CHAPTER 4

EXPERIMENTAL METHODS USED FOR FIBRE PRODUCTION AND POLYMER ANALYSIS

4.1 Chemicals, Apparatus and Instruments

4.1.1 Chemicals

The chemicals used in this research project were as shown in Table 4.1.

Table 4.1 Chemicals used in this research project.

Chemicals	Usage	Grade	Supplier
Polypropylene	Polymer	Commercial	TPC*
Poly(L-lactic acid-co-ε-caprolactone)	Polymer	Purified	Research sample
1,2,3,4-Tetrahydronapthalene	Solvent	Lab. reagent	May & Baker
Acetone	Solvent	Lab. reagent	E. Merck
Chloroform	Solvent	AR Grade	E. Merck
Sodium di-hydrogen phosphate dihydrate	Immersion medium salt	AR Grade	E. Merck
Di-sodium hydrogen orthophosphate	Immersion medium salt	AR Grade	BDH Chemicals
Sodium hydroxide	pH adjuster	Lab. reagent	E. Merck
Water	Immersion medium	Deionized	E. Merck

*TPC = Thai Plastic and Chemical Public Co., Ltd.

4.1.2 Apparatus and Instruments

The main items of apparatus and instruments used were as given in Table 4.2.

Table 4.2 Apparatus and instruments used in this research project.

Apparatus and Instruments	Company	Model
Small-Scale Melt Spinning Apparatus	Bradford University Research Ltd.	-
Differential Scanning Calorimeter	Perkin-Elmer	DSC 7
Thermogravimetric Analyzer	Perkin-Elmer	TGA 7
Optical Microscope	Nikon	Optiphot-2
Instron Testing Machine	Instron	4301
Vacuum Oven	Lab-Line Instruments	3620-1
Vacuum Oven	Eyela	VOS-300 SD
pH meter	Radiometer Copenhagen	PHM 61
Incubator	Memmert	-
Autoclave	Hirayama	HL 42 ADY

4.2 Preparation of Polypropylene Rods

The various melt spinning apparatus accessories used in the preparation of polypropylene rods are shown in Fig. 4.1 below.

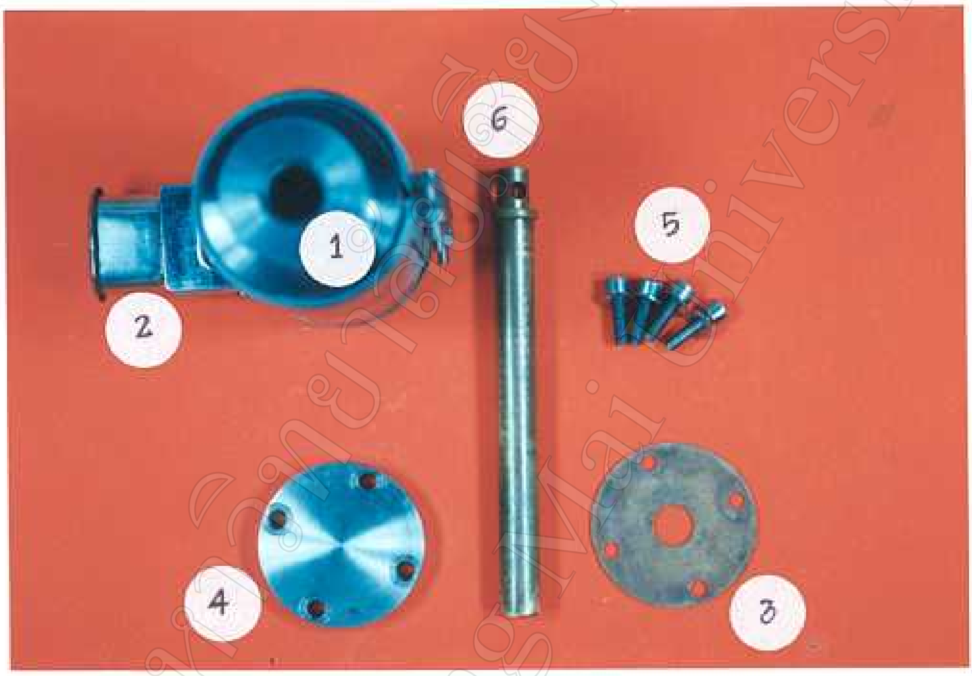


Fig. 4.1 The various melt spinning apparatus accessories used in the preparation of polypropylene rods.

1. pre-forming cylinder
2. heater band
3. copper gasket
4. plain blanking plate
5. 6 x 20 mm cap screws
6. piston

The 30 ml pre-forming cylinder was chosen and the large band heater was clamped around it (CAUTION: when the band heater was clamped around the pre-forming cylinder, the heater was positioned in such a way that it did not cover the thermocouple hole which was close to the bottom face of the cylinder. The heater was positioned so that its plug was approximately in line with the thermocouple hole). The gasket and the plain blanking plate were bolted to the base of the cylinder respectively by means of 6 x 20 mm cap screws. These screws were lubricated with an anti-seizure compound. Finally, the pre-forming cylinder was assembled as shown in Fig. 4.2.

Fig. 4.2 The assembled pre-forming cylinder used for making polypropylene rods.

The polypropylene beads which had previously been dried in an oven at 100°C for 3 hours were filled into the assembled pre-forming cylinder. The cylinder was purged with dry nitrogen during filling. The assembled pre-forming cylinder was then placed in the extrusion unit as shown in Fig. 4.3.

Fig. 4.3 The assembled pre-forming cylinder in position in the main extrusion unit.

To commence the pre-forming operation, the heater plug was inserted into its socket and the thermocouple inserted into its hole. (It was ensured that the thermocouple was fully inserted as far as it could go.) The temperature was set to 145°C to soften the polypropylene beads (CAUTION: the temperature should not make the polymer melt) and the heater switched on. As the cylinder was heating up, the piston was placed in position and the motor switched on to let the piston down into the cylinder. The speed of the piston used was 45 mm/min (ram speed). As the piston came into contact with the beads, the beads were compressed and the load (shown on the front control panel) increased until it became constant at its pre-set limiting value (approx. 400 kg) at which the motor would cut out automatically and the piston would stop. As the beads softened, the load would decrease and the motor would restart for compressing the beads further. When the temperature reached 145°C, the polymer was kept at this temperature for about 5 mins., after which the heater was switched off. The direction of the motor was reversed to bring the piston up to partially release the load. When the temperature had fallen by about 20°C, the base of the cylinder was removed. Finally, the piston was used to push the polymer rod out of the cylinder.

