Physical Ageing

In Semi-Crystalline

Polyethylene Terephthalate

A thesis submitted for the degree of MRes Science and Engineering of Materials

David Nicholls

The School of Metallurgy and Materials

The University of Birmingham

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Abstract

The polymer industry is growing at an extremely large rate and with the recycling of plastics and polymers from packaging and containers at an all time high, there is a greater need to understand the physical elements that affect the structure of these polymers.

There has been much previous work in the field of crystallisation, glass transition and polymer ageing. Many scientists have studied their findings on the work of L.C.E Struik who led the way in polymer science. However, there has been, as far as research shows, no work on Polyethylene Terephthalate (PET) and the effects ageing can have on this polymer.

Two sets of testing were performed, the first on a Thermo-mechanical Analyser (TMA) and the second on a Differential Scanning Calorimeter (DSC). The glass-transition temperatures and physical ageing effects were tested on the TMA, whilst on the DSC, only the physical ageing effects were tested.

During the ageing experiments 3 samples of varying crystallinity were created, one sample was completely amorphous (0% crystalline), the other samples were 28% crystalline and 65% crystalline.

The results showed that physical ageing can take place in PET. The definitive conclusion is that as the crystallinity increased the amount of ageing decreased. This shows that physical ageing primarily affects the amorphous regions of polymers; it is here that there is no organisation within the microstructure giving molecules larger areas of free volume to occupy.

Acknowledgements

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Contents

1 Introduction

1.1 Polymers

The principle characteristic of polymeric materials is that they consist of long-chain molecular structures, which are produced when many thousands of small monomer molecules join up to form macromolecules with repeated unit.

Polymers are used all around us in many different aspects of life. They are used in fundamental medical applications (Hip replacements and biomaterials) and more common applications (Sporting equipment, packaging). It is necessary to understand that whenever polymers are used, within any application, they will continually be affected be ageing which can affect their mechanical and overall performance.

1.2 Morphology

There are many techniques that have been used to study Polyethylene Terephthalate (PET) in the past, these include, Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) [1-4]. All the techniques for studying PET and other similar polymers take into account that semi crystalline polymers consist of a two-phase system. According to the two-phase model [4], it is assumed that any semi-crystalline polymer is composed of an amorphous part (W_a) and a crystalline part (W_c), as shown in equation 1.

$$\mathbf{W_a + W_c = 1} \qquad \mathbf{(1)}$$

During the last few years, there have been various independent studies in the literature, employing different experimental techniques such FT-IR spectroscopy, temperature modulated differential scanning Calorimetry (TMDSC) and X-ray diffraction (XRD) scattering techniques that have shown a three-phase model (*equation 2*) is more appropriate to describe the microstructure of PET [3, 4]. According to this model the previous relation is transformed to the following:

$$\mathbf{W_{MAF} + W_{RAF} + W_c = 1} \qquad \mathbf{(2)}$$

W_{MAF} relates to the 'mobile amorphous fraction', which, as the material cools from the melt through the crystallisation temperature is the proportion of the amorphous phase that remains completely amorphous.

W_{RAF} relates to the 'rigid amorphous fraction' which is believed to be associated with the interface between the crystalline and the mobile amorphous phases and has properties that are intermediate between them. In this W_{RAF} state the molecular mobility is restrained to a greater extent than in the "perfect" glass.

The three-phase model still shows the basis of an amorphous region and a crystalline region within the PET, so it is essential to understand these regions in more detail, and how they react together and independently during different tests.

1.2.1 The Amorphous State

Amorphous polymers (or the amorphous phase in polymers) have no order or regularity as there are no crystallites present. Due to a lack of crystallites, there is a distinct lack of structure meaning that the long-chain molecules are all intertwined and coiled within each other. Amorphous polymers can impose their mechanical properties by having more entanglements, it is also stated that properties scale with the number of repeat units within the polymer [5, 6].

As it is known, in the solid state all amorphous polymers are stiff and glassy, the macromolecular chains are randomly arranged in space and are entangled without any possibility of changing the conformations and consequently the morphology of the polymer [2]. The only movement that takes place in this state is the stretching, bending and rotating of macromolecular bonds. However, when an amorphous polymer (or an amorphous phase in a semi-crystalline polymer) is in the glassy state, it is out of thermo-dynamical equilibrium, and under constant environmental conditions (in particular a constant temperature and pressure) tends to approach equilibrium [7].

This (drive towards to equilibrium is known as 'physical ageing' or 'enthalpic relaxation'.

1.2.2 Crystallinity in Polymers

Semi-crystalline polymers get their name through being part crystalline and part amorphous. When a polymer is cooled from the liquid state it can result in the formation of crystals, called spherulites.

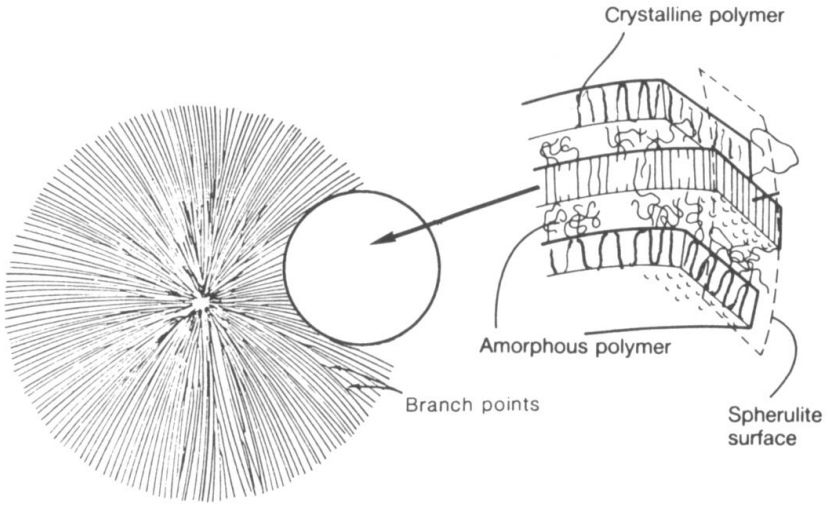

Figure 1 - Microstructure of Spherulite and close packing of lamella within a semi-crystalline polymer [5]

1.2.2.1 Spherulites

Spherulites form within a polymer during cooling from the liquid state. They can be induced with nucleating agents, but will naturally form in any polymer during the cooling process. The Spherulites grow outwards from a crystal nucleus allowing free space in between the individual branch points. This free space becomes occupied by the amorphous polymer, which produces a layered format. These layers are called Lamella.

The lamellae bring structure to the polymer and restrict the movement of the amorphous section; however, polymer chains can overlap from section to section to allow interaction between the amorphous and crystalline sections.

1.3 The Glass Transition

Polymers show certain properties at different temperatures. The glass-transition temperature (T_g) is a certain temperature where the polymer goes through a change of properties; it will go from glass properties (which are below the glass-transition temperature) to liquid properties (which are above the glass transition temperature). The actual value of the T_g depends on the cooling rate adopted during the cool from the liquid state as well as the heating rate adopted in the experiment [8].

On cooling (at constant pressure) from the equilibrium liquid, a transformation to a glass occurs when the molecular rearrangements, needed for the material to accommodate to the changing temperature, slow down to such an extent that they require a time-scale longer than that available by virtue of the imposed cooling rate [9, 10]. In effect, a structure, which may be characterised by T_g, is "frozen in", and will be retained as long as the same cooling rate continues.

When the polymer is below the T_g its molecular mobility is virtually zero, meaning that there is very limited motion which helps to lead to physical ageing. Whenever the polymer is above the T_g, its molecular mobility is relatively high.

When chains are coiled and entangled it makes co-operative motion along the chain difficult, this means that local motion becomes necessary for chains to move around each other, during this local (crankshaft) motion it is the repeat units that move. However, for this segmental mobility to take place there needs to be a certain amount of free space (a hole) in the system that the atoms can move into, this space is called free volume. Within polymers there is always a significant amount of free volume due to poor packing of chains in the system [3, 8, 11].

1.3.1 Free Volume

The concept of free volume originated from attempts to describe the variation of the viscosity (η) of liquids above T_g, and is the basis for just one of several empirical equations proposed. The temperature dependence, for example, was proposed by Vogel [1], Fulcher [12] and Tammann and Hesse [13] in the form often expressed as:

$$\ln \eta = \frac{A}{T - T_o}$$

(5)

Where A is a constant and T_0 is a temperature some distance below T_g. This is frequently referred to as the VTF equation.

An alternative empirical equation was later proposed by Doolittle describing the viscosity in terms of the free volume fraction, f:

$$\ln \eta = a + \frac{b}{f}$$

(6)

Where a and b are constants, b being rather close to unity. The fractional free volume is defined as:

$$f = \frac{v - v_o}{v} = \frac{v_f}{v}$$

(7)

Where the free volume, Vf, is the difference between the actual volume, V, and an "Occupied volume", V_0.

Upon cooling the free volume, Vf, and segmental mobility, M, decrease simultaneously [4]. Since free volume is made up of holes and molecules can attract one another, the existence of free volume represents an increase in internal energy (U) with respect to the zero free volume state. This free volume exists because it is accompanied with an increase in entropy, ΔS. It is known, that in fact, VF has precisely the value for which U balances TΔS. When the temperature is lowered it leads to a decrease in the importance of the term TΔS, and Vf and the mobility, M, will decrease simultaneously. This can be seen schematically in *figure 2*, where a straight line is drawn for Vf vs. T, and which shows a curve for mobility M of a slope that decreases with increasing temperature (and therefore with increasing Vf).

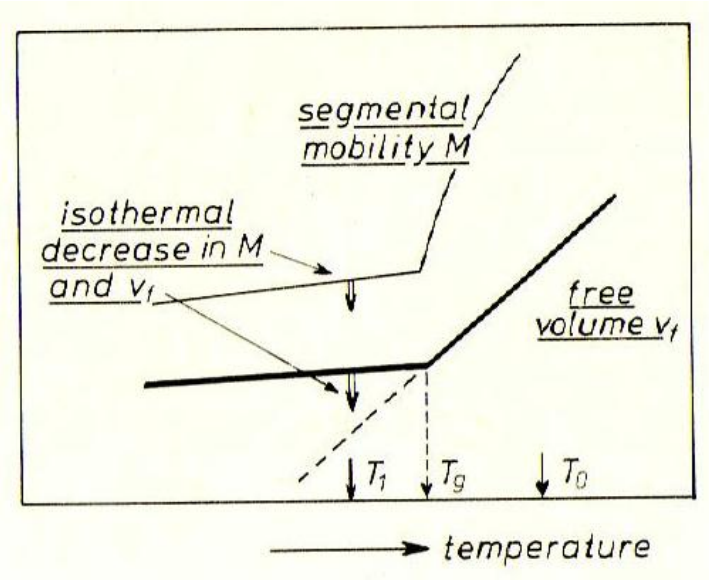

Figure 2 - The origin of ageing explained from the free-volume concept. [14]

The changes in the free volume are bought about by a rearrangement of the free space [15, 16]. The rate of this process is determined by the segmental mobility, M, so we have a closed-loop scheme: Vf determines M, while M determines the rate of dVf/dt at which vf changes (*Figure 2*) [4].

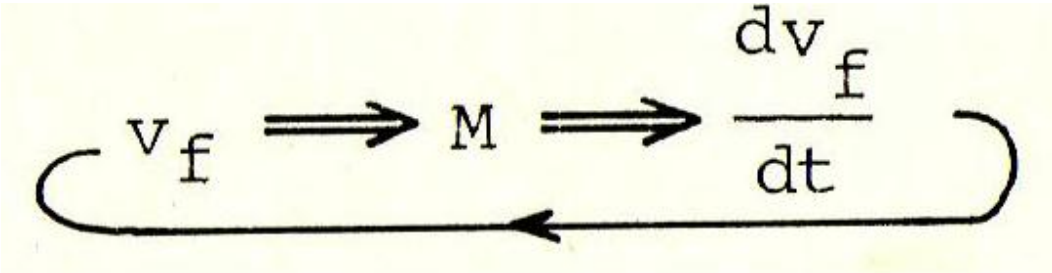

Figure 3 – Diagram of the closed-loop scheme between free volume and segmental mobility [14]

This closed-loop scheme (*figure3),* which implies that the volume-relaxation process is basically non-linear, is essential for an understanding of glass-transition and ageing. It shows that during cooling the free volume, vf, cannot decrease indefinitely, it also shows that below a certain temperature [11, 14], M becomes so small that Vf almost stops decreasing with temperature. The polymer will then pass through its glass transition. Upon further cooling Vf can only change slightly and slowly, likewise, M no longer changes rapidly with temperature, though it continues to decrease in thermal activation

(although segmental motion is primarily determined by free volume, it is also thermally activated) [17].

Another outcome of the closed-loop scheme is that below Tg the mobility cannot become zero. A decrease in M requires a decrease in Vf, and for this there must be some mobility [14]. Therefore, M cannot vanish in a finite time; the state of zero mobility can only be approached asymptotically.

Consequently when the polymer is cooled to a temperature T1 below its Tg, the mobility M, will be small, but not zero. Since at this stage Vf is greater than it would be at equilibrium, the volume will continue to push towards its natural equilibrium line and decrease slowly [18]. This contraction will be accompanied by a decrease in the mobility with concomitant changes in all those properties of the glassy polymer which depend on it.

1.3.2 Activation Energy

The activation energy refers to the amount of energy per amount of material (joule per mol) that is needed to be overcome for the glass transition to take place within a polymer. This activation energy will be different for all polymers, and is also dependant on the crystallisation and structure of the polymer. For the glass transition to BE distinguishable there should be a noticeable number of molecules with energy equal or greater than the activation energy [19].

1.4 Ageing in Polymers

Polymers can be affected by more than one type of ageing. They can undergo ageing from effects such as thermal degradation, photo-oxidation and physical ageing.

Thermal degradation is when molecular deterioration of materials such as resins and organic fibres occurs because of overheating. It occurs at a temperature at which some components of the material are separating or reacting with one another to modify the macro or microstructure.

Photo-oxidation is the induction of degradation through exposure of polymer surfaces to a combination of sun or artificial light, plus oxygen or other oxidising media. The consequences include embrittlement, discolouration, loss of gloss or transparency, changes in molecular weight (usually a decrease), and accumulation of oxidation reaction products such as peroxides and hydro peroxides.

Physical ageing is a gradual continuation of the glass formation that sets in around the Glass Transition temperature (Tg). Therefore it affects all those temperature-dependant properties which change drastically and abruptly at Tg. During aging these properties change in the same direction as during cooling through the Tg range; the materials become stiffer and brittle, its damping decreases, as do its creep and stress-relaxation rates [14]. However, the effects of physical ageing are reversible.

