CHARACTERISATION OF A CAVITY TRANSFER MIXER AS A CHEMICAL REACTOR

by

Roja Raghawa Wall

A thesis submitted to the University of Aston in Birmingham for the degree of Doctor of Philosophy.

October 1989

Department of
Interdisciplinary Higher Degree
The University of Aston in Birmingham

The University of Aston in Birmingham
Title of the thesis : Characterisation of a Cavity
Transfer Mixer as a chemical reactor.
Student : Mrs. Roja Raghawa Wall
The Degree : PhD
Year of submission : 1989

SUMMARY

This research project examined the feasibility of using a cavity transfer mixer (CTM) as a continuous reactor to perform reactions between either solid or liquid reagents and polymer melt; reactions which have previously been typically carried out in batch reactor systems. Equipment has been developed to allow uniform and reproducible introduction of reagents into the polymer melt. Reactions have also been performed using batch processing equipment to enable comparison with the performance of the CTM. It was concluded that:

a. there are certain reactions which cannot be carried out in a CTM, but which can be performed in a batch system such as a mill or a sigma blade mixer. This was found to be the case for some neutralisation reactions where the product was quasi crosslinked,

b. the reactions that can be carried out in a CTM are performed more efficiently in a CTM than on a batch process. For example, when monomers were to be grafted onto polymers, this was more safely and efficiently performed in the CTM than in a mill or a sigma blade mixer.

Residence time distributions (RTDs) for three CTMs were studied in order to gain an insight into the effect of CTM geometry on RTD, polymer melt flow pattern and reactor performance. A mathematical model has been developed to predict the influence of process parameters on RTD and the results compared with experimentally observed trends. The comparison was good.

A programme of research has been drawn up to form the basis of an industrially based sponsored development project of the CTM reactor. This work programme was successfully marketed to companies with commercial interest in modified rubber and plastics as an integral part of the research programme of this thesis and the sponsored research programme has parallelled the work reported here.

Key Words
Cavity Transfer Mixer
Polymer melt reactions
Residence Time Distribution
Marketing group sponsored projects
grafting

DEDICATED

TO MY HUSBAND

AND OUR CHILD

Acknowledgements

The author wishes to thank the following.

Dr. M. P.Wilson,

for his encouragement and constructive comments,

Dr. B.G.Willoughby,

for his supervision and for providing the experimental facilities,

Mr. K. W. Scott

for analysing the samples,

Rapra Technology,

for financing the work and providing the equipment required,

The Science and Engineering Research Council,

for financial support during the first two years of this work.

INDEX

Page No.

Page No.

Page No.

Page No.

APPENDICES

LIST OF TABLES

LIST OF FIGURES

Page No.

Page No.

1. INTRODUCTION

1.1 AIMS OF THE PROJECT

The main aims of the Project were to:

i. examine the feasibility of using a Cavity Transfer Mixer (CTM) as a reactor,

ii. select the reaction systems that are best suited to being performed in a CTM,

iii. determine the process limitations of a CTM,

iv. market a project to further characterise a CTM as a reactor,

v. initiate the flow modelling of a CTM.

1.2 BACKGROUND

1.2.1 REACTIVE PROCESSING: WHAT IS IT ?

Several definitions for reactive processing are available. Biesenberger et al[106] define "reactive processing" as the simultaneous processing and chemical formation of viscous fluids, typically chain building reactions. Their definition was applied to processing equipment of all types: moulds, extruders, mixing equipment etc., as well as to various kinds of polymerisation techniques including stepwise, chain and network reactions.

Beisenberger and Gogos[11] interpret "reactive processing" to connote the shaping of polymeric materials during the chemical formation.

Schmidt and Castro[104] attempted to clarify the definition of reactive processing. They explained that usually the chemical formation and shaping operations require separate equipment and are conducted at separate processing stages; reactive processing is the execution of both these operations in the same equipment.

It may be useful to note that the word "reactive" is also used to describe polymers. Hohfeld[52], for instance, defined "reactive" polymers as those polymers which have a "reactive" monomer, such as a chemically active acid group, grafted onto them. This use of the word reactive is distinct from its use in reactive processing.

Although Biesenberger and others explain the generic concept of reactive processing, the aspect of it covered in this thesis which the phrase " reactive processing" is intended to cover is a homogeneous chemical reaction, not necessarily polymerisation, in continuous processing equipment without necessarily going to a shaping stage. The definition excludes solution and emulsion reactions but includes modification reactions in melt phase and polymerisation reactions in the absence of solvents. The kinds of processing equipment that are included in this definition are a single screw extruder, a single screw extruder with a CTM, any type of twin-screw extruder and a ko-kneader. This does not include reaction injection moulding (RIM) technology which involves, as the name implies, reactions in injection moulding machines (which are intermittent processing equipment).

The kinds of reactions that could be potentially carried out by reactive processing include free radical, anionic, cationic, grafting and polycondensation[43].

1.2.2 WHY REACTIVE PROCESSING

Most of the products that could be made by reactive processing, for example SAN, ABS, Nylon, EP, are already produced by other means[3]. For instance, these products have been produced by reactions in solution or emulsion[108]. Any functionalities or property enhancers that are to be introduced into the polymer are introduced in two ways.

1) Either by modifying the polymer during polymerisation
   or
2) by redissolving the polymer and introducing the chemical group[102].

1.2.2.1 Comparison of melt reactions with solvent/emulsion based reactions

The advantages of melt reactions when compared to solution / emulsion reactions are listed below[129].

(1) Reduced costs due to temperature control of lesser mass (solvent / emulsion): Having to heat (and cool) the polymer and solvent (continuous phase), to maintain the optimum reaction temperature would be more expensive than heating (and cooling) the polymer by itself.

(2) Reduced material costs: The solvents or continuous phase may or may not be recoverable but the money is tied up in materials. This would increase the running costs of a plant.

(3) Reduced recovery costs: Solvents or continuous phase may have to be recovered, if not for recycling, then for pollution control. This can also significantly increase the running costs.

(4) Increased surface area : volume ratio:[11] The ability to continuously renew the surfaces leads to improved kinetics and heat transfer capabilities and controlled reaction propagation. Reaction propagation in a kettle type reactor (a typical batch reactor) is mostly random and hence is not as controllable.

(5) Achieve reaction temperature quicker:[36] Eise has given evidence that the residence time needed for reaction in continuous processing equipment can be substantially lower (60 to 150 minutes for a solution reaction to 0.5 to 30 minutes for melt reactions) even for the same reaction[148]. This could be due to the reduced time required to reach the reaction temperature.

1.2.2.2 Comparison of continuous with batch processing

Some commercial solution and emulsion reaction processes are batch, whereas reactive processing is continuous. Thus a comparison of the relative advantages of batch and continuous process is useful in comparing the available processing routes. Gouinlock et al[49] have identified the following factors for comparison between continuous and batch reactor systems.