Several polypropylene rods were prepared in this way and stored in a desiccator until required for melt spinning.

4.3 Melt Spinning

4.3.1 Polypropylene

The various accessories used in the melt spinning of the polypropylene rods were as shown in Fig. 4.4.

A schematic diagram of the melt spinning system is shown in Fig. 4.5. The system consisted of the extrusion unit, the filament guide and the final take-up unit.

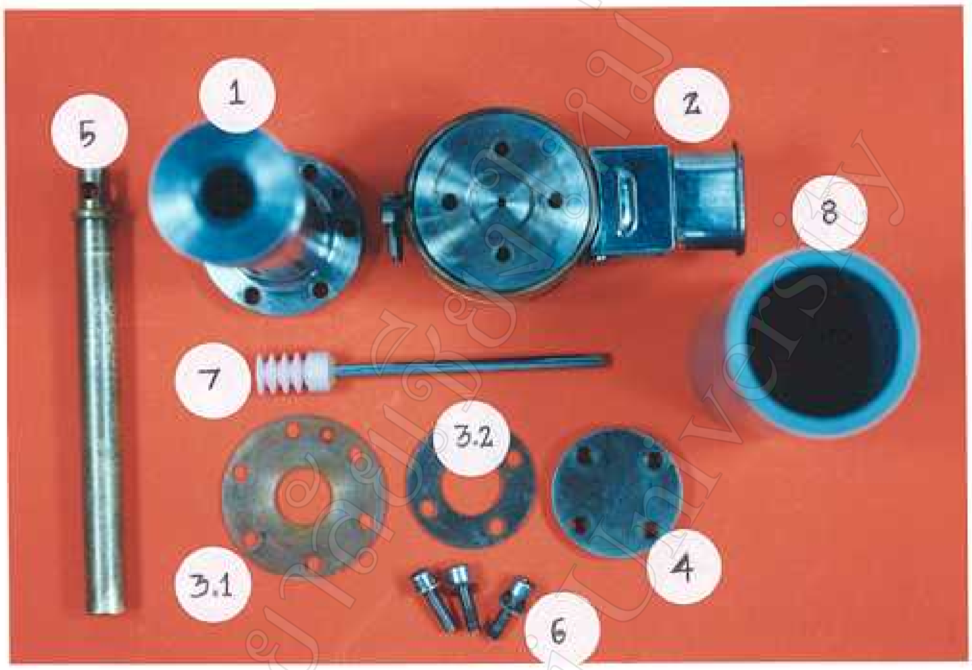


Fig. 4.4 The various accessories used in the melt spinning of the pre-formed polypropylene rods.

1. 30 ml extrusion cylinder
2. heater block
3. copper gaskets
   - 3.1 gasket used between the extrusion cylinder and the heater block
   - 3.2 gasket used between the heater block and the spinnerette
4. spinnerette (single hole, 1 mm diameter)
5. piston
6. 6 x 20 mm cap screws
7. filament guide
8. filament spool

spinnerette - guide (AB) distance = 120 cm
guide - floor (BC) distance = 20 cm
extrusion unit - take-up unit (DE) distance = 45 cm

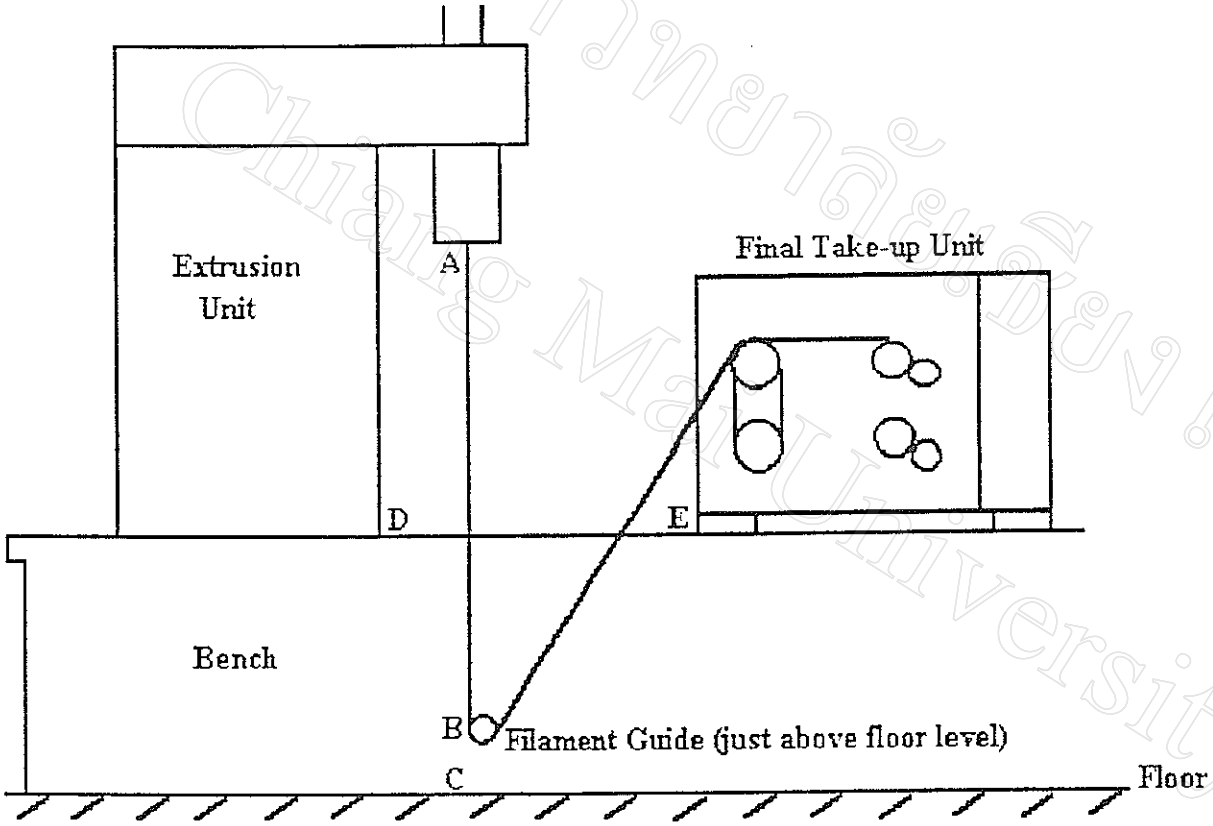


Fig. 4.5 Schematic diagram of the small-scale melt spinning apparatus [34].

