Investigation of Thermal Properties of Radiation Grafted Polystyrene / Polytetrafluoroethylene (PTFE) Copolymer Films

by

Md Aidi Bin Rais

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor Of Engineering (Hons)
(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Puan Jariah Bt Mohd Juoi)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2002

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MD AIDI BIN RAIS

ABSTRACT

Grafting was carried out using γ-radiation from a ^{60}Co source at dose rates of 1.32-15.0 $kGyh^{-1}$ at room temperature. The chemical structure and the crystallinity of the grafted PTFE films were studied by means of Fourier transform infrared (FTIR). Structural investigation of polystyrene grafted poly(tetrafluoroethylene) (PTFE) membranes prepared by radiation-induced grafting of styrene onto commercial PTFE films carried out by Fourier transform infrared spectrometer (FTIR) and the thermal stability of thermal gravimetric analyzer (TGA). The effect of the structural changes taking place in the film by grafting and the variation of the degree of grafting on melting temperature (T_m), glass transition temperature (T_g), heat of melting (ΔH_m), and degree of crystallinity was studied by using differential scanning calorimetry (DSC). Polystyrene grafted films prepared by radiation-induced grafting of styrene onto PTFE films were found to undergo considerable structural changes. The degree of crystallinity decreased upon grafted as well as deviation of the degree of grafting. The changes in melting temperature (T_m) was found to be insignificant regardless of the degree of grafting unlike glass transition temperature (T_g). The decrease in crystallinity was suggested mainly due to the effect of dilution on the original crystalline structure by incorporation of the amorphous polystyrene grafts. Furthermore based on the results and discussion and those on the original and grafted films is that the PTFE film surface undergoes structural changes in terms of chemical composition as a result of styrene grafting. The effect of grafting of polystyrene onto PTFE membrane on the thermal stability of the PTFE matrix is studied. It is found that the fluorinated-structure of the PTFE matrix has a thermal stability up to ~550°C followed by one-step degradation. Grafting of styrene, which led to the formation of polystyrene grafts in PTFE matrix introduces a two-step degradation pattern. The polystyrene grafts start to degrade at ~400°C and continue until ~480°C. This is followed by the degradation of PTFE backbone, which starts at ~550°C and continues to ~680°C. Styrene, which radiochemically grafted onto PTFE films leading to the formation of polystyrene grafted PTFE films. The grafted films were found to be very stiff compared to the original PTFE film.From DSC thermograms, the high value of T_g compared to that reported in literature (>20°C) [10,11], thus indicates that commercial PTFE film contains certain additive (filler such as glass fibres) that decreases the polymer chain mobility and gives rise to T_g.

The incorporation of polystyrene side chain grafts into PTFE film caused a shift in the T_g of the grafted film to higher temperature while significant changes took place in T_m. Grafting of styrene were found to reduce the heat of melting and the degree of crystallinity of PTFE films. In addition, the degree of crystallinity decreased in the original PTFE film to the grafted films.

ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

1.1 Problem Statement

At the beginning, the author was given a prepared sample and the task is to conduct research and experiment. The material used in the experiment are 5 samples of Polytetrafluoroethylene grafted polystyrene (PTFE-g-polystyrene) having unknown degree of grafting of between 5% to 36% and 1 sample of pure (virgin) PTFE. The films were prepared by using radiation-induced grafting method of polystyrene onto commercial PTFE which will be discussed further in section 1.6.

Structural changes occur as a result of grafting of styrene onto PTFE films. The changes do affect the properties of the PTFE films as a result of the grafted polystyrene. Thus the most important task is to study the effect of grafting on the thermal properties of the PTFE film. The thermal properties include the melting temperature (T_m), glass transition temperature (T_g), heat of melting (ΔH_m), thermal stability, degree of grafting and degree of crystallization.

This research is important to investigate the thermal properties of the new film, PTFE-g-polystyrene, since when deal with application, the thermal properties play an important role in indicating the stability and the temperature limitations.

1.2 Objectives

There are two main objectives that must be achieved at the end of the research. The objectives are:

i. To investigate the thermal and structural properties of radiation grafted Polystyrene / Polytetrafluoroethylene (PTFE) copolymer film.

ii. To establish correlations between the melting temperature (T_m), glass transition temperature (T_g), thermal stability and the degree of crystallization to the degree of grafting.

1.3 Scope of Study

In this research, the main task as has been mention before is only the main intention. The research will not go beyond the knowledge of the mechanical engineering area. As mention in the objectives, the particulars which are going to be investigated are done by using specific equipment such as Fourier Transform Infra Red Spectroscopy (FTIR), Thermal Gravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC). These equipments are available at laboratory of University Teknologi Petronas (UTP).

1.4 Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene (PTFE) was founded about 50 years ago by R. Plunckett, DuPont Company. PTFE had undergone modification with the introduction of new grades and even new forms to meet specific goals. Figure 1.1 shows the molecular structure of PTFE. The molecular structure consists of a core chain of carbon with fluorine sheath, which essentially completely shields the core from chemical attack. [1]

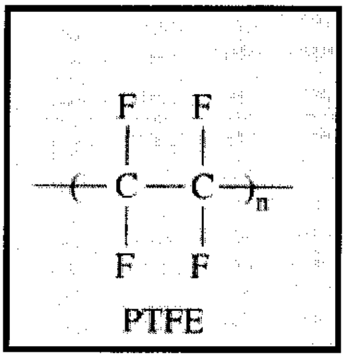


Figure 1.1: Polytetrafluoroethylene (PTFE) polymer repeating unit.

Good physical properties are taught to result from the entanglement of extremely long chain length, even though interchain forces are low. Polyethylene is the same structure as PTFE except that all the hydrogen in polyethylene is replaced by fluorine in PTFE. The differences in properties are because of the nature of the carbon-fluorine bonds. [1,2]

Fluorine is the most electronegative of all the atoms. Therefore, the carbon-fluorine bond is highly polar, with the negative end toward the fluorine. Hence, the electrons are held very tightly by the fluorine molecule. Thus, PTFE chains are very long, straight, and stiff, allowing PTFE molecules to pack together tightly. PTFE has the highest density of any plastic [2].

Polystyrene is produced by addition polymerization and the nature of it is amorphous. The monomer, styrene contains carbon-carbon double bond to which the benzene ring and three hydrogen are attached. The styrene monomer has a carbon-carbon double bond to which a benzene ring and three hydrogen are attached. This monomer is polymerized by the addition polymerization mechanism. PS is essentially 100% amorphous. The amorphous nature of PS allows light to pass through the structure without significant refraction and so PS is transparent and clear. Pellets of PS have a certain glitter or sparkle and so this unfilled, clear grade of PS has been referred to as crystal polystyrene. The term crystal PS refers to its appearance and not its crystallinity, which is near zero. [1, 5]

By grafting the PS onto the PTFE, new material with new properties is formed. Analyses have to be performed by establishing correlations between the variation of glass transition temperature (T_g), melting temperature (T_m), degree of crystallinity, and the amount of PS grafted therein, i.e. degree of grafting.

Graft polymerization is a common method for modifying polymer properties. Because the main chain and the branch chain are usually thermodynamically incompatible, most graft copolymers can be classified as multiphase polymers in the solid state, analogous to polymer blends, block copolymers, and interpenetrating polymer networks. [5]

1.4.1 Thermal Properties of virgin PTFE [3,4,6]

1.4.1.1 Thermal Stability

PTFE is one of the most thermally stable plastic materials. There are no appreciable decompositions at 260°C, so that PTFE, at this temperature, still possesses the greater part of its properties. Appreciable decomposition begins at over 400°C.

1.4.1.2 Transition points

The arrangement of the PTFE molecules (crystalline structure) varies with the temperature. There are different transition points, with the most important ones being the following: at 19°C corresponding to a modification of some physical properties and that at 327°C which corresponds to the disappearance of the crystalline structure: the PTFE assumes an amorphous aspect conserving its own geometric form.

1.4.1.3 Expansion

The linear thermal expansion coefficient varies with the temperature. In addition, because of the orientation caused by the working process, the PTFE pieces are in general anisotropic; in other words, the coefficient of expansion varies also in relation to direction.

1.4.1.4 Thermal conductivity

The coefficient of the thermal conductivity of PTFE does not vary with the temperature. It is relatively high, so that PTFE can be considered to be a good insulating material. The mixing of suitable fillers improves the thermal conductivity.

1.4.1.5 Specific heat

The specific heat is defined as the energy required to raise the temperature of a unit mass of a substance by one degree. Thus, the specific heat of virgin PTFE, as well as the heat content (enthalpy) increases with the temperature.

1.5 Polystyrene

Polystyrene is produced by addition polymerization and the nature of it is amorphous. The monomer, styrene contained carbon-carbon double bond to which the benzene ring and three hydrogen are attached. This monomer is polymerized by the addition polymerization mechanism. The repeating unit for PS is represented in Figure 1.2 below.

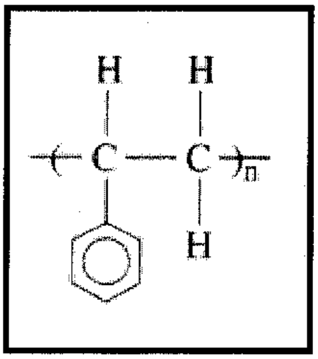


Figure 1.2: Polystyrene (PS) polymer repeating unit.

The size of the benzene pendent group is represented in Figure 1.2, where the benzene ring is much larger than any of the other pendent groups (hydrogen, CH_3, or Cl) associated with the other commodity resins. The benzene ring reduces the ability of the polymer chain to bend and interferes substantially with other parts of the molecule. These characteristics prevent crystallization. Therefore, PS is essentially 100% amorphous.

The amorphous nature of PS allows light to pass through the structure without significant refraction and so PS is transparent and clear. Pellets of PS have a certain glitter or sparkle and so this unfilled, clear grade of PS has been referred to as crystal polystyrene. The term crystal PS refers to its appearance and not its crystallinity, which is near zero. The chemical properties of PS are dictated largely by the presence of the benzene ring. Any molecule containing the benzene ring is called aromatic and has certain characteristic chemical properties. Among those properties is sensitivity to aromatic and chlorinated solvents. Therefore, PS can be dissolved in these solvents and will swell in the presence of small amounts of both aromatic and chlorinated solvents. Solvent adhesives employing these solvents are effective in joining PS. However, PS is resistant to water and has been used extensively for applications, such as food packaging, where water resistance and clarity are important.

1.5.1 Burning Test

PS will burn readily with a yellow flame and dark, sooty smoke. This type of burning is characteristic of polymers with aromatic pendent groups. When aromatic groups are in the backbone of the molecules, flammability is reduced in comparison to pendent aromatic groups.

1.5.2 Clarity [1-5]

The long-term clarity of PS is not good because of a tendency of the material to yellow with exposure to UV light and to oxygen. The material is subject to environmental stress cracking, which further limits its long-term use. PS is therefore most appropriate for applications of short duration (such as packaging) and not for long-term use (such as for outdoor signs). Perhaps the most troublesome use of PS was that often broke easily because of PS's brittleness.

1.5.3 Brittleness

Brittleness (low toughness) in PS is a result of the interference of the aromatic pendent groups with neighbouring molecules that prevents the molecules from sliding past each other. The strength of PS is strongly determined by the molecular weight [1-5].

1.5.4 Thermal Properties

The wide range between the softening point of PS (100°C, 212°F) and its decomposition temperature (250°C, 500°F) allows the viscosity of PS to be reduced by increasing the temperature. PS should not be held at temperatures above (150°C, 300°F) for long periods of time because some degradation can occur.

The glass transition temperature, T_g for Polystyrene is $100(105)^{O}$C (atactic), 100^{O}C (isotactic) the melting temperature, T_m for polystyrene is 240 (250) ^{O}C [1-5].

1.6 Polymer Grafting [5]

The applications for radiation processing are faster and more convenient crosslinking of thermosets, crosslinking of thermoplastics that would be difficult by conventional methods, control of molecular weight for viscosity modifiers, control of particle size, improved quality of crystalline structures due to atomic or molecular rearrangement, and medical sterilization. Several other applications are possible.

One important application is the modification of a polymer surface. The surface can be coated with a crosslinkable material and then crosslinked by radiative curing. This method avoids the problem that might be encountered when the polymer being coated softens or degrades with the heat normally required for crosslinking. This method of surface treatment can increase the toughness, scratch resistance, and stiffness of a material. Compact discs and computer floppy discs are improved by this technique.

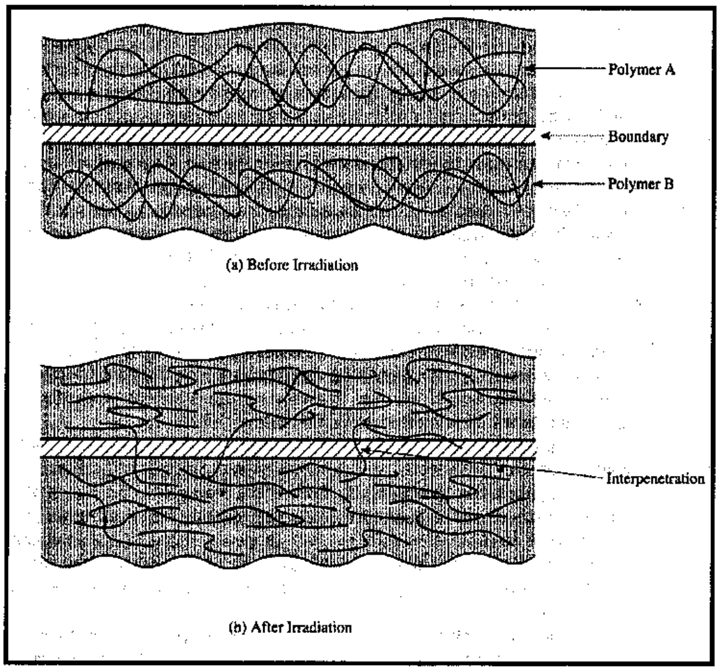


Figure 1.3: The increase in bonding in a polymer blend by interpenetrating polymer networks induced by radiation

A similar principle is involved in coating a low-priced material that forms the bulk of a product with a higher-priced material that can be crosslinked. This procedure cuts the cost of the overall product and still gives the required performance because the surface of the product may be the only part that requires the enhanced properties (such as plastic material that will be subjected to weathering).

A similar application is when some property is needed for the entire part (such as flexibility) but another property, such as abrasion resistance, is critical for the surface. This can be accomplished by making the bulk of the material from a polymer possessing the main property (flexibility) and then coating the outside with some other product that can be irradiated to obtain the desired surface property. Of course, the limited penetration of electron beam radiation allows this process to be accomplished without the need to coat the original material. Simply crosslinking the surface with radiation is sufficient to obtain the desired results.

The ability of radiation to cause molecular rearrangements has proven to be valuable in making polymer blends more stable. When these materials are irradiated, the molecules in the two materials migrate across their mutual polymer boundaries to form interpenetrating polymeric networks. These interpenetrating networks result in improved bonding between the two polymers (see Figure 1.3).

When radiation is used to join materials, the process is called polymer grafting. The result can be improved properties, stability of a blend of two or more polymers, or the joining of two polymers that would not otherwise join. The process for polymer grafting is the same as that shown in Figure 1.3.

If desired, two separate polymers can be joined by pressing them together and irradiating the junction. Bonding may or may not have already been done prior to irradiation. If the parts are already bonded, the irradiation is used to enhance the bonding. If they are not already bonded, the irradiation is used to create bonding. Usually, however, the bond strength obtained from bonding only with irradiation is not very strong.

1.7 Source of Samples [12]

As has been told earlier, the author was given a prepared samples which was prepared at Malaysia Institute for Nuclear Tecnology Research (MINT) [12]. PTFE film of 90μm thickness (Porghof, USA) was used as a base polymer. Styrene of purity more than 99 % (Fluka) was used as a grafting monomer without any further purification. Other chemicals were reagent grade and were used as received. Square pieces (5 cm x 5 cm) of PTFE film were washed with acetone and then dried in a vacuum oven (10 mbar) at 60°C to constant weight. The dried films were placed with a styrene solution of known concentration into glass ampoules and the grafting mixture was deaerated by bubbling with nitrogen for 8-10 min and the ampoule was sealed. The ampoule was irradiated at ambient temperature using γ-rays from a ^{60}Co source (Jlshepher and Associates, Model 109, USA) [12] at dose rates in the range 1.3215.00 kGyh-1 for the required period of time. The grafted films were removed, washed with toluene and soaked therein overnight to remove the residual monomer and homopolymer adhering to the films' surfaces. The grafted films were washed free of toluene with methanol, then dried in vacuum oven at 80°C to constant weight.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Literature Review [2,3,10]

Films or membranes which were prepared by radiation-induced grafting are receiving increasing attention in the field of polymer, solid state and separation science and technology. This is due to their potential to substitute similar membranes prepared by conventional polymerization methods in various applications of industrial interest such as pervaporation, dialysis, water electrolysers, sensors and fuel cells. In particular, radiation grafted membranes bearing sulfonic acid groups have been proposed as proton conductors in solid polymer electrolyte (SPE) fuel cells and proton exchange membrane (PEM) fuel cells. This is because of the complete dissociation of sufonic acid groups, which results in high current density. Experimental radiation grafted sulfonic acid membranes based on poly (tetrafluoroethylene-co-hexafluropropylene) (FEP) films were developed by Scherer and coworkers and found to be stable for 1400h in SPE fuel cells at temperatures up to 80°C. Recent experiments on commercial radiation grafted membranes showed a satisfying performance with an initial lifetime up to 1000h at an operating temperature of 60°C. Ion-exchange membranes bearing sulphonic acid groups are commonly prepared by grafting of styrene onto fluorinated polymers, and the graft copolymer is subsequently sulphonated [10].

For a membrane to be qualified for use in SPE fuel cells, it must combine high ionic conductivity ($10^{-2}\Omega^{-1}cm^{-1}$), mechanical strength, chemical/thermal stability and controlled swelling behaviour. Commercial perfluoronated sulfonic acid membranes such as Nafion (DuPont de Nemours Ltd), Aciplex (Asahi Chemical Co) and Dow development tal membranes (Dow Chemical Co Ltd) have been found to meet these requirements. However the high cost of these membranes has prompted the development of cheaper and better proton conducting membranes in the last few years [10].

Sulfonic acid membranes have received a considerable attention over the last decade due to their suitability to various electrochemical cells such as water electrolyzers and proton exchange membrane (PEM) fuel cells. In such cells, membrane plays a vital role as it severs as a separator and electrolyte. Nafion® and Dow® commercial membranes have been identified for use in PEM fuel cells where high current density and low resistance are required. However, these membranes are expensive and other membranes are needed to promote the PEM fuel cell systems.

Many efforts have been devoted world wide to develop very specific and cost-effective sulfonic acid membranes. The latest development of these membranes with respect to methods of preparation, properties and potential use in PEM fuel cells have been recently reviewed by Savadogo. Modification of polymer films by radiation-induced grafting of chemical functionality is an advantageous technique to prepare these membranes, particularly, in terms of the ability to control the composition and properties of the membranes by variation of grafting parameters. For stability reasons, sulfonic acid groups have been identified as functional groups and fluorinated films as base polymers in these membranes. However, grafting of a sulfonated monomer is very difficult due to the high incompatibility between sulfonic acid groups (strongly hydrophilic) and the polymer films (strongly hydrophobic). Hence, styrene is often grafted onto fluorinated polymer films to produce graft copolymers that can be easily sulfonated in a post-grafting reaction using chlorosulfonic acid. Membranes prepared by this method have shown a great potential to substitute the expensive commercial membranes in water electrolyzers and PEM fuel cells.

Recent study had used commercial poly(tetrafluoroethylene) (PTFE) film as a polymer matrix despite its radiation sensitivity. PTFE was selected because of its outstanding chemical, thermal and mechanical stability. Styrene was grafted onto PTFE films using a simultaneous irradiation technique under appropriate grafting conditions. Kinetics of the grafting were investigated in correlation with the grafting conditions, i.e. solvent type, irradiation dose, dose rate and initial monomer concentration. The degree of grafting was found to be a conditions and has a strong influence on the properties of the grafted films.

Grafting of styrene is well known to cause structural changes in the host fluorinated film. This is mostly induces changes in the thermal characteristics mainly due to the introduction of polystyrene, which has a different nature (hydrocarbon) from that of the fluorocarbon matrix. It is also very significant to determine the changes in structural characteristics of the membranes as they have a strong impact on the membrane operating parameters and the overall performance of the membrane cell.

