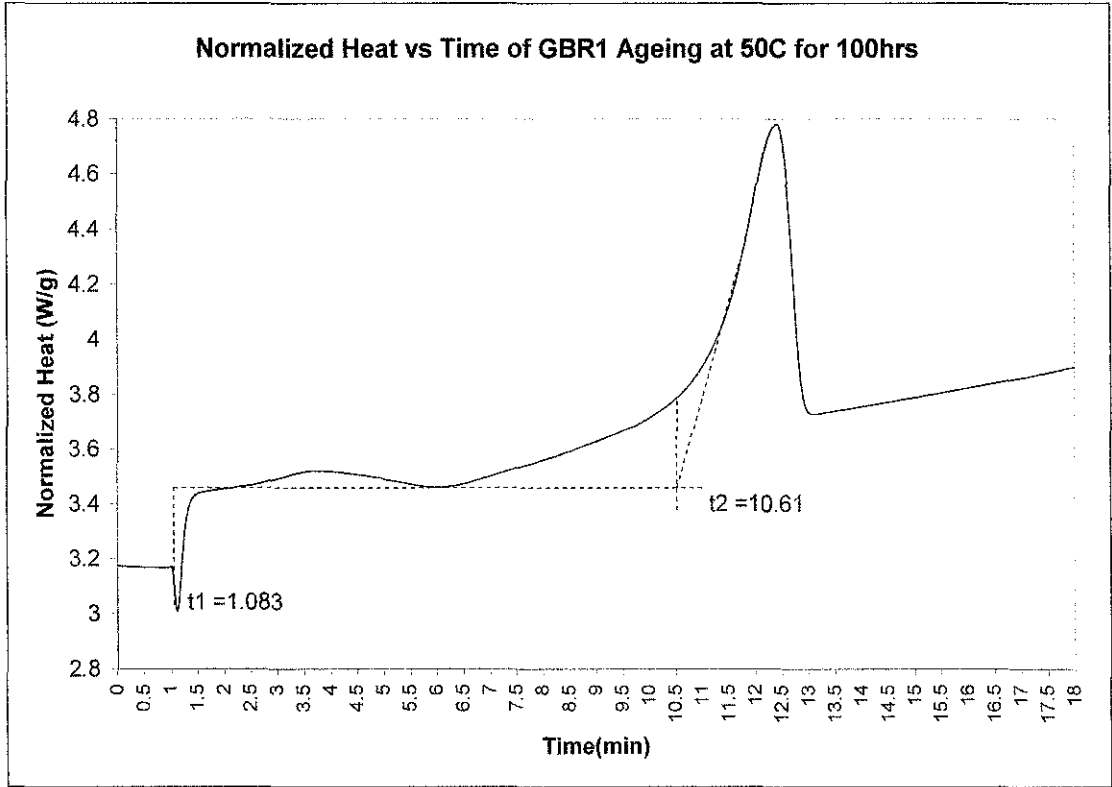


Figure 45: Determination of OIT for Ageing GBR1 samples at 50°C for 100hrs

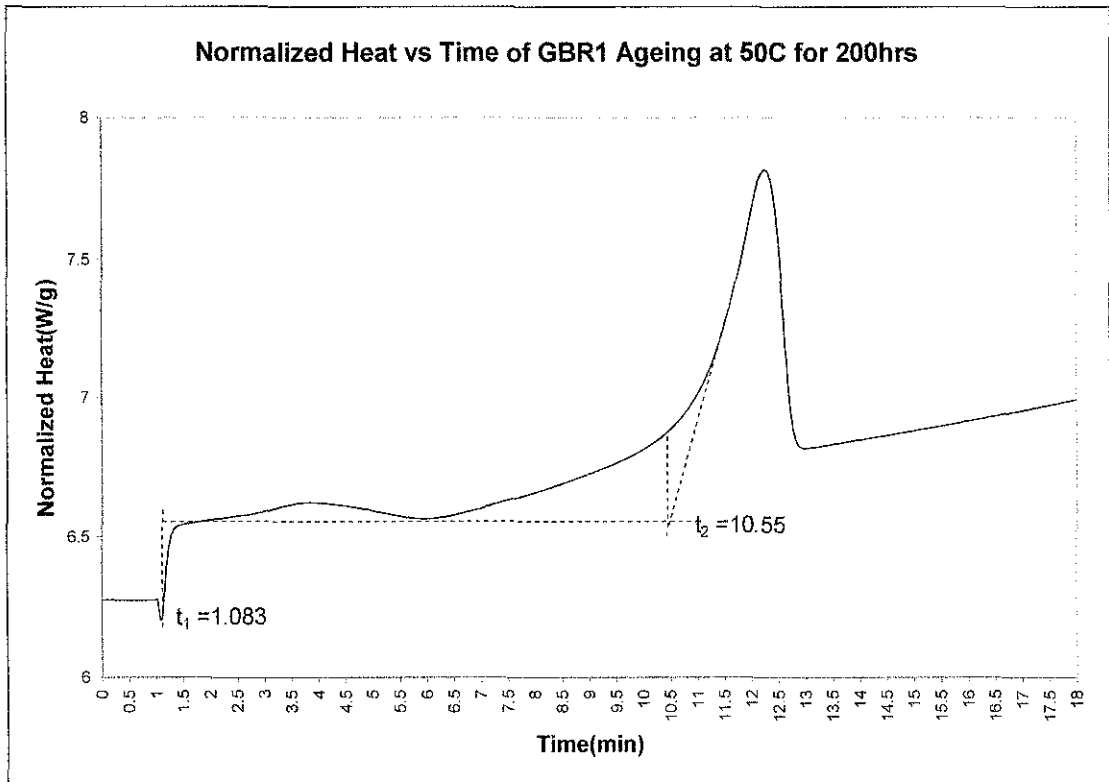