The extrusion cylinder was attached to the heater block by means of 6 x 20 mm cap screws that were lubricated with anti-seizure compound. The spinnerette was bolted to the lower face of the heater block. It was necessary to insert one disc of fine stainless steel gauze in the center of the heater block (the gauze was not a filter but a means of shearing the polymer melt) so as to assist the molten polymer to flow smoothly through the spinnerette. Solid copper gaskets were used between the heater block and both the cylinder and the spinnerette. These various devices used for melt spinning were assembled as shown in Fig. 4.6.

The extrusion cylinder was placed in the extrusion unit with the thermocouple and the heater plug connected as previously described. The extrusion cylinder was pre-heated to the recommended spinning temperature (205°C) for polypropylene [34] and then held at that temperature to ensure thermal equilibrium. A rod of polypropylene, pre-dried at 100°C for 3 hours, was then carefully inserted into the extrusion cylinder and the piston placed in position. An appropriate ram speed (e.g. 3 mm/min) was chosen and the piston let down to compress the polymer. When the polypropylene melt emerged from the spinnerette, the monofilament was drawn smoothly downward and around the filament guide near the floor. It was then wound 4 to 6 times in a clockwise direction around the two thread advancing rollers of the final take-unit and, finally, wound on to the take-up spool through the traversing guide.

Fig. 4.6 The assembled extrusion cylinder ready for melt spinning.

4.3.2 Poly(L-lactic acid-co-ε-caprolactone)

The poly(L-lactic acid-co-ε-caprolactone) P(LLA-co-CL) studied in this work was a research sample synthesized as part of another research project [33]. Interest in its melt spinnability stemmed from its intended biomedical application as an absorbable suture material. The method used for its melt spinning was similar to that described in the previous section for polypropylene, the only differences being:

(a) Due to the limited amount of copolymer available (< 10 g), a much smaller-sized 7 ml extrusion cylinder was used, as shown in Fig. 4.7.

(b) Since there was not enough material to make a pre-formed rod, the copolymer was melt spun directly from its original form by compacting it in the extrusion cylinder manually prior to heating.

(c) A spinning temperature of 160°C was found to be the most suitable temperature for controlled extrusion.

(d) Because the copolymer monofilaments produced were mechanically very weak (in comparison with polypropylene), they could not be wound up on the final take-up unit. Instead, they were taken up manually as carefully as possible to avoid pulling and breaking the thread.

Fig. 4.7 The smallest-sized extrusion cylinder used in the melt spinning of poly(L-lactic-co-ε-caprolactone).

4.3.3 Thermal Conditioning Zone

As a refinement to the melt spinning process (polypropylene only), a "thermal conditioning zone (TCZ)" was constructed from the following components:

1. electrical heating column (cylindrical, length 54 cm)
2. thermocouple
3. thermostat control
4. glass rod (length 60 cm)

The heating column was placed directly underneath the spinnerette. The thermocouple wire was attached to a glass rod which was then inserted down the center of the column and the column temperature measured at various positions along its height. Fig. 4.8 shown the thermal conditioning zone used in this work.

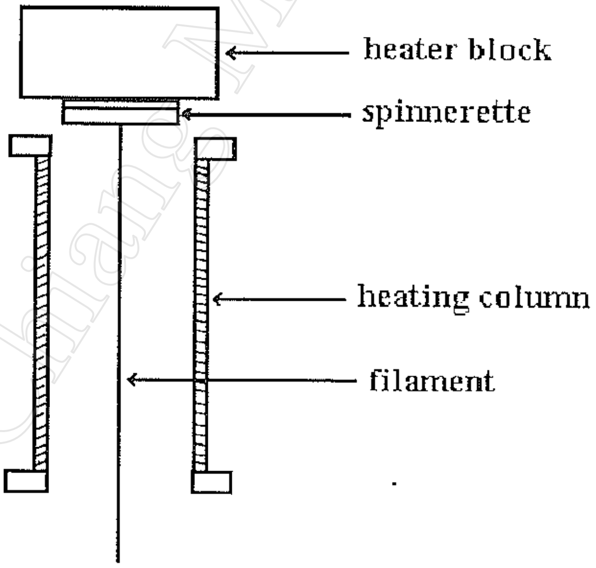


Fig. 4.8 Thermal conditioning zone used in the melt spinning of polypropylene

Thermal conditioning of the filament as it emerges from the spinnerette can, under certain circumstances, improve fibre properties by allowing the polymer to cool more slowly from the melt. It was the purpose of this subsidiary study to see if a TCZ could improve the properties of the polypropylene fibres produced.

4.4 Off-Line Hot Drawing

Off-line hot drawing of the melt-spun polypropylene fibres was carried out as a means of increasing the degree of chain orientation within the polymer, thereby strengthening the fibres in the direction of draw. The accessories used for achieving this were as follows:

1. initial take-up unit
2. hot-drawing unit
3. final take-up unit
4. two filament guides
5. stands
6. filament spool

It is often recommended that hot drawing of fibres be carried out as a separate operation from extrusion. As such, it is called "off-line hot drawing". The three main components of the process (the initial take-up unit, the hot-drawing unit, and the final take-up unit) were arranged in series, as shown in Fig. 4.9.