1. The throughput: The production rate of a batch system is restricted by the design of the plant. Production of much smaller quantities than the designed values will detrimentally influence the efficiency and product quality. On the other hand, increasing the throughput beyond the designed value is also not easily accomplished without adversely affecting the product quality. This is also true for continuous processing equipment if the residence time is important. The great advantage of some continuous processing systems is that for varying throughputs, the residence time may be held constant (or nearly so) by increasing the active volume of the reactor (for instance by adding modular cells to a twin screw extruder or a CTM). Demands for varying production rates can be satisfied since a given design of a continuous processing equipment, such as a twin screw extruder, can operate at production rates of less than 200 to 500 kg/hr.

2. The running costs: For continuous systems, capital costs are high and running costs are low compared to a

batch system. Hence, at low production rates the batch process is economical, but as the production rate increases the continuous process becomes commercially more attractive.

3. Increased surface area:volume ratio:[11] The ability to continuously renew the surfaces leads to improved heat transfer capabilities and controlled reaction propagation whereas reaction propagation in a kettle type reactor is mostly random and hence is not as controllable.

4. Sequential reaction initiation:[3] In a continuous flow process, reactants can be introduced exactly when they are needed along the process flow route.

5. Ready-to-use polymers:[55] Polymers can be produced by continuous processing in the required shapes by profile extrusion and the reprocessing step can be avoided.

1.3 PRELIMINARY COMPARISONS OF CTM WITH ALTERNATIVE REACTIVE PROCESSING OPTIONS.

The types of processing equipment used to achieve continuous melt reactions include single screw extruders, twin screw extruders, CTMs and ko-kneaders.

Their advantages and disadvantages will be described in detail later (Section 2.5) but it is worthwhile indicating here that in terms of operating flexibility, the CTM appears to offer advantages over alternative paths.

1.3.1 COST

Equipment for reactive processing may be compared on the basis of a cost of machine : production rate ratio. Approximate costs will be cited for each type of processing equipment producing 1 kg/hr of the product.

Twin Screw extruder	£50,000 - £75,000
Ko-kneader	£75,000
Single screw extruders	£15,000
CTM + Extruder	£25-30,000

All these are approximate 1987 prices for equipment without any downstream equipment.[132,133,134,135] The comparison is expected to be valid for complete production lines also since all the processing equipments need similar downstream equipment. Operating costs are also expected to be similar for all these equipments since they are all operated by electric motors. The cost benefit of the extruder with a downstream CTM is clear compared with the twin screw extruder and the ko-kneader. Single screw extruders have lower capital cost but may be less effective as reactors. The same contacts[132,133,134,135] comment that relative costs would be similar at higher throughputs as well.

1.3.2 OPERATING FLEXIBILITY

An advantage of a CTM over the ko-kneader and the single screw extruder is the pseudo independent control of the residence time. Since the CTM does not convey, it does not strongly influence the throughput; throughput is controlled by the extruder. Hence, the mean residence time can be altered by changing the volume of the CTM whilst keeping the rest of the equipment the same. This would give a great deal of flexibility to enable production of different reaction products demanding different residence times and would also provide flexibility in production rates.

The operation of a twin screw extruder is as flexible (Section 2.3.2) as an independently driven CTM, this could be why twin screw extruders are often used in industry for reactive processing (Table 2.4).

1.4 THE STRUCTURE OF THE PROJECT AND THE THESIS

Relevant literature in the fields of polymer processing equipment and reactive processing is described. The project described in this thesis examines the feasibility and flexibility of a CTM as a reactor.

Initial experiments are described which examine the feasibility of the CTM as a reactor. This feasibility is examined for reaction between

polymers and solids
polymers and liquids

and for cases in which the rheological properties of the product are:

a) vastly different from that of the reactants,
b) not greatly different from that of the reactants.

This stage of assessing the CTM for reactor application involved extensive equipment modification. The development of the extruder/CTM and its commissioning as an effective reactive processing system is detailed.

As part of the Project, hands-on experience was gained with certain batch reactors, such as a mill and a sigma blade mixers, with a view to gaining a working knowledge of the influence of reaction on processing.

Once the feasibility of using a CTM as a continuous melt reactor had been established, industrial collaboration was sought. This was an important element of the programme whereby the commercial applicability of the product would be verified. An approach to industry for the marketing of a research project on reactive processing is outlined and the success of this approach is indicated.

Once the project had been shown by this approach to attract an industrial interest, a programme of research was initiated to establish the optimisation of the reactor performance and to give an indepth understanding of the performance of a CTM as a reactor. It was not expected that the final optimisation of the process conditions would be achieved within the time span or scope of this research programme. It was anticipated that this project would establish feasibility and enable reliable operation of the equipment. The thesis analyses data and performance of the extruder/CTM system and makes recommendations as to its industrial application and to future research work.

2. LITERATURE REVIEW

2.1 INTRODUCTION.

In this section, the background to rubber and plastic development is briefly discussed and then the salient processing stages are summarised. The different pieces of continuous equipment used in the polymer industry are described. An outline is given of the continuous polymer processing equipment used for reactive processing, briefly discussing their advantages and disadvantages.

Mathematical modelling of flow and attempts to model some continuous polymer processing equipments are then described.

2.1.1. BACKGROUND.

The growth of the rubber and plastics industry was accelerated in the first half of this century initially to supply resources for the Second World War[8]. The true versatility of polymers was realised during this period and the years that followed saw a rapid development in applications for polymers until today when they can be found in almost every area, from disposable packaging to recreational aids and even in highly demanding engineering applications.

Each polymer has its inherent physical properties which dictate how suitable it will be for a particular job[93]. How fully the true "strengths" of the polymer are realised depends to a large extent on how it is processed from the reaction stage to the finished product. The correct choice of processing equipment and optimum operating conditions will result in minimum degradation of the polymer and in some cases, even enhance the physical properties.

But there are further criteria that govern which equipment should be chosen for the process line[8]. How efficiently the production line handles the material can often dictate what is feasible and what is not feasible, in terms of running costs. Plant efficiency often determines the size of equipment to be bought and this is directly related to its capital cost. Capital cost alone may prohibit a project from progressing any further despite its merits on a production line.

2.1.2 OUTLINE OF THE DIFFERENT PROCESSING STAGES.

This literature review examines publications dealing with the different processing stages, and the equipment, required to convert raw polymeric or monomeric material so that they are suitable for shaping.

In tracing the processing steps, several different stages may be identified[75]: a) metering, b) preblending, c) compounding, d) let-down, e) forming and f) reactive processing. The final product will have been through one or more of these stages. The equipment to be discussed can usually be identified with an individual stage, or sometimes with more than one stage.