Figure 46: Determination of OIT for Ageing GBR1 samples at 50°C for 200hrs

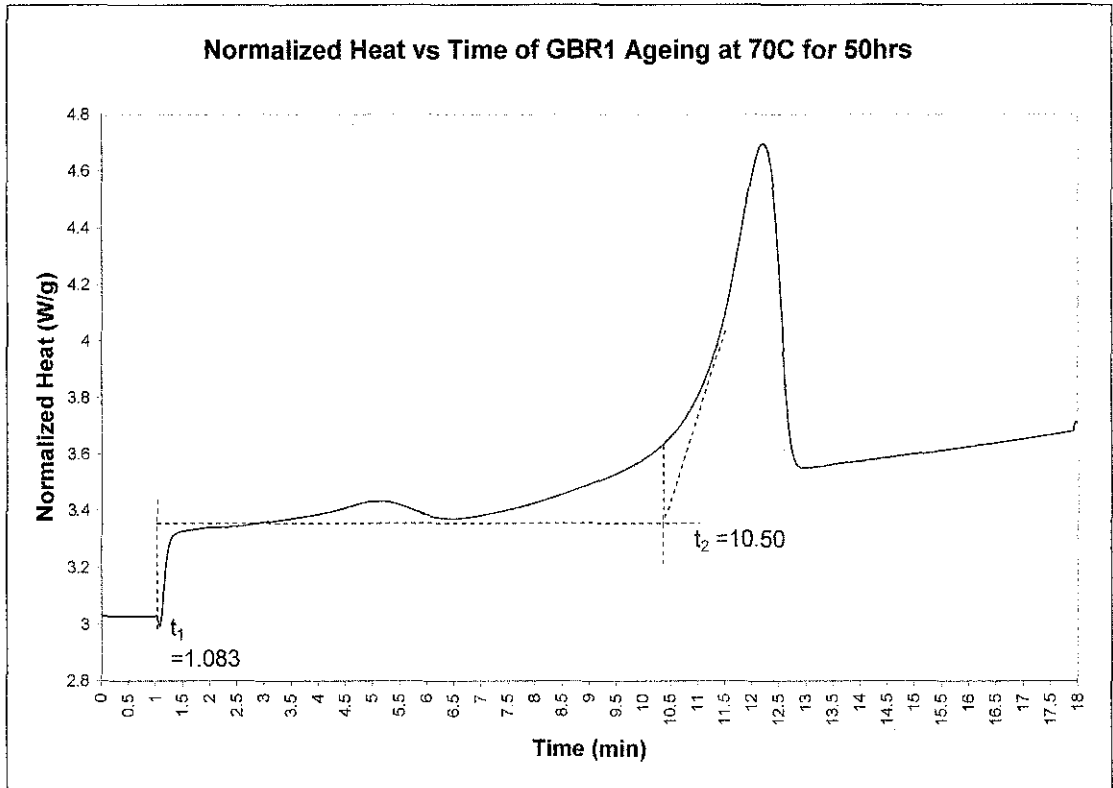


Figure 47: Determination of OIT for Ageing GBR1 samples at 70°C for 50hrs