The desired temperature of the hot drawing unit was set and the unit allowed to stabilise. The initial take-up unit was switched on and set to run at 5 m/min. to take up the filament from the filament spool which was placed beneath the tensioner. Then, the filament was led to the tensioner and wrapped several times around the lower two rolls of the initial take-up unit in an anti-clockwise direction. Two stands, each of 24 cm height with a grooved guide at the top, were placed at points A and B (Fig. 4.9) to guide the filament as it passed through the hot-drawing unit. After the filament had passed along the groove of the second stand (point B), it was re-directed back through the hot-drawing unit so as to increase its "effective residence time" inside the heater block. The filament from the hot-drawing unit was led to the final take-up unit by wrapping it several times around the thread-advancing roller in a clockwise direction and onto one of the take-up spools. The speeds of the final take-up unit were set at 10, 20, 30 and 40 m/min. to produce the required "draw ratios" of 2, 4, 6, and 8 respectively.

4.5 Annealing

Annealing is a post-spinning process designed to increase the polymer's % crystallinity. This is achieved by heating under vacuum at a temperature just below the melting range. As a result, annealing oftens brings about an increase in the mechanical strength of the fibre.

In practice, after ambient storage, the spin-drawn/off-line hot drawn polypropylene fibres were cut into short lengths and placed in a petri-dish. The samples were then annealed under vacuum at 3 different temperatures: 145°C, 150°C and 155°C (to study the effect of temperature), and for 2 different periods of time: 1 hour and 5 hours (to study the effect of time).

In the case of the two poly(L-lactic acid-co-caprolactone) 8:2 and 7:3 samples, annealing was carried out under vacuum at 140°C and 90°C respectively, each for 9 hours.

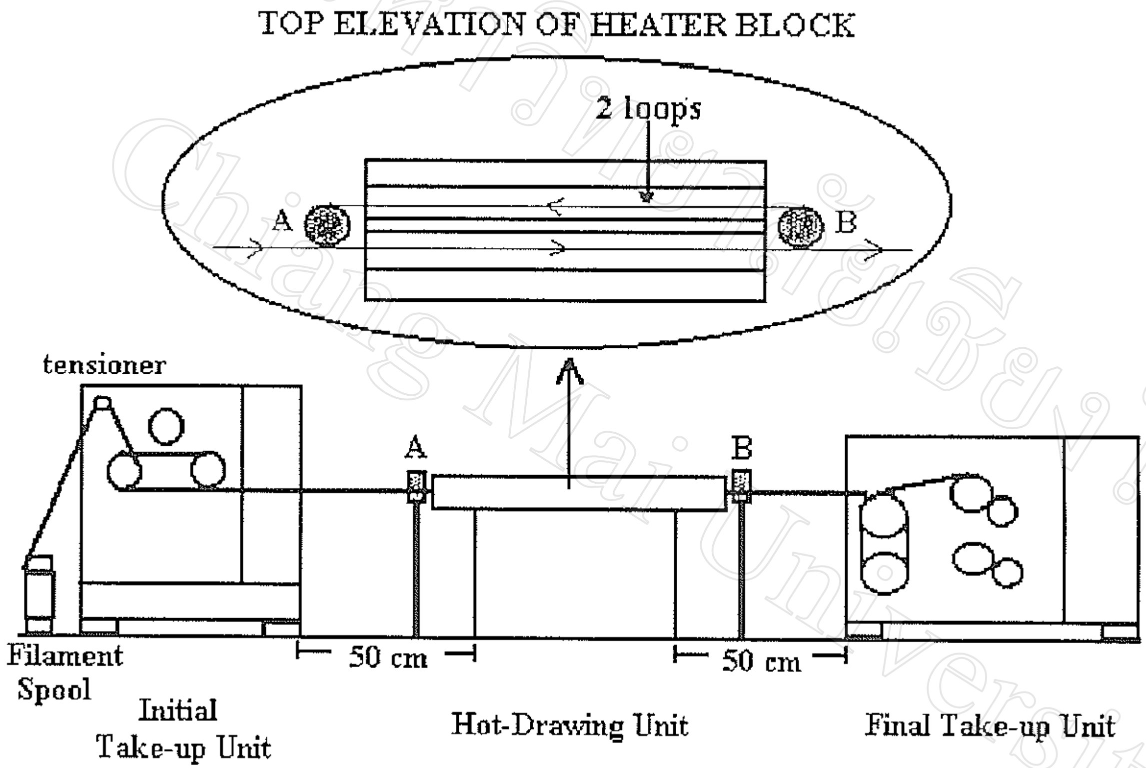


Fig. 4.9 Schematic arrangement used for off-line hot drawing.

4.6 Thermal Analysis [35]

Thermal analysis (TA) is the generic name given to a series of techniques which measure changes in the physical or reactive properties of materials as a function of temperature and time.

The advantages of thermal analysis over other physical characterization tests include:

1. Short test times: typically less than 30 mins
2. Small sample sizes: usually less than 50 mg
3. Minimal sample preparation
4. Automated instrumentation
5. Easy correlation with end-use properties
6. Quantitative results

4.6.1 Thermal Analysis Instrumentation

There are three components to any thermal analysis system, as shown in Fig. 4.10.

- A programmable temperature controller for regulating the sample temperature
- An analysis module which contains a furnace and transducers for measuring changes in the sample's physical properties
- An output device for data storage, data analysis and printer or plotter for reporting the results