It is the latter of these types of ageing (Physical ageing) that is relevant to this thesis.

1.5 Physical Ageing in Polymers

Physical ageing is a general phenomenon that is a basic feature of the glassy state. It should be found in all glasses, irrespective of their chemical nature and of their being polymeric of monomeric [14]. This has been confirmed in present work, there have been very similar ageing effects in amorphous glassy polymers [2, 14]. Physical ageing results in structural changes that increase both the density and the brittleness of the material and change the electrical properties [2], along with this, the polymers enthalpy, entropy, volume and other physical properties change continuously [3].

As physical ageing is a continuation of the glass formation, it is necessary to understand through the literature how the glass-transition temperature can be affected and how this, in turn, can affect the physical ageing of a polymer.

Most physical ageing and glass transition experiments have been performed using a Differential Scanning Calorimeter (DSC) or a Thermo-Mechanical Analyser (TMA). The DSC is a more popular piece of equipment to use for experimenting on polymers as it can easily distinguish and show such things as phase transitions where these are endothermic or exothermic. DSC can also detect subtle phase changes such as the

glass transition, it is for this reason that DSC is widely used in industrial settings as a quality control instrument – it has the applicability in evaluating sample purity and studying polymer curing.

Alves et al. [3] found that when using the DSC to trace a fully amorphous PET through its T_g, that it's thermogram *(figure 5)* produced what was expected for an amorphous polymer with a relatively narrow glass transition temperature interval. This agrees fully with the work off Karagiannidis et al. [4, 20] which showed a trace of an amorphous PET with a narrow T_g area and the same T_g region interval between 60-80 Celsius.

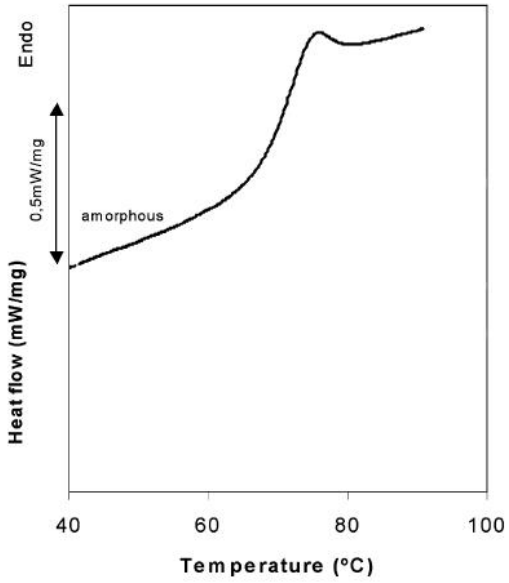

Figure 5 - DSC Trace of amorphous PET [21]

However, the only difference in the work is that Karagiannidis et al. state that they could quench the PET quick enough to only have a very few crystals present, meaning that their amorphous PET was found to have a crystallinity ratio of 0.4% [20], where as Alves et al. could only quench the PET from heating at a slow rate and therefore produced a crystallinity of 19% [22]. Although there is rather large difference between the two degrees of crystallinity the DSC traces are very similar between the two pieces of work. These traces and results also agree with the work of Hay [1] (*figure 6*) which states that the low temperature transition, observed as a step change in specific heat, is a transition from glass to liquid – the glass transition (T_g).

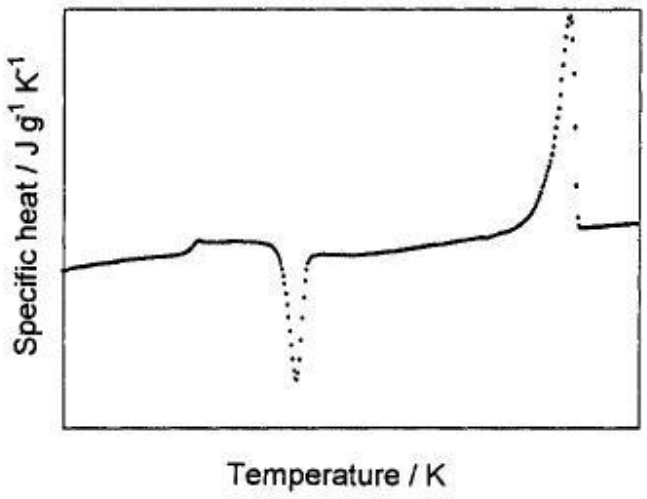

Figure 6 - DSC curve of amorphous crystallisable polymer [22]

As well as comparing results from amorphous PET, it is also necessary to compare the results of crystallised PET so that it is easier to understand the full aspects of PET and how the results vary with different levels of crystallinity.

Alves et al. [21] worked not only with amorphous PET, but also did tests on PET that was crystallised at temperatures of 131, 133, 135 and 163 °C. It is clear that the degree of crystallinity within PET makes a great difference to the DSC traces (*figure 7*) and therefore will make a vast difference to the physical ageing and structural relaxation of the different samples of PET. It is clear from the traces that the glass transition temperature of the samples crystallised at 135 or 163 °C, which are the samples with the highest crystallinity, are both very different from that of the amorphous PET. Where as the sample that was crystallised at 131 °C has the lowest crystallinity and gives a similar trace to that of the amorphous PET.

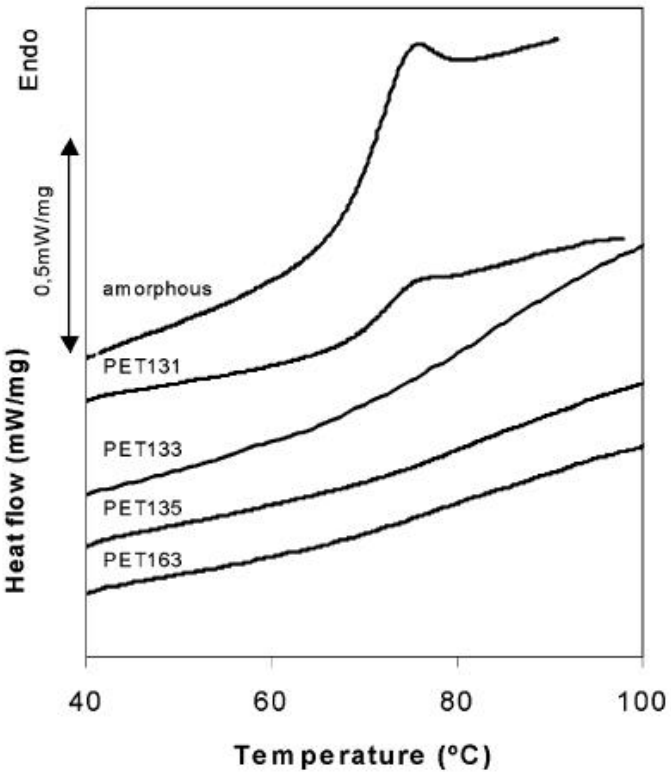

Figure 7 - Thermo grams obtained on heating scans on samples of PET [21]

These traces show and agree with the work of Hay [1], Jenkins [7], Struik [14] and Karagiannidis [20] which is mentioned before that the more crystallised a polymer is the less rotational movement of molecules takes place, giving a decrease in the heat flow.

Alves et al. found that the equilibrium relaxation times in the semi-crystalline polymers are longer than in amorphous PET for a temperature, or equivalently, that the whole relaxation process is shifted towards higher temperatures in the semi-crystalline PET with respect to the fully amorphous sample. This work from Alves et al. was in agreement with work performed by Hay, which states that the morphology, in the particular the size of the lamellar crystals, primarily determines the value of the T_g and so the enthalpic relaxation characteristics.

Hutchinson [23] mentions how it is common practice to quench the sample from just below the T_g to a lower temperature and to start a DSC scan from there, this is in order to overcome some problems of thermal inertia; this procedure is valid as no enthalpy

changes occur during the short period of time that the sample spends below T_a (Ageing Temperature). Given sufficient aging time at T_a, the enthalpy relaxation will process to equilibrium, where the enthalpy is H_∞ [11, 23]. This agrees with the practical work of Struik [14], who states that his samples that were tested were first annealed – to remove any internal stresses generated by original compression mouldings or extrusions – then heated to a certain temperature above the T_g and then were quenched to a temperature just below the T_g and then kept at this temperature.

The extensive work of Struik [11, 14, 24-28] on a very wide range of polymeric and other materials shows a remarkable universality in respect of physical ageing behaviour. The most commonly adopted explanation is in terms of changes in free volume. In the simplest situation, following a quench from above to below T_g, the reduction in molecular mobility as the free volume reduces implies a lengthening of the viscoelastic timescale. This leads to stress relaxation which seems to work rather well in the linear viscoelastic region, even though vertical shifting is occasionally necessary, and suggest that the free volume hypothesis is largely correct.

There have been complications that have arisen when the ageing studies are extended to semi-crystalline polymers. Struik [14] developed a rather detailed explanation of the behaviour of semi-crystalline polymers in terms of an extended glass transition, resulting from the amorphous phase existing in two states, W_{MAF} and W_{RAF} (as mentioned previously [4]). This can explain why semi-crystalline polymers can age above there supposed glass transition.

The physical aging of polymers can be reviewed in three broad areas: the changes in bulk thermodynamic properties, namely volume and enthalpy; various micro-structural evidence for structural changes; and changes in mechanical properties. It is concluded that there is a remarkably good correlation between these aspects, and that they may broadly be linked through the concepts of free volume and free volume distribution [4, 8, 11, 14, 20, 23, 25, 29-32]. However, there remain a number of controversial areas where disagreement may arise for a number of reasons. Since these areas frequently include those situations which are of practical or engineering relevance, such as the application of high stresses or the use of semi-crystalline polymers, there is a clear need for these problems to be resolved.

1.6 Polyethylene Terephthalate (PET)

Polyethylene Terephthalate is a relatively hard, stiff, strong and dimensionally stable material that absorbs very little water $(0.16\ 1/\mathrm{cm})$. It has a good gas barrier property and also has a good chemical resistance, except to alkalis (which hydrolyse it). The level of crystallinity can vary from amorphous to high crystallinity. It can become highly transparent and colourless when amorphous, however the thicker, more crystalline sections, will be an off-white or opaque colour.

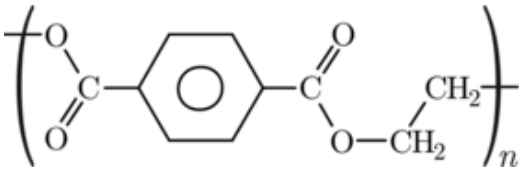

Figure 4 - Chemical Structure of PET [33]

PET is a polymer produced from the monomers ethylene glycol, a di-alcohol, and dimethyl terephthalate, a diester [33] . By the process of transesterification, these monomers form ester linkages between them, yielding a polyester, during this process methanol is also produced, but this is evaporated to drive the reaction forward.

1.7 Scope of the work

The primary objective of the project is to study the effects of physical ageing within Polyethylene Terephthalate and to see how this ageing varies with an increase in crystallinity of the polymer. This will allow a greater understanding of how ageing affects semi-crystalline and amorphous polymers.

The work will also cover other aspects of polymer transitions and will show the effects of different heating and cooling rates on Polyethylene Terephthalate; this will give a much better guide to the aspects of glass transition.

2 Materials and Methods

2.1 Material

Samples of PET were supplied by Goodfellow Cambridge Ltd. The samples that were supplied were PET grade ES303050 in the form of a sheet dimensions 10cm x 10cm and also as PET grade ES306310 in the form of granules.

Both PET samples were received as semi-crystalline polymers.

2.2 Differential Scanning Calorimetry

A Perkin Elmer DSC2B interfaced with a PC was used to measure the variation of relative heat flow with temperature for PET. The DSC unit consisted of separate sample and reference cells enclosed by platinum lids.

Both cells had separate heaters and platinum resistance temperature sensors. The heaters were coupled such that the differential power required to maintain both cells at the same temperature in a thermal scan could be measured. Samples in the form of discs (1mm thick and 3mm diameter) were contained in aluminium pans and an empty pan was used as a reference.

The temperature scale of the calorimeter was calibrated using the melting point of 100% Indium.

2.2.1 Production of an Amorphous PET sample

It was essential to produce amorphous PET to allow the creation of samples with a known thermal history and defined crystallinity.

The samples of PET were heated from room temperature (23 ^{o}C) to a temperature above the known melting point of PET (290 ^{o}C). To be sure of a molten state, the experiment was performed with an open pan and the head of the DSC equipment removed. Once

the sample had visibly become molten it was removed from the DSC with tweezers and immediately placed into liquid nitrogen.

Placing the sample in liquid nitrogen allowed it to be immediately quenched to below the Tg thus preventing crystallisation. The speed at which the liquid nitrogen cooled the sample did not allow the formation of spherulites and therefore produced an amorphous sample.

2.2.2 Production of a Semi-Crystalline PET sample

Two semi-crystalline samples were created to explore the affect of morphology on the ageing process. The procedure to make the sample was as follows.

An amorphous sample was heated through its glass-transition temperature and held at the crystallisation temperature of 95^{o}C for 120 minutes, this allowed the sample to become full crystallised. After the holding time, the sample was cooled back to room temperature at a rate of 10^{o}C/minute.

A second sample was heated to above the melting point (290^{o}C) at a rate of 10^{o}C /minute and was then cooled to the crystallisation temperature (210^{o}C). It was held at this temperature for 120 minutes to allow sufficient time for complete crystallisation and then cooled to room temperature at a rate of 10^{o}C/minute. This method was necessary to avoid ageing whilst the sample was crystallised at such a high temperature.

2.2.3 Measurement of Glass-Transition Temperature of PET by Differential Scanning Calorimetry (DSC)

As the crystallinity of a polymer affects its glass-transition temperature, it was a necessity to obtain this transition temperature before any physical ageing experiments could take place. Once the glass transition temperature was determined an ageing temperature, ΔT, could be specified. Where $\Delta T = Tg - Ta$.

Tg was determined using a fixed heating rate of 10 ^{o}C/minute. Samples were heated from room temperature to 100 ^{o}C and the Tg was measured using the method discussed

by Richardson [34]. It was necessary to determine the value of Tg as comparing the extent of ageing at a fixed ageing temperature is unreliable as any variation in Tg caused by the presence of crystalline regions will confound the comparison. Therefore the samples were aged at identical values of ΔT. To specify the ΔT, the Tg of each sample was measured.

2.2.4 Physical Ageing in PET

After establishing the glass transition temperature of the samples the appropriate ageing temperatures (ΔT) could be determined. On each sample, this was decided to be a ΔT of 10 (10^{o}C below the Tg). For the experimentation to be valid, it was essential that each sample was aged at a ΔT of 10 in respective to the glass transition temperature.