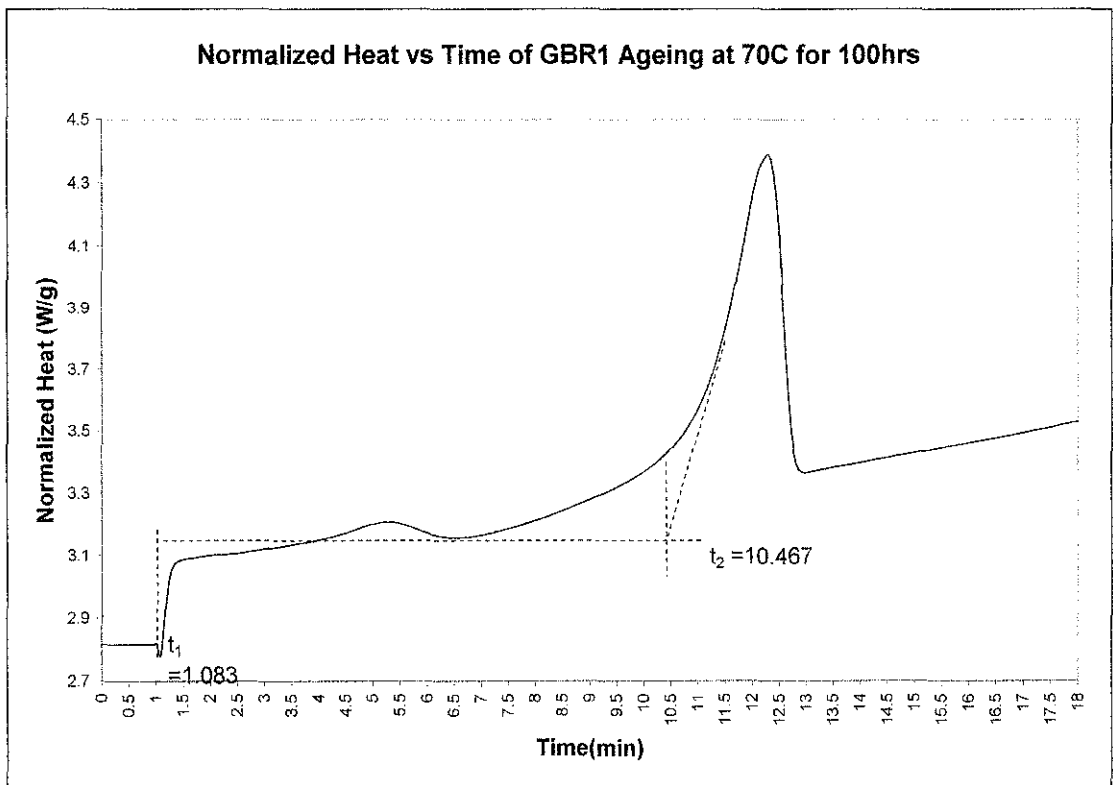


Figure 48: Determination of OIT for Ageing GBR1 samples at 70°C for 100hrs

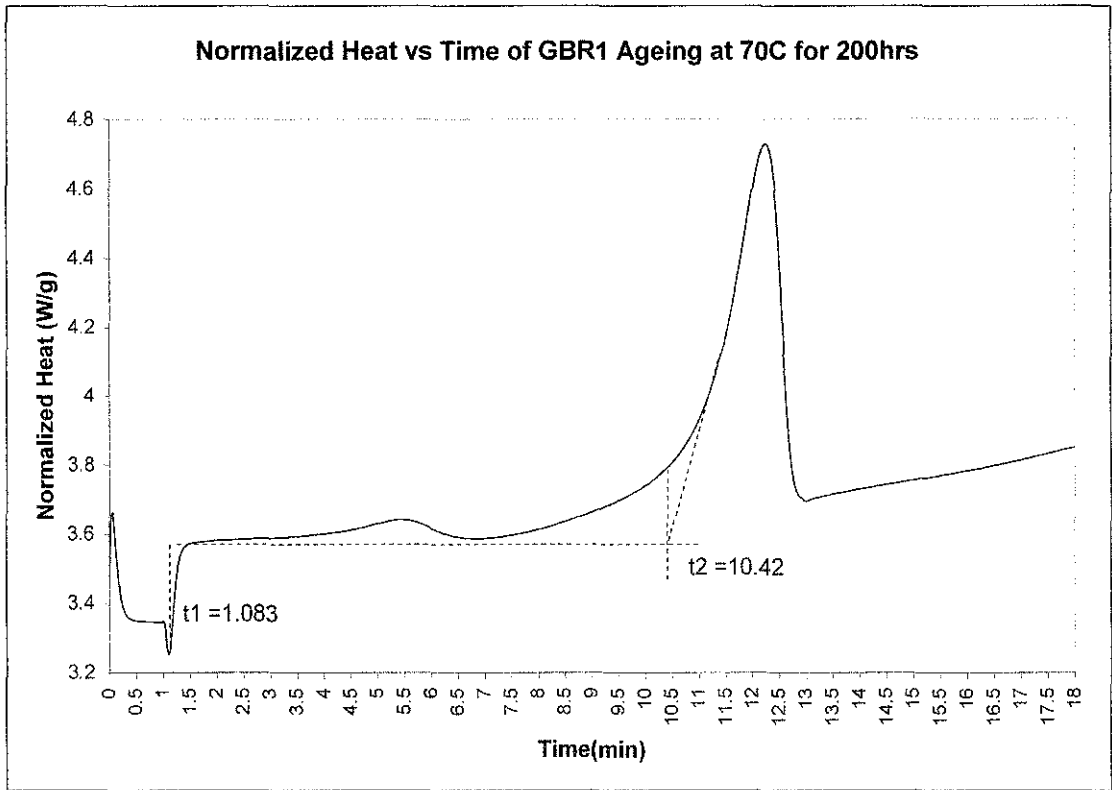