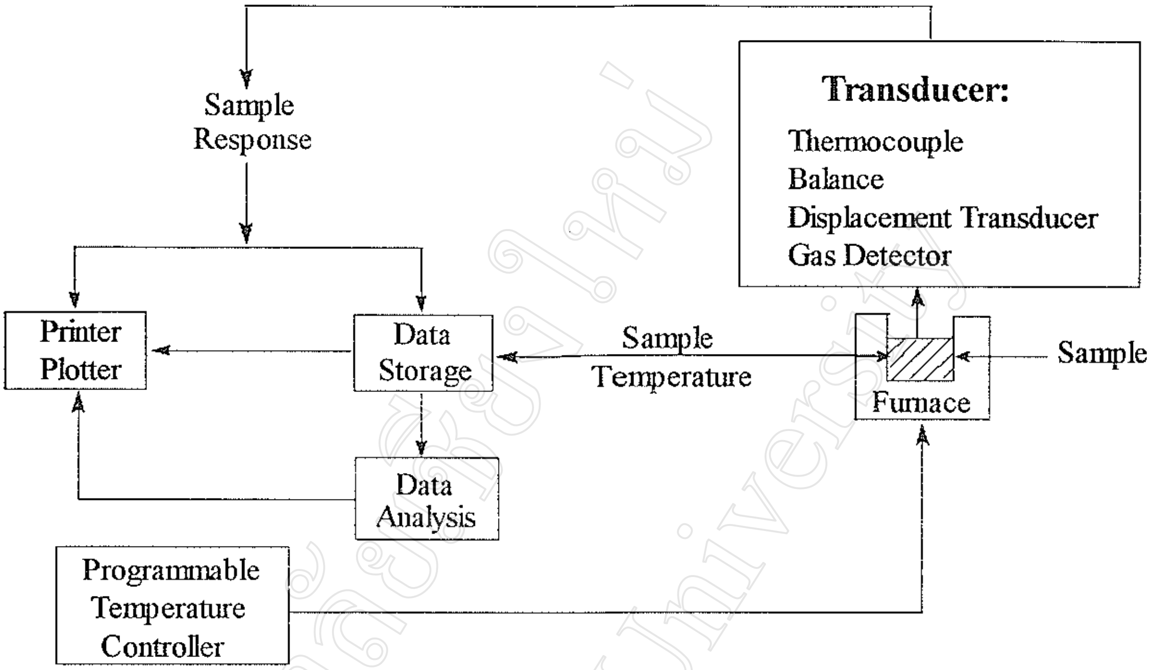


Fig. 4.10 Thermal analysis system components [35].

The TA techniques used in this research were Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG).

4.6.2 Differential Scanning Calorimetry (DSC) [36, 37]

DSC is a technique in which the difference in energy input into the sample and a thermally inert reference is measured as a function of temperature while the sample and the reference material are subjected to a controlled temperature program. The measurement of heat flow in this technique, either into or out of the sample, provides valuable data on the sample's crystallization rate, percent crystallinity, glass transition temperature, melting point and specific heat.

For precise measurements of heats of transition, it is necessary to add two further conditions:

(1) precise weighing of the sample
(2) precise calculation of the peak area under the endotherm or exotherm caused by the transition

From the DSC curve, the melting point of a sample is easily determined. The knowledge of a plastic's melting point is useful for determination of its optimum processing conditions. The relative amount of crystallinity in a semi-crystalline polymer is easily determined by DSC from a single heating experiment. The area under the melting endotherm is the heat of fusion (ΔH_f), usually expressed in joules per gram of sample (J/g), and is directly related to the degree of the crystallinity. The higher the degree of crystallinity, the higher the heat of fusion. The percent crystallinity in a polymer is important because it affects end-use properties and because it is an indication of the polymer's thermal history during processing.

The DSC operating conditions which were employed in this work for each sample analysis were as shown in Tables 4.3 and 4.4. In addition, nitrogen gas (99.9%, dry, oxygen-free grade) was used as the purge gas at a pressure of 20 lbs/in^2 (flow rate = 40.0 ml/min). Indium (T_m = 156.60 °C, ΔH_f = 28.45 J/g) and tin (T_m = 231.90 °C) were used for temperature and energy calibration of the Perkin-Elmer DSC7 instrument which was used in this work.

Table 4.3 DSC operating conditions used for polypropylene analysis.

Parameters	Conditions
Final Temp: 250.0°C	End Condition: Load Temp.
Start Temp: 50.0°C	Load Temp: 25.0°C
Scanning Rate: 10.0°C/min	Go to Temp Rate: 50°C
Y range: 40.0 mW	Event 1 Time: 0.00 min
*Sample Weight:	Event 2 Time: 0.00 min
	Time at T start: 0.00 min
	Time at T Final: 0.00 min
	Y Initial Value: 10.0 mW

* variable according to sample

Table 4.4 DSC operating conditions used for poly(L-lactic acid- co-ε-caprolactone) analysis.

Parameters	Conditions
Final Temp: 250.0°C	End Condition: Load Temp.
Start Temp: 20.0°C	Load Temp: 25.0°C
Scanning Rate: 10.0°C/min	Go to Temp Rate: 50°C
Y range: 40.0 mW	Event 1 Time: 0.00 min
*Sample Weight:	Event 2 Time: 0.00 min
	Time at T start: 0.00 min
	Time at T Final: 0.00 min
	Y Initial Value: 10.0 mW

* variable according to sample

4.6.3 Thermogravimetry (TG) [38, 39, 40]

Thermogravimetry (TG) is a most useful method for the investigation of the thermal decomposition and stability of a polymer. Thermogravimetry is generally defined as a techique in which the weight of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. The thermal stability of plastics varies with the type of plastic and concentration of additives. It affects both processing and end-use performance of the plastic part. In processing, it is important that incoming materials are able to handle the high temperatures generated by processing equipment without thermal decomposition. Thermogravimetry may be divided into two types:

(1) Isothermal thermogravimetry, in which the method is to record the change in weight of the sample as a function of time at a constant temperature
(2) Non-isothermal (or dynamic) thermogravimetry, in which the change in weight of the sample is recorded as a function of both temperature and time as the temperature is increased at a constant heating rate. This was the technique used in this research.

The most important variables which must be controlled in order to obtain meaningful TG data are:

- The heating rate in dynamic TG, which must be made linear with time but slow enough to separate successive reactions
- The sample size, which must be kept as small as practicable to minimize mechanical difficulties
- The atmosphere, which must be either absent (i.e, *in vacuo*) or inert to prevent reaction with the sample

The dynamic TG operating conditions which were employed for each sample analysis in this work were as shown in Tables 4.5, 4.6 and 4.7. In addition, pure nitrogen gas (99.9%, dry, oxygen-free grade) and pure oxygen gas (for polypropylene only) were used as the purge gases at a pressure of 30 lbs/in^2 for the (lower) sample zone and 50 lbs/in^2 for the (upper) balance zone in the Perkin-Elmer TGA 7 instrument used.

Table 4.5 Dynamic TG operating conditions used for polypropylene analysis using N_2 as the purge gas.