The samples were aged in a vacuum oven for 72 hours at their respective ageing temperatures; the ageing time was restricted to 72 hours as a full kinetic analysis was outside the scope of the project and would have taken longer to complete than the 12 months permitted. Once the 72 hours ageing was complete the sample was removed from the oven and placed in one of the aluminium pans of the DSC machine.

Once in the aluminium pan, a simple heating test was performed on the sample. The sample was heated from room temperature (23 ^{o}C) to 180 ^{o}C at 10 ^{o}C/minute. This temperature range allows the sample to pass through its glass transition step change and simultaneously show the effects of the physical ageing. The sample was then cooled back to room temperature before a reheat over the same temperature range. The reheat was necessary to produce a baseline to measure the peak area developed during ageing.

2.3 Thermo Mechanical Analysis

A TA Instruments Thermo-mechanical analysis (TMA), figure 8, was used to perform the experimental procedures. The TMA was interfaced with a PC.

The Thermo-mechanical analysis was used to measure the dimensional changes, of PET with changes in temperature.

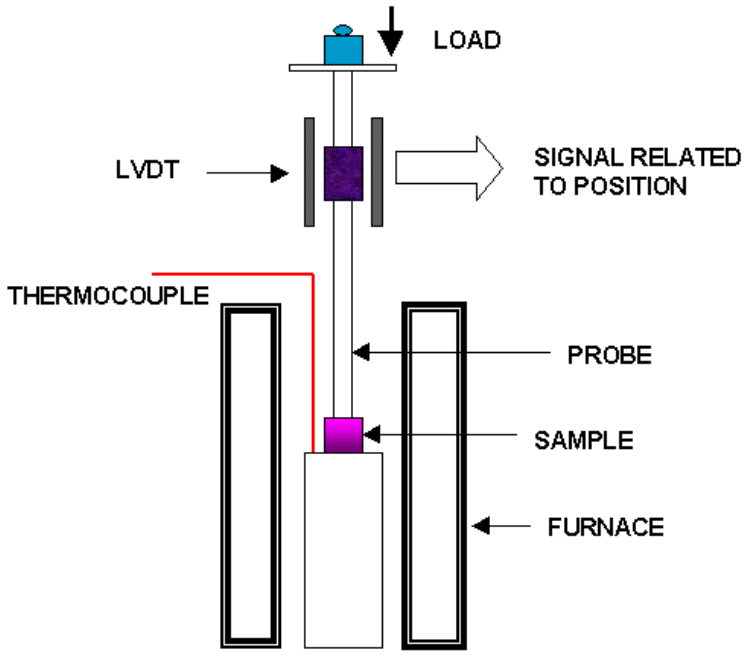

Figure 8 – TA instruments TMA

A sample was placed on a support within the furnace. A constant load of 10mN was supplied to the sample by the probe that measures the changes in length. This change in length is distinguished by a linear variable displacement transducer (LVDT). A thermocouple that is located underneath the sample indicates the temperature. The probe and support are made from a materials such as glass quartz (vitreous silica), which has a low reproducible, an accurately known coefficient of thermal expansion and also has low conductivity. This helps to isolate the sensitive transducer from the changes in temperature in the furnace.

2.3.1 Sample Preparation

The PET was cut into cubic samples of 6mm sides. Once the samples were the correct size the edges were smoothed using wet/dry paper to allow the sample to be in full contact with the support.

2.3.2 Measurement of the Glass Transition of PET

The glass transition of a polymer can be affected by a change in heating and cooling rates. The TMA is able to show these movements in the glass transition temperature with the changing variables.

The samples were heated at increasing rates from room temperature to 120^{o}C, and were cooled at a constant rate of 10^{o}C/minute. The resultant graphs were plotted and the glass transition temperatures were identified.

A similar experiment was used to test for the effects of cooling rates on the Tg. However in this series of tests, the samples were heated at a constant rate of 10^{o}C/minute and cooled at increasing rates. The resultant graphs were plotted and the glass transition temperatures were identified.

2.3.3 TMA Physical Ageing of PET

Firstly, a Tg was established, this was 73^{o}C. With a definitive Tg it was a necessity to decide on ageing temperatures that were to be used below this temperature. It was decided that the temperatures for ageing were 58^{o}C, 61^{o}C, and 63^{o}C – respective ΔT of 15, 12 and 10 respectively.

The samples were heated through their Tg to 120^{o}C at a rate of 5^{o}C/minute, after being held for 1 minute at 120^{o}C the sample was cooled to its respective ageing temperature at 5^{o}C/minute and held there for 1000 minutes. Once the ageing was complete, it was cooled back to room temperature at the same rate of 5^{o}C/minute.

3 Results and Discussion

3.1 Thermo-mechanical Analysis (TMA) of the Glass-transition temperatures of Semi-crystalline Polyethylene Terephthalate (PET)

A Differential Scanning Calorimetry test was first run on the “received” PET.

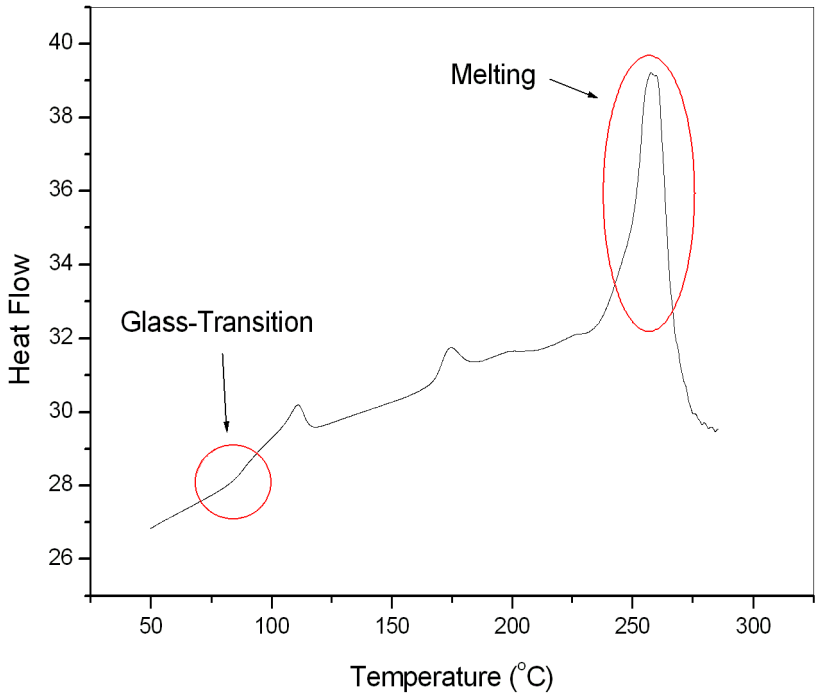

Figure 9a – DSC trace of the “as received” PET from Goodfellow.

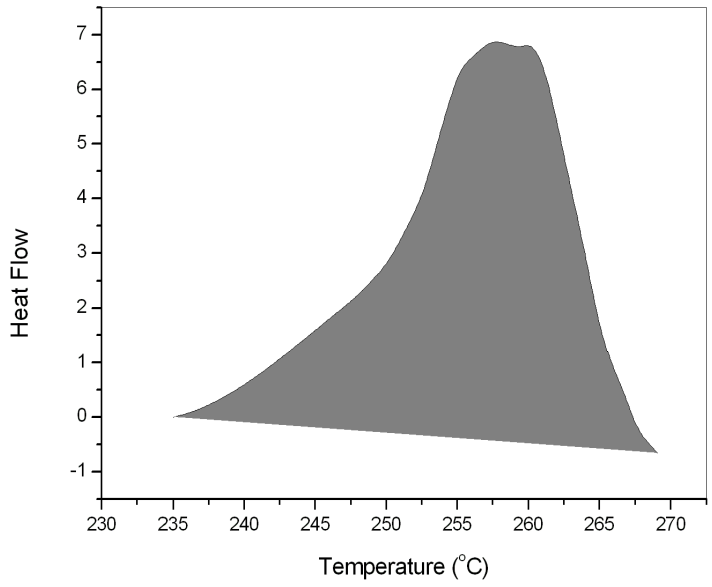

Figure 9b – The melting peak of the DSC trace allows to calculate the degree of crystallinity within the PET.

The heat of fusion, ΔH1, was found to be 87.3 J/g.

The corresponding value, ΔH1, for 100% crystalline PET is 239 J/g

Therefore:

Therefore:

$$\text{Degree of Crystallinity} = (\Delta H1/\Delta H) \times 100$$

$$\text{Degree of Crystallinity} = (87.3/239) \times 100$$

$$\text{Degree of Crystallinity} = 40.5\%$$

3.1.1 Effect of Heating Rate

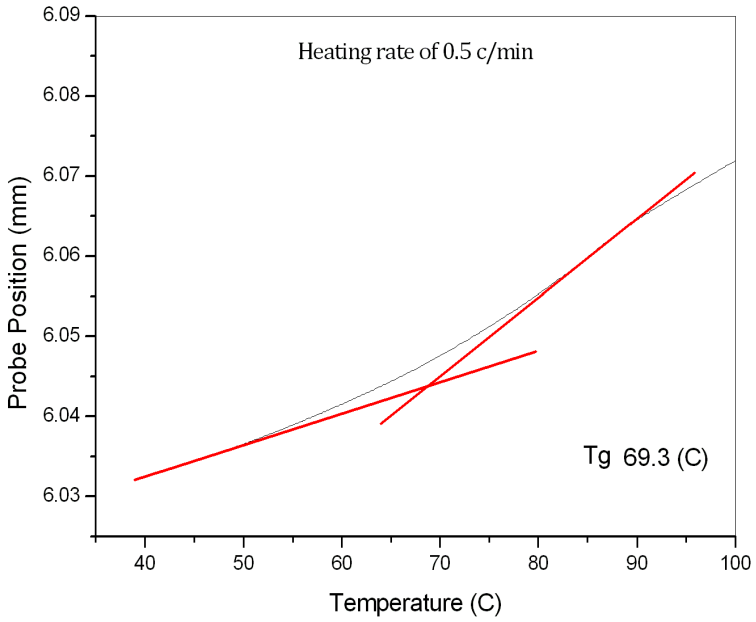

Figure 10 - The glass-transition temperature after a heating rate of 0.5°c / minute was found to be 69.3°c

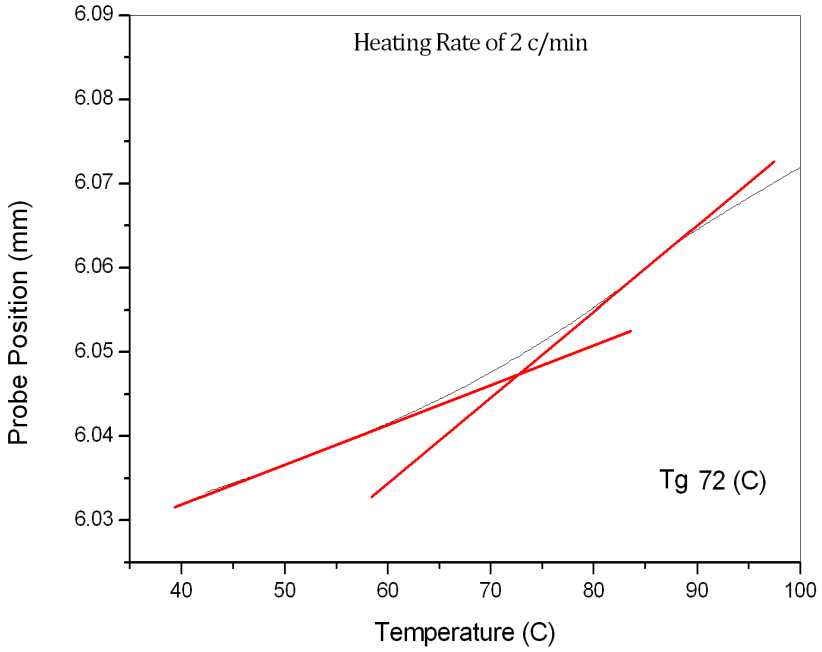

Figure 11 - The glass-transition temperature after a heating rate of 2°c / minute was found to be 72°c

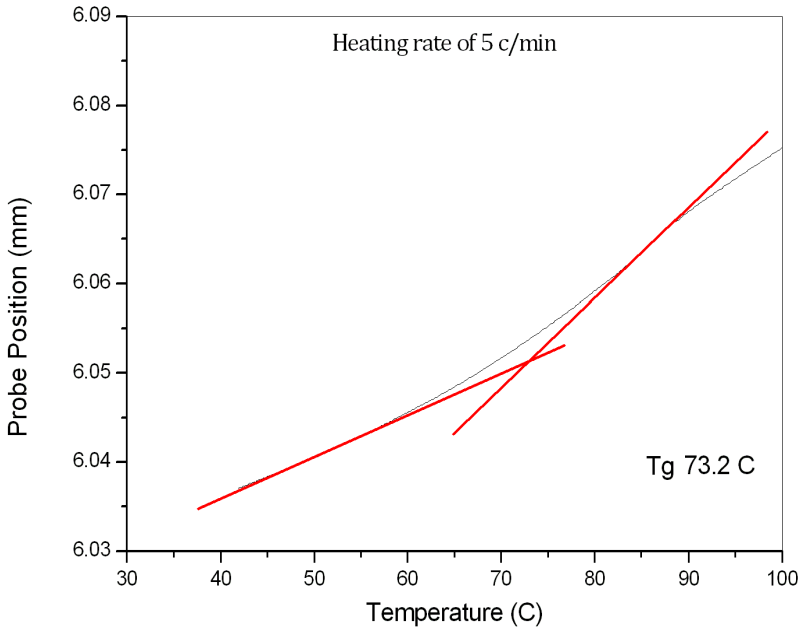

Figure 12 - The glass-transition temperature after a heating rate of 5°c / minute was found to be 73.2°c