Figure 49: Determination of OIT for Ageing GBR1 samples at 70°C for 200hrs

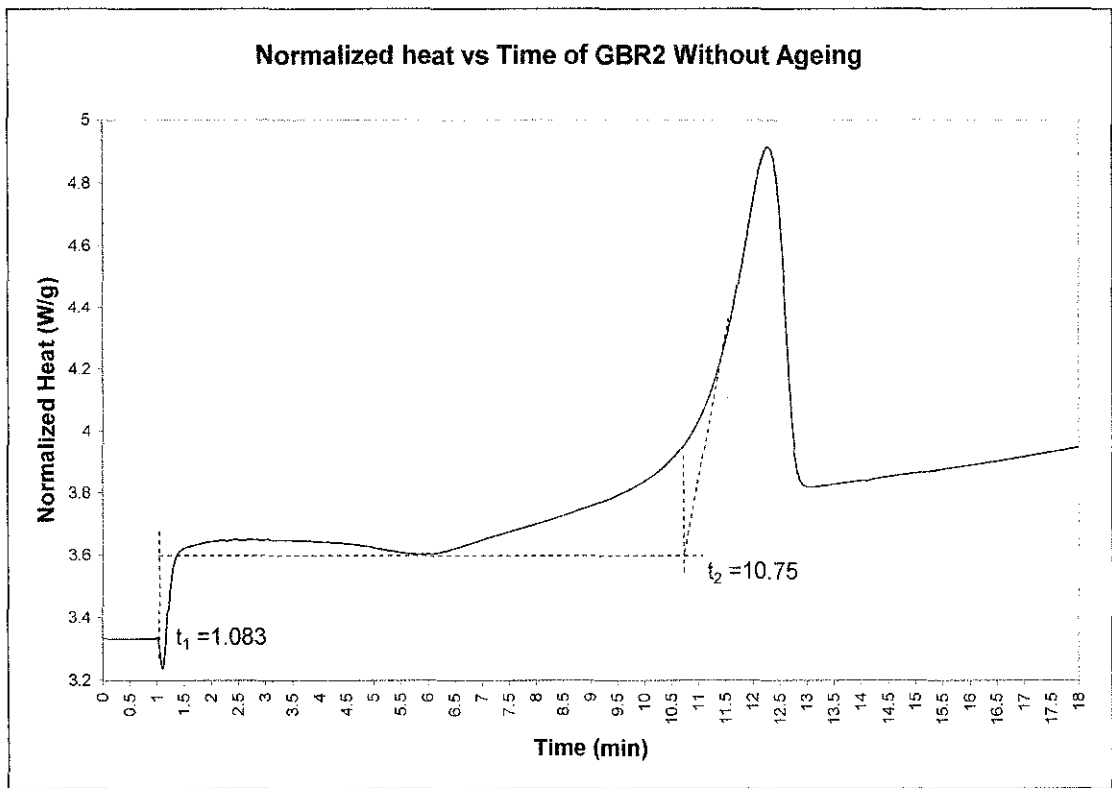


Figure 50: Determination of OIT for Without Ageing GBR2 samples