2.2 MIXING

The mixing of liquid or solid additives into a matrix of low or high viscosity is discussed in this section. In discussing mixing, it is important to recognise the significance of material properties and how they influence the flow of material. This is important since the flow properties of a material influence the forces experienced by the material. These "forces" are responsible for the mode of mixing achieved in these materials

2.2.1 INTERRELATIONSHIP BETWEEN SHEAR RATE, FLOW AND VISCOSITY.

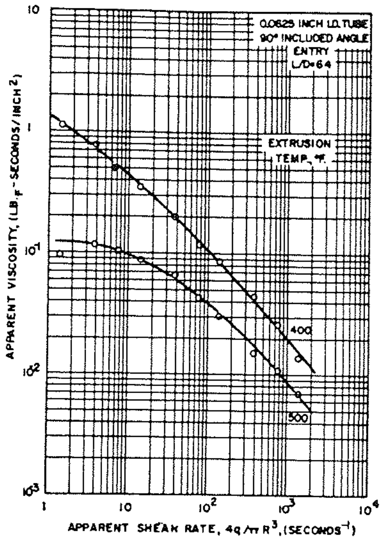
The flow of material and the forces experienced due to flow influence the rheological behaviour of some liquids. For low-molecular weight systems, the coefficient of viscosity is typically not a function of the shear rate and becomes the constant of proportionality in the Equation 2.1. This is the Equation which describes purely viscous liquids and such liquids are called Newtonian.

$$R = -\mu\dot{\gamma} \qquad 2.1^{(14)}$$

However, for the majority of fluids encountered in polymer processing, viscosity is shear and/or time dependent and such fluids are called non-Newtonian.

It should be noted that all polymer melts exhibit, to a greater or lesser extent, pseudoplastic behaviour - with their viscosity reducing with increasing shear rates. An example of the kind of dependance observed in polymer melts between the shear rate and viscosity is shown in the Figure 2.1 given below.

Figure 2.1: The influence of shear rate on viscosity for polystyrene at 400 & 500 °F.



The bulk properties of the liquid (eg. the viscosity, the density) and equipment parameters (eg. the diameter of the pipe and the velocity of the liquid in this pipe) influence the flow behaviour. One of the ways this is represented is by the dependence of Reynolds number on viscosity. Reynolds number is given by the Equation below:

$$NRE = \frac{\rho v d}{\mu} \qquad 2.2^{(14)}$$

Typically, the Reynolds number (NRE) defined in the above equation needs to be greater than 2,100 for turbulent flow to exist in a straight pipe of circular cross section.

2.2.2 MIXING IN DIFFERENT SYSTEMS.

Having examined the different parameters that may influence mixing, the different modes of mixing may now be distinguished. (Although mixing can be quantified using certain British standards, qualitative descriptions are often useful in describing the different modes of mixing.)

Gale's definition[136] for different modes of mixing are reproduced here along with some explanatory notes.

Dispersive mixing : "an operation which reduces the agglomerate size of the minor constituent to its ultimate particulate size". This operation is usually relevant in the context of mixing solids (agglomerates) into a matrix. Studies[7] have been carried out which indicate that such mixing requires high shear stresses.

Distributive mixing : "an operation employed to increase the randomness of the spatial distribution of the minor constituent within the major base with no change in the size of the minor particle".

Mixing of liquids is usually distributive since there are no agglomerates to break down. Distributive mixing can be achieved by agitation - where agitation is defined as "the creation of a state of activity such as flow or turbulence"[53]. This is only practical for obtaining distributive mixing in low viscosity liquid matrices. For high viscosity matrices, strain experienced by the mixture is used as a measure of distributive mixing. However it has been suggested[86] that reoriented flow would lead to a better mix. This was the basis for the design of several static and dynamic mixers one of which is the cavity transfer mixer.

2.2.3 DEPENDANCE OF THE MODE OF MIXING ON VISCOSITY.

As has been stated previously, the viscosity of the fluid influences the mode of flow that is exhibited in a flowing system. It has also been observed that the flow behaviour would influence the forces that would be exerted on the matrix. Hence, it is logical to assume that matrices of different viscosities would favour different modes of mixing; this dependance of mixing on the viscosity of the matrix is discussed in Section 2.2.3.

2.2.3.1 Mixing in high viscosity systems.

Dispersive and distributive mixing in high viscosity systems are discussed in this subsection.

2.2.3.1.1 Dispersive mixing in high viscosity systems.

Dispersive mixing, as mentioned before, requires high shear stresses. As seen in Equation 2.2, high viscosity increases the shear stress experienced by the polymer and hence, for a given shear rate, the ability to disperse a polymer is increased as the viscosity of the matrix increases. Since high levels of filler increase viscosity[40], dispersive mixing is carried out in masterbatches containing high filler loadings and these are subsequently let down by blending with more polymer (Section 2.4.4).

2.2.3.1.2 Distributive mixing in high viscosity systems.

Distributive mixing is not as easy to obtain as dispersive mixing in high viscosity systems as it depends on the strain levels that can be achieved; this is true for systems such as single screw extruders where the flow is not reoriented. However improved distribution may be achieved by a sequence of reorienting and then cutting the flow stream - this principle has been used in the design of a mixer, called a cavity transfer mixer (CTM), which is studied in this research project.

2.2.3.2 Mixing in low viscosity liquid systems.

Dispersive and distributive mixing in low viscosity liquid systems are discussed in this subsection.

2.2.3.2.1 Dispersive mixing in low viscosity systems.

As seen in Equation 2.1, a lower viscosity fluid is subjected to lower shear stress, at a given shear rate. As shear stress is necessary to break down agglomerates, dispersion in low viscosity liquids is not easily achieved. However, equipment is available where very high shear rates are exerted to achieve dispersion in low viscosity systems.

2.2.3.2.2 Distributive mixing in low viscosity systems.

Turbulence is more easily achieved in low viscosity systems (Section 2.2.2). In the turbulent flow regime, distributive mixing is efficient since distributive mixing is enhanced by the eddies existent in the turbulent flow regime.

2.3. CONTINUOUS PROCESSING EQUIPMENT.

In this section, details are given of some of the important continuous processing equipment suitable for polymer processing applications.

2.3.1 SINGLE SCREW EXTRUDER

A single screw extruder is commonly used for melting, conveying and for let-down of compounded material. With appropriate attachments and modifications, it can be used to compound certain fillers.

The processing parameters that can be altered in a single screw extruder are the rotational speed of the screw, the barrel temperature, and sometimes also the temperature of the screw. The throughput, for a single-screw extruder, is determined by the rotational speed and the die head pressure.

2.3.1.1 Design of a single screw extruder.

The influence of the screw design on the flow pattern, pressure build-up and the power requirements has been mathematically examined by Booy[20]. Design modifications, such as grooved screws, have been used to improve conveying of elastomers[95] and low bulk density powders[8].

The equation developed by Maddock[72], which describes the throughput when it is controlled by the metering section, is given below:

$$Q_V = \frac{\pi^2 D^2 h \sin \phi \cos \phi N}{2} - \frac{\pi D h^3 \sin \phi \Delta P}{12 L \mu} \tag{2.3}$$ (72)

Figure 2.2 A single screw extruder flight showing the symbols used in Equation 2.3.