2.2 Theory

2.2.1 Glass Transition Temperature (T_g)

Most polymers are either completely amorphous or have an amorphous-like even if they are crystalline. Such materials are hard, rigid glasses below a fairly sharply defined temperature known as the glass transition temperature, T_g [3]. The glass transition temperature, T_g also plays a role in determining the physical properties of semi crystalline polymers, whose amorphous portions melt or soften at T_g while the crystalline portions remain solid up to the melting temperature, T_m [4].

2.2.2 Glass transition

Polymeric material becomes much stiffer as it goes through a certain temperature range when a it is cooled from the liquid or rubber state. This *stiffening* is the result of one of two possible events: *crystallization* or *glass transition*. For crystallization to occur, the polymer molecules must be sufficiently regular along their length to allow formation of crystalline lattices and cooling rate must be slow enough for the crystallization process to take place before the molecular motions become too sluggish or too slow. When the polymer fails to crystallize for either reason, the amorphous, liquid-like structure of the polymer is retained, but the molecular motion becomes frozen and the material turns into a glass. Such a glass transition occurs over a finite temperature interval, but is still realized abruptly enough to merit the term "transition". The glass transition can be recognized by the change in many of the properties of the material, the most important from a practical point of view being the increase in the modulus of the material by several orders of magnitude. [1]

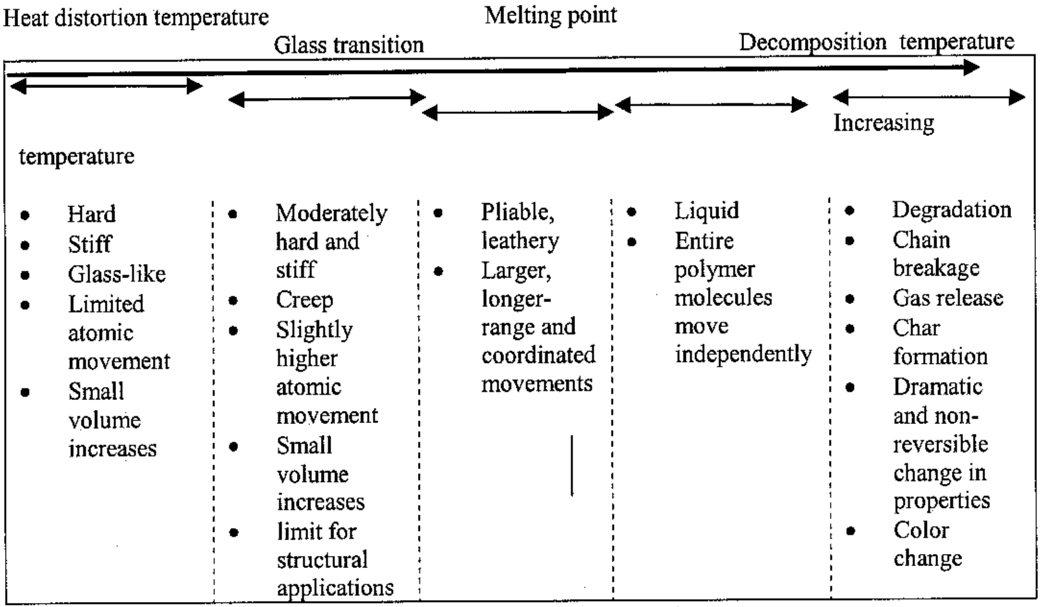
Glass formation can be achieved with many low molecular weight materials and with certain metallic alloys by special preparation techniques such as rapid quenching. With polymers, the opportunities for irregularity along the chain are numerous and the crystallization rate is inherently slow; as a result the formation of the glassy state is a more common occurrence. Thus the glass state is a state of polymeric materials equal in importance to the semicrystalline state and the rubbery state. Also, the melting temperature T_m and the glass-transition temperature T_g, are the two most important parameters of a given polymer that characterize its properties over a wide temperature range. [1,2,3]

The most important method for determining T_g is the differential scanning calorimetry (DSC) test (ASTM D3417 and D 3418). This test involves measuring the heat absorbed by a sample when that sample goes through thermal transitions. The DSC test allows these transitions to be identified for a plastic material by noting the absorption of heat from a plot of heat versus time as the sample is gradually heated. Results identify the temperatures of the transitions. Where previously (below T_g) the polymer was rigid and hard, with the long-range movements of several adjacent atoms that occur above the glass transition temperature, the polymer becomes pliable and leather like. (T_g is called the glass transition temperature, because glass behaves similarly) [4,5].

2.2.3 Melting

When more heat above T_g is put into the polymer, the thermoplastic polymer continues to soften and become more pliable, because larger and larger segments of the polymer become excited and gain coordinated movements. The polymers continue to disentangle from each other. Eventually, the polymer has so much internal energy that entire polymer molecules are moving freely relative to all the other polymers in their vicinity, and melting occurs. (If the polymer is joined to those neighboring polymers by covalent bonds, it is a thermoset, and melting does not occur, as explained later.) Hence, melting is simply the process of polymer chains gaining sufficient energy to move independently. Initially only a few polymers have sufficient energy to move independently, but with increased thermal input, all the polymers will gain this freedom. The temperature at which this occurs is called the melting point or melting temperature, T_m, and it is a thermal transition as defined previously for T_g. Figure 3 shows the relative position of the melting temperature and the other thermal transitions which have already been discussed [1,2,5].

The thermal transitions are also depicted in Figure 4, where the differences between thermoplastics (both amorphous and crystalline) are shown and compared with a thermoset. Note that in a typical amorphous thermoplastic the polymer is hard and stiff below the T_g and passes through the HDT and then to T_g. Above T_g, the polymer would be leathery up to the melting temperature, where it would, of course, melt to a liquid.



• Hard • Stiff • Glass-like • Limited atomic movement • Small volume increases	• Moderately hard and stiff • Creep • Slightly higher atomic movement • Small volume increases • limit for structural applications	• Pliable, leathery • Larger, longer-range and coordinated movements	• Liquid • Entire polymer molecules move independently	• Degradation • Chain breakage • Gas release • Char formation • Dramatic and non-reversible change in properties • Color change

Figure 2.1: Idealized plastic.

In the amorphous thermoplastic polymer, the melting point, T_m, is shown as a range over which melting would occur. This melting range is caused by the wide variations in entanglement, chain length, and secondary bonding between polymer chains that often occur in amorphous plastics [5].

Figure 2.2 shows that for the case of crystalline thermoplastics, there is no T_g. In highly crystalline polymers where the crystal bonding energies are strong, resulting in tightly held molecules, almost no translation motions occur until the input energy is sufficient to overcome the crystal bonding energies. The crystalline structure prevents the long-range, coordinated atomic motions that are characteristic of the change from rigid structures to leathery structures. When the energy reaches the threshold energy equal to the crystal bonding energies, the crystal lattice breaks apart and the molecules become free to translate. Therefore, crystalline thermoplastics remain quite rigid up to the crystalline melting point, which is quite sharp (narrow temperature range). The temperatures at which the crystalline areas break apart are usually high enough that other effects, such as secondary bonding and differences in chain length, have little effect on the melting point sharpness.

This behaviour is obviously important in certain applications where the plastic material must give structural support. Hence, crystalline materials are more likely to be used in structural applications than are amorphous polymers. The melting point for a crystalline thermoplastic is typically somewhat higher than for an amorphous thermoplastic (all other things being equal), because of the higher energy required to break the crystalline bonds. Most real polymers are mixtures of crystalline and amorphous regions. The two types of regions act independently in thermal transitions. Therefore, the crystalline regions have sharp melting points and the amorphous regions have glass transitions and broad melting temperatures.

In addition, crosslinks largely prevent the formation of crystal regions. Most thermosets will, however, exhibit a glass transition temperature. The T_g is related to the number of crosslinks formed, because higher crosslinking will give further restrictions to the molecules and require higher temperatures to effect the long-range movements that are characteristic of the glass transition. This direct relationship between T_g and crosslink density has led to the use of T_g as an indicator of the extent of cure (crosslinking). Because T_g is one measure of the maximum use temperature of the plastic for structural applications, the use range can be increased by increasing the number of crosslinks, which in turn raises T_g [1,2,5].

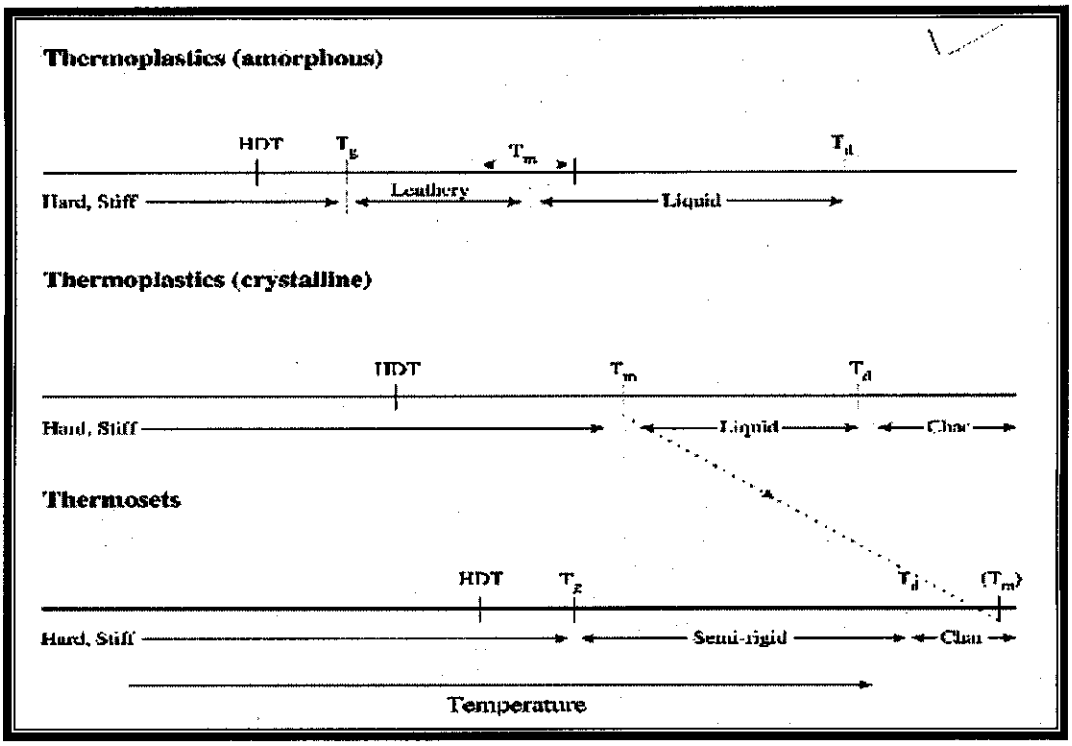


Figure 2.2: General thermal behaviour for thermoplastic and thermoset plastics.

In crosslinked thermosets the melting point is dramatically increased relative to thermoplastics. When molecular size effects are examined, the larger the molecule, the greater the energy that needs to be input to melt it, thus raising the melting point. For thermosets, the increase in molecular weight is so great that the melting point is raised above the decomposition temperature, thus creating a situation where there is no real melting point because the thermoset material will start to decompose before it will melt [5]

Characteristics of the polymer that raise T_g or T_g have a tendency to raise its maximum structural use temperature as well. Therefore, in general, thermoplastics have lower thermal stability temperatures than thermosets because the crosslinks in thermosets raise T_g and T_m. Other polymer characteristics that raise the amount of energy required to impart internal movements and, therefore, raise the maximum use temperature are higher degrees of aromatic character, hydrogen bonding, and the stiffness of the polymer backbone [2,4,5].

2.2.4 Nature of the Glassy State [1,2]

The volume-temperature relationship of a typical polymer is depicted in Figure 2.3. Upon crystallization at temperatures moderately below T_m, the specific volume of the polymer decreases significantly in comparison to that of the amorphous polymer. If crystallization is prevented, either because of irregularities in the polymer chain or because of a rapid cooling rate, the material undergoes a glass transition manifested not by a change in specific volume but by a change in the thermal expansion coefficient, α. If the enthalpy of the polymer is measured by DSC and plotted against temperature, the resulting enthalpy-temperature relationship would be very similar to the plot in Figure 5. In any first-order transition, such as melting or boiling, the volume and entropy, which are both first derivatives of the free energy, undergo a discontinuous change. In the second-order transition, the second derivatives of the free energy, such as a and heat capacity, undergo a discontinuous change. The glass transition gives the appearance of the second-order transition in this sense. The glass transition phenomenon as observed ordinarily is, however, a nonequilibrium phenomenon.

2.2.5 Factors Determining T_g.

Tg value is influenced with structural and compositional factors. The most fundamental of which are chain stiffness and interchain cohesive forces. The copolymer films (specimen) have the new structure which has some amorphous properties (polystyrene). In other words, the new material will intend to accommodate the properties of the major composition (PTFE) and the minor composition material (PS). [4,5]

Crosslinking is another structural factor which can affect Tg. Tg increases with increasing crosslink density. The average molecular weight of polymer chains also influenced the T_g value. Tg increases asymptotically, with increasing number-average molecular weight M_n, to its limiting value fo the high polymer as $M_n \rightarrow \infty$ [5].

The presence of additives, fillers, unreacted residual monomers and/or impurities, whether deliberately include in the formulation of a resin, or left over as undesirable by-products synthesis. For example, plasticisers of low molecular weight generally decrease Tg. In this research, samples preparation is done by using virgin PTFE which grafted with PS. So there are no additives in the samples under study and this factor is neglected.

Thermal history also one of the factor that can affected the value of T_g. The annealing (or "physical aging") of test specimens at elevated temperature below T_g usually result in an increase of Tg. [4,5]

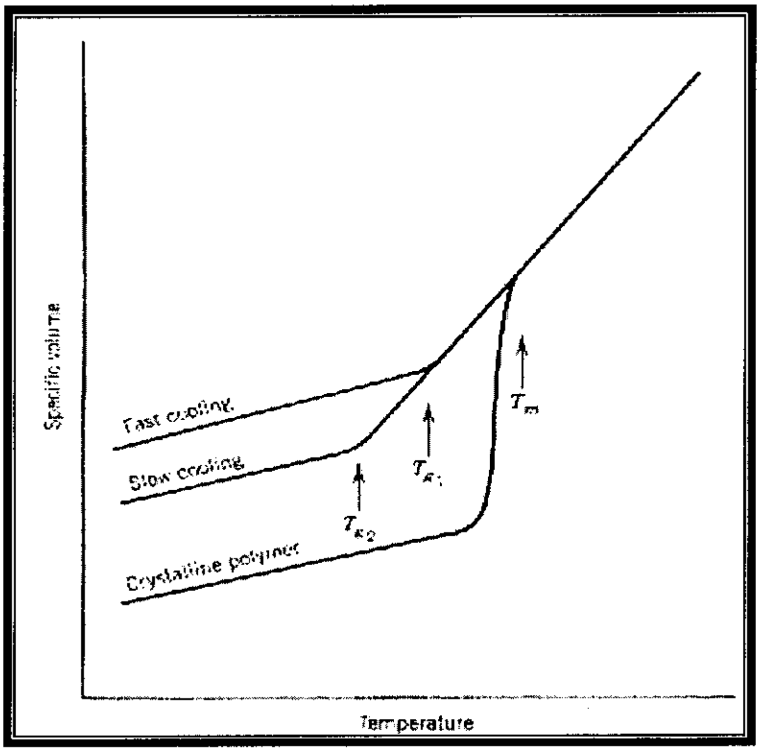


Figure 2.3: Schematic illustration of the volume-temperature relationship of a typical polymer. When the polymer is prevented from crystallization, it is brought to temperatures below T_m in an amorphous state and is then turned into a glass at the glass-transition temperature T_{g1}, or T_{g2}, which depends on the cooling rate.

Crystallinity has a big impact of T_g. The presence of the crystallites, and the interphase regions ("tie molecules") between amorphous and crystalline regions, often increases the observed value of Tg. In addition , the decrease of the amorphous fraction of the polymer naturally leads to the decrease in the strength (intensity) of its amorphous relaxations. With the decrease of strength of the glass transition at a given percent crystallinity normally being larger than the decrease in the strength of the secondary (sub-Tg) relaxations. The pressure also affects the value of T_g. Most measurements of Tg are performed under normal atmospheric pressure is very seldom considered in any details in correlations of T_g [2,4,5].

CHAPTER 3

METHODOLOGY

There are 3 tools that going to be used in this project. The tools are:

1. Differential Scanning Calorimeter (DSC)
2. Thermal Gravimetric Analyzer (TGA)
3. Fourier Transform Infrared (FTIR) Spectrometer

Differential Scanning Calorimeter (DSC) is to be used in determining Tm and Tg. Thermal Gravimetric Calorimeter (TGA) is to be used in determining heat (thermal) resistance of the films. And Fourier Transform Infrared Spectrometer (FTIR) is used to identify the composition of the material based on some inherent pattern of energy absorption

3.1 Differential Scanning Calorimeter [5,7,8]

In this project, differential scanning calorimeter (DSC) (ASTM D 3417, ASTM D 3418) is to be used in determining Tm and Tg. DSC is the dominant technique for the thermal analytical investigation of polymeric materials. It measures the difference in energy inputs into a substance and a reference material as they are subjected to a controlled temperature program. Furthermore, it is used in the determinations of heat capacity, heat of transitions, heat of reaction, and temperature of transition (eg. glass-transition temperature) for polymeric material with a quick and accurate data.

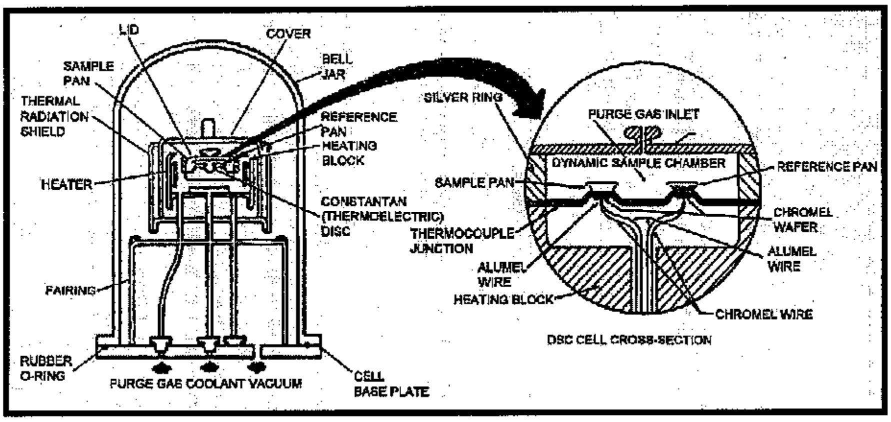


Figure 3.1: Schematic of DSC

3.1.1 Differential Scanning Calorimeter Theory

In differential scanning calorimetry (DSC), the most widely used thermal analysis technique, the heat flow rate to the sample (differential power) is measured while the temperature of the sample, in a specified atmosphere, is programmed. Because all materials have a finite heat capacity, heating or cooling a sample specimen results in a flow of heat in or out of the sample. The two most common types of commercial DSC measuring cells are shown in Figure 3.2. The heat flux DSC employs a disk containing sample and reference positions which are heated by a common furnace. The differential heat flow to the sample is proportional to the temperature difference that develops between sample and reference junctions of a thermocouple. The power compensations approach controls a temperature enclosure around the sample and reference individually. Through amplified feedback from platinum resistance thermometers, it records the differential energy flow necessary to maintain the sample on the specified temperature program.

The test procedure is simple. A small quantity of sample, usually 5-10 mg, is weighed out into an inert capsule (usually made of aluminum). The encapsulated sample is placed in the DSC sample holder or onto the sample platform of a DSC cell disk. In the attached control module or computer, the operator selects a temperature range and heating rate, or perhaps a more complex temperature program. The test is started. (A hypothetical DSC curve showing both endothermic and exothermic changes in a polymer is shown in Figure 3.3) Initially, constant energy input is required to heat the sample at a constant rate. This establishes a baseline. At a transition point, the sample requires either more or less energy depending on whether the change is endothermic or exothermic. For example, when the glass transition point is reached, the heat capacity increases. The midpoint is taken as the glass transition temperature. Adding plasticizers to a formulation lowers T_g . When a polymer reaches the melting point, it requires more energy (endothermic) to melt the crystalline structure. The area of the peak in units of energy is the enthalpy of fusion, the heat of melting. The temperature dependence of the peak and its shape give information about degree of crystallinity, the molecular-weight distribution, degree of branching, copolymer blend ratio, and or processing history. Often quality procedures involve comparing the melting profile to that of a standard "good" material.