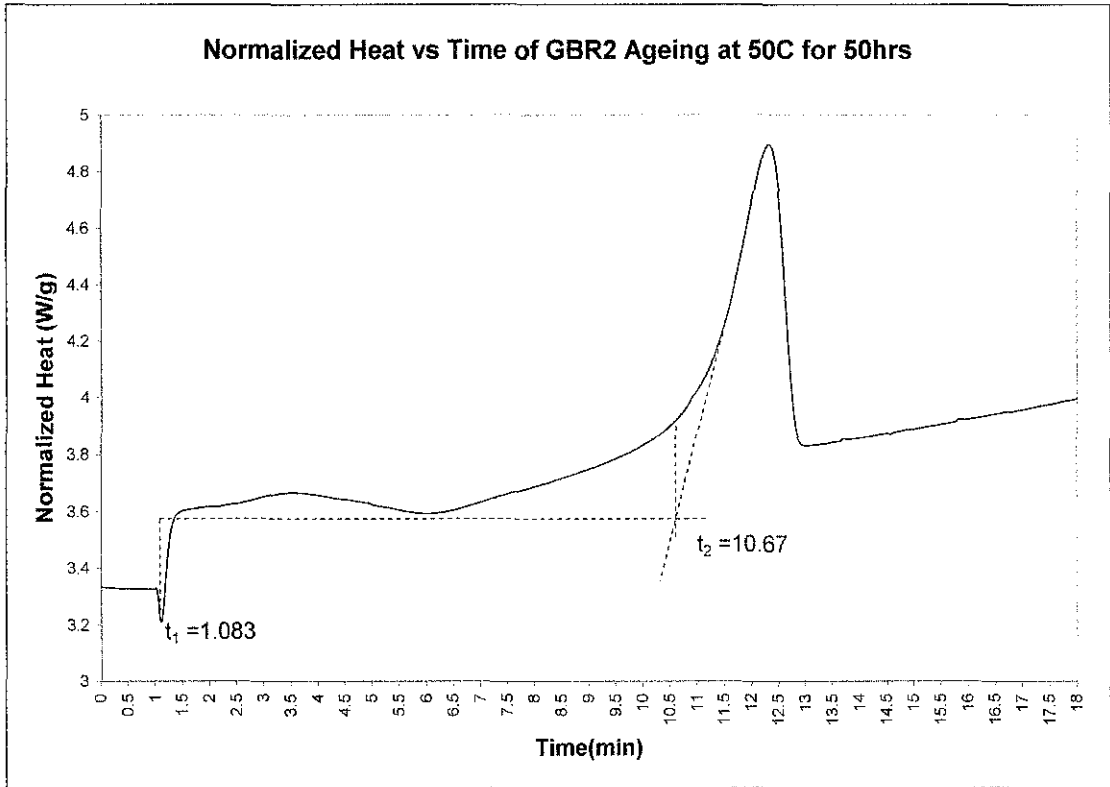


Figure 51: Determination of OIT for Ageing GBR2 samples at 50°C for 50hrs

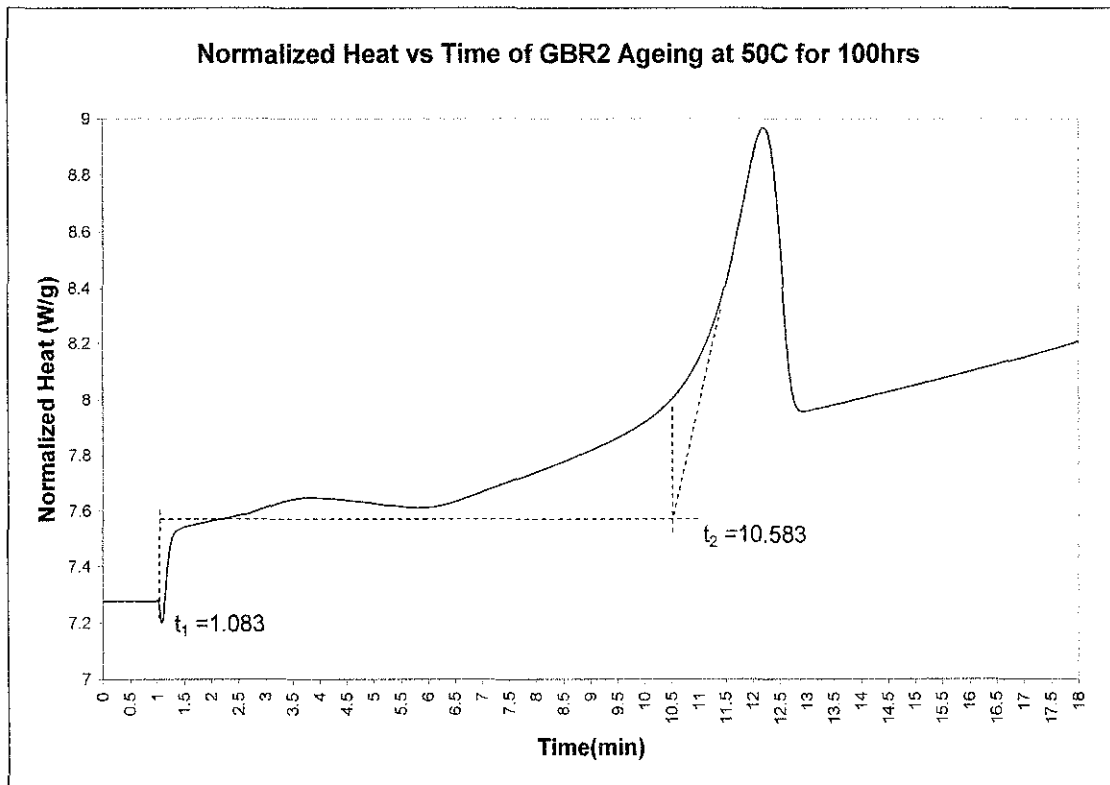