Parameters	Conditions
Final Temp: 600.0°C Start Temp: 50.0°C Scanning Rate: 20.0°C/min Y range: 100.0 *Sample Weight:	End Condition: Load Temp. Load Temp: 50.0°C Go to Temp Rate: 200°C Event 1 Time: 0.00 min Event 2 Time: 0.00 min Delay time: 0.00 min Y Range (L/H): L

* variable according to sample

Table 4.6 Dynamic TG operating conditions used for polypropylene analysis using O_2 as the purge gas.

Parameters	Conditions
Final Temp: 600.0°C Start Temp: 50.0°C Scanning Rate: 20.0°C/min Y range: 100.0 *Sample Weight:	End Condition: Load Temp. Load Temp: 50.0°C Go to Temp Rate: 200°C Event 1 Time: 0.00 min Event 2 Time: 0.00 min Delay time: 0.00 min Y Range (L/H): L

* variable according to sample

Table 4.7 Dynamic TG operating conditions used for poly(L-lactic acid-co-ε-caprolactone) analysis using N_2 as the purge gas.

Parameters	Conditions
Final Temp: 550.0°C Start Temp: 50.0°C Scanning Rate: 20.0°C/min Y range: 100.0 *Sample Weight:	End Condition: Load Temp. Load Temp: 50.0°C Go to Temp Rate: 200°C Event 1 Time: 0.00 min Event 2 Time: 0.00 min Delay time: 0.00 min Y Range (L/H): L

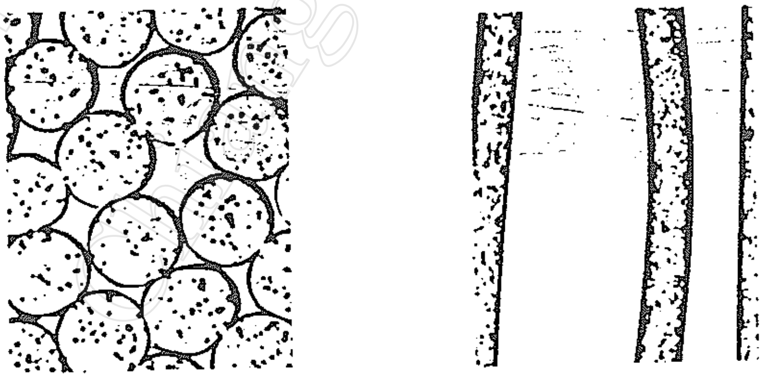
* variable according to sample

4.7 Optical Microscopy [41, 42]

Both optical and electron microscopes are commonly used in materials science. These instruments aid in investigations of the microstructural features of all three material types: metal, ceramics and polymers. Most microscopic techniques employ photographic equipment in conjunction with the microscope; the photograph on which the image is recorded is called a photomicrograph. In this research project, an optical microscope was used to examine the microstructural surface features of the fibres obtained from melt spinning.

With optical microscopy, the light microscope is used to study the microstructure: optical and illumination systems are its basic elements. For materials that are opaque to visible light (all metals and many ceramics and polymers), only the surface is subjected to observation, and the light microscope must be used in a reflecting mode.

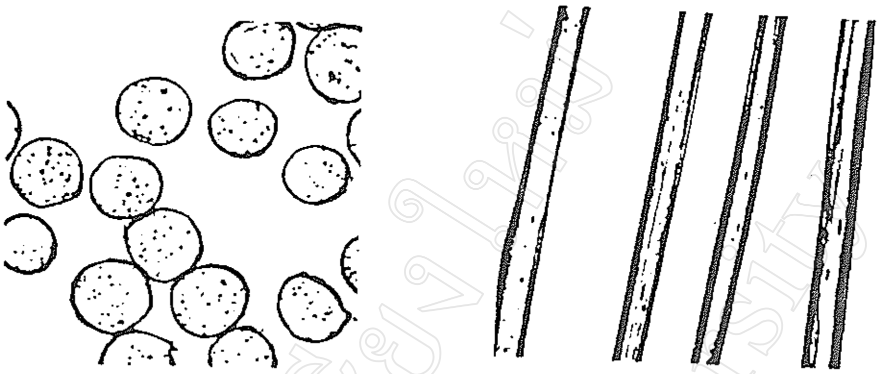
The longitudinal and cross-sectional views of the most common fibres are shown in Figs. 4.11 and 4.12.



cross-sectional view

longitudinal view

Fig. 4.11 Cross-sectional and longitudinal views of melt-spun polypropylene fibres [42].



cross-sectional view longitudinal view

Fig. 4.12 Cross-sectional and longitudinal views of solution-spun viscose rayon fibres [42].

In this research project, longitudinal mounts for the polypropylene fibres were easy to make. It was necessary that the lens and objectives of the microscope, as well as the slides and cover glasses, must be clean and free of scratches. The light source was adjusted for maximum visibility prior to looking at prepared slides. The basic steps for making a longitudinal mount were as follows. The fibres were cut into short lengths and placed side-by-side on the slide. Then, a cover glass was placed over the fibres. The slide was placed on the stage of the microscope and the objective lowered slowly and carefully before trying to focus the slide (since it is very easy to damage the objective by scratching it). The fibres were observed at a low power magnification of 10 to see if more than one type of fibre was present. With the microscope focussed at that magnification, the microscope's fine adjustment was adjusted very slowly until the surface contours became visible. Again they were observed carefully to see if more than one fibre type was present. Finally, the fibres were photographed to provide an image (photomicrograph) exactly as seen through the microscope.

4.8 Linear Density [15]

The usual method of designating fibre size is by its so-called "linear density" in units of mass per unit length. In fibre and textile terminology, three special linear density units are used : denier, grex, and tex. The tex system has been adopted by the ASTM as the standard unit for designating the linear density of textile fibres. The tex is also acceptable as part of the SI system, although rigorously, the SI unit is kg/m.

The tex as a measure of fineness or linear density is defined as 1g/1000m (10^{-6}kg/m). This unit has replaced the denier which is defined as 1g/9000m (1.111×10^{-7} kg/m); 1 denier = 0.1111 tex. A grex is 0.1 tex.

In this work, the linear density of fibres was determined by direct weighing of a known length (1 m) of fibre. Direct weighing is feasible for continuous synthetic filaments where a sufficient length for accurate weighing can be obtained.