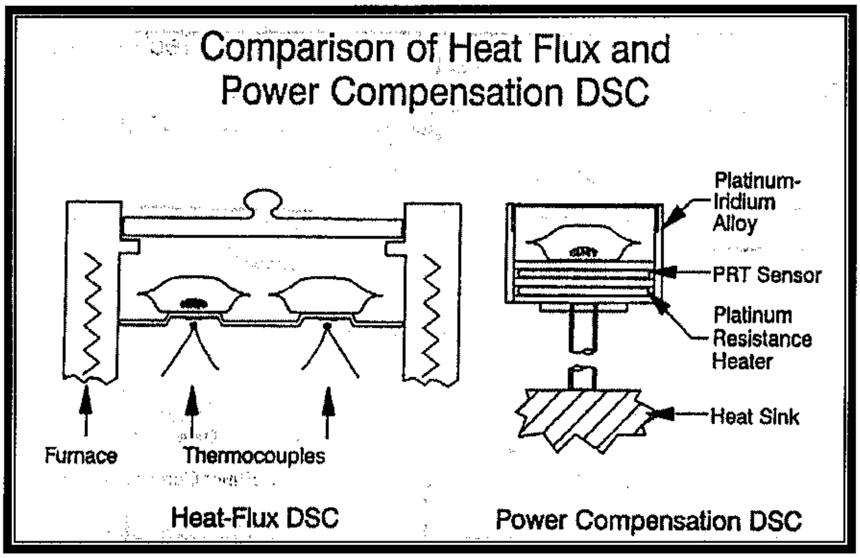


Figure 3.2: Two most common types of DSC measuring cells.(Courtesy PerkinElmer Corporation)

When a sample cures, more energy is usually released, and the change is exothermic. The area of the curing peak is proportional to the number of crosslinks that were formed. This indicates degree of cure. The shape of the curing curve can be analyzed to obtain the reaction kinetic parameters.

In this research, DSC is used in determining melting temperature (T_m), glass-transition temperature (Tg), and the heat capacities of the of the samples [5,7,8].

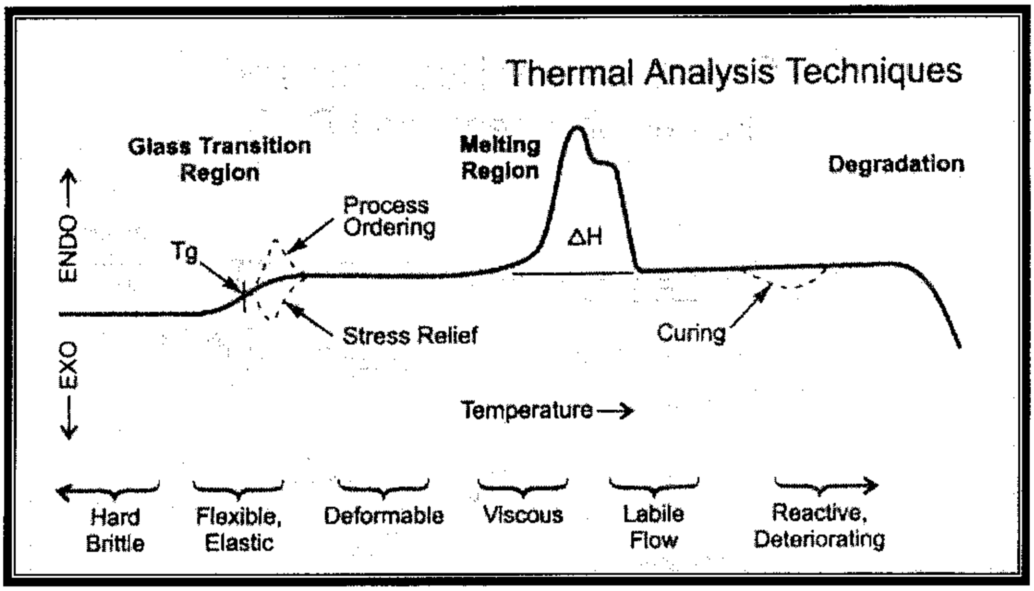


Figure 3.3: A typical DSC thermogram. (Courtesy Perkin-Elmer Corporation.)

3.2 Thermal Gravimetric Analyzer (TGA) [5,7,8]

In this experiment, TGA is used to determine the heat (thermal) resistance of the copolymer films. TGA also has been employed in measuring the rates of sorption; amounts of volatile contaminants, monomer, plasticizers, additives, etc; solubility of gases and vapours in the polymers; diffusion and permeation constant of gases and vapours through polymer matrices. Anyway, the traditional role for TGA investigation of polymers is the study of thermal degradation in vacuum and inert and active (e.g. oxygen) atmosphere. Figure 3.4 shows the schematic diagram of TGA and Figure 3.5 shows the example of output (thermograms) of TGA.

The ability of investigation of TGA is enhanced by or combined with techniques that measures change in functional groups and volatile products. For example, TGA is run in tandem with Fourier Transform Infrared Spectroscopy (FTIR).

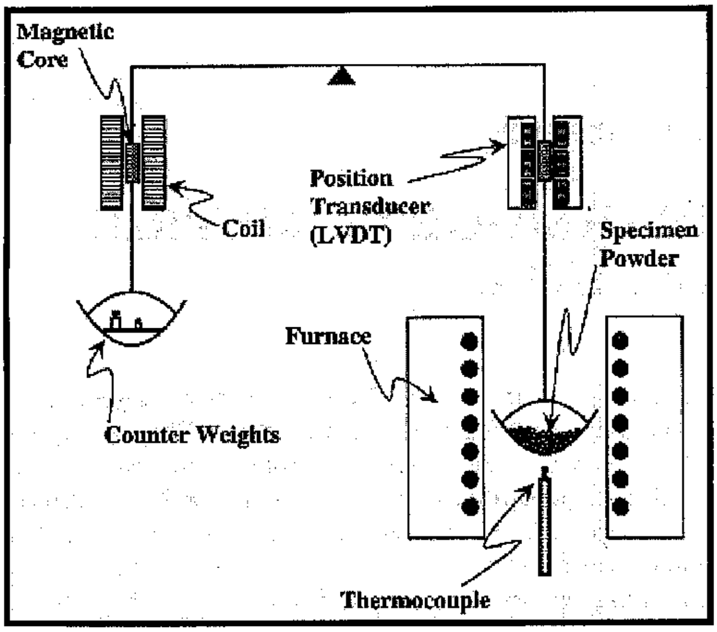


Figure 3.4: Schematic of TGA

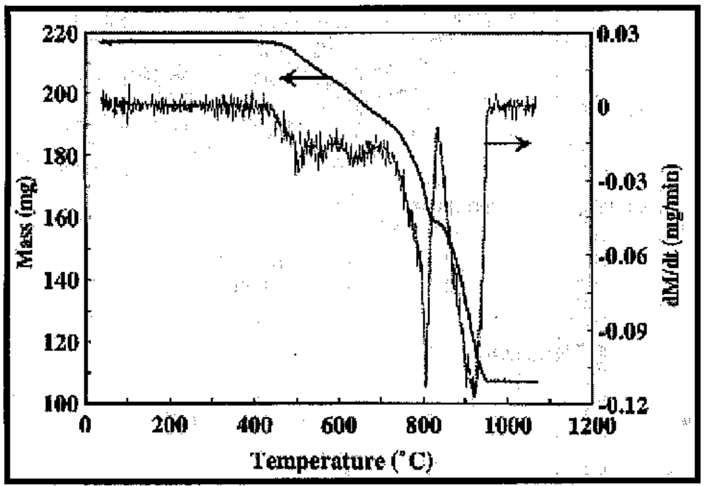


Figure 3.5: Example output of TGA

3.2.1 Thermogravimetric Analysis (TGA) Theory

Thermogravimetric analysis (TGA) is a test procedure in which changes in the weight of a specimen is monitored as the specimen is progressively heated. The sample weight is continuously monitored as the temperature is increased either at a constant rate or through a series of steps. The components of a polymer or elastomer formulation volatilize or decompose at different temperatures. This leads to a series of weight-loss steps that allow the components to be quantitatively measured. A typical high-performance apparatus consists of an analytical balance supporting a

3.3 Fourier Transform Infrared Spectroscopy (FTIR) [5,7,8,14]

Infrared spectroscopy has been one of the most widely used material analysis techniques for over 70 years. Fourier Transform Infrared Spectrometer (FTIR) is used to identify the composition of the material based on some inherent pattern of energy absorption. In this method, sample is exposed to infrared light through or reflected off the sample. The transmitted or reflected light of the sample is compared with the nondisturbed light to view the various absorptions. These absorptions correspond to internal molecular motions of the polymer. The motions are the characteristic of a polymer type and by comparing the spectrum obtained for a sample with a library of spectra obtained from many different materials; the sample can be identified. The model of equipment used is PerkinElmer Spectrum FTIR.

3.3.1 Fourier Transform Infrared Spectroscopy Theory

An infrared spectrum represents a fingerprint of a sample with absorp tion peaks that correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. This fact allows a positive identification of polymeric materials. By studying the size of the peaks in the spectrum, one can also determine the amount of material present.

A newly developed technique called Fourier transform infrared (FTIR) spectrometry overcomes the limitations encountered with the traditional infrared technique. The original infrared instruments were of dispersive type, which separated the individual frequencies of energy emitted from infrared source using a prism or grating. These instruments measured each frequency individually, making the entire process painfully slow. Modern FTIR instruments can process as many as 100 samples per day compared to only 2 to 4 samples per day. FTIR spectroscopy is fast, precise, and simple, requiring a very small amount of sample for a successful amalysis. In FTIR spectroscopy, infra red radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents molecular absorption and transmission, creating a molecular fingerprint of the sample. Figure 3.7 graphically illustrates this process.

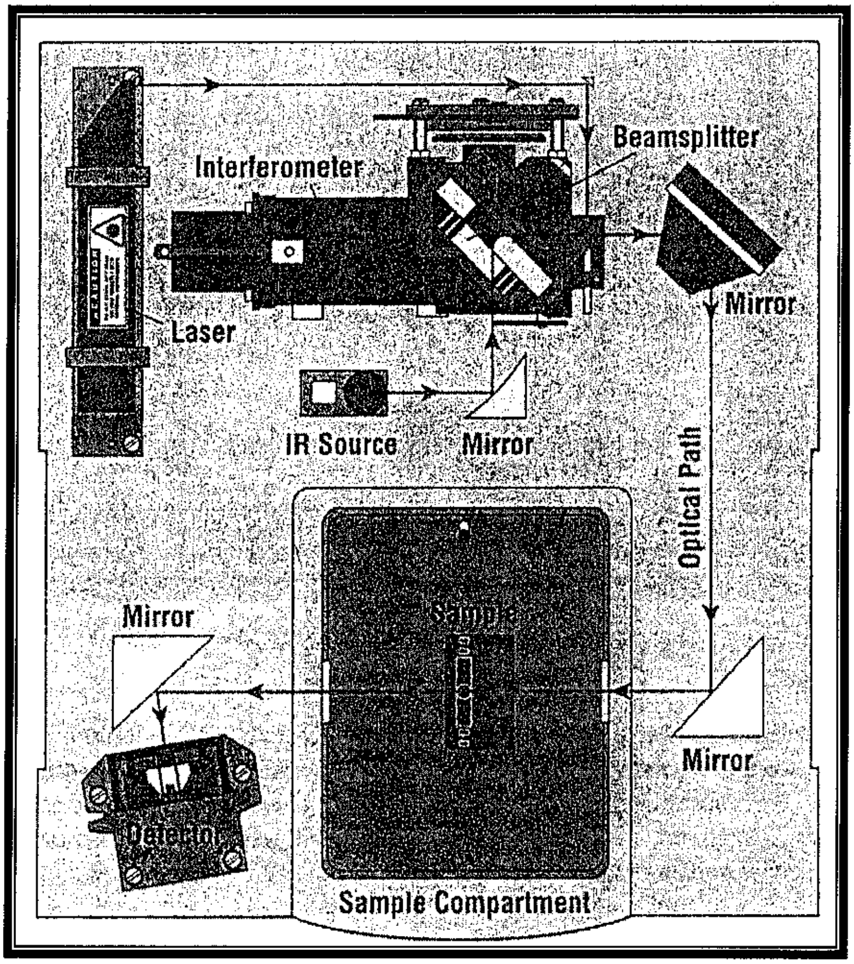


Figure 3.7: Sample spectrometer layout. (Courtesy Nicolet Instruments.)

The sample analysis process is quite simple using a modern spectrometer coupled with a powerful computer. Infrared energy is emitted from a glowing black-body source. This beam passes through an interferometer where the "spectral encoding" takes place. The re sulting interferogram signal then exits the interfermeter. Next, the beam enters the sample compartment where it is transmitted though or reflected off the surface of the sample. This is where the specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed. The beam finally passes through a detector and the signal is sent to computer where a mathematical technique called the Fourier transformation takes place. The infrared spectrum is displaced on the CRT for analysis and interpretation.

The computer is equipped with a collection of thousands of known polymer and additive FTIR spectra for easy comparison and identification. A spectral library search can identify a polymer, additive, or contaminant within minutes, making the entire process fast and efficient. Figures 13 illustrate the entire FTIR process and a commercially available FTIR instrument. The example of output (spectra) of FTIR is shown in Figure 3.8 [5,7,8,14]

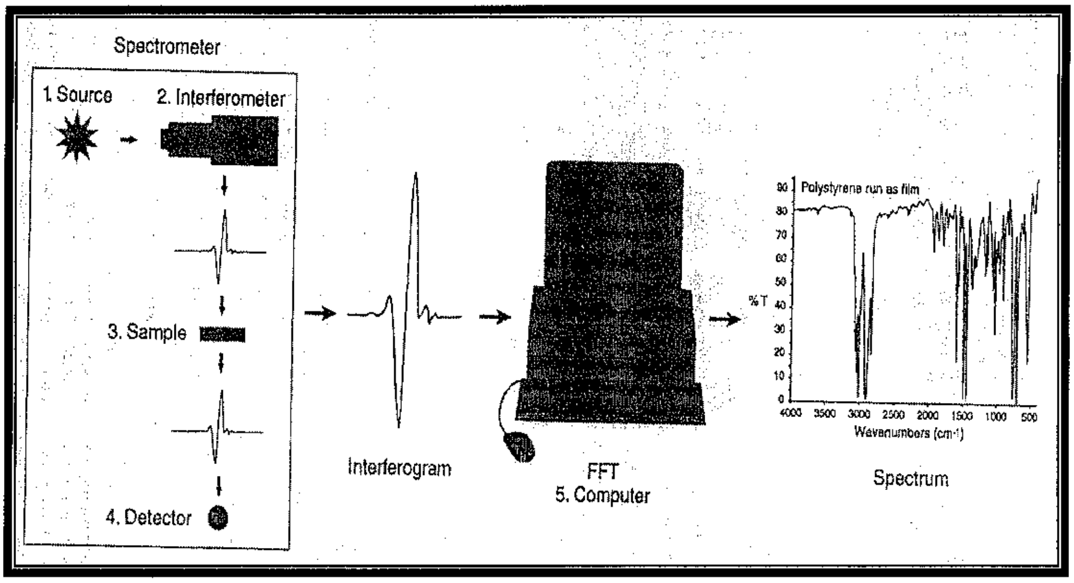


Figure 3.8 Sample analysis process. (Courtesy Nicolet Instruments.)

3.4 Experimental

3.4.1 Membrane preparation [12]

As has been mention earlier, PTFE grafted Polystyrene films were prepared using radiation-induced grafting technique, styrene (Fluka, purity of > 99%) was grafted onto commercial PTFE film (Porghof, USA) using simultaneous irradiation technique [12]. The grafting mixture hosted in tightly sealed and nitrogen flushed glass ampoule was irradiated using γ-rays from a ^{60}Co source (located at Malaysia Institute for Nuclear Technology Research) under nitrogen atmosphere and at room temperature [12]. The grafted films were thoroughly washed with toluene and dried under vacuum few times until a constant weight was obtained [12]. The degree of grafting was determined as the weight gain according to the following equation 1:

$$\text{Degree of grafting [21] (\%)} = \frac{W_g - W_0}{W_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where, W_g *and* W_0 are the weights of grafted and original PTFE films, respectively.

In this experiment, the degree of grafting is assumed to be the same as the percentage (%) reduction of mass of the first order according to the TGA thermograms. This is because, the radiation-induced grafting technique is proven to give stability of a blend of two or more polymers (section 1.6).

3.4.2 Differential Scanning Calorimetry Analysis

Thermograms of membrane samples having various degrees of grafting (5-36%) were measured by DSC (model Perkin-Elmer Pyris-1 DSC). Original and grafted PTFE films were used as reference materials. Typical membrane samples of weight ranging from 5 to 10 mg were used. Thermograms were obtained in a temperature range of 50-100°C at a constant heating rate of 20 min^{-1} and under nitrogen atmosphere.

3.4.2.1 Calculations of the degree of crystallinity [12,14]

The overall degree of crystallinity of the samples was calculated using Eq. (2).

$$X_c\ [14] = H_m/H_{m100} \times 100 \ldots\ldots\ldots\ldots (2)$$

where, H_m is the heat of melting of PTFE and H_{m100} is the heat of melting of 100% crystalline PTFE polymer which equal 92.9 J/g [12].

Since the incorporated polystyrene has an amorphous nature, the crystallinitiy in the grafted films and the final sulfonated membranes is always referred to the fraction of PTFE matrix [12]. The weight fraction of PTFE in grafted films (W_{PTFE}) is obtained using Eq. (3):

$$W_{PTFE}\ [21] = m_{PTFE}/(m_{PTFE}+m_{PS}) \ldots\ldots\ldots (3)$$

where, m_{PTFE} is the weight of PTFE and m_{PS} is the weight of the grafted polystyrene. Using Eq. (2), the degree of crystallinity of PTFE fraction in the grafted PTFE film is calculated as follows [12]:

$$(X_C)_{grafted}\ [12] = H_{mgrafted}/H_{m100}\ X\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

3.4.3 Thermal Gravimetric Analysis

In this project, about 10 mg-20 mg weight of each specimen is used for TGA measurements. The thermograms will be obtained in the temperature range of 50°C-700°C. The heating runs will be made at a constant heating rate of 30°C/min under nitrogen atmosphere [5,8,9]. The model of equipment used in this experiment is PerkinElmer Pyris 1 TGA.

As has been mention earlier, from the results (TGA thermograms) the degree of grafting is assumed to as the same as the first order mass reduction of the samples.

3.4.4 Fourier Transform Infrared Spectrometer Analysis

The chemical structure of the original and the grafted PTFE films were determined using a PerkinElmer Spectrum FTIR Spectroscopy equipped with an Attenuated Total Reflectance (ATR) accessory having a KRS5 crystal with face angle of 45 degree. The FTIR spectra (results) are determine by using PerkinElmer Spectrum FTIR Spectroscopy software which presented in percentage (%) of transmittance versus wavelength (cm^{-1}).

CHAPTER 4

EXPERIMENTAL RESULT AND ANALYSIS

4.1 Experimental Results

4.1.1 Fourier Transform Infrared Spectroscopy Result

Figure 4.1 (next page) shows the spectra of virgin PTFE (top) and spectra of sample 2. Other results, for sample 1, sample 2, sample 3, sample 4 and sample 5 were presented in Appendices section (Appendix 1-6). The absorption bands were refered to infrared correlation tables which could be refered to Apendix 7.

4.1.2 Thermal Gravimetric Analyzer Result

Table 4.1: Result for TGA

Sample	Curve shape	Mass reduction (%)	Degree of grafting (%)
Virgin PTFE	1-step	0	0
Sample 1	2-step	4.37	4
Sample 2	2-step	12.60	13
Sample 3	2-step	13.67	14
Sample 4	2-step	26.83	27
Sample 5	2-step	13.59	14

Figure 4.2 (next page) shows the TGA thermograms for all samples presented in one graph. Other results, for virgin PTFE, sample 1, sample 2, sample 3, sample 4 and sample 5 were presented in Appendices section (Appendix 8-13).