Figure 52: Determination of OIT for Ageing GBR2 samples at 50°C for 100hrs

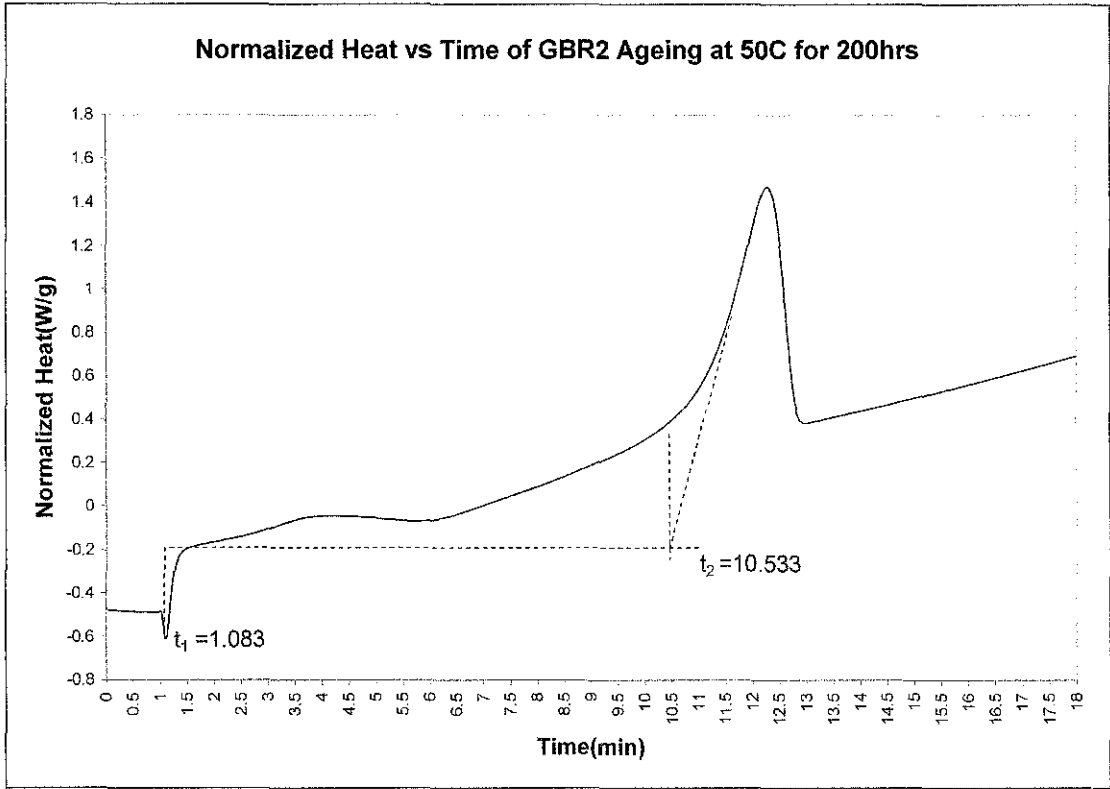


Figure 53: Determination of OIT for Ageing GBR2 samples at 50°C for 200hrs