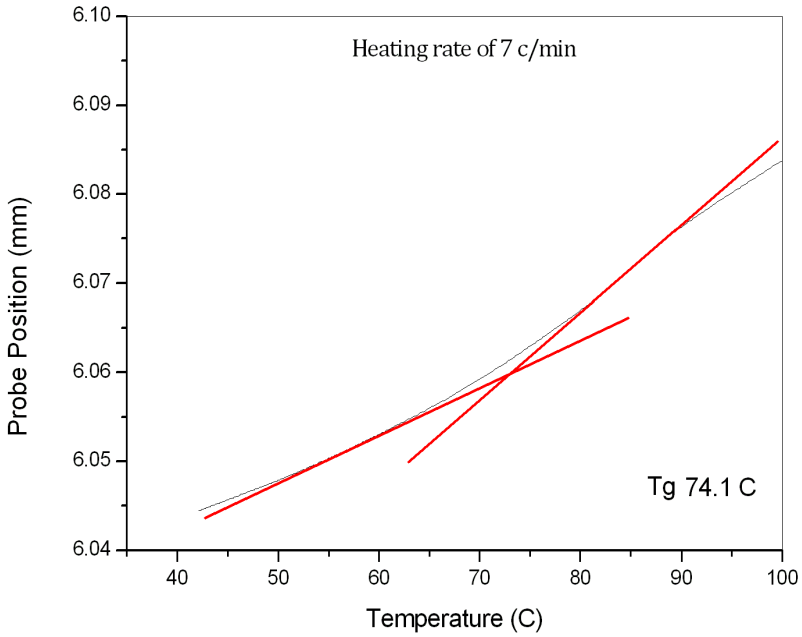

Figure 13 - The glass-transition temperature after a heating rate of 7°c / minute was found to be 74.1°c

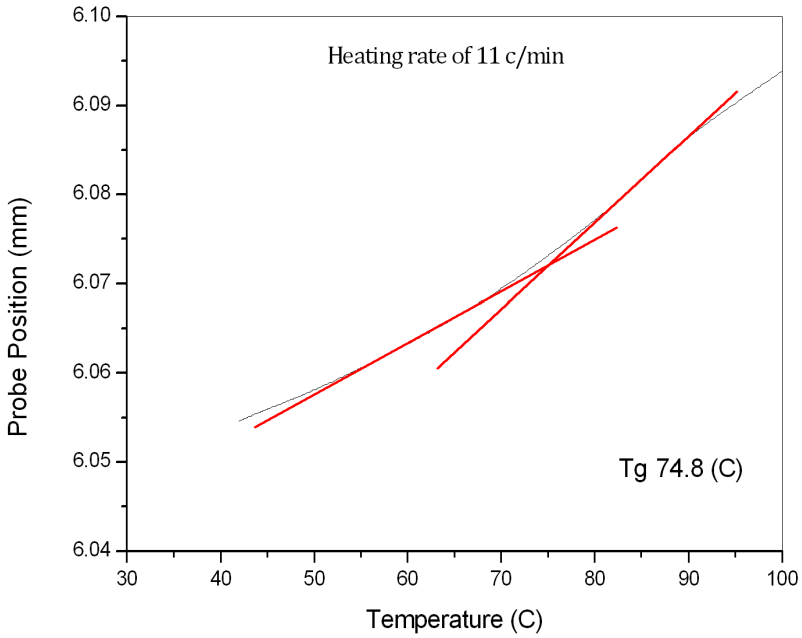

Figure 14 - The glass-transition temperature after a heating rate of 11°c / minute was found to be 74.8°c

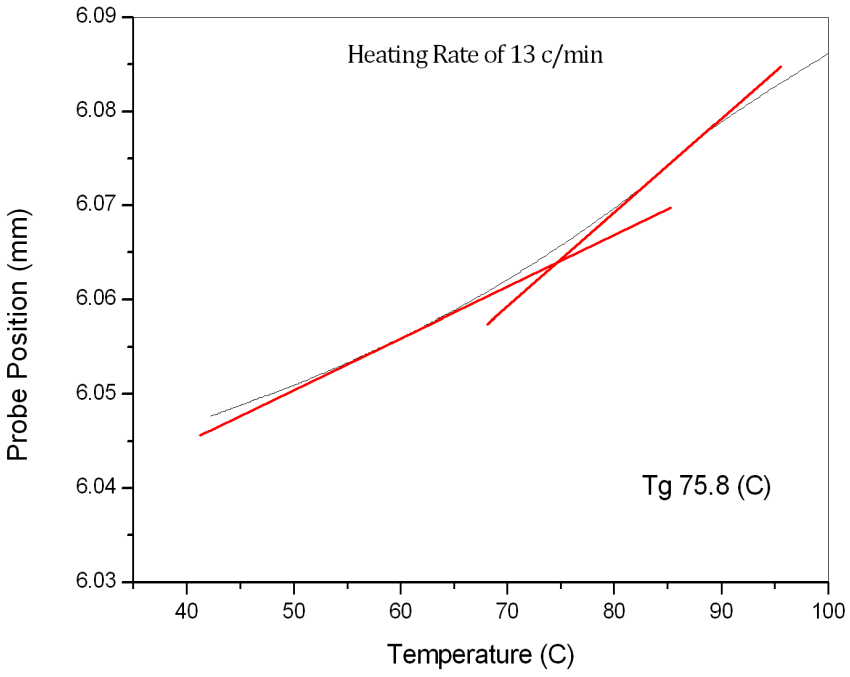

Figure 15 - The glass-transition temperature after a heating rate of 13°c / minute was found to be 75.8°c

3.1.2 Discussion

Figure 16 shows that when the PET is heated at a faster rate the resultant Tg is at a higher temperature. This is mainly due to an aspect of the heating regime called 'Thermal lag'.

Thermal lag is when there is a subsequent difference between the temperature of the sample and the actual temperature of the thermometer within in the thermo-mechanical analyser. Due to the nature and properties of polymers (high heat capacity and low conductivity), thermal lag can have an effect on the readings of the glass-transition temperatures.

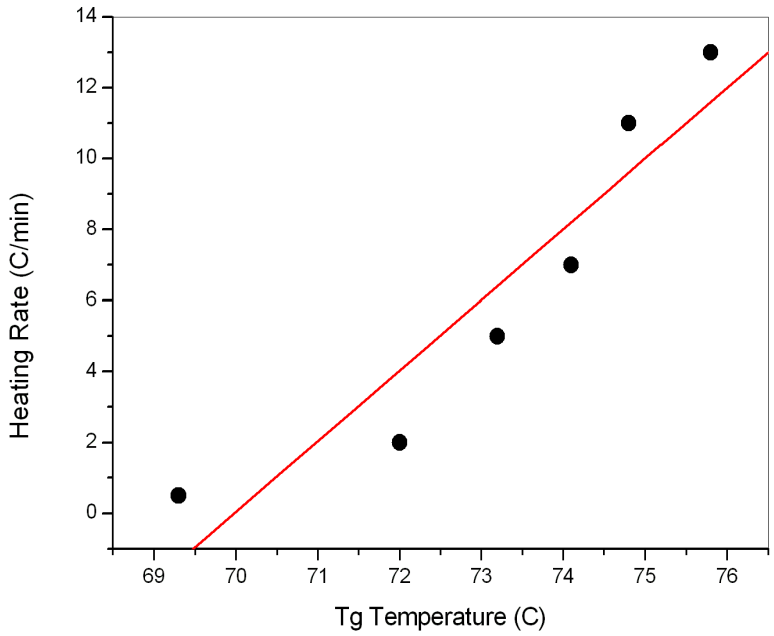

Figure 16 - Graph to show change in Tg with varying heating rates

As the heating temperature is increased, there is more thermal lag between the sample and the actual temperature that is being transmitted to it. Therefore a slower heating rate will give a more accurate Tg reading as the whole sample has a chance to heat to a

uniform temperature, whilst the faster heating rates will not actually give the sample enough time to be uniform in its temperature.

As the crystallinity of the samples were constant and the only primary reason for the shift in the glass transition temperature is due to thermal lag.

3.2 Effect of Cooling Rate

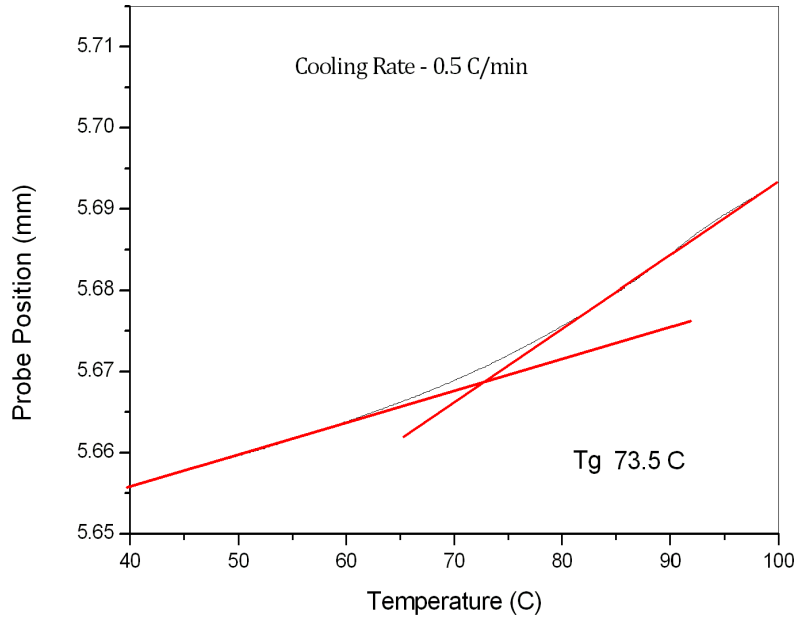

Figure 17 - The glass-transition temperature after a cooling rate of 0.5°c / minute was found to be 73.5°c

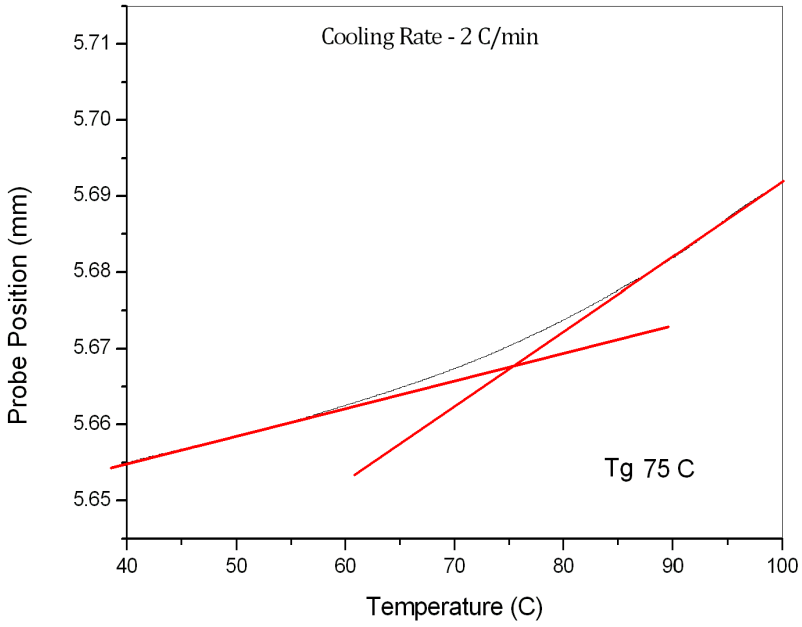

Figure 18 - The glass-transition temperature after a cooling rate of 2°c / minute was found to be 75°c

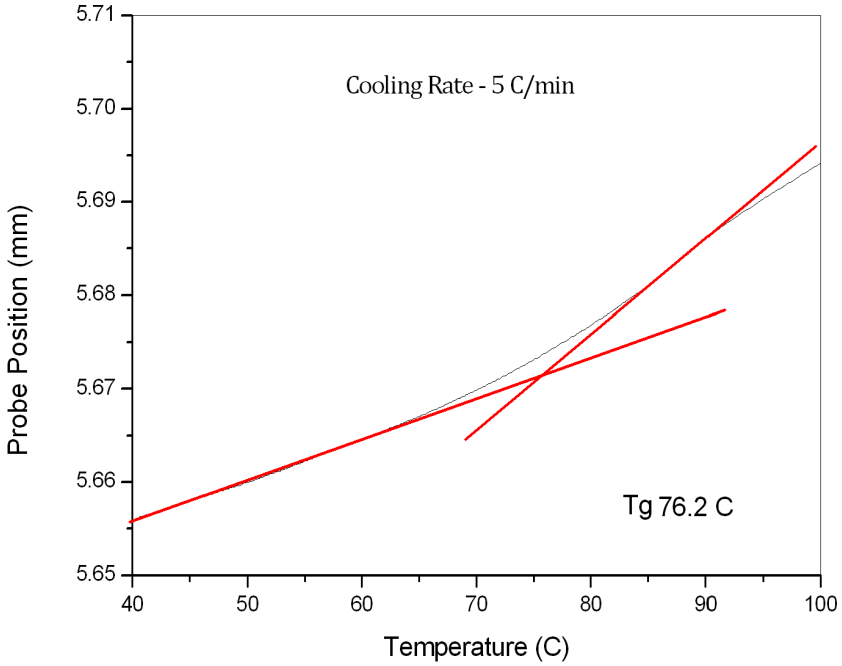

Figure 19 - The glass-transition temperature after a cooling rate of 5°c / minute was found to be 76.2°c

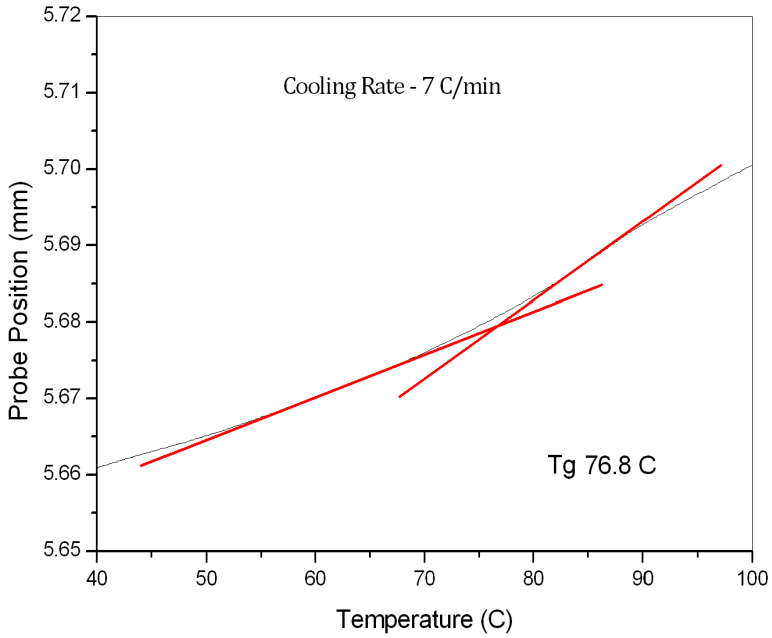

Figure 20 - The glass-transition temperature after a cooling rate of 7°c / minute was found to be 76.8°c