4.9 Mechanical Tests [42, 43]

A fibre must possess sufficient strength to withstand processing by available textile machinery and provide the desired durability in its end use. The strength of a specimen subjected to tension load is usually reported when fibre properties are compared.

4.9.1 Tensile Strength

Any one of a number of different laboratory instruments can be used to apply a tension load to a fibre. Most tension tests are continued until the fibre breaks. The load at that point is called the breaking load or breaking force. The units for measuring breaking force include pounds, grams and newtons or millinewtons, abbreviated lbf, gf, N and mN, respectively.

To compare the breaking strengths of materials of varying sizes, it is necessary to express breaking load in terms of the dimensions of the material being tested. When relatively large material specimens are tested. the comparison may be made based on the cross-sectional area of the unstrained specimen, generally expressed as pound-force per square inch (psi), gram-force per square millimeter (gf/mm^{2}) or newton-force per square millimeter (N/mm^{2}). These are units for expressing the tensile strength of materials, that is: the maximum resistance of the material to deformation in a tensile test carried to rupture, expressed in force per unit cross-sectional area of the unstrained specimen.

4.9.2 Tenacity

Since individual fibres have very small cross-sectional areas, the conventional units for tensile strength are normally not used. Instead, breaking strength is expressed in terms of the linear density of the material, that is the mass or weight per unit length. The tensile stress expressed as force per unit linear density of the unstrained material is referred to as the tenacity, or specific stress, of the material.

4.9.3 Modulus of Elasticity (Young's Modulus)

The modulus of elasticity can be determined from the slope of the stress-strain curve. The stress-strain curve of a typical polymer is shown in Fig. 4.13.

When stress-strain curves are not linear, the modulus of the polymer can be measured in several different ways. There are four different techniques, as shown in Fig. 4.14.

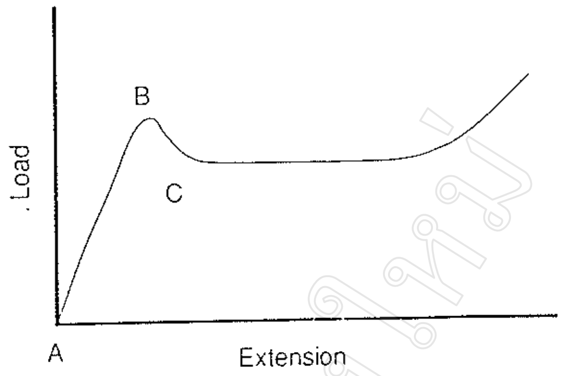


Fig. 4.13 A typical stress-strain curve for a drawn polymer [43].
A: application of load B: yield point
C: necking or cold drawing

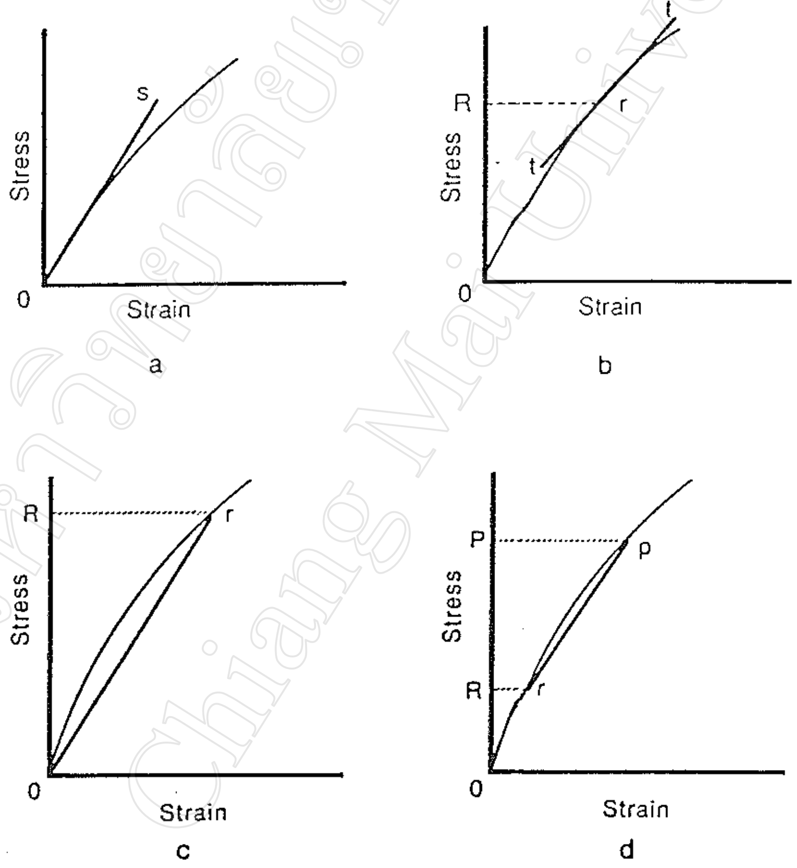


Fig. 4.14 Four accepted methods of determining the elastic modulus from a non-linear stress-strain diagram [43].

(a) initial tangent modulus [s is initial slope of curve]
(b) tangent modulus at stress R [t is tangent to curve]
(c) secant modulus between origin and stress R
(d) chord modulus between stresses R and P

4.9.4 Elongation

In a breaking strength or tensile test, a fibre is extended until it breaks. The change in length due to stretching is referred to as extension. Elongation, or percent elongation, is defined as the ratio of the extension of a material to the length of the material prior to stretching. This relationship is shown by the following equation:

$$\%\ \text{elongation} = \frac{(\text{extended length} - \text{original length})}{\text{original length}} \times 100$$

Traditional classifications can be used to decribe the performance of a polymer under load, as shown in Fig. 4.15.

Soft, Weak. These are polymers that show low modulus, low (or no) yield point and low elongation at break.

Soft, Tough. These materials have low modulus, low yield point but very high elongation at break.

Hard, Brittle. These polymers have high modulus, no yield point and very low enlongation at break.

Hard, Tough. These polymers have high modulus, high yield strength and relatively high elongation at break.

Hard, Strong. These materials have high modulus, high yield strength and relatively low elongation at break.