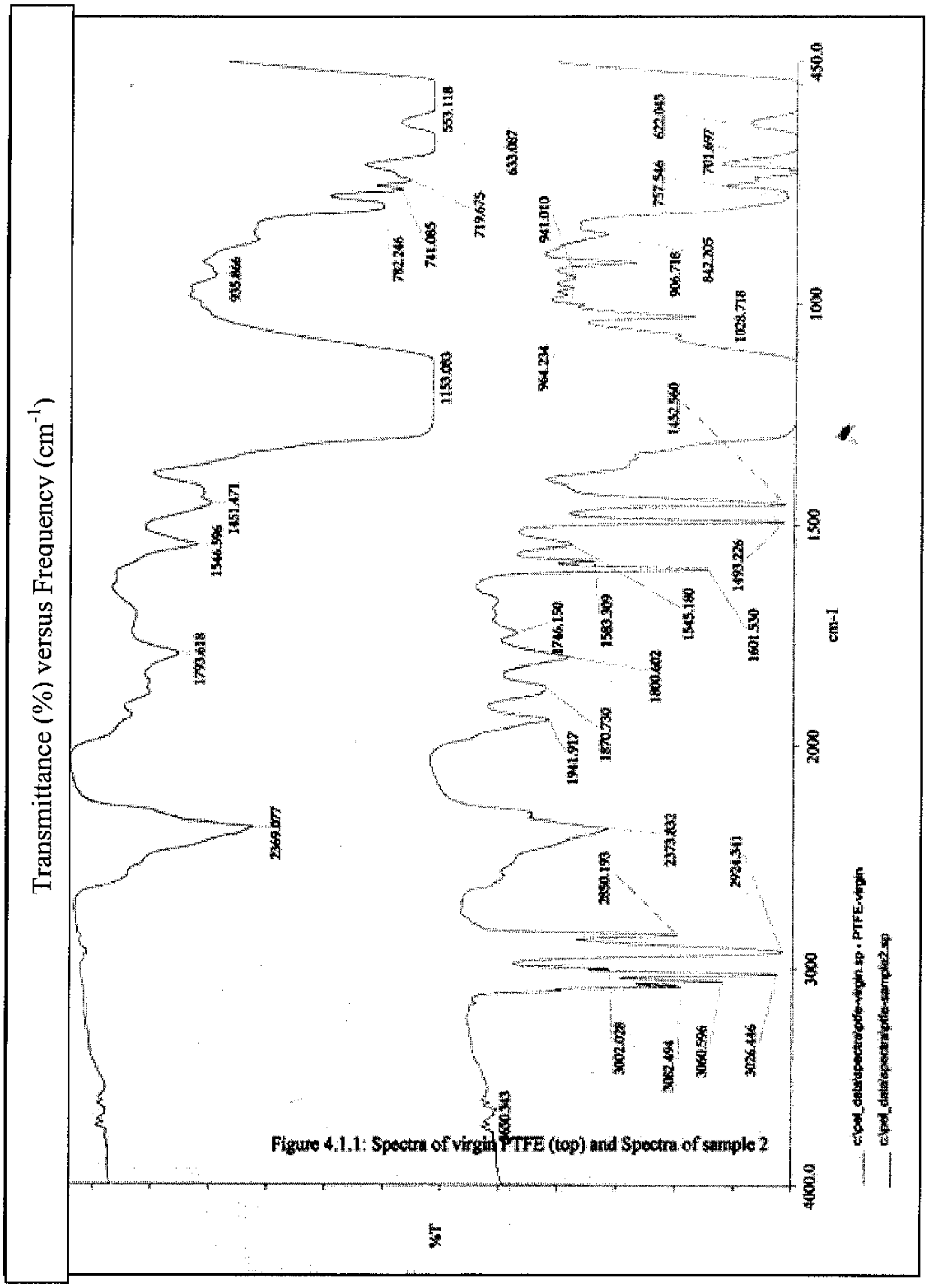


Figure 4.1: Spectra of virgin PTFE (top) and Spectra of sample 2

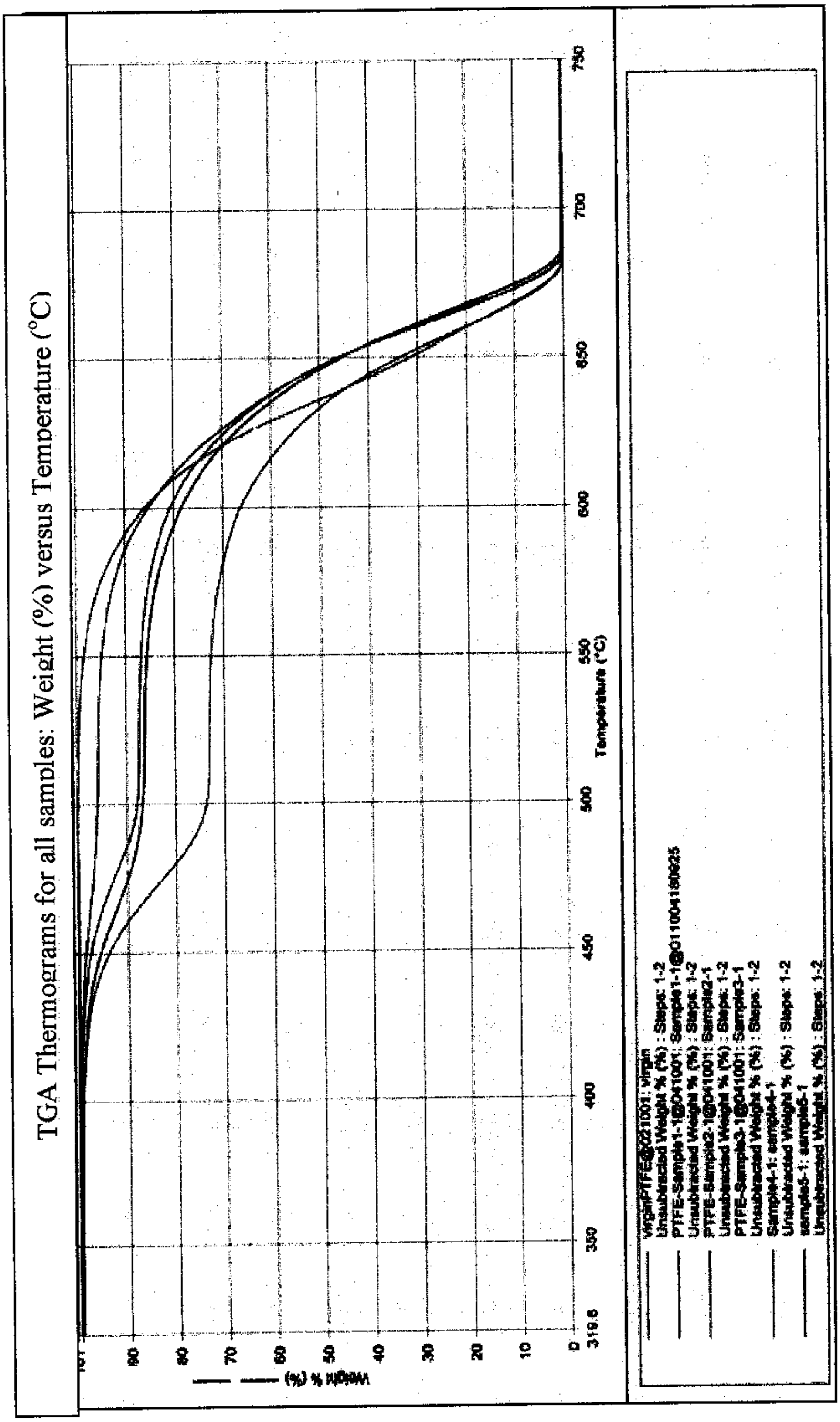


Figure 4.2: TGA thermograms for all samples

4.1.3 Differential Scanning Calorimetry Result

Table 4.2: DSC Result

Sample	**T_g (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**Degree of Crystallinity $(X_C)_{grafted}$ (%)**
Virgin PTFE	163.33	331.82	38.54	41.49
Sample 1	119.52	334.26	40.00	43.05
Sample 2	114.04	346.72	21.89	23.56
Sample 3	113.22	346.97	26.89	28.95
Sample 4	113.61	348.43	14.52	15.63
Sample 5	113.07	347.23	27.37	29.46

Figure 4.3 (next page) shows the DSC thermograms for all samples presented in one graph. Other results for virgin PTFE, sample 1, sample 2, sample 3, sample 4 and sample 5 were presented in Appendices section (Appendix 14-19).

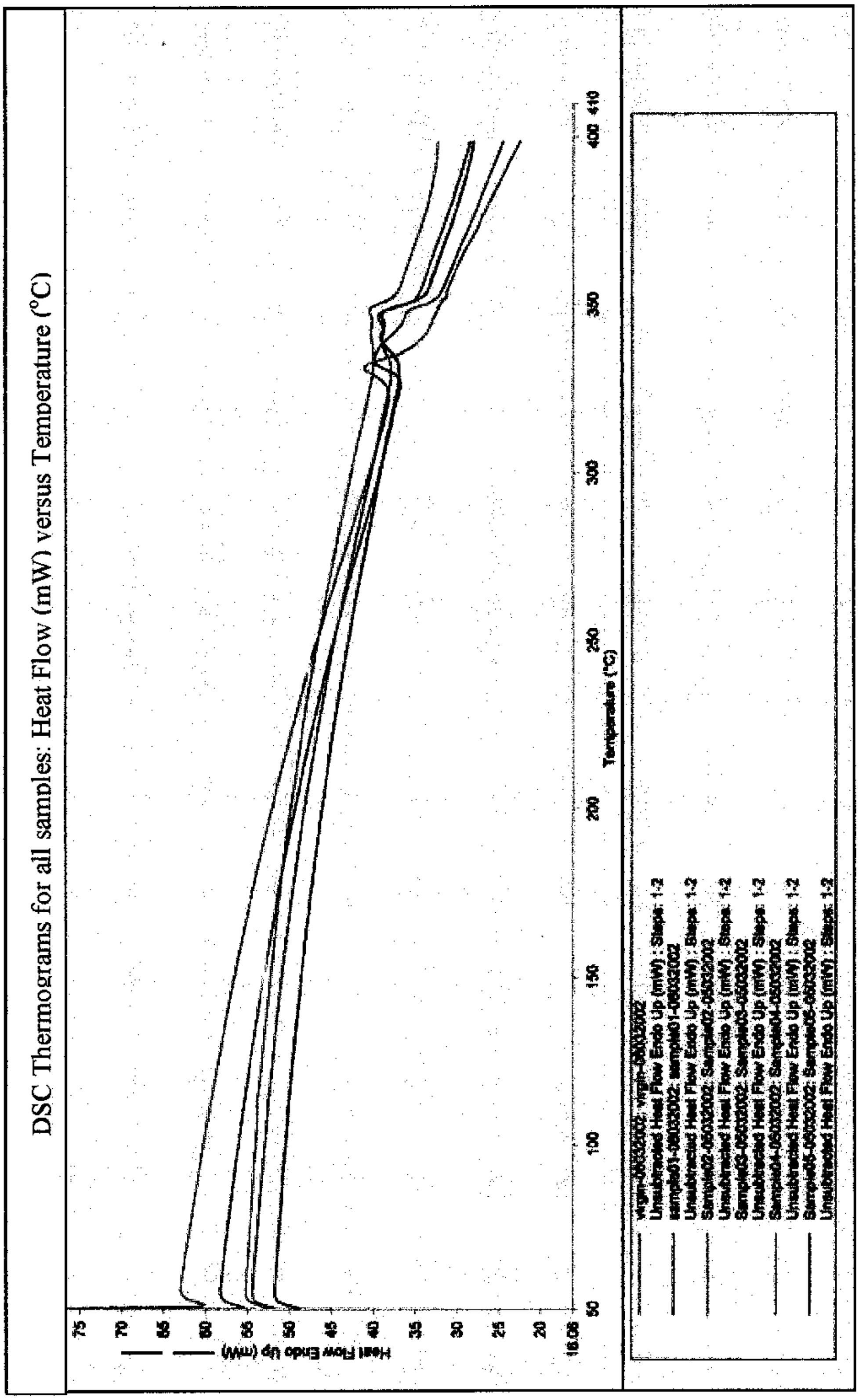


Figure 4.3: DSC thermograms for all samples

4.2 Analysis

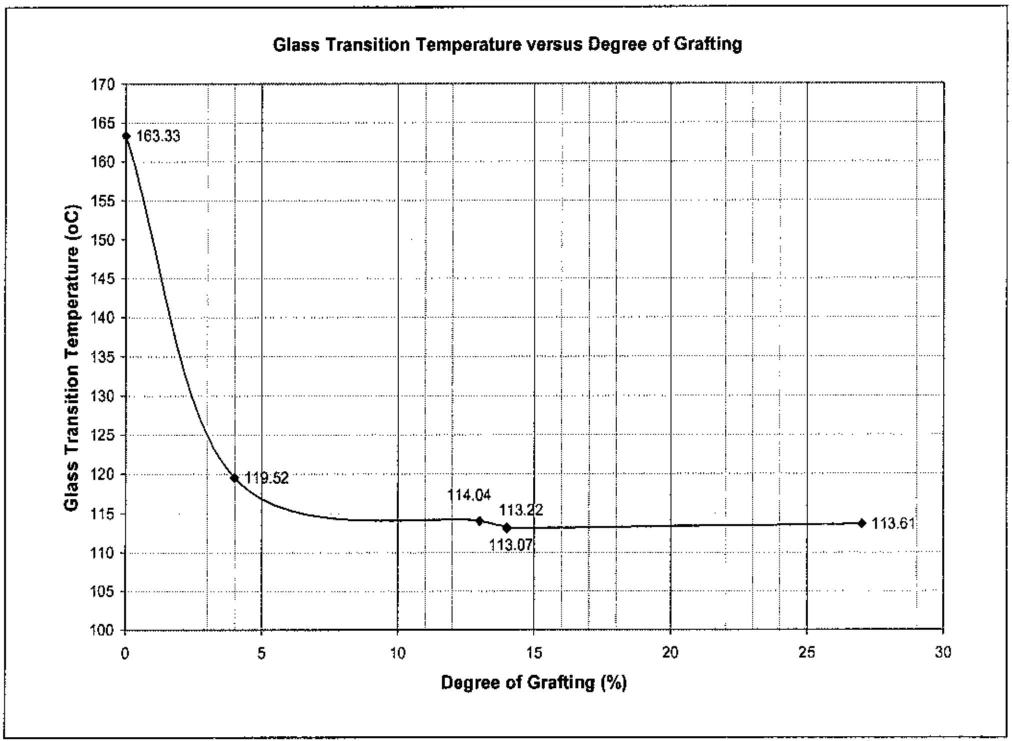


Figure 4.4: The relationship between glass transition temperature (^{o}C) and the degree of grafting (%)

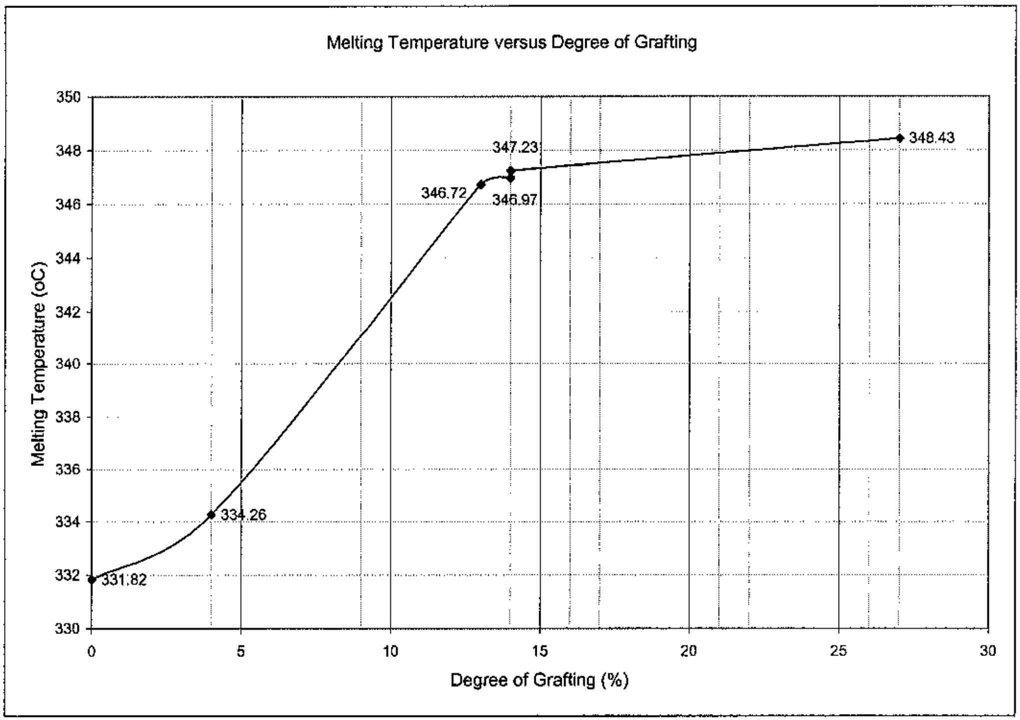


Figure 4.5: The relationship between melting temperature (^{o}C) and the degree of grafting (%).

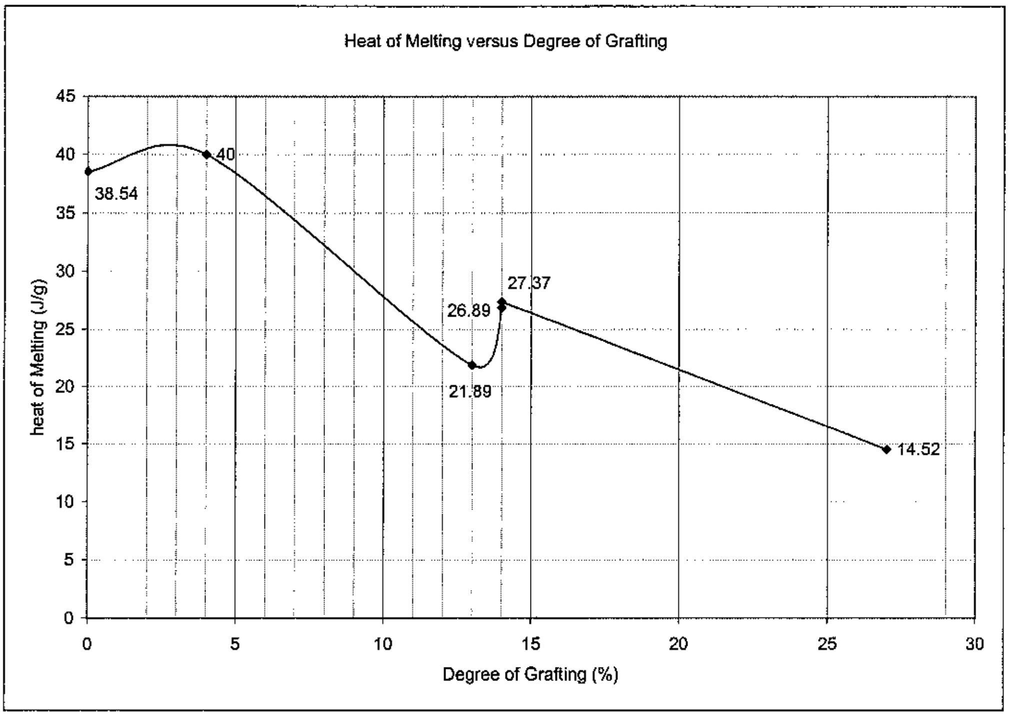


Figure 4.6: The relationship between heat of melting (J/g) and the degree of grafting (%)

From the tables and the graphs plotted, it shows that sample 3 and sample 5 have the same degree of grafting. The value of Tg, Tm, ΔH_m and $(X_C)_{grafted}$ for these samples are almost the same. There are only marginally differences of these values and they are acceptable.

CHAPTER 5

DISCUSSIONS

5.1 Characteristic of the Grafted Films

Typical FTIR-ATR spectra of original and grafted PTFE films having various degrees of grafting are shown in Apepndix 1 to Appendix 6. The characteristics bands at 1150-1250 cm^{-1} are assigned for stretching vibration of the CF_2 groups present in the original PTFE film. The presence of the benzene rings of polystyrene grafts is established by the =C-H stretching vibration at 3050 cm^{-1} and the skeletal C=C in-plane and stretching vibrations at 1500 cm^{-1} and 1600 cm^{-1}, respectively. The mono-substitution of the benzene ring is confirmed by the aromatic out-of-plane C-H deformation band at 860 cm^{-1}, C-H out-of-plane bending overtone and the combination band patterns in the 1660-2000 cm^{-1} region.

The transmittance bands at 2800-2900 cm^{-1} and 2900-3000 cm^{-1} are assigned to symmetric and asymmetric stretching of aliphatic CH_2 groups, respectively. It is clear that the features of the spectra of the grafted films confirm the successful grafting of styrene onto the PTFE backbone.