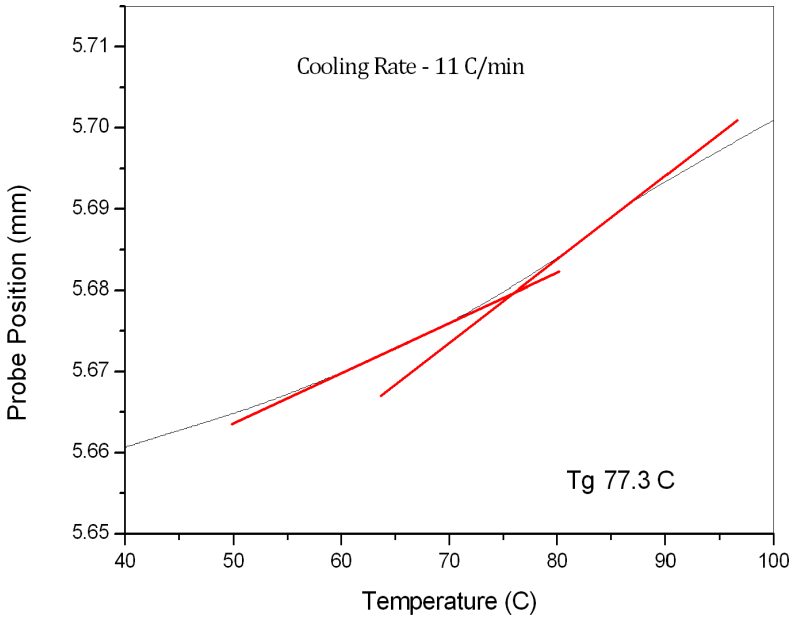

Figure 21 - The glass-transition temperature after a cooling rate of 11°c / minute was found to be 77.3°c

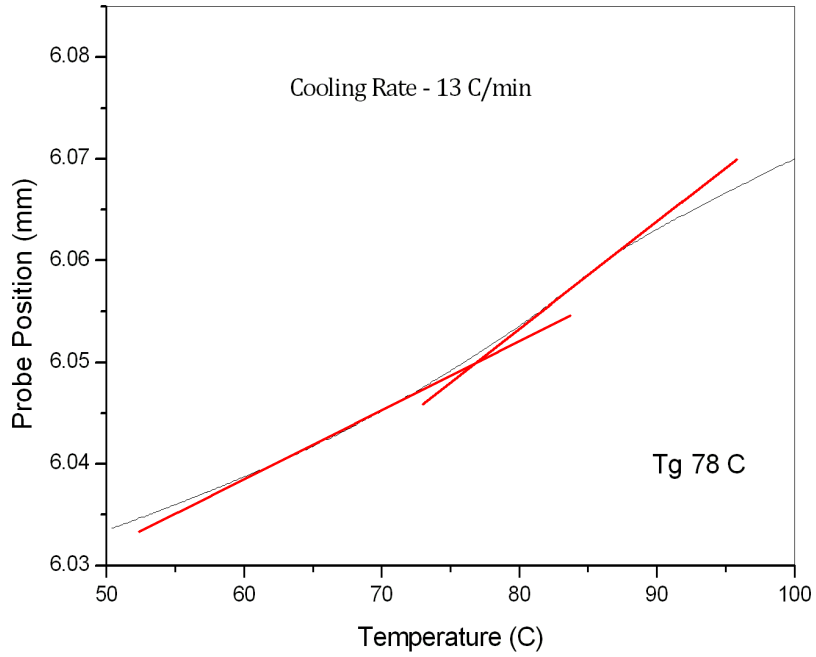

Figure 22 - The glass-transition temperature after a cooling rate of 13°c / minute was found to be 78°c

3.2.1 Discussion

Figure 23 clearly shows that the cooling rate has an impact on the glass transition temperature of PET. As the cooling rate increases the chance for the amorphous phase in the semi-crystalline polymer to become organised decreases and therefore the Tg increases due to more entanglements between the long chain molecular structures.

During this experiment the PET is not put through its 'melting temperature' which therefore means the crystallinity of the polymer will be constant. This means that during these experiments the cooling rate affects how much structure and order there is, rather than the level of crystallinity, of the polymer. A faster cooling rate will not allow the amorphous sections to be trapped closely between the lamella, and so will be 'frozen' in place with many entanglements in between the crystalline sections of PET.

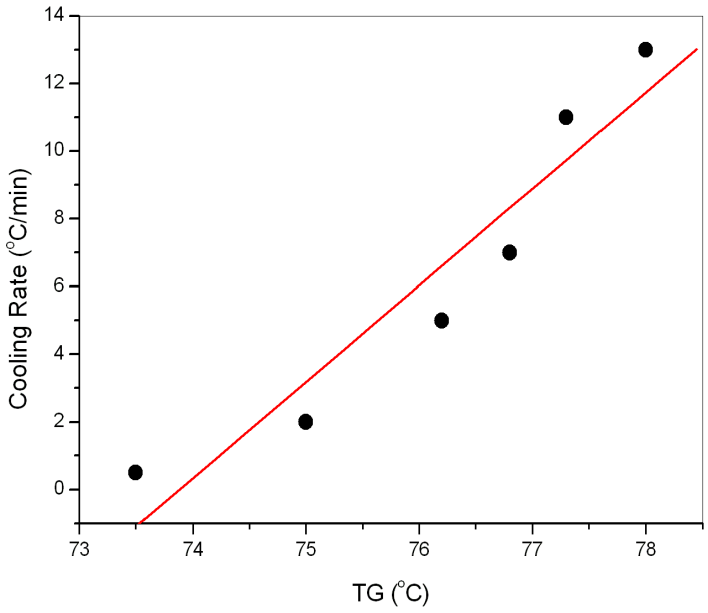

Figure 23 - Graph to show the change in Tg with cooling rate

Using the analysis of the change in Tg with varying cooling rates give the ability to calculate the activation energy of the semi–crystalline PET.

3.2.2 Calculation of the Activation Energy

Figure 15 shows the variation of the glass transition temperatures with the increasing cooling rates, this information can be used to determine the activation energy for the glass-transition process.

The Activation Energy (Ea), of a polymer is the minimum amount of required energy to allow the polymer to change from a glass to a liquid state.

Table 1 shows the information needed to calculate the activation energy for the glass-transition temperature within the semi-crystalline PET.

Cooling Rate (C/min)	Tg (C)
0.5	73.5
2	73.9
5	75.4
7	75.9
11	77.1
13	77.5

Cooling Rate (K/sec)	Tg (K)
304.15	347.65
394.15	348.05
574.15	349.55
694.15	350.05
934.15	351.25
1054.15	351.65

Ln Cooling Rate (Ln K/sec)	1/Tg (1/K)
5.717521	0.0028765
5.976732	0.0028732
6.352891	0.0028608
6.542688	0.0028567
6.839637	0.002847
6.96049	0.0028437

Table 1 – Table showing changes in Tg with change of cooling rates

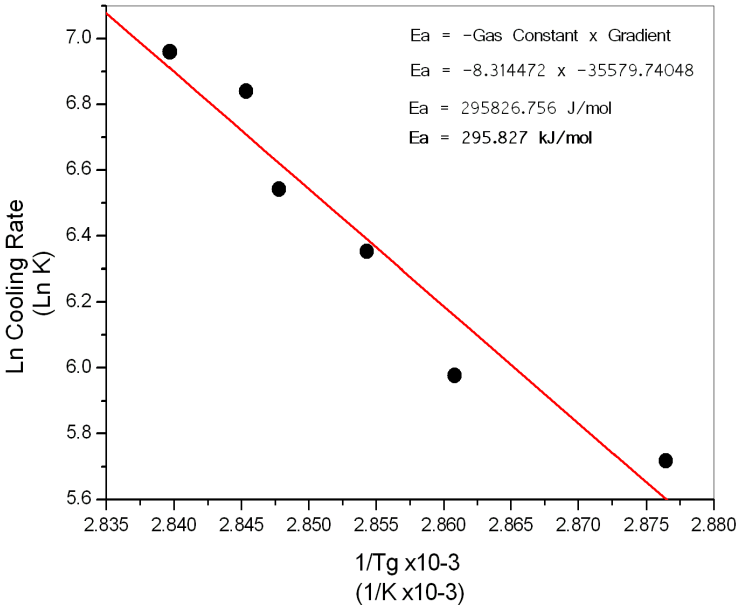

Figure 24 - The Activation Energy of semi-crystalline PET

The activation energy can be found using the equation:

$$E_a = -RT \ln\left(\frac{k}{A}\right) \qquad \textbf{(2)}$$

This equation can be more simply written as:

Energy Activation / Gas Constant = Gradient **(3)**

Therefore the activation energy becomes:

Activation Energy = - 8.314472 x -35579.74048

Activation Energy = 295826.756 J/mol

Activation Energy = 295.827 kJ/mol

3.3 Thermo-mechanical Analysis (TMA) of Physical Ageing within Semi-crystalline Polyethylene Terephthalate (PET)

The first test was performed at a ΔT of 15, which gave an ageing temperature of 58°c.

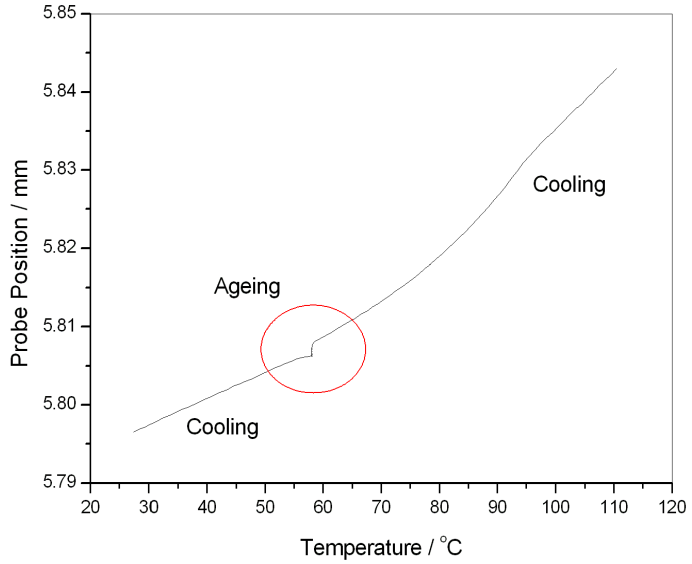

Figure 25a - The effects of physical ageing when the sample is held at a temperature of 58°c for 1000 minutes

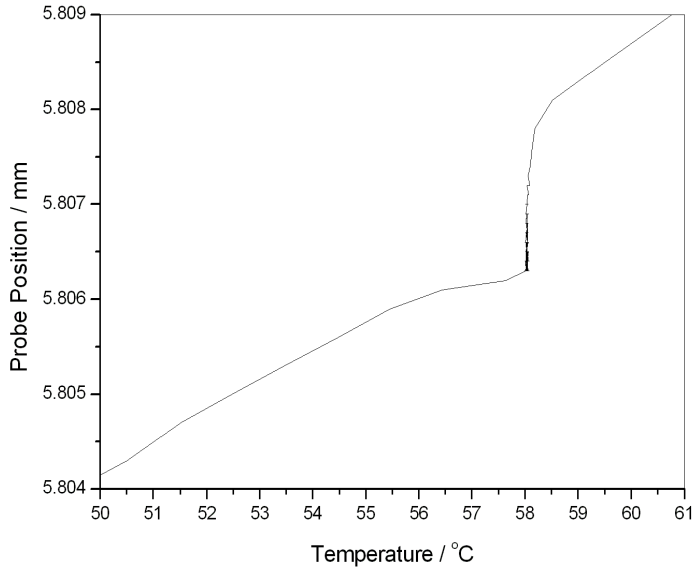

Figure 25b – Focusing on the physical ageing process, the sample is tending towards natural equilibrium.

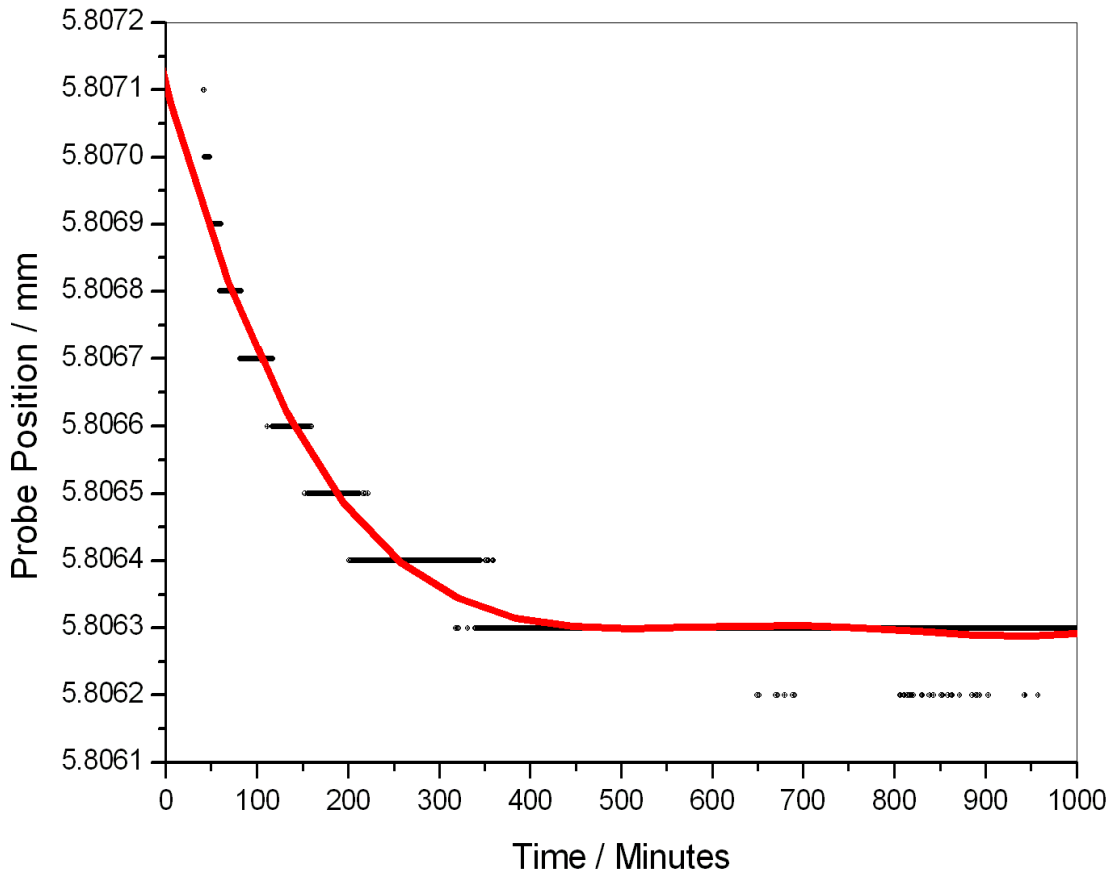

Figure 25c –The ageing effects against time when the sample is held at 58°c. The solid line is a 4th order polynomial to help guide the eye and to represent the overall data. The fluctuations and stepping of the results is due to a lack of resolution in the equipment.