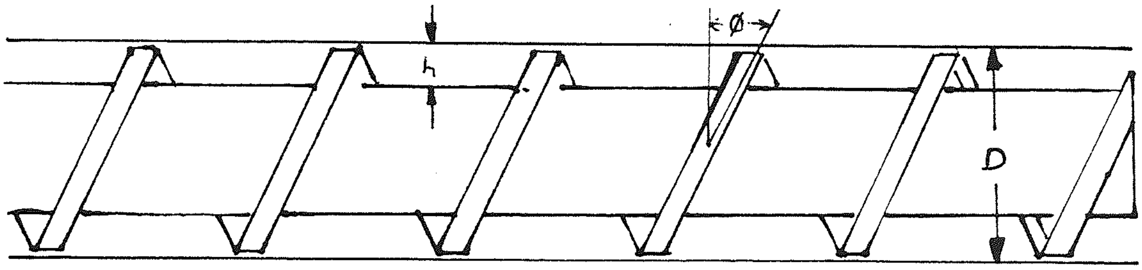
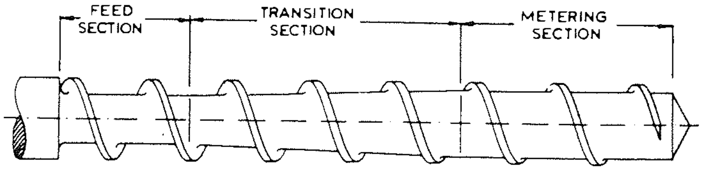
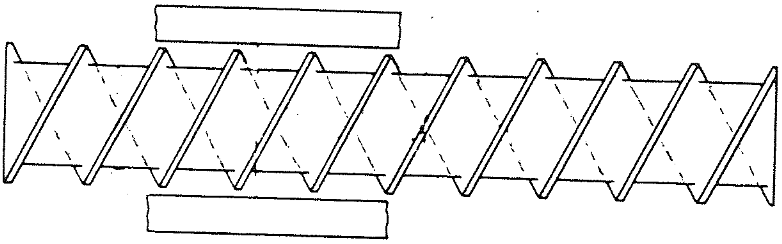


Figure 2.3 A figure showing the different regions in a typical single screw extruder.



The pitch of the screw and the speed of rotation determine the throughput. Usually a square-pitched screw (pitch length equalling the diameter of the screw) is chosen. Variable pitch screws can be manufactured in order to optimise the pitch in the different zones (solids conveying, melting and melt metering) of the extruder, but this increases the manufacturing cost and is only financially attractive for the production of value added products. Two-start screws (Figure 2.4) are also used to achieve higher throughputs. However, the product quality from such an extruder may not be satisfactory (especially for elastomers[76] because of the high shear rates in such machines which would lead to high temperatures in polymers of high viscosity such as rubbers).

Figure 2.4: A figure of a two start single screw extruder.
(the flight consists of a double helix).



The depth of the channel is often reduced as the screw approaches the die head. The ratio of the channel depth at the feed section to that at the metering section is known as the compression ratio.

A single screw extruder can be designed for compounding; salient design features of such extruders are discussed here: they usually have large length to diameter ratio (L:D) ranging from 30:1 to 40:1, and typically have shallow channels. There are various kinds of attachments available to effect dispersion; there are certain attachments which restrict the flow of material so that it has to flow through a tortuous path (for example, studs, pins, maddack barrier screw), there are other attachments which enable the material to flow through a high shear rate region (for example; a shear cone unit, kneaders, shear heads)[87,4,54,79]. Details of these devices are not given here but they are adequately discussed in the literature[87,4,54,79].

2.3.1.2 Screw designs[127]

The screw design is selected after consideration of the process conditions and the materials to be handled. A high compression ratio is used if:

a) the pressure at the die head needs to be high,
b) the difference in density between the pellet/powder and the molten polymer is great.

High compression ratios lead to excessive shear heating. Therefore ratios over 3:1 are not recommended for processing shear sensitive materials such as PPO and TPU (Table 2.1).

It is advisable to use a gradually compressing screw if a material to be processed:

1) is shear or temperature sensitive like PVC or rubber,
2) has a wide softening temperature range like PC,
3) is degradable like rubber and polyether ester.

The zone where the channel depth decreases is where the majority of the solids melting is designed to occur. Consequently, if the material[127] to be processed has a narrow melting point (e.g. Nylon 6,6), a short (approx. 0.2L) compression zone is chosen. On the other hand, if the material is such that too much shear stress should not be introduced into the material at once (e.g. rubber), the compression zone is "stretched" over a longer region.

Typical compression ratios used for processing a variety of polymers are listed below.

Table 2.1: Recommended compression ratios for some polymers[127].

Polymer	Compression ratio	Comments
Polyethylene[152]	2.5:1 to 4:1	Gradual transition
Poly Vinyl Chloride[154]	1.8:1 to 2.3:1	Gradual transition
Polycarbonate[153]	2:1 to 4:1	
ABS and rubber	1.6:1	Gradual transition
Nylon 6	2.2:1	Length of compression = 0.2L
Fluorinated EP	3:1	Rapid transition
PBT	2:1	Rapid transition
PEEK	2.2:1	Rapid transition
PET	2:1	Gradual transition
PPO	1.8:1 to 3:1	If > 3:1, will result in degradation
PSU	2:1	

The design variables for a single-screw extruder which are altered to suit the processing system include: the pitch, the number of starts, the depth of the channel, the flight width and the design of the die[77].

2.3.1.3 Operation of a single screw extruder.

As may be seen, from Equation 2.3, increasing the depth of the channel (h), increases the throughput (Q). The influence of some process parameters on the operation of a single screw extruder are briefly discussed below.

1. Temperature : The advantages of operating an extruder adiabatically have been emphasised by McKelvey and Bernhardt[75]. A couple of these advantages are listed below.

i. the mode of introduction of heat into the polymer: heating using external heaters requires temperature gradients whereas heat generation due to increased mechanical energy dissipation does not require any thermal gradient; this would alleviate the problem of uneven temperature in the polymer melt.

ii. the throughput from an adiabatically operated extruder would be higher because if the extruder is heated from an external source, the rate at which the heat is transferred to the polymer melt would limit the throughput. Even with adiabatic operation of the extruders, heaters would be required to fine tune the temperature profile in an extruder[75].

The influence of temperature profile on the melting behaviour in an extruder has been assessed by Tadmor et al[119] and a previous mathematical model was modified to take this influence into account although their mathematical predictions were not tested against experimental evidence.

The thermal requirements ie. the heat that needs to be introduced into the polymer, of an extruder have been established by Menges et al[76].

2. Pressure : Severs[107] and Colwell et al[29] examined the influence of pressure drop on throughput; an increase in throughput is found to be accompanied by an increase in pressure drop.

3. Loading : The effect of partially filled screw channels on the pumping efficiency of an extruder was predicted and experimentally verified by Squires[114] although, in practice, single screw extruders are operated with their channels full.