The variation in the intensity of polystyrene characteristic bands manifest the difference in the degrees of grafting.

5.2 Thermal Stability of the Grafted Films

Radiation grafting of styrene onto PTFE film resulted in PTFE-g-polystyrene membranes having a degree of grafting ranging from 5% to 36%. A generalized structure of a PTFE-g-polystyrene film is given in Fig.5.1.

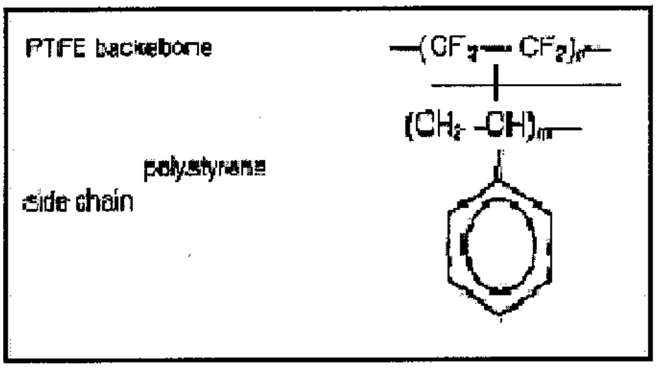


Figure 5.1: A generalized molecular structure of PTFE-g-styrene membrane: (a) PTFE main chain and (b) polystyrene graft.

The effect of grafting of polystyrene onto PTFE membrane on the thermal stability of the PTFE matrix is studied. Fig. 4.1 shows TGA thermograms of original film and all samples of PTFE-g-polystyrene having a degree of grafting of between 5% to 36%. It is found that the fluorinated-structure of the PTFE matrix has a thermal stability up to ~550°C followed by one-step degradation as depicted from thermogram Fig. 4.2A. Grafting of styrene, which led to the formation of polystyrene grafts in PTFE matrix introduces a two-step degradation pattern. All grafted film components show two distinct degradation temperatures as depicted in Fig. 4.2B to 4.2F. The polystyrene grafts start to degrade at ~400°C and continue until ~480°C.

This is followed by the degradation of PTFE backbone, which starts at ~550°C, The polystyrene grafts that have pure hydrocarbon structure seem to be incompatible with the fluorocarbon structure of the PTFE matrix. Therefore, phase separated microdomains were formed in PTFE-g-polystyrene film. In the second step the degradation begins at ~550°C and continues to ~680°C.

5.3 Effect of Grafting T_m,T_g and ΔH_m.

Appendix 14 to 19 show typical DSC thermograms of the original PTFE and grafted PTFE (sample 1 to sample 5) which the grafting is varied from 5-36%. The effect of grafting on T_m,T_g and ΔH_m of PTFE film is presented in Table 4.2.

Styrene was radiochemically grafted onto PTFE films leading to the formation of polystyrene grafted PTFE films. The grafted films were found to be very stiff compared to the original PTFE film. A closer look on the effect of grafting on thermal characteristics such as glass transition (T_g) and melting (T_m) temperatures could be obtained form the DSC thermograms.(Appendix 14-19)

Figure 4.3 shows typical DSC thermograms of original PTFE and sanple 1 to sample 5 of grafted PTFE film. The deviation of the melting temperature (T_m) and the glass transition temperature (T_g) with grafting is simplified in Table 4.2. As can be seen from Appendix 14, the original PTFE film shows a small transition at 163.3°C, which can be assigned for T_g and a strong transition (endothermic peak) at 331.8°C representing T_m. The high value of T_g compared to that reported in literature (>20°C) indicates that commercial PTFE film contains certain additive (filler such as glass fibres) that decreases the polymer chain mobility and gives rise to Tg [11]. The incorporation of polystyrene side chain grafts into PTFE film caused a shift in the T_g of the grafted film to higher temperature (119.5°C) while no significant change took place in Tm (334.3°C) as depicted from Appendix 15. T_m is referring to the melting point of the original PTFE film and the main melting peak in both thermograms (Appendix 14 and 15). It can be noticed that the melting endotherm peak took the shape of bimodal (two melting peaks) in the thermograms of both grafted PTFE.

The effect of grafting on the heat of melting and degree of crystallinity of PTFE film is presented in Table 4.2. The heat of melting (H_m) was calculated from the area under the melting endotherms. Whereas, the degree of cystallinity of original (X_c), and only grafted PTFE ($(X_C)_{grafted}$) were calculated using Eqs. (2) and (4) respectively. Grafting of styrene were found to reduce the heat of melting and the degree of crystallinity of PTFE films. H_m declined from 38.54 (J/g) in the original PTFE film to 27.37-14.52 (J/g) upon grafting. In addition, the degree of crystallinity decreased from 41.49% in the original PTFE film to 43.05-15.63% in the grafted films. This indicates that there is a strong possibility for transition to more disordered material under the influence of grafting [11]. Moreover, this implies a considerable decrease in the melting temperature. However, there are changes found to take place in T_m upon grafting ,which the T_m increase between 2°C to 17°C. In term of percentage, the increament is between 6% to 54%. Since any change in T_m is a sign of crystallite defects [11], it can be recommended that grafting bring significant damage to the original crystalline structure.

In addition, from Table 4.1, the value of the degree of ghrafting of sample 3 and sample 5 is the same. Moreover the value of Tg, Tm, ΔH_m and $(X_C)_{grafted}$ for these samples are almost the same. There are only marginally differences of these values and they are acceptable.

From the results and analysis, although PTFE is well known as a highly crystalline polymer, but the degree of crystallinity observed in commercial PTFE films used in this work is found to be low compared to that reported for virgin PTFE resin (92-98%) in literature [11]. The high crystallinity of the virgin PTFE is due to the high strength of interatomic bonds between carbon and fluorine atoms and the nonpolarity. While the low degree of crystallinity of the commercial PTFE film used in this study is perhaps due to the presence of fillers such as glass or asbestos fibers, which are being added to enhance the mechanical properties of PTFE [10,11]. Moreover, low degree of crystallintiy may be also resulted from fast cooling during film processing [10,11]. Therefore, it can be reasonably suggested that PTFE film used in this study is rather semicrystalline [10,11].

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Polystyrene grafted films prepared by radiation-induced grafting of styrene onto PTFE films were found to undergo considerable structural changes. The degree of crystallinity decreased upon grafted as well as deviation of the degree of grafting. The changes in melting temperature (T_m) was found to be insignificant regardless of the degree of grafting unlike glass transition temperature (T_g), which showed an increasing trend with the degree of grafting. The decrease in crystallinity was mainly due to the effect of dilution on the original crystalline structure by incorporation of the amorphous polystyrene grafts

Based on the results and discussion and those on the original and grafted films is that the PTFE film surface undergoes structural changes in terms of chemical composition as a result of styrene grafting.

It is clear that the features of the spectra of the grafted films confirm the successful grafting of styrene onto the PTFE backbone. The variation in the intensity of polystyrene characteristic bands manifest the difference in the degrees of grafting.

The effect of grafting of polystyrene onto PTFE membrane on the thermal stability of the PTFE matrix is studied. It is found that the fluorinated-structure of the PTFE matrix has a thermal stability up to ~550°C followed by one-step degradation as depicted from thermogram Fig. 4.1A. Grafting of styrene, which led to the formation of polystyrene grafts in PTFE matrix introduces a two-step degradation pattern. All grafted film components show two distinct degradation temperatures as depicted in

Fig. 4.1.2B to 4.1.2F. The polystyrene grafts start to degrade at ~400°C and continue until ~480°C. This is followed by the degradation of PTFE backbone, which starts at ~550°C and continues to ~680°C.

Styrene, which radiochemically grafted onto PTFE films leading to the formation of polystyrene grafted PTFE films. The grafted films were found to be very stiff compared to the original PTFE film.

From DSC thermograms, the original PTFE film shows a small transition at 163.3°C, which can be assigned for T_g and a strong transition (endothermic peak) at 331.8°C representing T_m. The high value of T_g compared to that reported in literature (>20°C) [10,11], thus indicates that commercial PTFE film contains certain additive (filler such as glass fibres) that decreases the polymer chain mobility and gives rise to Tg. The incorporation of polystyrene side chain grafts into PTFE film caused a shift in the T_g of the grafted film to higher temperature while there are significant changes took place in T_m. The T_m of the grafted film increased between 2% to 54% from the original PTFE films.

The effect of grafting on the heat of melting and degree of crystallinity of PTFE film is presented in Table 4.2. Grafting of styrene were found to reduce the heat of melting and the degree of crystallinity of PTFE films. H_m declined from 38.54 (J/g) in the original PTFE film to 27.37-14.52 (J/g) upon grafting. In addition, the degree of crystallinity decreased from 41.49% in the original PTFE film to 43.05-15.63% in the grafted films. This indicates that there is a strong possibility for transition to more disordered material under the influence of grafting. Moreover, this implies a considerable decrease in the melting temperature. However, only insignificant changes were found to take place in T_m upon grafting. Since any change in T_m is a sign of crystallite defects,it could be recommended that grafting do not bring any significant damage to the original crystalline structure.

From the results and analysis, although PTFE is well known as a highly crystalline polymer, but the degree of crystallinity observed in commercial PTFE films used in this work is found to be low compared to that reported for virgin PTFE resin (92-98%) in literature. The high crystallinity of the virgin PTFE is due to the high strength of interatomic bonds between carbon and fluorine atoms and the nonpolarity. While the low degree of crystallinity of the commercial PTFE film used in this study is perhaps due to the presence of fillers such as glass or asbestos fibers, which are being added to enhance the mechanical properties of PTFE. Moreover, low degree of crystallintiy may be also resulted from fast cooling during film processing. Therefore, it can be reasonably suggested that PTFE film used in this study is relatively semicrystalline.

6.2 Recommendations

1. The chemical structure and the crystallinity of the grafted PTFE films were studied by means of Fourier transform infrared (FTIR). It is an advantage and more accurate if the research were also using electron spectroscopy for chemical analysis (ESCA) and X-ray diffractometry (XRD) to study the chemical structure and the crystallinity of the grafted PTFE films [11,12,13].

2. The thermal stability was investigated in correlation with the film preparation procedure, grafting by using TGA. In order to understand and discover further about the thermal stability, surface analysis of the films were recommended to be studied and the equipment suggested is electron spectroscopy for chemical analysis ESCA [11,12,13].

3. From the results of DSC (appendix 14-19), the results for T_g are not so accurate and visible from the thermograms because, usually it is hard to get the T_g easily. So, it is recommended that, in the experiments, the heating rate which was set at 20°C/min be decreased to 10°C/min.

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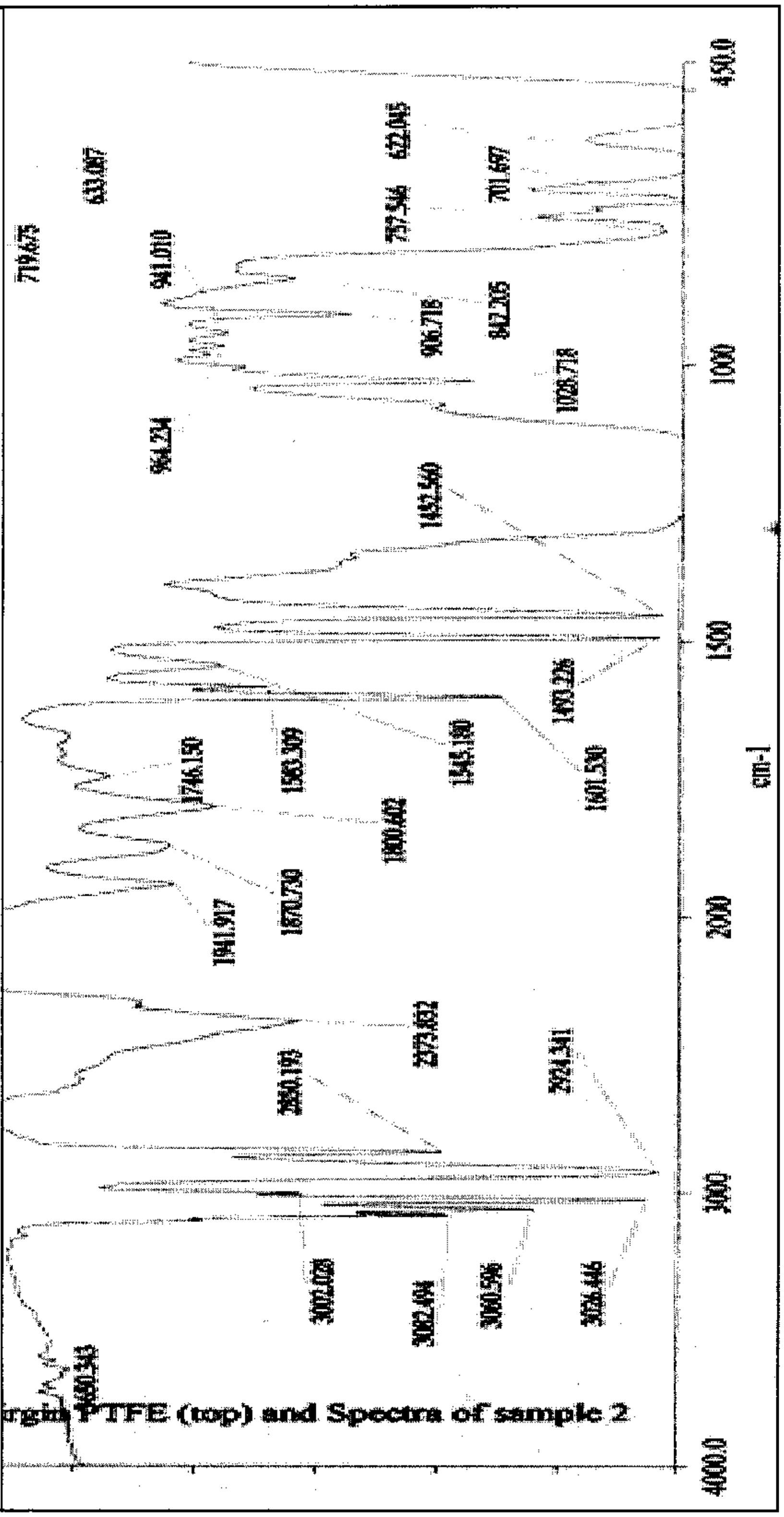
APPENDICES

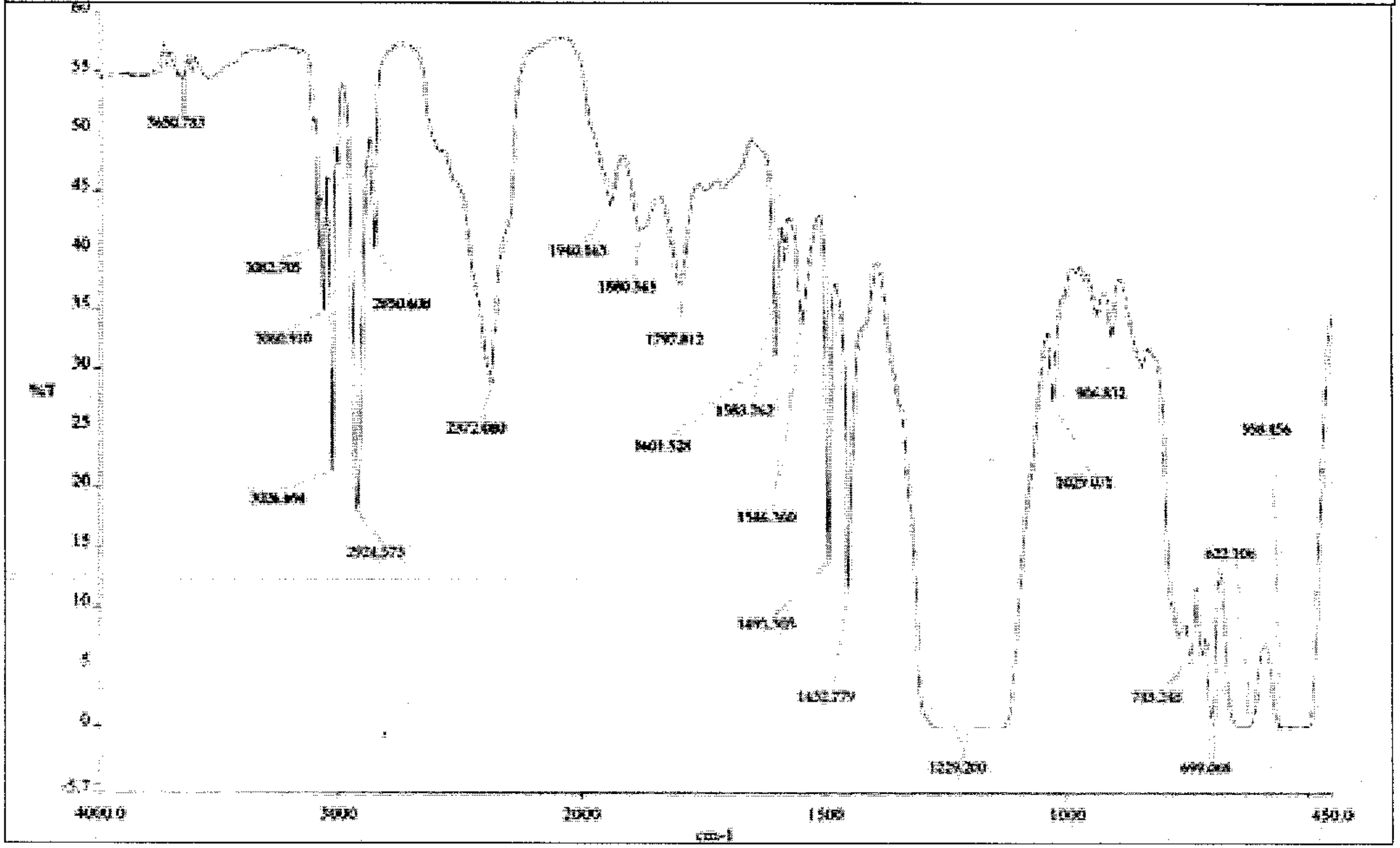
Appendix 1: Spectra of virgin PTFE

FTIR Spectra for Virgin PTFE: Transmittance (%) versus Frequency (cm^{-1})

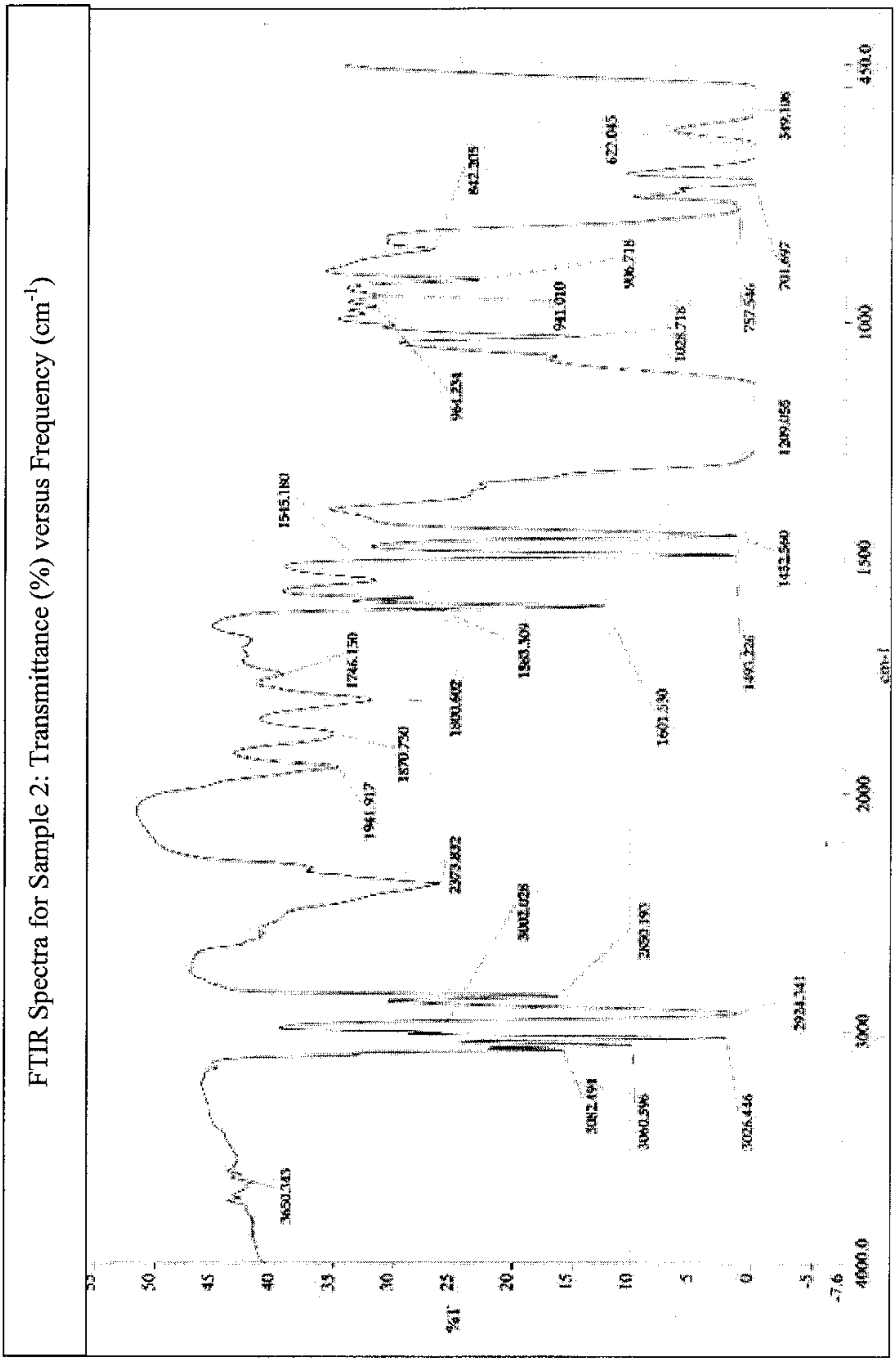


Appendix 2: Spectra of sample 1

FTIR Spectra for Sample 1: Transmittance (%) versus Frequency (cm^{-1})