The second test was performed at a ΔT of 12, which gave an ageing temperature of 61°c.

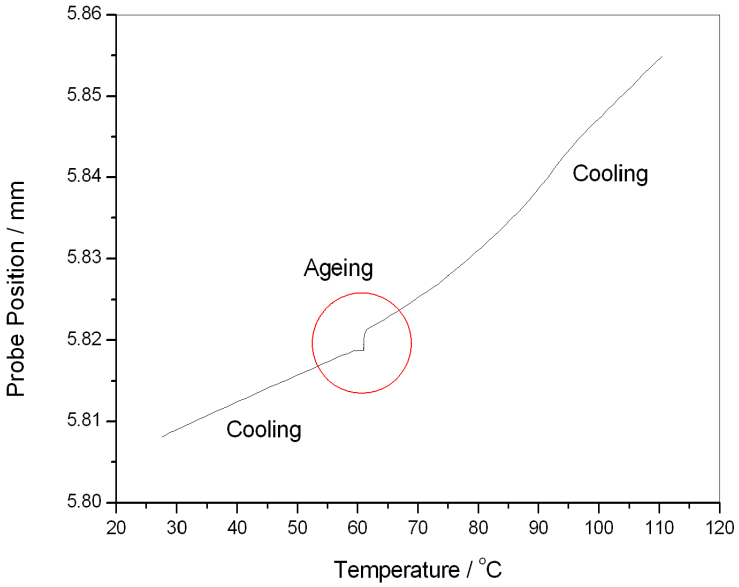

Figure 26a - The effects of physical ageing when the sample is held at a temperature of 61°c for 1000 minutes

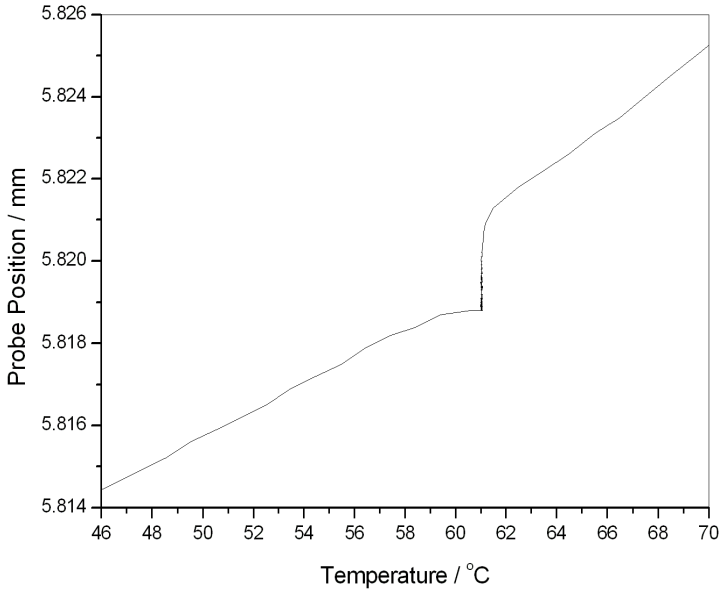

Figure 26b – Focusing on the physical ageing process, the sample is tending towards natural equilibrium.

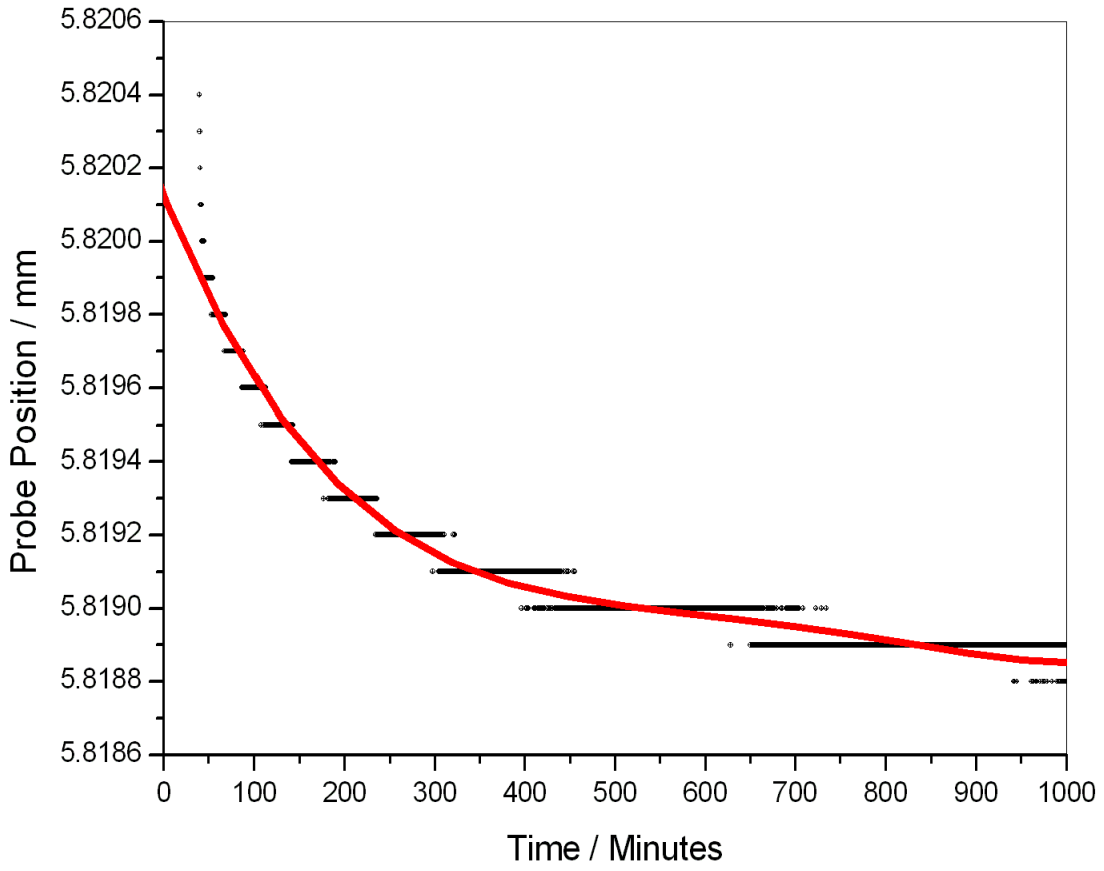

Figure 26c –The ageing effects against time when the sample is held at 61°c. The solid line is a 4th order polynomial to help guide the eye and to represent the overall data. The fluctuations and stepping of the results is due to a lack of resolution in the equipment.

The third test was performed at a ΔT of 10, which gave an ageing temperature of 63°c.

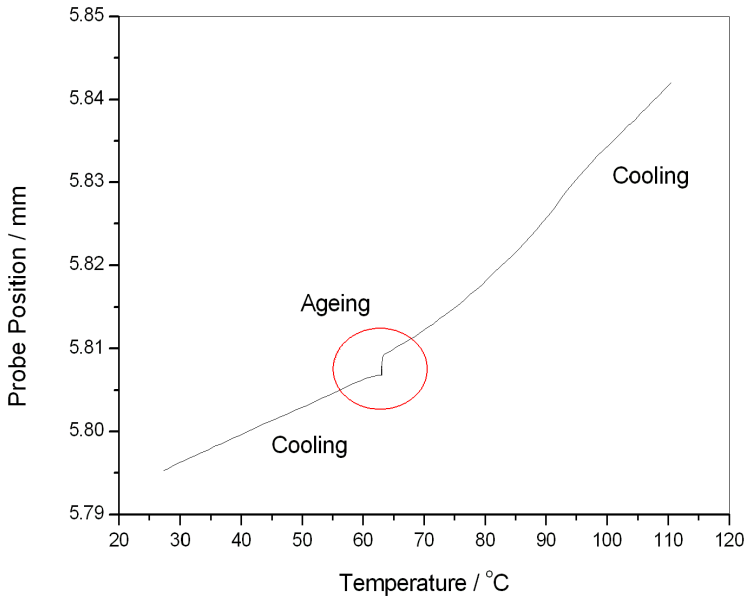

Figure 27a - The effects of physical ageing when the sample is held at a temperature of 63°c for 1000 minutes

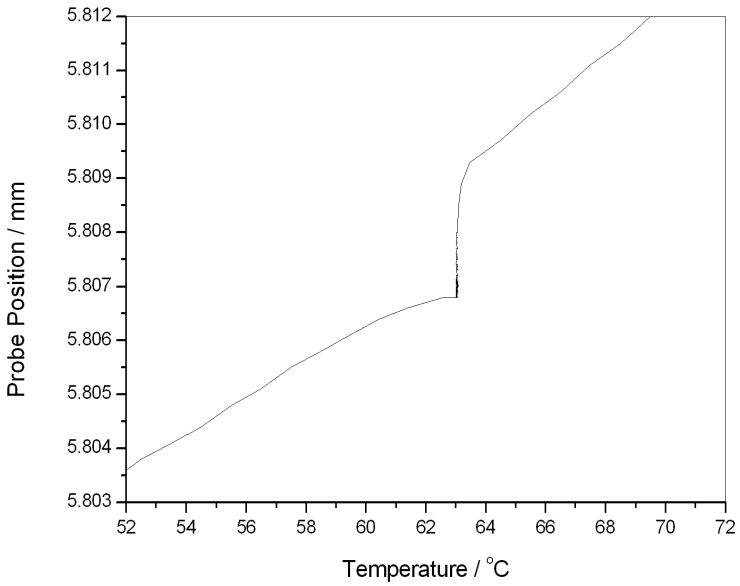

Figure 27b – Focusing on the physical ageing process, the sample is tending towards natural equilibrium.

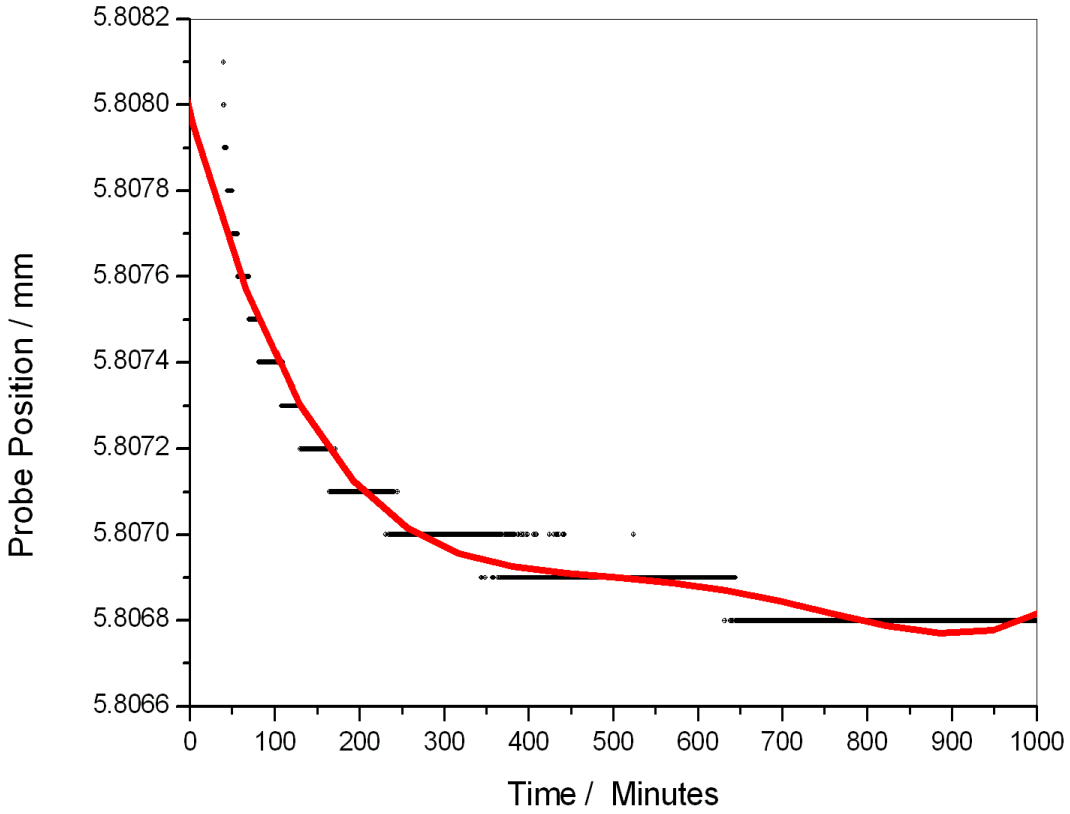

Figure 27c –The ageing effects against time when the sample is held at 63°c. The solid line is a 4th order polynomial to help guide the eye and to represent the overall data. The fluctuations and stepping of the results is due to a lack of resolution in the equipment.

3.3.1 Discussion

It is clear to see that physical ageing has taken place during the testing via TMA. Over the ageing period, the sample is forcing itself towards equilibrium as described by Atkinson et al. [2]. This can be seen by the decrease in probe position when the sample is held at it ageing temperature (Graphs 25b, 26b and 27b).

When considering the ageing period against time, it is clear to see that the decrease in probe position is similar for all three of the samples, ranging from 0.0014 mm to 0.0008mm. This is due to the constant crystallinity of the sample. The results do show to an extent that the probe position varies and increases with an increase in ΔT. However, as the time scale for this experiment is limited, the extent of the variation in the results is not easily recognisable.

The probe was in constant contact with the top of the sample, which allowed an accurate reading of the height of the polymer, as the sample softened the position of the probe changed as described by Karagiannidis et al.[4]. Therefore, as the probe position decreases during the ageing the period this shows the sample is 'softening'. This softening is an aspect of the Tg. The results show that the sample is trying to force itself to equilibrium as it goes through the ageing process and is around its Tg.

However, TMA is not the ideal piece of equipment to study the physical ageing effects on any semi-crystalline polymer. The long-term stability and the accuracy of the TMA is not suitable, this is evident in the fluctuations seen in graphs 25c, 26c and 27c.

3.4 Measurement of Physical Ageing within Semi-crystalline Polyethylene Terephthalate (PET) using DSC

The first test was performed on an amorphous sample of PET.