4. Materials : Dettaven[33] developed a technique to estimate the performance of a single screw extruder with a range of pseudoplastic materials.

2.3.1.4 Residence time distribution in single screw extruders. (RTD defined on p93).

Residence time distribution (RTD) in an extruder has also been examined. Potente and Lappe[97] calculated the RTD in a plasticating screw (which melts a polymer pellet into a polymer melt) using the mean and minimum residence time as variables in their model. They[97,150] also examined the influence of the physical properties of the tracer on the measured RTD. Sebastian and Biesenberger[106] did experimental work to conclude that flow in an extruder did approximate to plug flow.

2.3.1.5. The scale-up of a single screw extruder.

The extruders used in industry are about 20 times larger (in diameter of the extruder screw) than those typically used for research and development[24] which explains the need for scale-up work. This necessitates the development of scale-up laws[60,72]. For example, relationships are drawn between the diameter of the screw, the power of the drive and the throughput rate[60]. Maddock[72] discussed the rationale behind the scale-up of extruders using the ratio of the screw diameters as the scale-up factor. He investigated how this factor would influence the performance of a single screw extruder. However, experience and empiricism still play a major role in scaling up due to the complicated interactions between design and process parameters[72].

2.3.2 TWIN SCREW EXTRUDERS[37,36,131,6,67,9,123,32]

Twin screw extruders are often used, in the polymer industry, for compounding. In recent years, they have also been used as a reactor - for reactive processing; their use in reactive processing will be discussed in Section 2.6.3. The design and operation of twin screw extruders will be discussed in this section.

2.3.2.1 Design of twin screw extruders.

There are a two main types of twin screw extruder , one with counter rotating screws and the other with co-rotating screws. In both these models, they can be non-intermeshing, semi-intermeshing or fully intermeshing. The residence time distribution, the flow patterns and the shear rate generated in the machine are dependent on the design of the screw. Some of these extruders are designed so that they are self cleaning ie. the flight of one screw wipes the surface of the other; this is thought to reduce (eliminate) dead spots[125] .

Counter rotating twin screw extruders are not usually modular; they consist of two Archimedian screws of set lengths. It is possible that distributive mixing would not be efficient in these extruders, since they do not encourage transfer of material between screws[83] .

The screw design, in a co-rotating machine, is modular allowing it to be built-up to meet the exact process requirements[100] . In this way, it overcomes the restriction placed on other compounders of having to use only one of a few standard designs[77, 100] . The design of the co-rotating twin screw extruder is such that material is transferred from one screw to the other readily. This would result in good distributive mixing[83] . This design is not as good at conveying as the counter rotating model[100] .

2.3.2.2. Screw designs: The modular structure.

There are a range of modules available for the co-rotating model. An advantage of the modular arrangement is that it can satisfy the exact process requirements. By altering the arrangement of the modules, the required flow path and the shear range can be obtained. It also means that, for a given throughput, the mean residence time can be altered by increasing or decreasing the internal volume of the reactor zone (usually the kneader section). The more frequently used modules are: a single start conveying section, a twin-start conveying section, kneading elements and a reverse-threaded screw[131,6,67,9].

The kneaders are usually manufactured as individual units and are assembled at different angles; the magnitude of the angle between adjacent kneader elements influences:

1) the flow pattern,
2) the shear stress experienced by the process stream and
3) the conveying capacity of the train of kneaders.

The kneading elements contribute to both distributive and dispersive mixing by:

1) the high shear rate generated in the region between the two kneaders leading to dispersive mixing,
2) the design of the kneader influencing the transport of material in the radial direction, leading to distributive mixing.

The conveying screws are usually of standard lengths. The reverse threaded screw region is capable of generating high shear rates because of the flow pattern generated; the overall motion of the material is towards the die and the design of the screw (reverse threaded) pushes the material towards the hopper. This conflict of flow patterns generates increased radial mass transfer.

2.3.2.3 The operation of twin screw extruders.

The counter rotating extruders consist of two standard Archimedian screws and their speeds of operation are usually low (approx. 30-35 rpm); consequently the throughputs are also lower than those of a co-rotating twin screw extruder of a similar diameter. Since the throughputs are lower, they operate with their channels full.

The co-rotating screws consist of modular sections (Section 2.3.2.2) and rotate at speeds of up to 500 rpm. They are usually starve fed. These extruders have to be starve-fed since flood feeding would result in overloading the extruder drive unless a low bulk density material is used[100]. Since they are not operated at their full capacity, they cannot be gravity fed; they need to be fed using weigh feeders, or fed by volumetric feeders. Either preblends could be used or each component could be metered individually. (Starve fed conditions are defined on p6I)

The barrel is heated or cooled with either a fluid medium or by electrical means. Heat transfer coefficients as high as 0.7 KW/cm^2 K have been claimed by certain manufacturers[36].

Rauwandaal[100] showed that dispersive mixing in a counter rotating model was better than that in the co-rotating model. He postulated that this was due to the small gaps between the screws in a counter rotating model generating high shear rates (as in a two roll mill).

2.3.2.4 Residence time distributions in twin screw extruders.

The residence time distribution plays an important role especially when the equipment is used for reactive processing.

Rauwandaal[100] examined the effect of throughput and rotational speed on residence time distribution in both co-rotating and counter rotating twin screw extruders. The extruders he tested were not fully intermeshing. Partially intermeshing twin screw extruders are expected to be more positively conveying than the non-intermeshing models.

Rauwandaal[100] showed the following trends for both designs of extruder , the co-rotating and the counter rotating.

a. Increasing the throughput narrowed the RTD.

b. Increasing the speed of rotation of the twin screw extruder broadened the RTD.

The second observation agrees with Stuber and Tirrel's prediction and inferences from continuous polymerisation work performed in a twin screw extruder[116].

One major difference between the two models he[100] found was that the counter rotating model had a narrower RTD than the co-rotating model.

Hermann and Eise[51] investigated the influence of various modules on the RTD in closely intermeshing co-rotating twin screw extruders. They found that:

i. a combination of right and left hand pitched kneading elements gave a broad RTD and a longer mean residence time (low conveyance),

ii. the conveying element has a medium residence time distribution and a medium mean residence time and

iii. a right hand pitch kneading element has a narrowest RTD and the shortest mean residence time demonstrating its efficiency of melt conveying.

2.3.2.5 The scale-up of twin screw extruders.

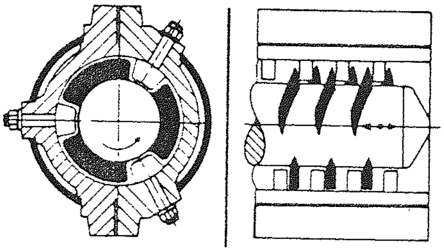
Scale-up of twin screw extruders (both counter and co rotating models) was attempted by Potente[96] using "model laws". He compared the theoretically obtained values for process parameters, such as throughput, power requirement, with values for a commercially available twin screw extruder. This comparison showed that the scale-up "laws" he used are serviceable. The parameters he used to scale-up included the temperature profile, the pressure upstream of the die, the screw diameter, the torque requirements, the length of the screw, the rotational speed of the screw and the depth of the screw thread.