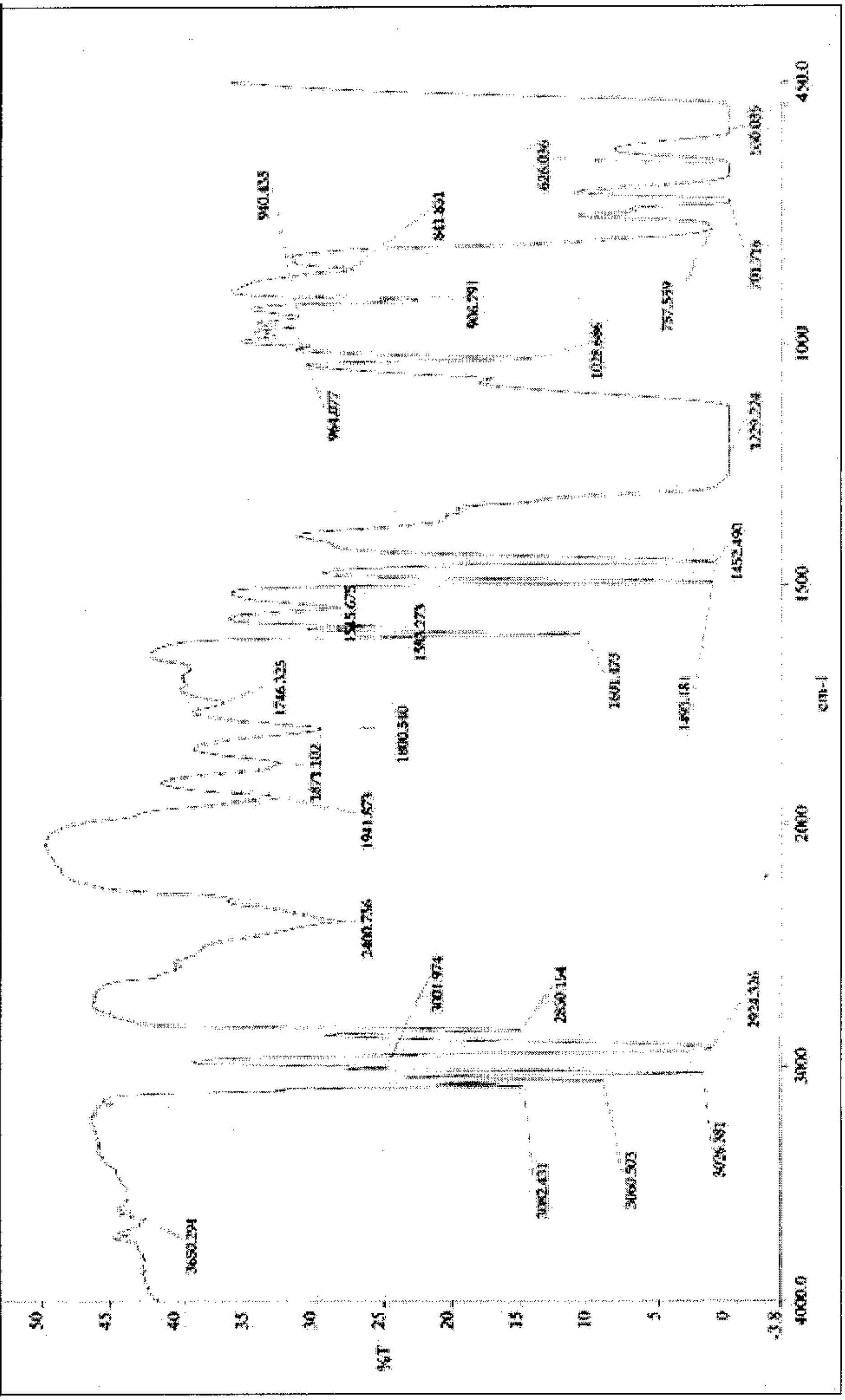


Appendix 3: Spectra of sample 2

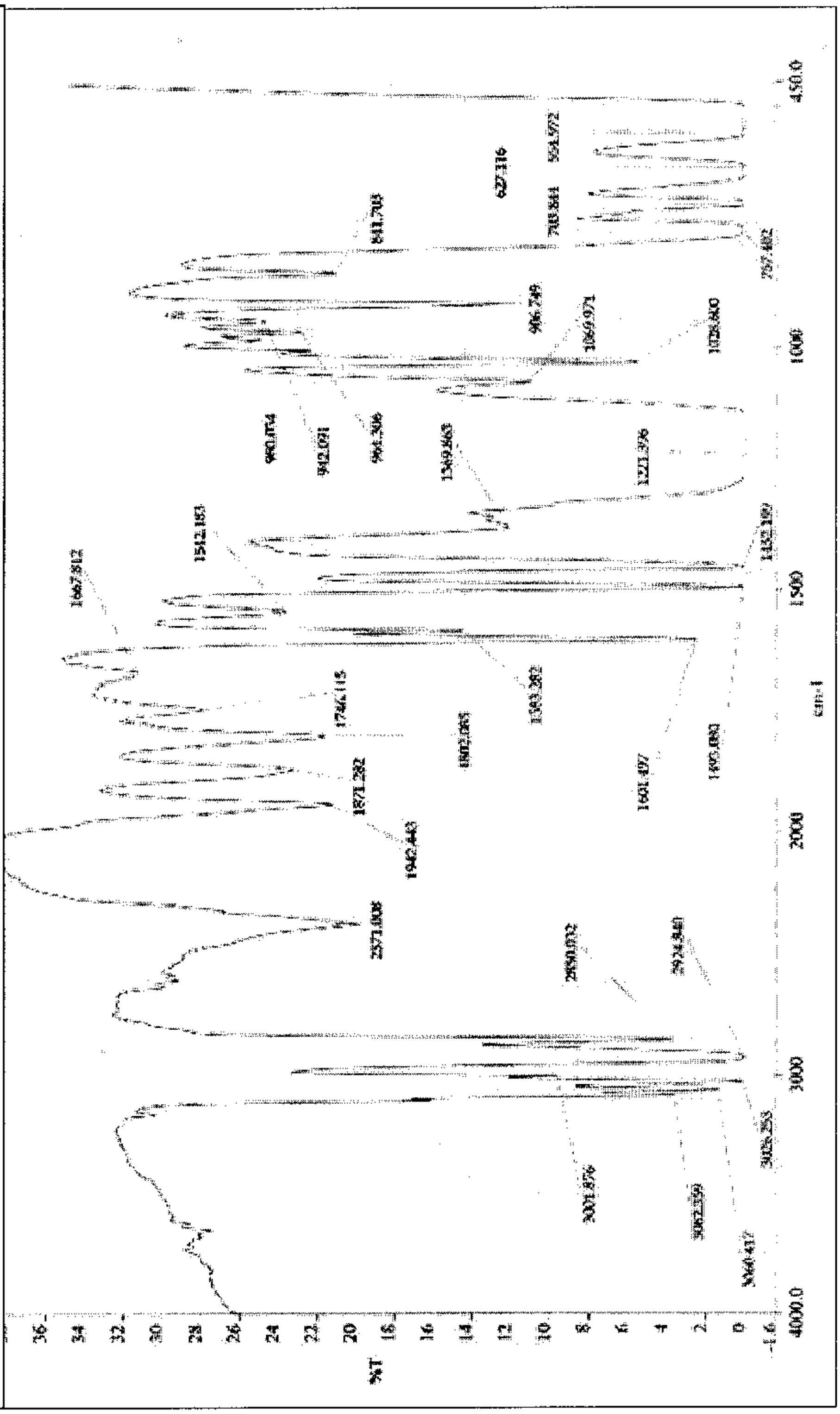


Appendix 4: Spectra of sample 3

FTIR Spectra for Sample 3: Transmittance (%) versus Frequency (cm^{-1})



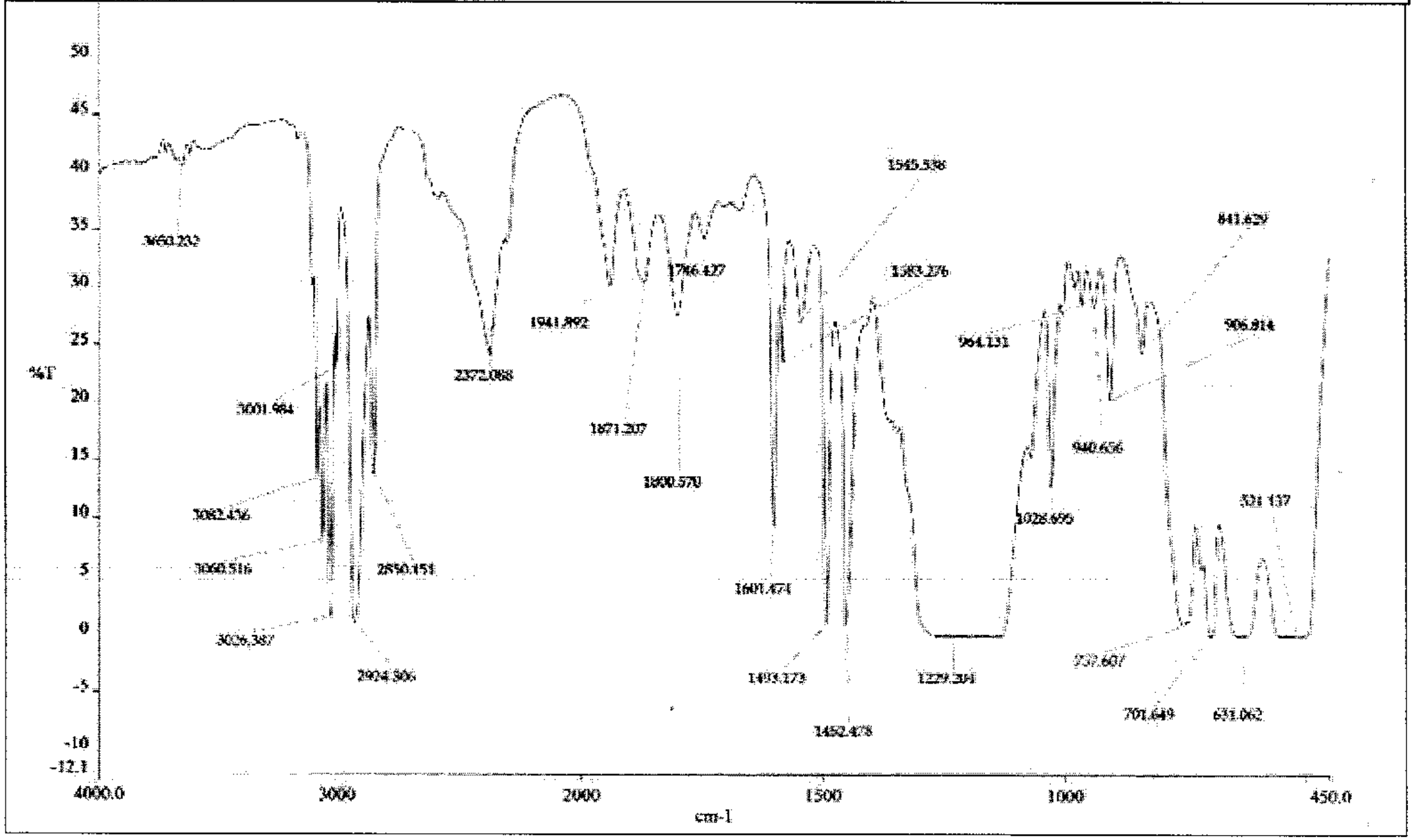
Appendix 5: Spectra of sample 4



FTIR Spectra for Sample 4: Transmittance (%) versus Frequency (cm^{-1})

Appendix 6: Spectra of sample 5

FTIR Spectra for Sample 5: Transmittance (%) versus Frequency (cm^{-1})