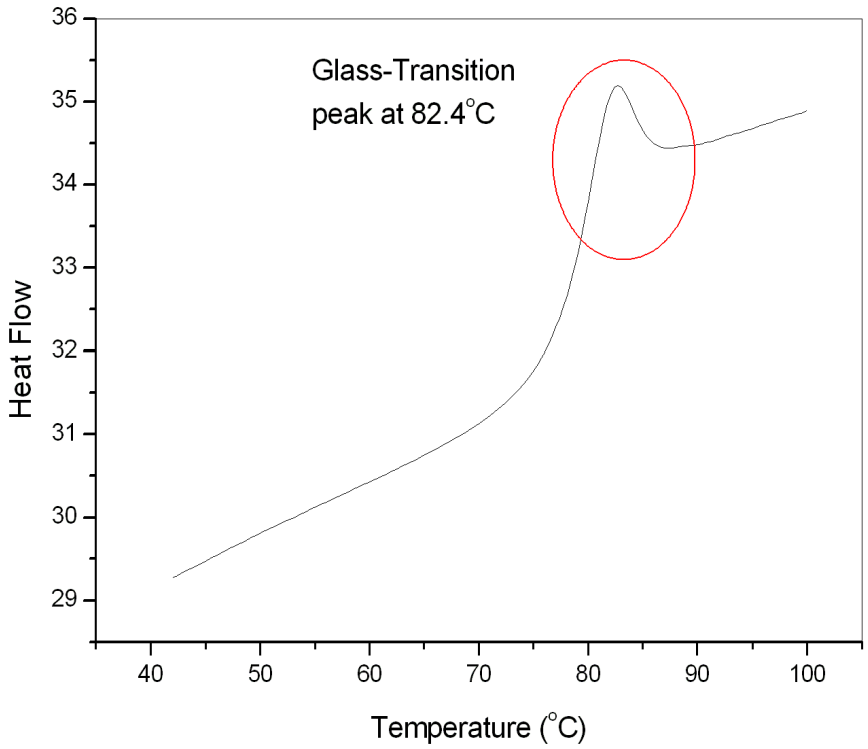

Figure 28a –Before any ageing experiments could take place there was a need to find the Tg of the amorphous sample of PET. This was found to be 82.4°C.

Once the Tg was found, a ΔT could be defined. This was decided to be a 10°C below the Tg.

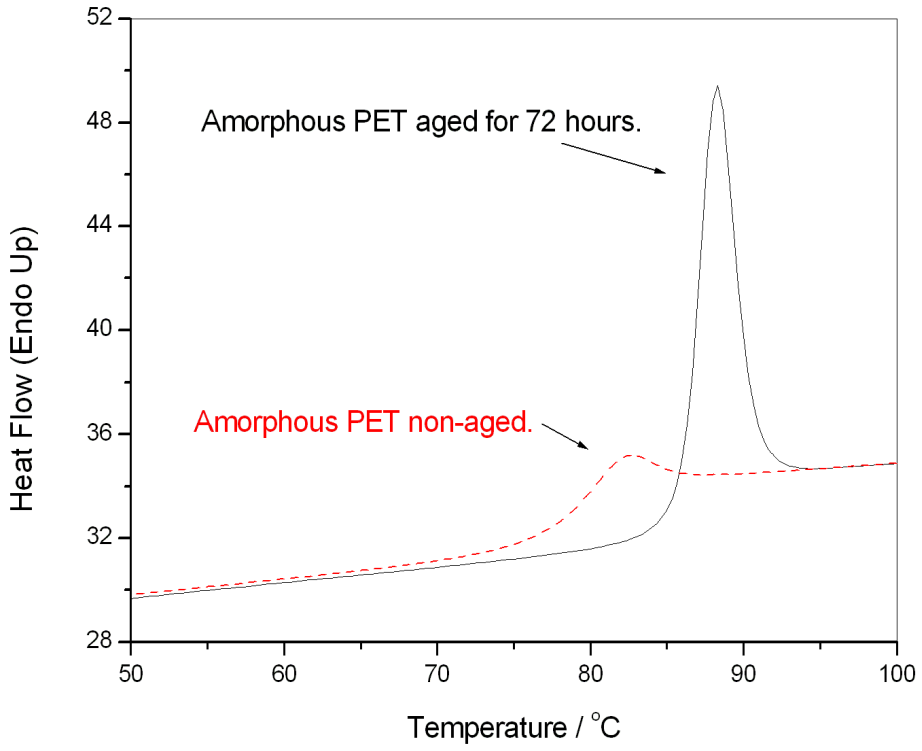

Figure 28b –The ageing effects against temperature. The solid line is the amorphous polymer after being aged at a temperature of 72°C (ΔT of 10) for 72 hours. The dotted line is the original trace for amorphous PET

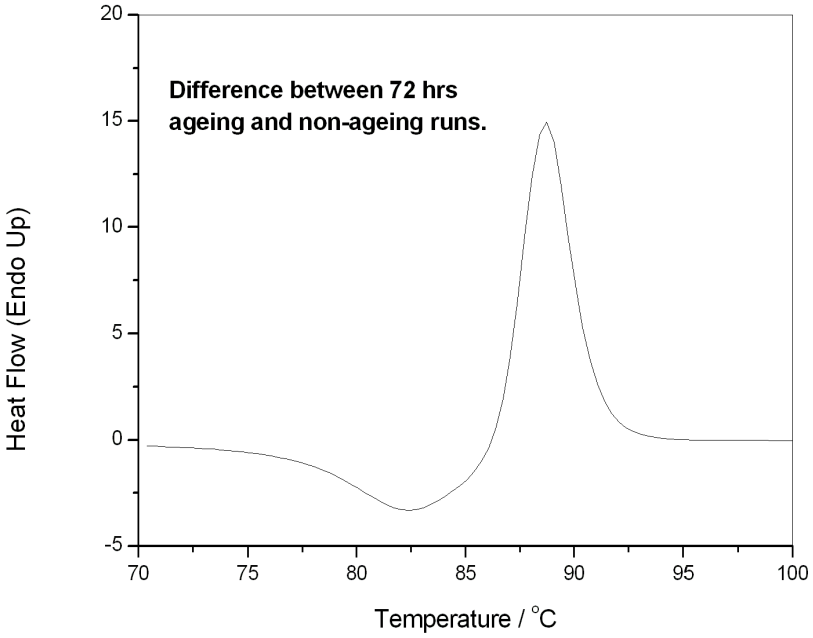

Figure 28c –The difference shown when the ageing line is subtracted from the baseline (the original amorphous trace)

The second test was performed on a semi-crystalline sample of PET that was crystallised at 95°c.

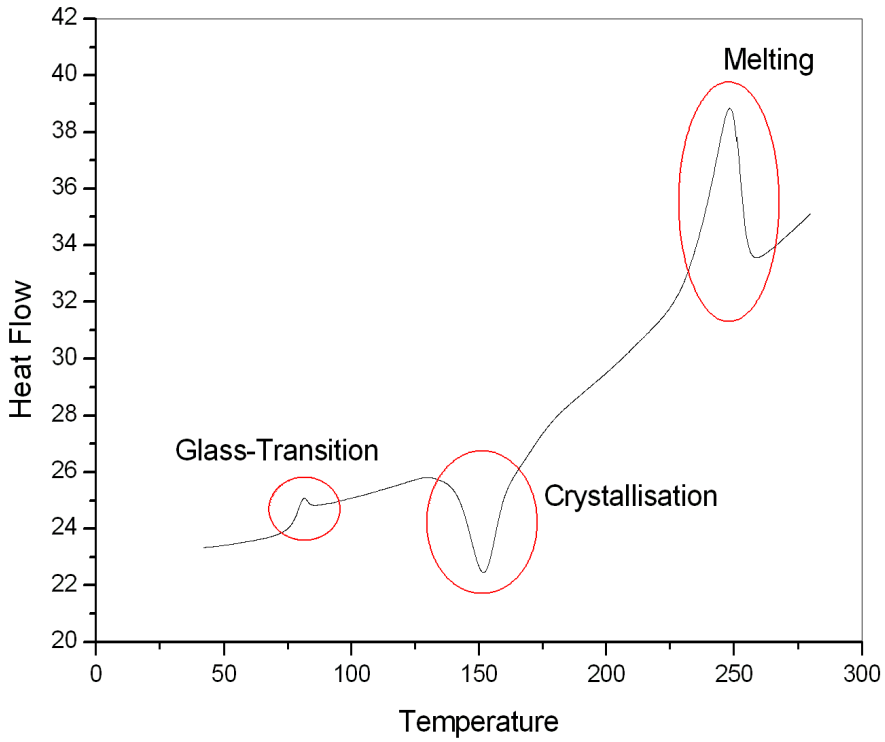

Figure 29a (i) –Before any ageing experiments could take place there was a need to find the Tg of the 95 semi-crystalline PET. This was found to be 84.3°C.

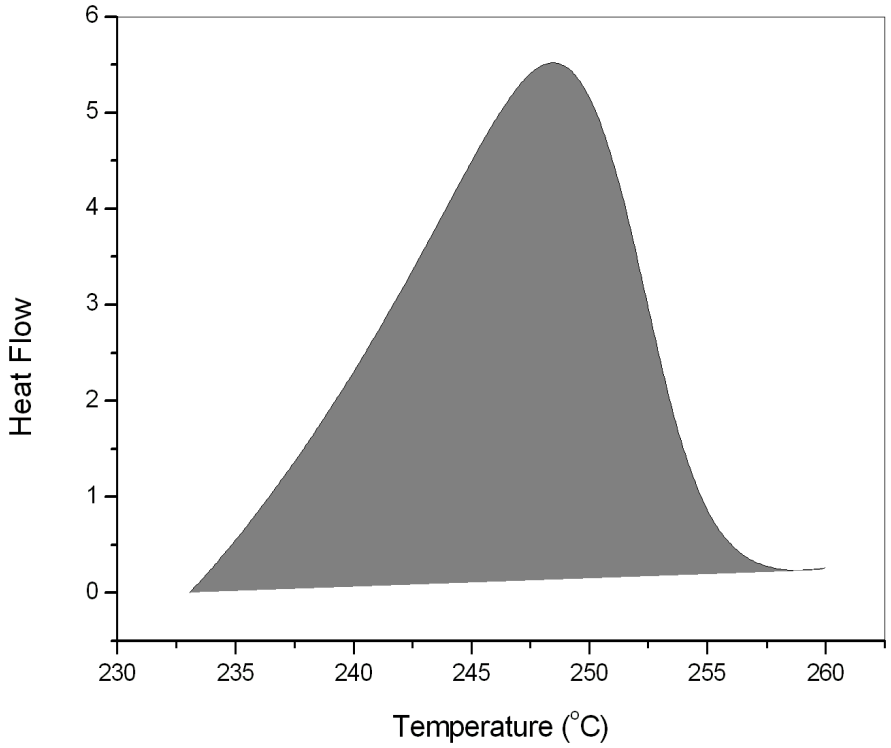

Figure 29a (ii) –Using the melting peak, it is possible to calculate the crystallinity of the sample. The area under the melting peaks is the enthalpy of the sample.

The heat of fusion, ΔH1, was found to be 67.2 J/g.

The corresponding value, ΔH1, for 100% crystalline PET is 239 J/g

Therefore:

Therefore:

$$\text{Degree of Crystallinity} = (\Delta H1/\Delta H) \times 100$$

$$\text{Degree of Crystallinity} = (67.203/239) \times 100$$

$$\text{Degree of Crystallinity} = 28\%$$

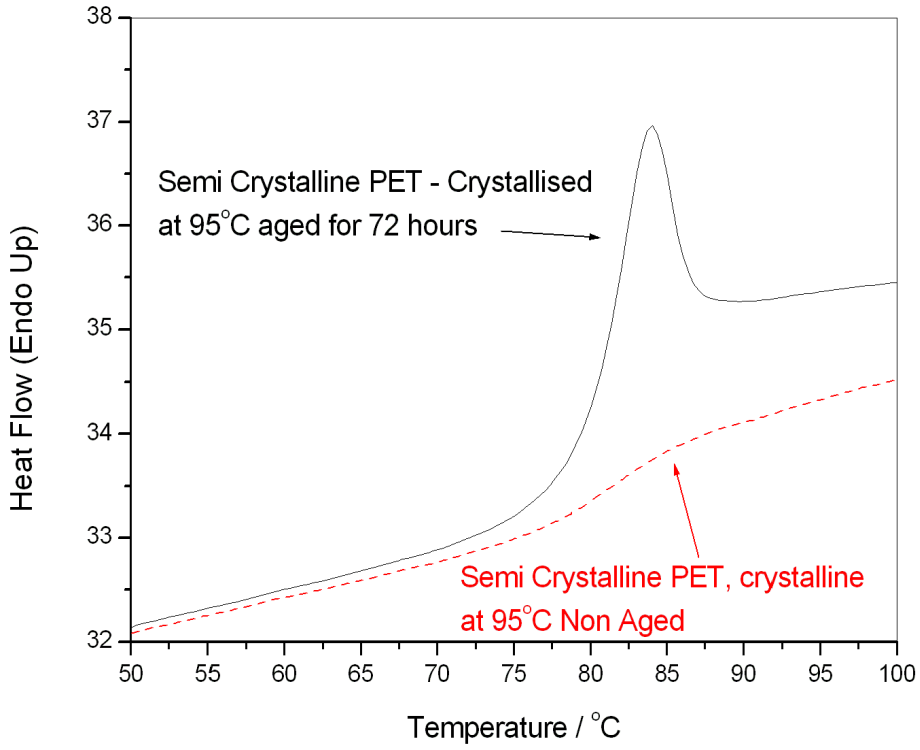

Figure 29b –The ageing effects against temperature. The solid line is the semi crystalline polymer after being aged at a temperature of 74°C (ΔT of 10) for 72 hours. The dotted line is the original trace for the 95 semi-crystalline PET

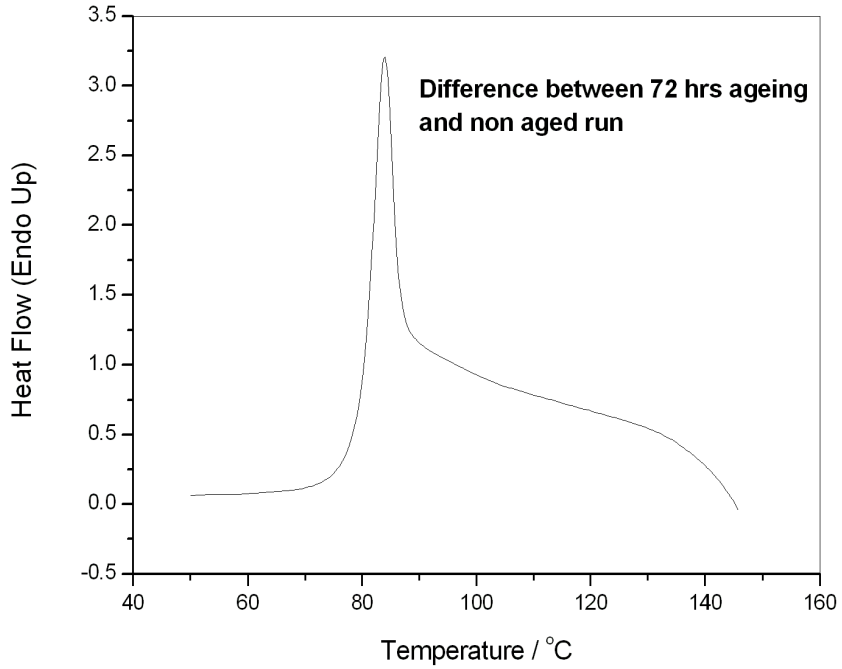

Figure 29c – The difference shown when the ageing line is subtracted from the baseline (the non-aged trace of 95 semi-crystalline PET)

The third test was performed on a semi-crystalline sample of PET that was crystallised at 210°c.