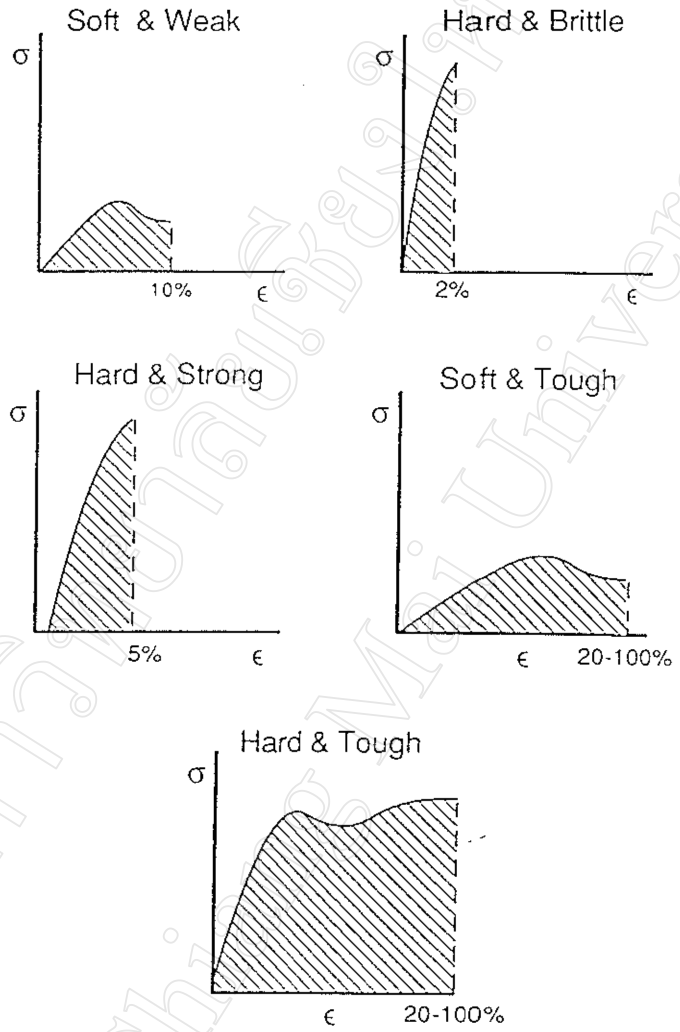


Fig. 4.15 Classification of engineering stress-strain curves for polymers [43].

σ = applied stress

ε = resulting strain

The mechanical tensile tests in this project were performed on an Instron Testing Machine, model 4301. All tests were carried out on single monofilaments using a gauge length of 30 mm and a crosshead speed of 15 mm/min. The average of five determinations was reported for each sample. The testing conditions used for all of the samples studied are given in Table 4.8.

Table 4.8 Mechanical tensile testing conditions and instrument settings used for the various fibres studied.

Testing Conditions	**Monofilament Fibres**			
	Spin-Drawn PP	Spin-Drawn/ Off-Line Hot Drawn PP	P(LLA-co-ε-CL)	Commercial Sutures
gauge length (mm)	30	30	30	30
crosshead speed (mm/min)	15	15	15	15
load cell (N)	10	10	10	100
x position (mm)	9.5	19	9.5	38
load range (%)	100	100	25	50[a] 100[b]

[a] For Monocryl 4-0 and PDS(II) 4-0 sutures

[b] For Monocryl 2-0, Maxon 2-0 and PDS(II) 2-0 sutures

4.10 *In Vitro* Biodegradation Studied

4.10.1 Experimental Method

The sample chosen for this biodegradation study was poly(L-lactic acid-co-ε-caprolactone) 7:3 melt-spun monofilaments [33]. As mentioned previously, the P(LLA-co-CL) was a prototype absorbable suture material which would need to be biodegradable (hydrolysable) within the human body. The results obtained are compared in the following Chapter 5 with corresponding data for commercial MAXON 2-0 sutures reported in an earlier study [28].

All glassware items were sterilized before use by steam autoclaving at 120°C for 20 mins. In this research project, a 0.2 M phosphate buffer of pH 7.40 was used as the immersion medium. This type of immersion medium is commonly used in polymer biodegradation studies [44].

4.10.2 Phosphate Buffer Immersion Medium (pH 7.40)

A 0.2 M phosphate buffer of pH 7.40 was prepared from anhydrous disodium hydrogen orthophosphate, Na_2HPO_4 (salt), and sodium dihydrogen phosphate 2-hydrate, $NaH_2PO_4.2H_2O$ (acid). From the Henderson-Hasselbach Equation:

$$pH = pKa + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad (1)$$

$$pH = pKa + \log\frac{[Na_2HPO_4]}{[NaH_2PO_4.2H_2O]} \qquad (2)$$

and the "Handbook of Chemistry and Physics" [45], the pKa of this phosphate mixture is 7.21. By calculation, a 0.2 M phosphate buffer (pH 7.40) was prepared from 17.2584 g of Na_2HPO_4 and 12.2401 g of $NaH_2PO_4.2H_2O$ dissolved in 1 l of deionized water. The pH of the solution, which was almost 7.40, was adjusted to exactly 7.40 with 2M NaOH.

4.10.3 Sample Preparation

All the samples were in the physical form of monofilament fibres of approximately 0.1 - 0.2 mm diameter. The samples were pre-dried in a vacuum oven at 60°C to constant weight and their weights were accurately recorded. Approximately 0.25 g samples of each were placed into screw-top glass bottles, each containing 25 ml of the pH 7.40 phosphate buffer. The bottles were then immediately placed in an incubator, thermostatically controlled at 37.0 ± 0.1°C for the *in vitro* biodegradation experiments to begin (zero time). The experiments lasted for a total of 11 weeks.

4.10.4 Sampling Procedure

At time intervals of 1 week, one bottle was removed from the incubator and the sample filtered off, washed carefully with deionized water and dried to constant weight in a vacuum oven at 60°C. Its weight was accurately recorded and its % weight retention calculated. Various thermal properties of the sample were then determined by DSC such as its melting point and heat of fusion. The pH of the medium was also re-measured since the hydrolytic mechanism of polyester biodegradation is well-known to be pH-dependent.