Appendix 7: Correlation Table

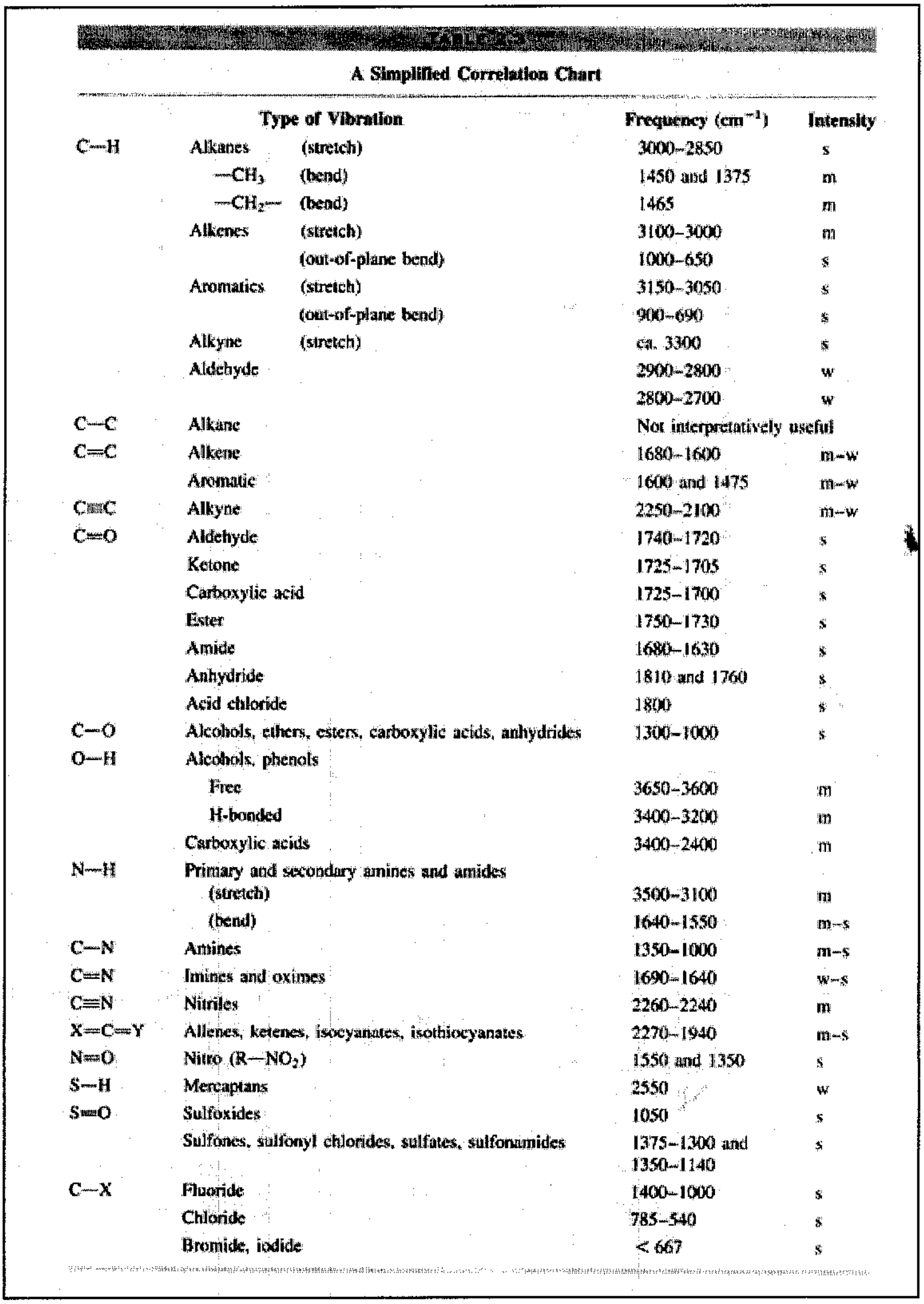


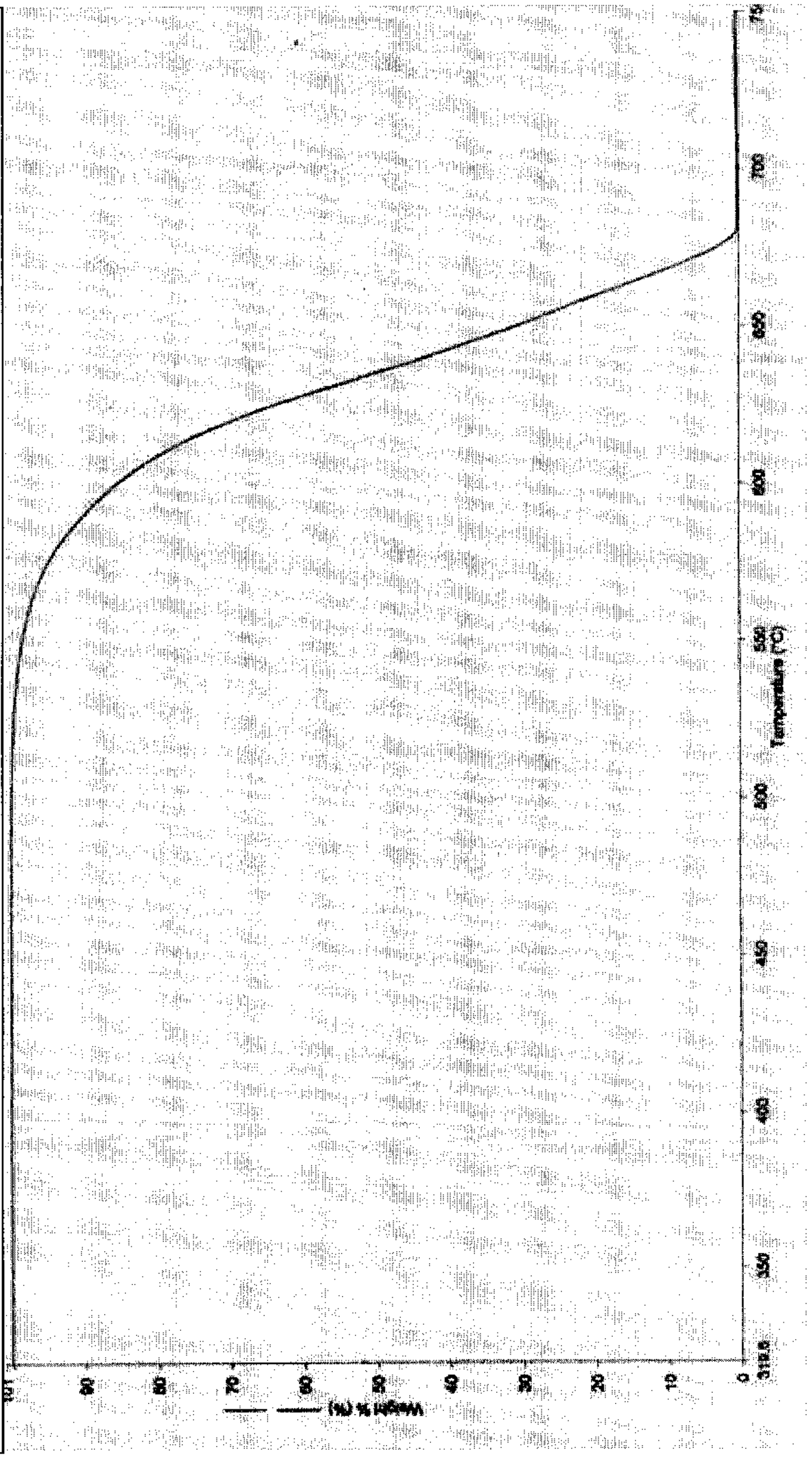
TABLE 2.3

A Simplified Correlation Chart

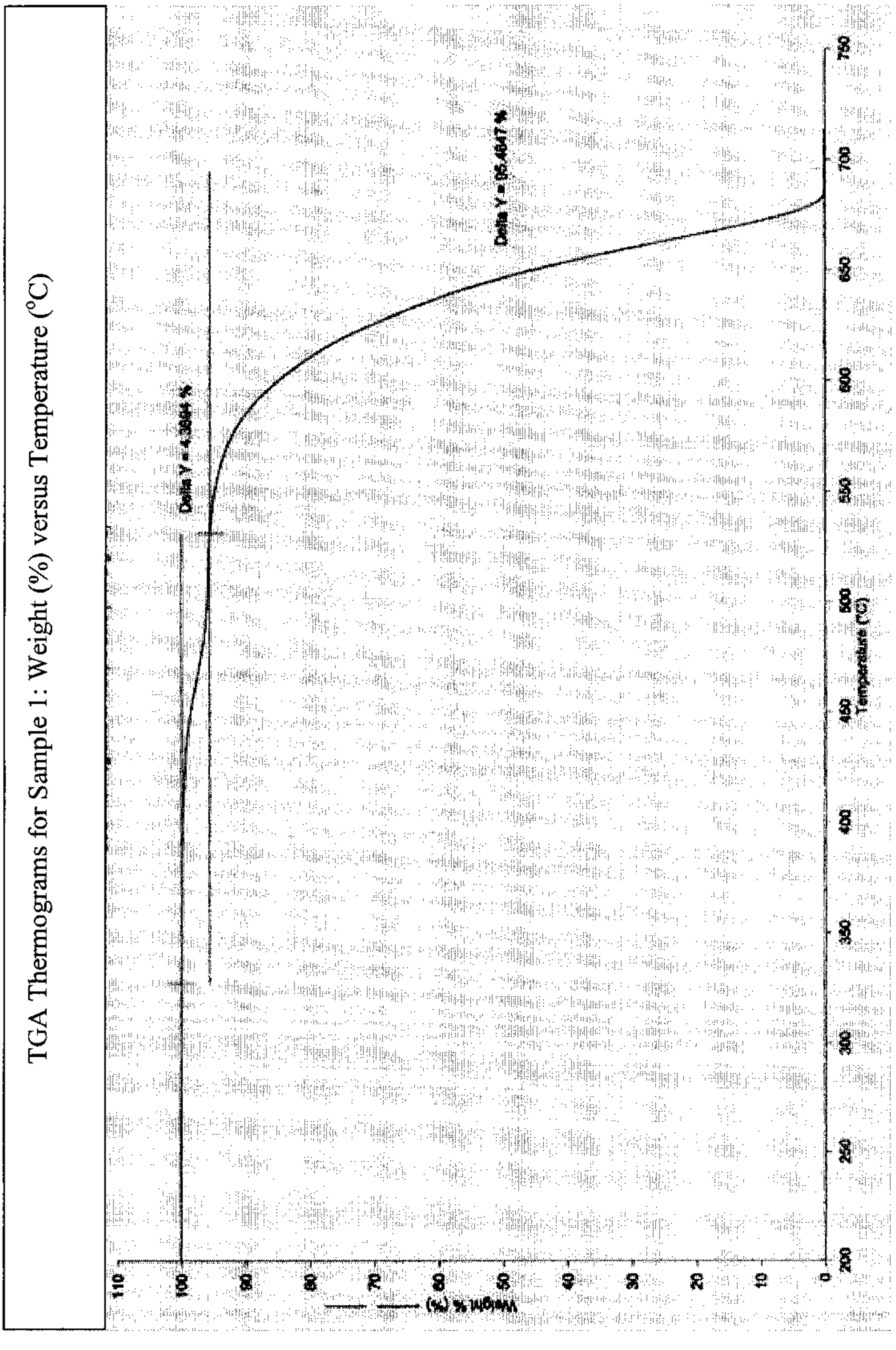
	Type of Vibration		Frequency (cm^{-1})	Intensity
C—H	Alkanes	(stretch)	3000–2850	s
	—CH$_3$	(bend)	1450 and 1375	m
	—CH$_2$—	(bend)	1465	m
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane		Not interpretatively useful	
C=C	Alkene		1680–1600	m–w
	Aromatic		1600 and 1475	m–w
C≡C	Alkyne		2250–2100	m–w
C=O	Aldehyde		1740–1720	s
	Ketone		1725–1705	s
	Carboxylic acid		1725–1700	s
	Ester		1750–1730	s
	Amide		1680–1630	s
	Anhydride		1810 and 1760	s
	Acid chloride		1800	s
C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s
O—H	Alcohols, phenols			
	Free		3650–3600	m
	H-bonded		3400–3200	m
	Carboxylic acids		3400–2400	m
N—H	Primary and secondary amines and amides			
	(stretch)		3500–3100	m
	(bend)		1640–1550	m–s
C—N	Amines		1350–1000	m–s
C=N	Imines and oximes		1690–1640	w–s
C≡N	Nitriles		2260–2240	m
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates		2270–1940	m–s
N=O	Nitro (R—NO$_2$)		1550 and 1350	s
S—H	Mercaptans		2550	w
S=O	Sulfoxides		1050	s
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides		1375–1300 and 1350–1140	s
C—X	Fluoride		1400–1000	s
	Chloride		785–540	s
	Bromide, iodide		< 667	s

Appendix 8: TGA Thermogram of Virgin PTFE

TGA Thermograms for Virgin PTFE: Weight (%) versus Temperature (°C)



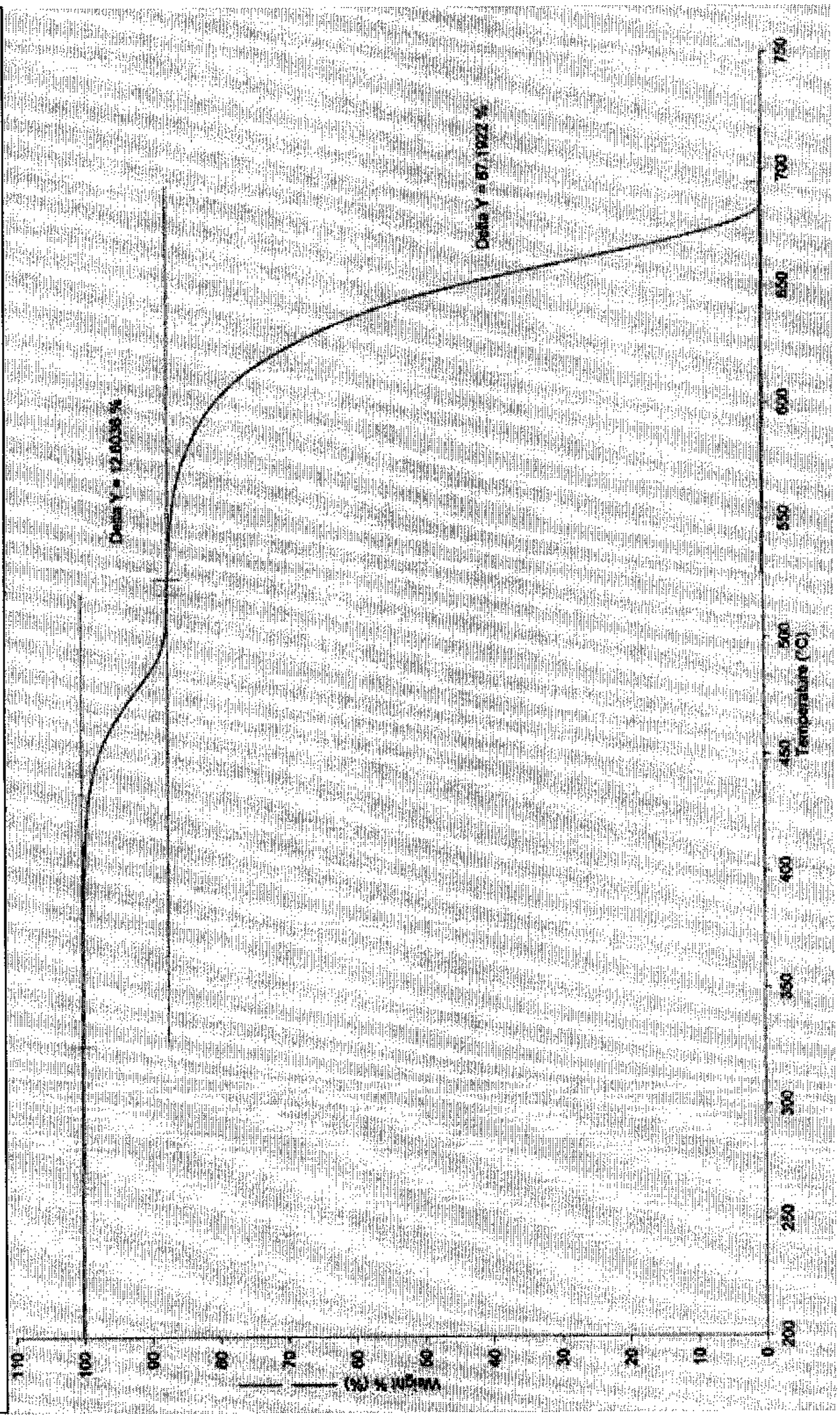
Appendix 9: TGA Thermogram of sample 1



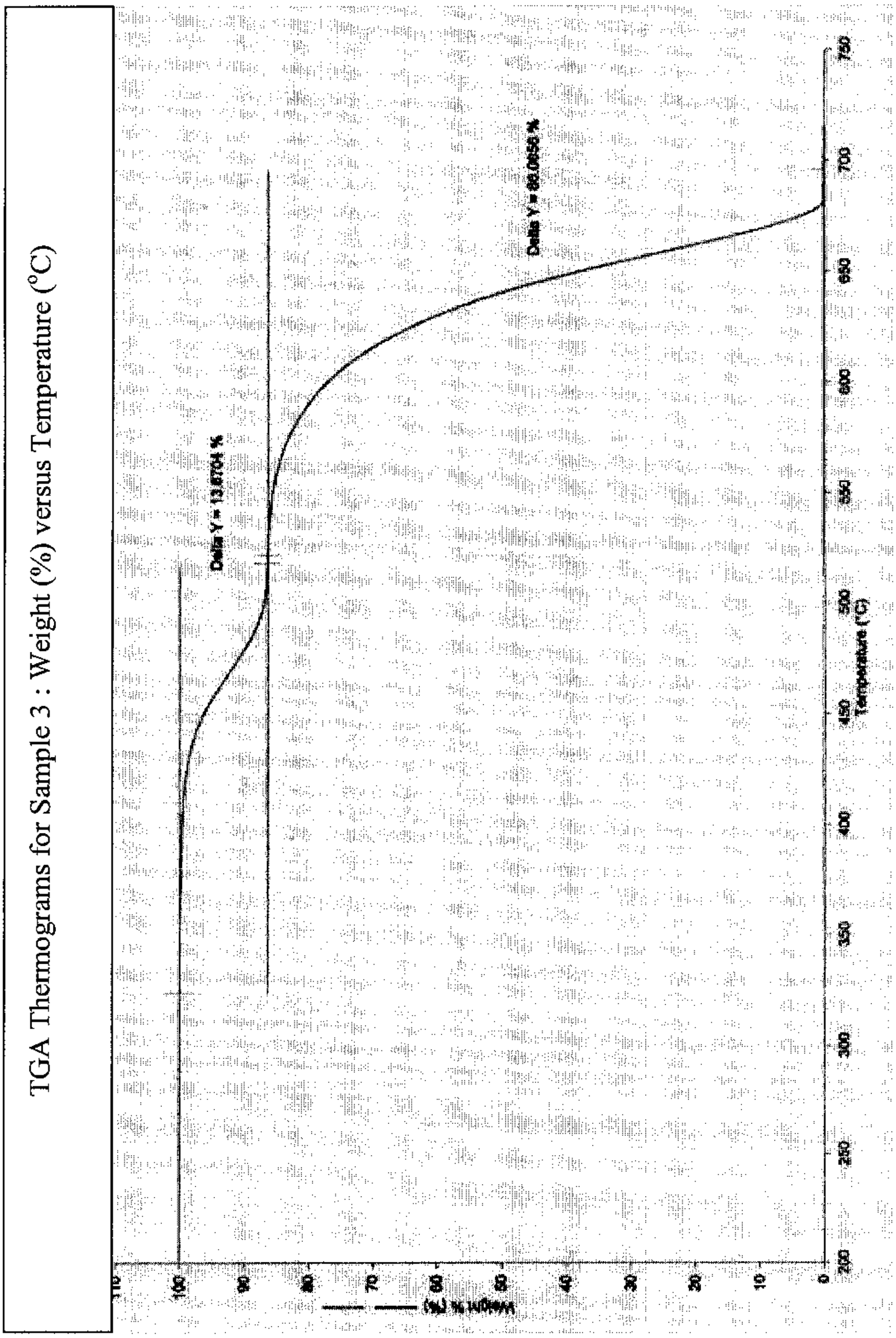
TGA Thermograms for Sample 1: Weight (%) versus Temperature (°C)

Appendix 10: TGA Thermogram of sample 2

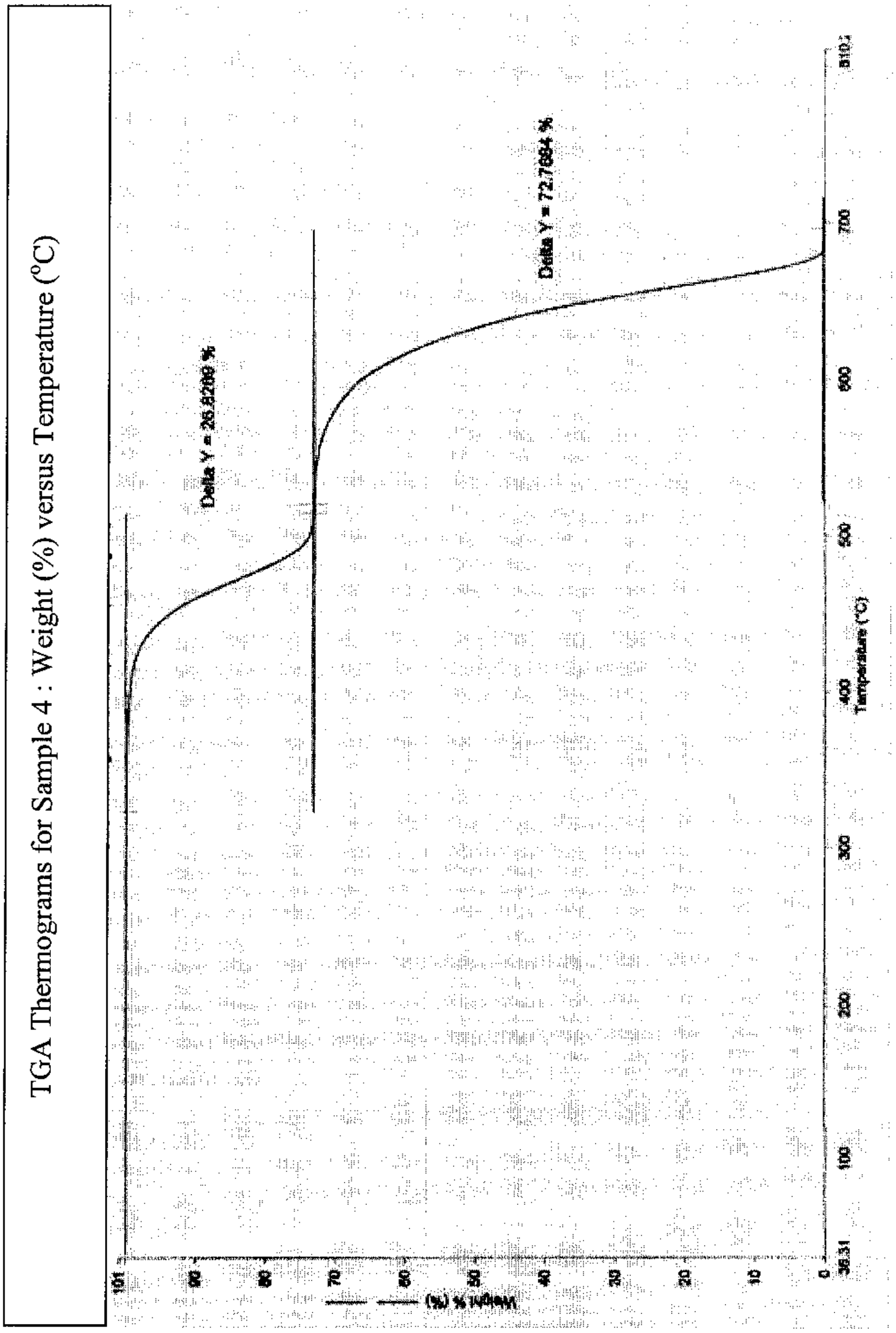
TGA Thermograms for Sample 2 : Weight (%) versus Temperature (°C)