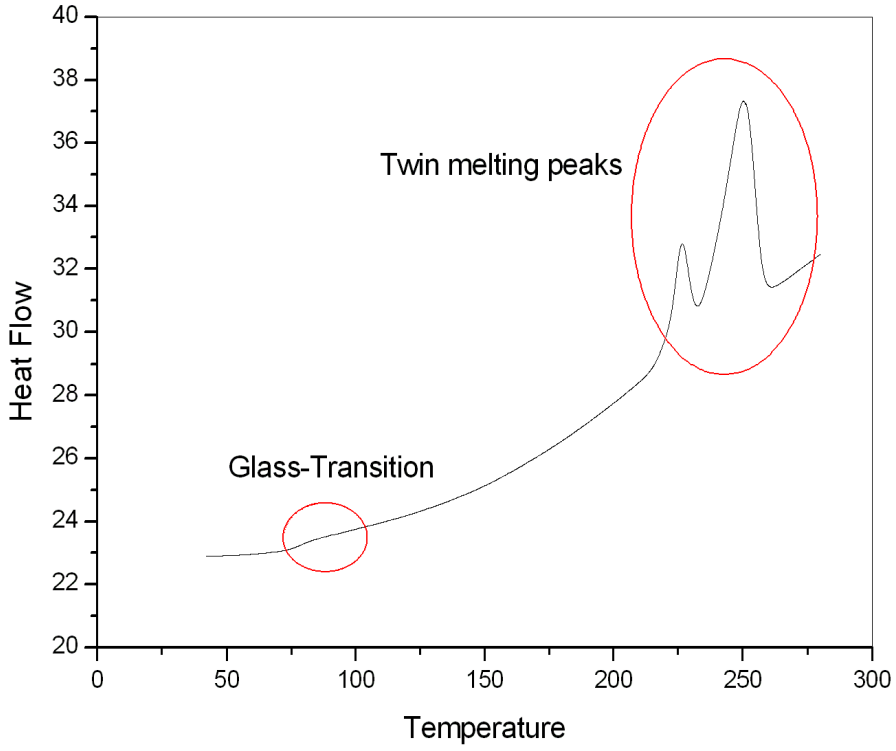

Figure 30a (i) –Before any ageing experiments could take place there was a need to find the Tg of the 210 semi-crystalline PET. This was found to be 88.6°C.

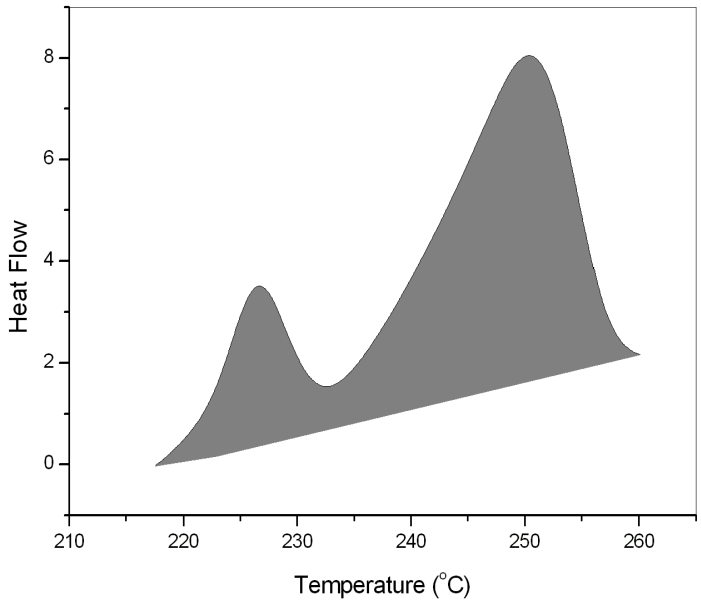

Figure 30a (ii) –Using the melting peaks, it is possible to calculate the crystallinity of the sample. The area under the melting peaks is the enthalpy of the sample.

The heat of fusion, ΔH1, was found to be 155.4 J/g.

The corresponding value, ΔH1, for 100% crystalline PET is 239 J/g

Therefore:

$$\text{Degree of Crystallinity} = (\Delta H1/\Delta H) \times 100$$

$$\text{Degree of Crystallinity} = (155.433/239) \times 100$$

$$\text{Degree of Crystallinity} = 65\%$$

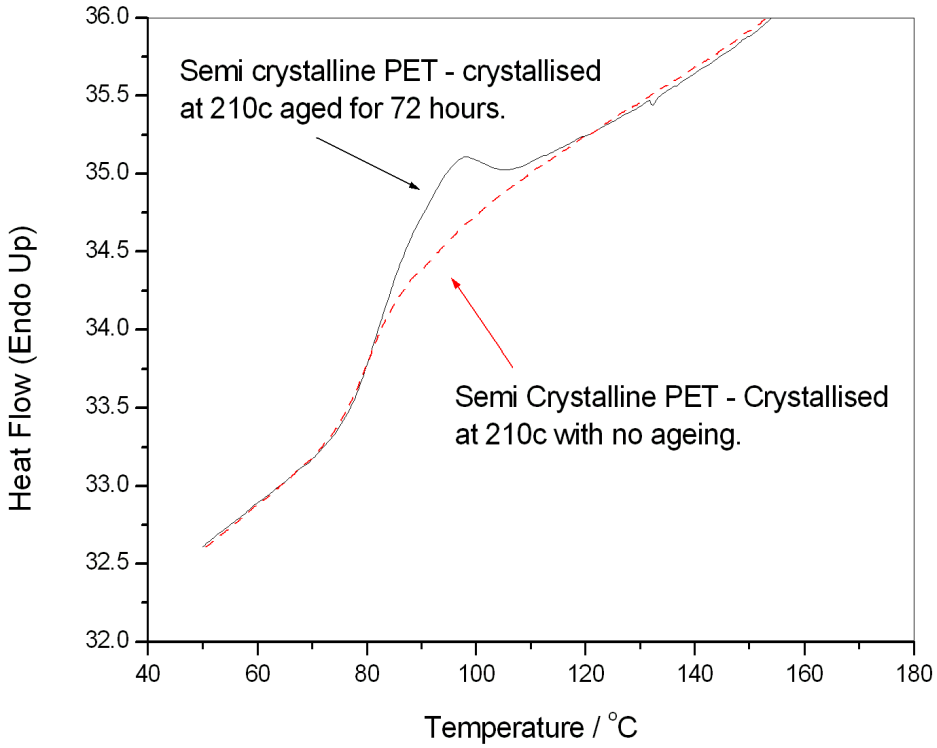

Figure 30b –The ageing effects against temperature. The solid line is the semi crystalline polymer after being aged at a temperature of 78°C (ΔT of 10) for 72 hours. The dotted line is the original, non-aged trace for the 210 semi-crystalline PET

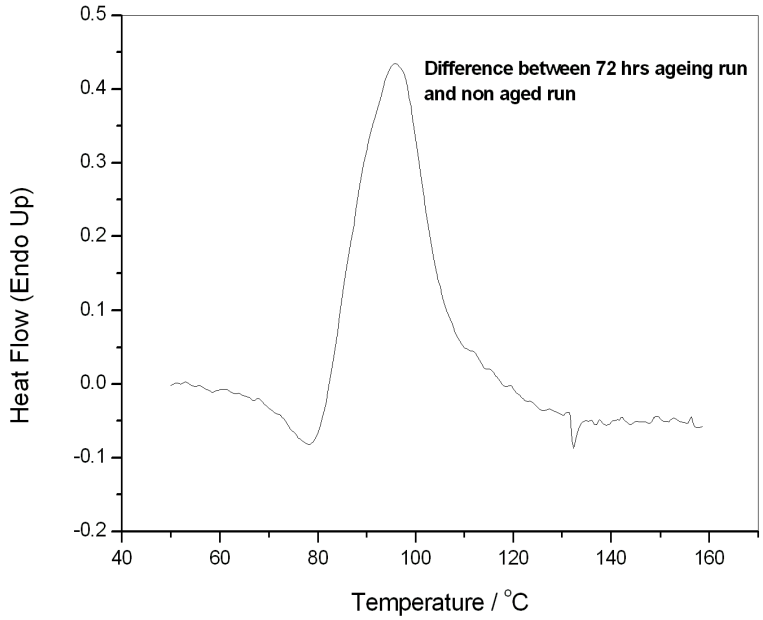

Figure 30c –The difference shown when the ageing line is subtracted from the baseline (the non-aged, 210 semi-crystalline trace)

3.4.1 Discussion

It is clear to see from figures 28b, 29b and 30b that physical ageing has taken effect on the samples. The ageing effects change with the varying degree of crystallinity of the samples. The amorphous sample (figure 28b) has a large amount of heat flow in comparison to its original run without ageing, showing that the ageing affects have changed the properties of the sample. The increase in heat flow shows that the amorphous regions, when unrestricted and free of any “order” have much more free-volume to move into, and can all easily rotate and have local motions whilst going through the ageing temperature and its glass transition.

Although this is evident in all the samples, Figure 31 shows us that the heat flow becomes much more restricted as the crystallinity within the polymer increases. This is due to the formation and density of the crystals within the Polyethylene Terephthalate. The amorphous inter-lamella region is composed of irregular chain folding, chain ends and polymer chains incorporated in several lamellae. Consequently, the segmental mobility will be lower in this region than in the “amorphous only” region. Because of this different segmental mobility, the intensity of the heat flow peaks will be reduced as the crystallinity of the polymer increases.

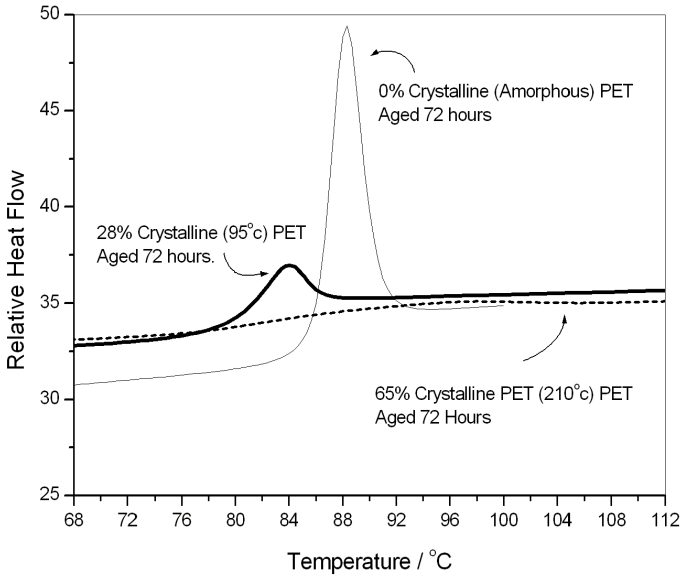

Figure 31 – When comparing ageing effects it is clear to see that there is a much larger relative heat flow between the amorphous polymer and the semi-crystalline samples of PET.

The higher the crystallisation temperature the higher the crystalline content meaning the restrictions of the segmental mobility in the inter-lamella amorphous regions area also greater. The main peak from the amorphous sample is caused by the ageing process which affects the amorphous region, meaning that the smaller peaks seem to be a response of the amorphous section within the crystalline samples. The 65% crystalline sample has the smallest heat flow peak where the spherulites practically fill the whole volume of the polymer, reducing the amount of the amorphous region, whilst increasing the restrictions of segmental mobility.

4 Conclusions

This thesis has examined the effects of physical ageing across different samples of Polyethylene Terephthalate.

The results from the TMA and the DSC both conclude that ageing can take place in semi-crystalline PET. However it is the DSC results that show in more depth the results of varying crystallinity and its impact on ageing.

Involved in the DSC testing were; a completely amorphous sample, a sample that was crystalline close to the glass transition temperature (Crystallised at 95^{o}C), and the final sample that was crystalline at close to the melting temperature (Crystallised at 210^{o}C).

The main findings of the tests performed show that physical ageing can take place within the polymer, although the degree of ageing varies with the degree of crystallinity of the polymer.

- As the crystallinity of the sample increases the effects of ageing are reduced. This is due to the constrictions of the Spherulites that are produced during crystallisation. The lamella constricts the movement of the amorphous sections of the semi-crystalline polymer and therefore reduces the amount of ageing that can take place.

- The increase in crystallinity reduces the free-volume within the polymer and so there is a lack of space for molecules to move into – restricting the polymer's push towards equilibrium and therefore reducing the effects ageing.

- The change in crystallinity is subsequently changing the morphology in the lamellae within the polymer. This change in morphology is what ultimately affects the effects physical ageing.

The data gathered during the TMA testing concludes and agrees with much previous work by others that heating and cooling rates can affect the glass-transition temperature of semi-crystalline PET.

The results that were concluded from the cooling rates also allowed the activation energy to be determined and this was found to be similar that of the value found in the literature.

The overall results from this investigation have shown that although physical ageing primarily takes place in amorphous PET, it can also take place in the amorphous regions of semi-crystalline PET, however, the increase in crystallinity of the polymer (and therefore the reduction in the amorphous section) will reduce the amount physical ageing undertaken within the polymer.

5 Future Work

Future work to follow on from this investigation would include:

- SEM (Scanning Electronic Microscopy). This would allow more knowledge of the microstructure of the polymer.

- Study into lamella thickness. To assess how the variation of lamella thickness with constant crystallinity affects physical ageing.

- Vary ageing time with crystallinity. This would show if the ageing time or the degree of crystallinity gives a larger physical ageing affect on semi-crystalline PET.

Due to time restrictions some parts of the experimental procedures had to be reduced. These would also be changed in future work:

- More samples with a higher crystallinity range would be created to give a more definitive answer for ageing variation with crystallinity.

- Crystallinity variation on the TMA testing. This would show the TMA ageing results with samples of different crystallinity to back-up the data from the DSC.

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