2.3.3. KO-KNEADER [57,58,10,23]

The ko-kneader is a special modification of a single screw extruder and it is different enough in design to warrant a separate discussion. It consists of a single screw with usually three interruptions per revolution and a barrel with stationary teeth corresponding to these interruptions. The size and shape of the stationary teeth and the interruptions in the flight can be modified to adjust the distributive and dispersive action in the kneader. There are modular attachments available which can alter the functioning of the ko-kneader and these include reverse thread screws, special kneading elements and other such attachments.

The pitch of the screw can also be different in the modules, if the process requires such an action.

The screw not only rotates but also oscillates, leading to a flow pattern where the flow stream is continually separated and later rejoined with other streams. This leads to an efficient distributive action in the ko-kneader. One of the side effects of the oscillating movement is that the output is always pulsating. To overcome this, the output is discharged into a single screw extruder. The cascade arrangement is selected to fit in with the plant layouts and process systems [23].



2.3.4 CAVITY TRANSFER MIXER (CTM)

A Cavity Transfer Mixer (CTM) was designed and patented by Dr. G. M. Gale of Rapra Technology. It has been selected for investigation in this project for reasons outlined in Section 3.3.2. The concept behind the design of a CTM, the actual design features and its performance as a mixer are discussed in this section. Discussions of its potential as a reactor are outlined in Section 2.6.4 and further use of a CTM as a reactor was examined in this PhD project. (Refer to Figure 2.4b). A CTM cannot convey and hence has to be connected to a processing equipment that can.

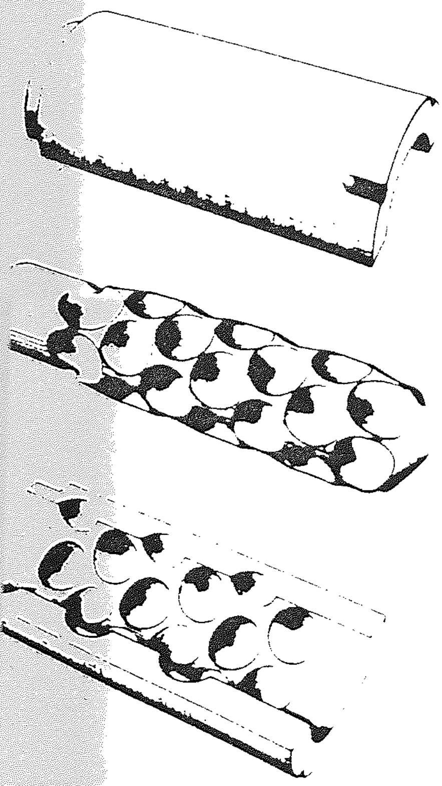
2.3.4.1 A CTM: What is it?

A CTM was designed to improve distributive mixing, with minimal pressure drop, of polymer melt containing fillers. Gale used Ng[86] and Spencer and Wiley's[113] hypothesis that improved distributive mixing is achieved if the melt stream is reoriented (Section 2.3.4.2.1). Hence, the CTM was designed with hemispherical cavities in the rotor and the stator in a bid to achieve such a motion. The melt pressure drop across the CTM was expected to be minimised by reducing landed areas. The basic design features of a CTM are summarised below.

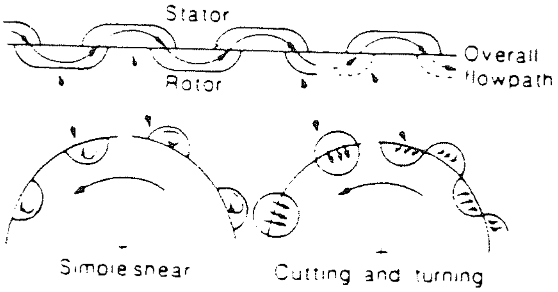
1. The cavities are nominally hemispherical with circular openings.
2. The cavities are arranged in staggered rows, so that the following criteria are satisfied.

(a) At any point during rotation, each cavity is open to

Figure 2.4b : A drawing of a cavity transfer mixer and the mixing action in it.



The Cavity Transfer Mixer



Mixing action of the CTM

3 opposite cavities with a large overlapping area being possible. This minimises pressure drop and variation in cross sectional areas during rotation.

(b) Land lengths are minimal so that shear rates are minimised.

(c) The configuration is streamlined with no corners; this is to prevent stagnation.

(d) Shape is conducive to circulatory flow which can link opposite cavities.

2.3.4.2. Reorientation and its influence on mixing.

The fundamental basis of the design of the CTM is that reorientation of flow leads to improved mixing. The theory behind this premise is discussed in this section.

The easiest way to visualise the Equations 2.4 - 2.6 is to consider a matrix with two separate layers, of say different colours but of the same rheological properties. The Si in the equations would then be the initial surface area between these two layers. This surface area of contact between the two layers is expected to increase as a result of mixing. The factor Sf/Si would represent the increase in surface area due to mixing. The values α and β describe the motion experienced by the matrix during the mixing process.

Spencer and Wiley[113] studied mixing in viscous liquids and related the angle between the orientation of the flow and the shear strain to the increase in the surface area. This is given by the equation below:

$$\frac{Sf}{Si} = \sqrt{1 - 2\left(\frac{\partial x}{\partial Y}\right) \text{Cos}\,\alpha\ \text{Cos}\,\beta + \left(\frac{\partial x}{\partial Y}\right)^2 \text{Cos}^2\alpha} \qquad 2.4$$

It follows from Equation 2.4 that "for very large surface ratios (Sf/Si), the undeformed surfaces should cut perpendicularly across the displacement sectors".

Erwin[112] in 1978 further studied mixing and developed equations (Equations 2.5 - 2.6) to quantify mixing in a single screw extruder. The Equation 2.4 can be reduced to the Equation 2.6 below when flow is not reoriented.

$$\frac{Sf}{Si} = \sqrt{1 - 2\left(\frac{\partial x}{\partial Y}\right) \text{Cos}\,\alpha\ \text{Cos}\,\beta + \left(\frac{\partial x}{\partial Y}\right)^2 \text{Cos}^2\alpha} \qquad 2.4$$

$$\frac{Sf}{Si} = \frac{\partial x}{\partial Y}\,\text{Cos}\,\alpha \qquad 2.5$$

and when $\alpha = 0^\circ$; $\text{Cos}\,\alpha = 1$, i.e. there is no reorientation

$$\frac{Sf}{Si} = \frac{\partial x}{\partial Y} \qquad 2.6$$

Equation 2.6 predicts a linear rate of mixing , i.e. rate of increase of surface area is linearly related to the stress strain experienced by the fluid, when the flow is not reoriented. This is the mode of mixing expected in a single screw extruder.