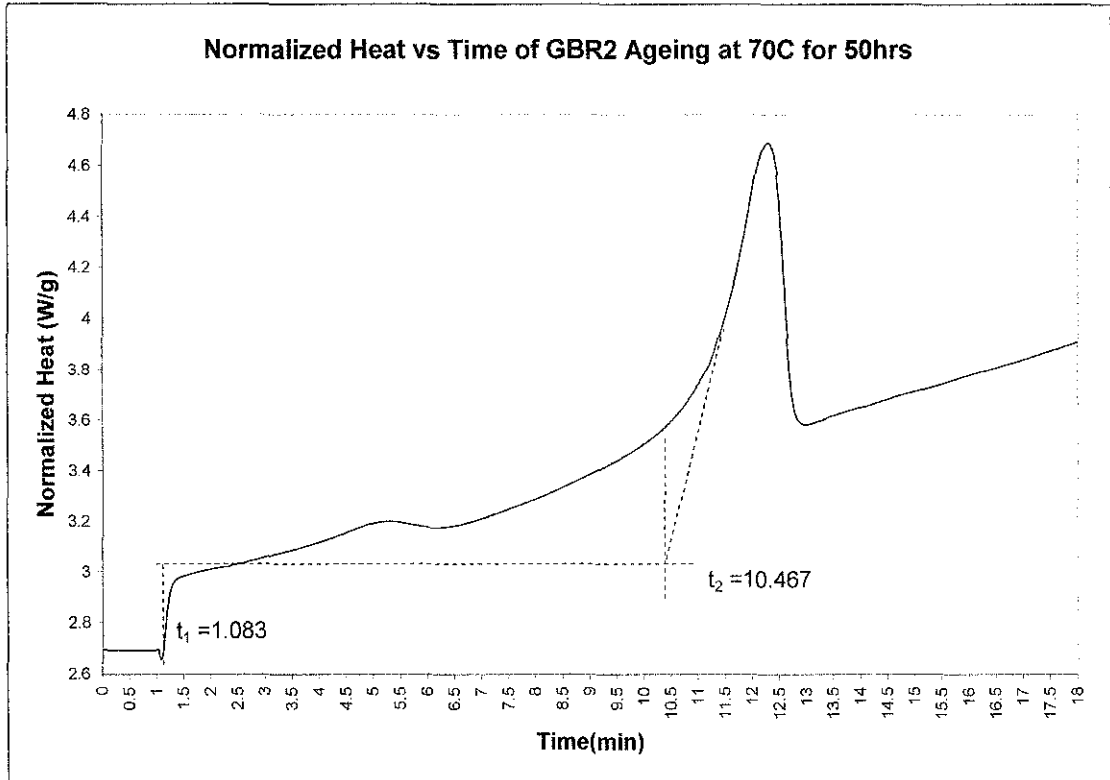


Figure 54: Determination of OIT for Ageing GBR2 samples at 70°C for 50hrs

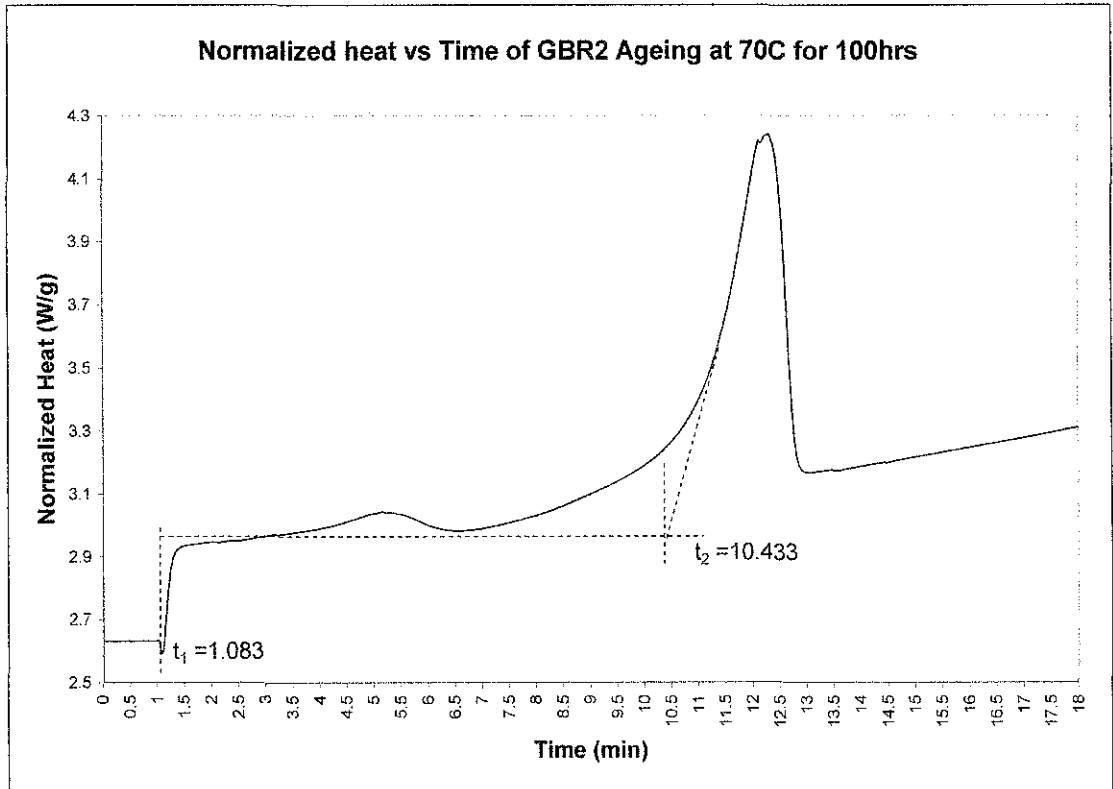