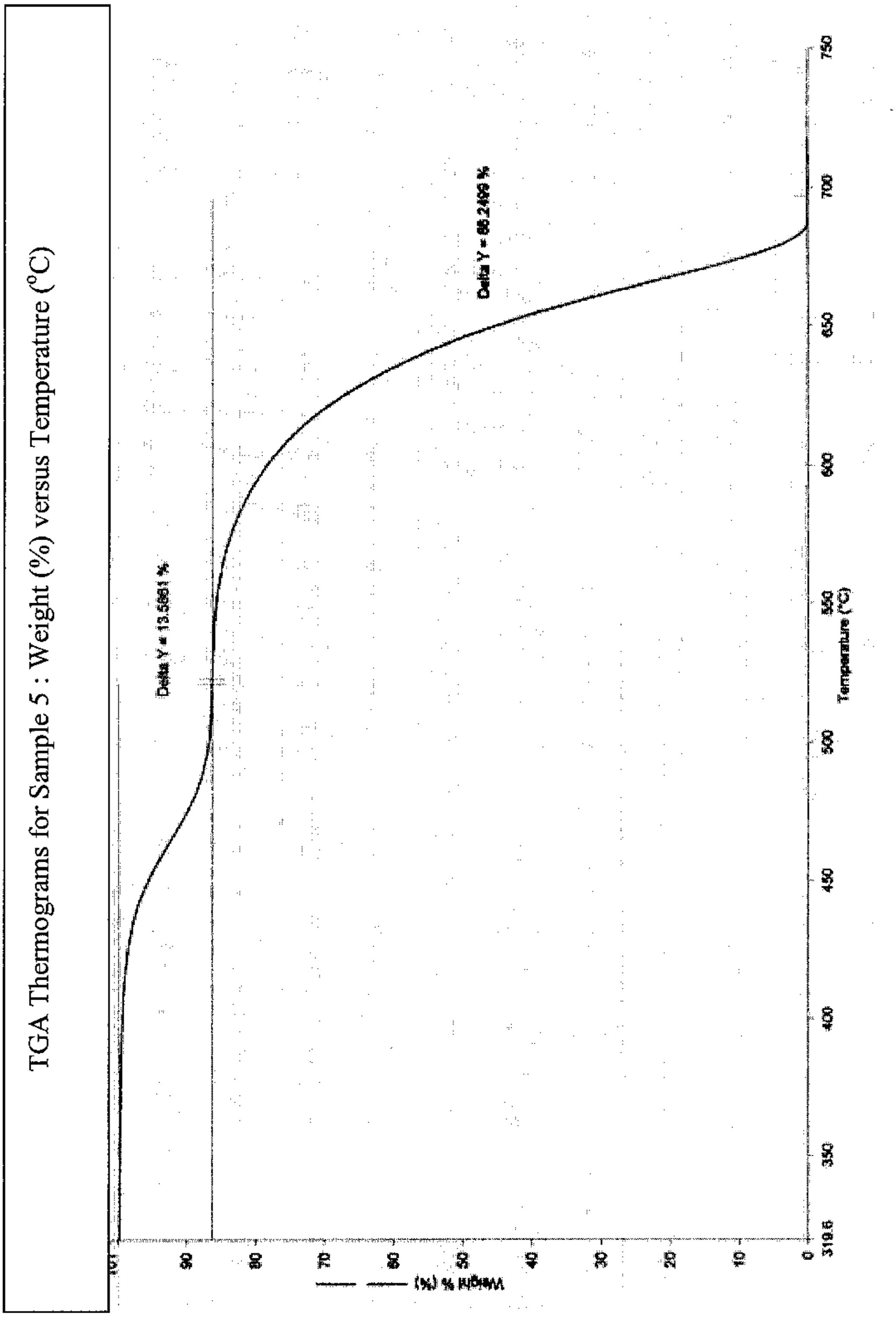
Appendix 10: TGA Thermogram of sample 3



Appendix 12: TGA Thermogram of sample 4

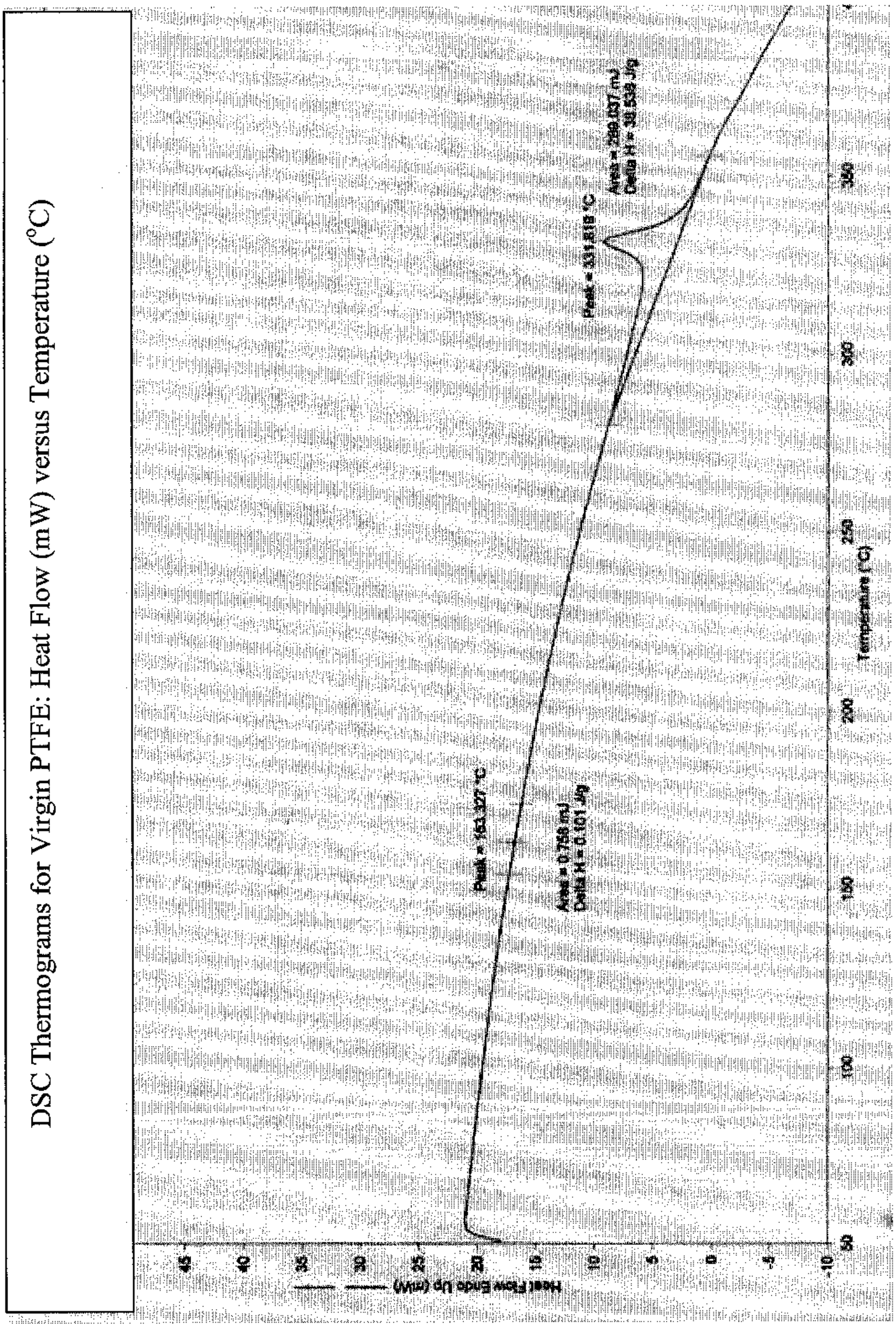


Appendix 13: TGA Thermogram of sample 5



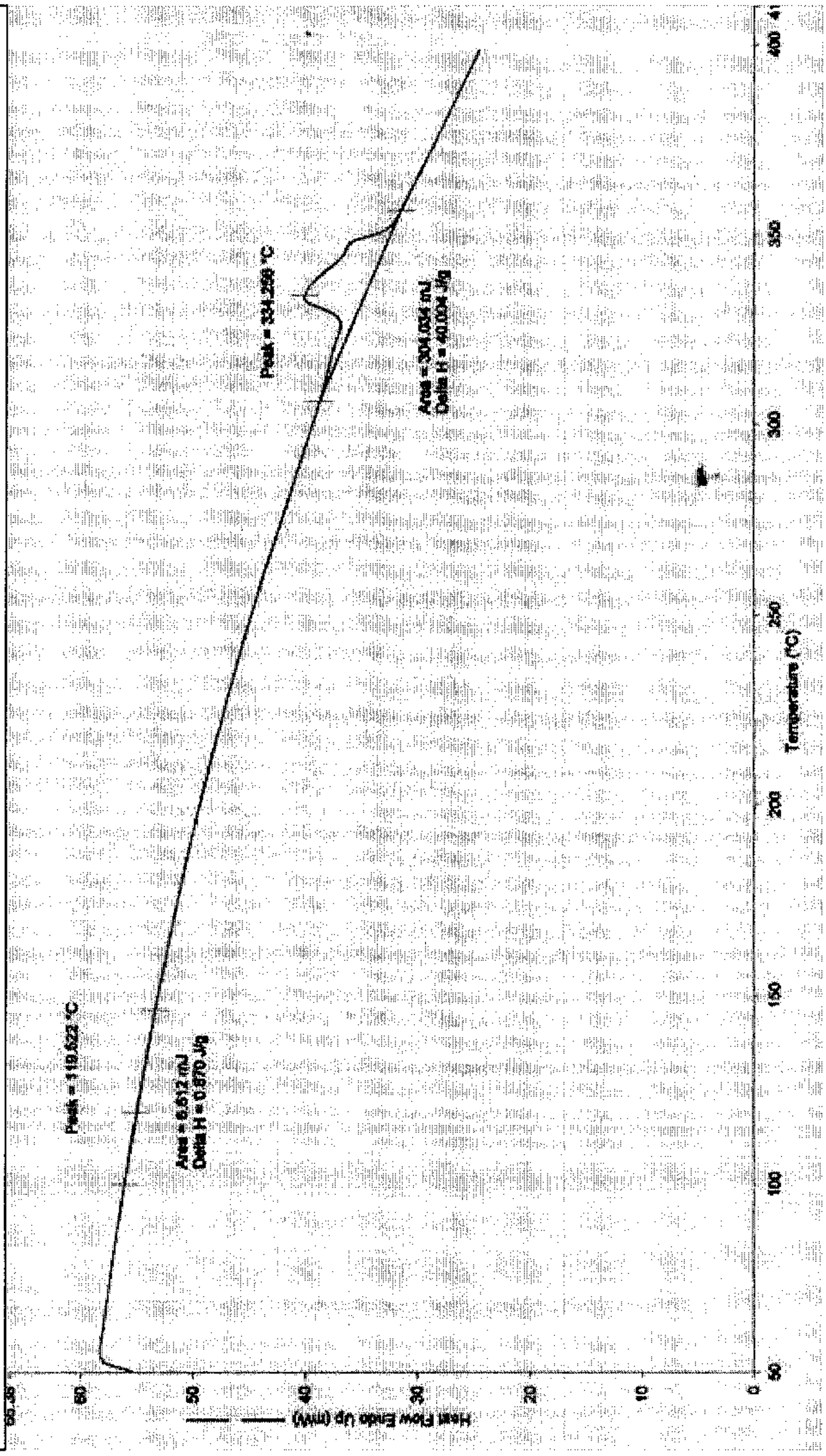
TGA Thermograms for Sample 5 : Weight (%) versus Temperature (°C)

Appendix 14: DSC Thermogram of virgin PTFE



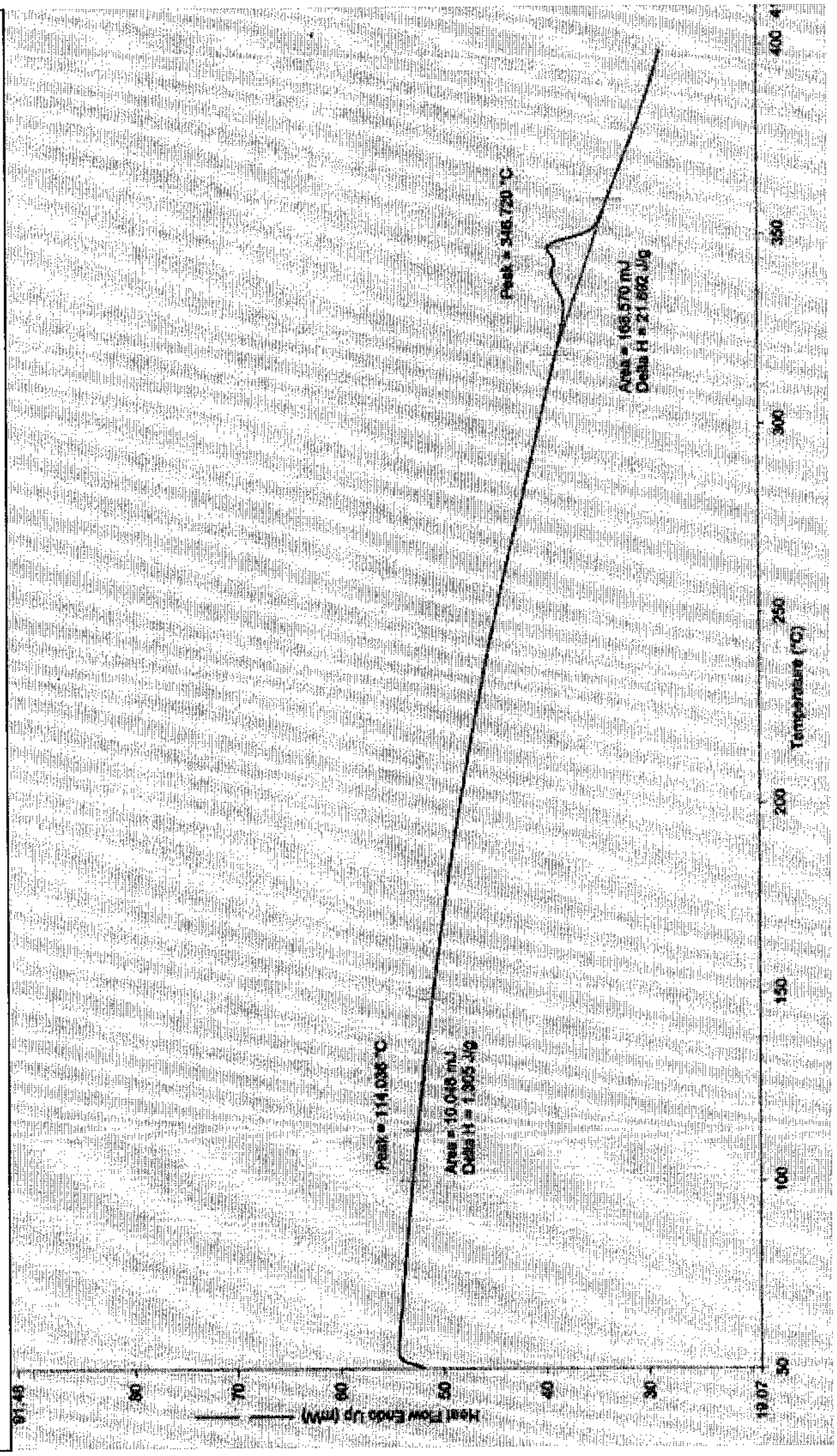
Appendix 15: DSC Thermogram of sample 1

DSC Thermograms for Sample 1: Heat Flow (mW) versus Temperature (^oC)



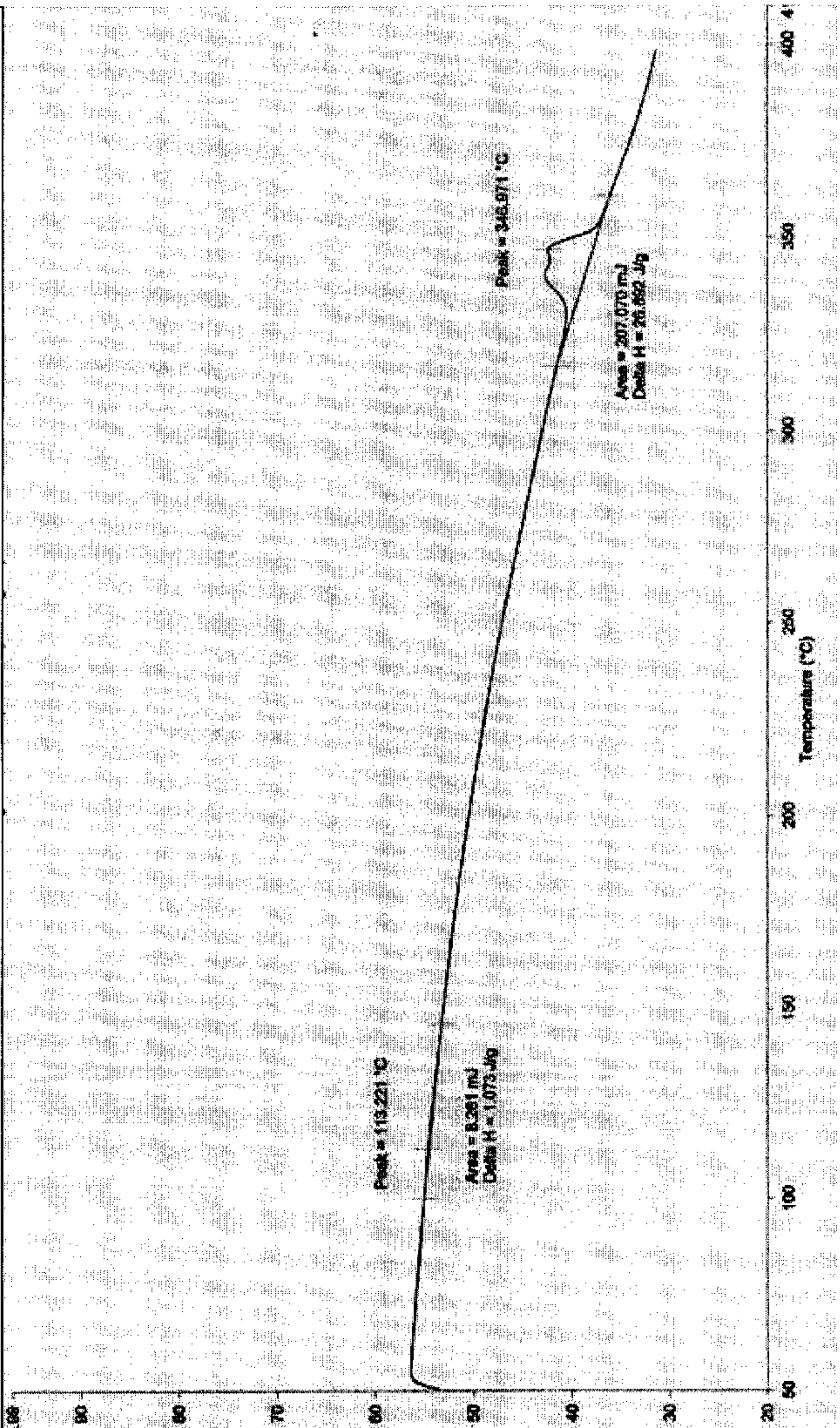
Appendix 16: DSC Thermogram of sample 2

DSC Thermograms for Sample 2: Heat Flow (mW) versus Temperature (°C)



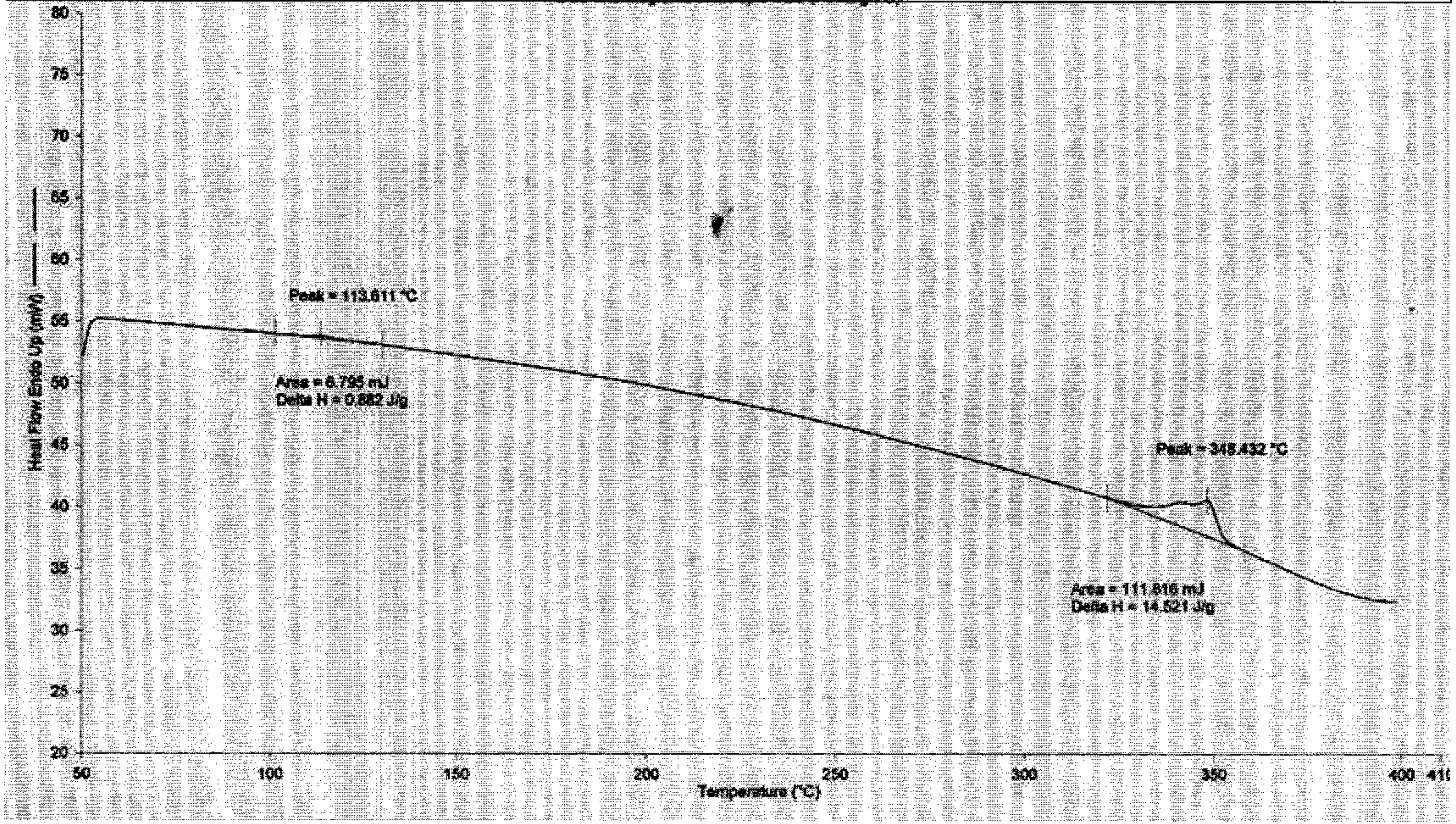
Appendix 16: DSC Thermogram of sample 3

DSC Thermograms for Sample 3: Heat Flow (mW) versus Temperature (°C)



Appendix 17: DSC Thermogram of sample 4

DSC Thermograms for Sample 4: Heat Flow (mW) versus Temperature (^oC)



Appendix 18: DSC Thermogram of sample 5

DSC Thermograms for Sample 5: Heat Flow (mW) versus Temperature (^{o}C)