Bigio et al[13] (in 1985) also assessed the performance of a single screw extruder as a mixer. They, like Spencer and Wiley[113], comment on the improvement in mixing due to reorientation of flow by 90°... "reorienting the mixture during processing will enhance the mixing effectiveness of shear".

Ng et al[86] agree with the ideas put forward by Spencer and Wiley[113]. Ng et al[86] go on to state that if a mixer with N-1 mixing sections, each of which optimises the interface for subsequent strain, and having N shearing sections, each of equal straining magnitude ($\partial x/\partial y$), causes mixing defined by:

$$\frac{Sf}{Si} = \left[\left(\frac{\partial x}{\partial y}\right) \Big/ N\right]^N \qquad 2.9$$

$$\text{Since} \qquad Si \propto 1/ri \quad \& \quad Sf \propto 1/rf \qquad 2.10$$

where r is the striation thickness and hence is inversely proportional to the surface area S.

$$\frac{ri}{rf} = \left[\left(\frac{\partial x}{\partial y}\right) \Big/ N\right]^N \qquad 2.11$$

$$\lg \frac{ri}{rf} = N \lg\left[\left(\partial x/\partial y\right) \Big/ N\right] \qquad 2.12$$

Equation 2.12 predicts a logarithmic relationship between the rate of mixing and the number of mixing stages; "the interfacial area grows much faster than linearly with one or more reorientations incorporated in the mixer"[86]. The CTM was designed on this principle.

2.3.4.3 Mixers designed to improve the mixing performance of a single screw extruder.

Kosel[65] (1971) compared the mixing action of a single screw extruder and a barrel and screw pins (pineapple) mixer by examining the quality of extrudate. He found that the barrel and screw pins improved the mixing performance of the assembly. (Subsequent studies by Gale[45] on microtomed sections showed that a CTM produced a more homogeneous mixture than a pineapple mixer.)

Bigio et al[13] reported that the rate of increase of striation thickness/total strain rate was 0.055 for an extruder screw and increased to 0.1 for a screw with mixing pins. This showed that a screw with mixing pins is a more "efficient" mixer since it led to a greater reduction in striation thickness for a given total strain.

2.3.4.4 Development of a CTM.

In 1978, Gale[137] investigated the flow in a single screw extruder in order to identify how improvements in mixing could be achieved. He studied the addition of a Maddock screw to a single screw extruder and reported on the improvement achieved by this mixing zone. The comparison of goodness of mixing was mostly on microtomed sections of samples. For a given screw speed, it was found that 8% reduction in throughput resulted due to this addition of the mixing aid.

In 1980, Penny[138] investigated an addition of a roller bearing mixer to a single screw extruder to improve mixing. Microtomed sections did show improvement in mixing due to the roller bearing mixer. However, the temperature increase due to the passage through the roller bearing was significant (at 80 rpm, 15°C for LDPE, 40°C for Alathon 7030 HDPE).

A crosshead arrangement, with the "pineapple" mixer on the crosshead, was then investigated by Gale[137]. It was reported that, as the mixer speed decreased, for a given extruder speed, the temperature rise across the mixer increased. It was observed that although the mixer provided adequate mixing for certain polymers, for others such as LDPE, mixing performance with this mixer was inadequate.

Gale[139] then investigated a device called a cross cavity mixer. This is referred to as the A2-B2 mixer in his paper. An increase in melt temperature was noticed due to this mixer; it was 20°C for the LDPE. The pressure increase due to the mixer was approximately 200 psi. There was a significant reduction in striation thickness due to this mixing (reduced from approximately 1000 microns to 0.01 microns after going through the 7 row mixer). Although the mixing performance and the temperature increase criteria set by Gale were satisfied by this mixer, the pressure increase was too high.

In an attempt to reduce the pressure build-up due to the mixer, another mixer was developed (A3-B3) with angled rotor cavities and curved stator cavities. However, because of the reduction in the number of cavities in the mixer (due to the difference in cavity design), the mixing was not as good as that obtained with the A2-B2. The desired melt pressure reduction was also not achieved.

This work formed the basis for the design of a Cavity Transfer Mixer (CTM)[136]. Examination of microtomed sections of extrudate revealed that mixing was most effective in a CTM. The striation thickness measurements showed that a CTM provided more efficient mixing than A2-B2. It was also found that a CTM with deeper cavities required less power to drive than a CTM with shallow cavities for LDPE, HDPE and PP. Both the CTMs required less power to drive than the other mixers studied. The pressure drop was also lower for the deeper cavitied CTM than the shallow cavitied CTM. In both the CTMs, the pressure drop was lower than for the majority of other mixers (for LDPE, HDPE and PP). Melt temperature rise was usually lower for the deeper cavitied CTM (for HDPE and PP).

From the experiments performed, it was deduced that a CTM would not be suitable for dispersive mixing.

2.3.4.5 Residence time distribution in a CTM.

Bevis and Lin[71] examined the use of a CTM on-line an injection moulding machine. They assembled an injection moulding machine with a CTM downstream and analysed the improvements in mixing obtained in the product due to the presence of the CTM and also its influence on RTD. They noticed that there was both an increase in mean residence time and broadening of residence time distribution when a CTM was used on-line. However, when the residence time distribution was plotted against dimensionless time, ie. time/mean residence time, it was seen that the assembly with the CTM had the narrowest residence time distribution.

N.B. Plotting the residence time distribution against dimensionless time takes into account the broadening of residence time distribution due to the increase in mean residence time and compares RTDs as if they had the same mean residence time.

It was also noted in their work that mixing (according to BS 2978 part 8: Method 823A and 823B for measuring carbon black dispersions in polyethylene and BS 2782) was better in the assembly with a CTM than one with a vent zone which was better than one with a standard compression screw.

2.3.4.6 Applications of CTMs.

Some researchers have examined the various applications of CTMs; a few of these are listed below.

N.B It is not always possible to comment on improvements in performance due to the addition of a CTM since such comparative studies are rare.

(1)[136] Blotchiness, pronounced when extruding LLDPE at high throughputs, was eliminated by the use of a CTM.

(2)[136] When extruding coloured materials, a reduction in the masterbatch level was acceptable with a CTM in-line compared to when an extruder was used by itself. This was attributed to the better distribution of the masterbatch in the polymer.

(3)[136] A CTM could be used in forming systems, such as the extrusion of pipes and blow moulding of bottles.

(4)[136] Let down of pigmented EPDM using a 50mm extruder was accomplished with a CTM in-line.

(5)[136] Compounding of butylene/poly(alkylene ether) terephthalate with desiccant, stabiliser, pigment and flame retardant using a 50mm extruder was possible with an in-line CTM.

(6)[136] Blown film of a mixture of 90 parts LDPE and 10 parts HDPE with CTM allowed higher blow-up ratio without flaws than when an extruder was used by itself.