Figure 55: Determination of OIT for Ageing GBR2 samples at 70°C for 100hrs

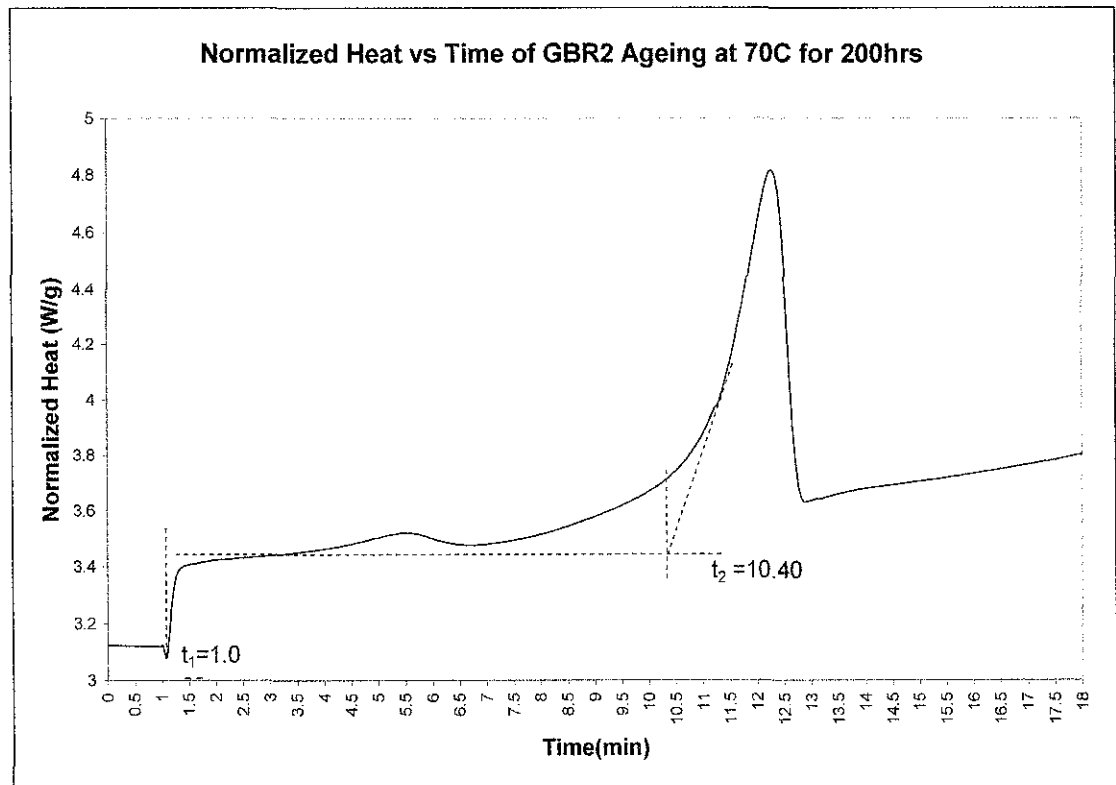


Figure 56: Determination of OIT for Ageing GBR2 samples at 70°C for 200hrs