(7)[136] The possibility of blending SAN (MFI 0.28g/10 min) and polycaprolactone (MFI 34g/10 min) was established with a CTM.

(8)[136] Liquids such as glycol, colour dispersion, DOP, dispersion containing blowing agents and activators could be injected into and mixed in a CTM. This operation would not be possible with an extruder alone because it would result in slippage.

(9)[140] Hindmarch reported the use of a CTM for blending in the rubber industry. Improved properties, i.e. electrical resistance, were reported when the blends were prepared in a CTM. This is seen to be due to the better mixing achieved in a CTM.

(10)[140] Another application is the extrusion of rubber with reproducible electrical properties. "A CTM improved the distribution of ingredients sufficiently to give some advantages in mixes destined for a microwave heater... the variability of resistivity within a sheet of rubber was improved very considerably by using the CTM."

[illegible]

(11)[140] The use of a CTM to attain higher throughputs from extrusion lines was also attempted. The throughput could be doubled without penalising the product quality if a CTM were used instead of an extruder by itself.

(12)[71] A CTM was used on-line in an injection moulding machine where it was found that its presence improved the mixing efficiency of the line.

(13) The use of a CTM as a reactor will be discussed in Section 2.6 and Chapter 6.

2.3.4.7 Financial attractions of a CTM.

The cost advantages of using a CTM for reactive processing are outlined in Section 1.3.1. Cost analysis was carried out by Gale[136] for when the CTM was used as a mixer; it was calculated that, for say PP compounding on a 114 mm extruder, the CTM would (in 1984) cost £7,000 but would save £203,000/year. Savings around £50,000 to £100,000/year are predicted from these calculations for processes ranging from compounding to blown film to PU coating.

2.4 PROCESSING STAGES IN A REACTIVE PROCESSING TRAIN.

Equipment available to perform the various processing stages in the polymer industry is outlined in this section of the review. The Table below summarises the available equipment for each stage. There follows a more detailed description of each stage and its characteristics.

A chart outlining a) the processing requirements and b) the equipments used to satisfy these flow requirements.

Function	Mixing Requirements	Flow Requirements	Equipment Available
Metering Section 2.4.1		Uniform flow	Volumetric feeders, weigh feeders such as single screw, vibrating tray and belt feeders
Preblending Section 2.4.2	Distributive mixing	Flow pattern is the important factor	high speed mixer, ribbon blender, trough and tumble blenders
Compounding Section 2.4.3	Dispersive mixing	High shear stress is needed so as to break down the agglomerates, which is an essential part of compounding	internal mixers, two roll mills, multiple screw extruders, large L:D ratio single screw extruders and ko-kneaders
Let-Down Section 2.4.4	Distributive mixing	Flow pattern is the important factor	internal mixers, two roll mills, single screw extruders, CTMs
Reactive Processing Section 2.6	Good interfacial contact	Requirement in positive conveying of material with a narrow RTD	All compounding, let-down and forming equipment are used for reactive processing

2.4.1 METERING

Before ingredients of any formulation are put into the preblending cycle or into the compounding stage, they must be metered in the required proportions. This is simple for a batch process; ingredients are weighed out by the operator and added to the mixer in the correct ratios. Obtaining scales with sufficient resolution to provide the necessary accuracy for weighing out purposes is relatively easy; the main errors to the proportioning being due to operator error.

For a continuous process, the ingredients must be metered continuously into the mixing cycle in the correct ratio. The choice of metering equipment will depend on the physical form of the ingredients, metering accuracy and cost restrictions. The metering equipment discussed in this section can also be used for metering <u>preblended</u> mixtures into a starve fed system such as into a twin screw extruder or a ko-kneader. (Starve fed conditions are said to exist when the channels in the extruder are only partially full. In other words, the throughput would be dependent on the metering device setting and not on the conveying capacity of the extruder.)

N.B. The subjective statements in this metering section (Section 2.4.1) are only made after extensive technical discussions with both the manufacturers and users of metering devices.

2.4.1.1 Metering of solids[149, 94, 61].

The two different systems for handling solids are volumetric feeders and weigh feeders. The volumetric feeders can be operated within an error margin of 2-3% but these are cumulative errors. If greater accuracies of, typically 1%, are required, weigh feeders are used. Cumulative errors in weigh feeder systems can be eliminated by using control systems that interconnect different weigh feeders and can maintain the ratios of the feed rates as a constant. Since the weigh feeders are usually about three times as expensive as a volumetric feeder, their applications are restricted to areas where greater accuracies are required. A cost comparison between a volumetric feeder and a weigh feeder is given below.

	output range (lt/hr)	price
volumetric single screw feeder	0.6 - 4400	£ 3740
weigh single screw feeder	0.6 - 4400	£11740

The range is not for any given model but for the range of feeders for which the price is valid[61].

2.4.1.1.1 Volumetric feeders.

There are various types of volumetric feeders in use and some of the commonly used models are: single-screw, twin-screw, belt and vibrating tray feeders.

Since some of the costs were only available for weigh feeders, the cost comparison between these feeders is given for weigh feeders in Section 2.4.1.1.2.

2.4.1.1.2. Weigh feeders.

Weigh feeders, even at increased expense compared to volumetric feeders (Section 2.4.I.I.I) have a significant market demand, especially in multi-feeder systems, where they perform with greater accuracies since they can avoid the cumulative errors associated with their counterparts in volumetric feeders.

Screw feeders, vibrating trays and belt feeders can all be used in weigh-feeder systems. Weigh feeders usually function on two principles: either loss-in-weight or stream weight. Typically, screw feeders function on loss-in- weight principle. The belt feeders and the vibrating tray feeders more frequently use the stream weight to control their throughput (the throughputs are controlled by altering the belt speed, the screw speed or the vibration intensity)[61].

Weigh feeders also have some disadvantages. The equipment, being more elaborate, is prone to damage by operators and care should be taken during mounting this type of equipment since it is susceptible to interference due to mechanical vibrations and electrical circuitry. These shortcomings however can be overcome by good equipment design and operator training[61].

A cost comparison is given below for the different weigh feeder designs commercially available. Comments are made on the applications for the various feeders.

Table 2.2 Cost comparison between different designs of weigh feeders (1989 prices)[61].

metering device	output range (lt/hr)	applications	price
single screw feeder	0.3 - 4400	powder pellets mixes, free flowing powders	£13900
twin screw feeder	0.8 - 1500	sticky or fine powders	£14800
belt feeder	20 - 15000	pellets,flakes agglomerates	£13100
vibrating tray feeder	8 - 80	fragile materials eg.glass fibres	£10700

The range is not for any given model but for the range of feeders for which the price is valid[61].

2.4.1.2 Metering of liquids.

Liquids can be introduced into mixing cycles of either batch or continuous processes. This is a more straightforward operation for batch systems compared to continuous systems. In the latter case, the injection conditions and the properties of the liquid play a deciding role in the selection of the pump. When the liquid being injected into the system needs to be heated, greater care in material selection should be taken to ensure minimised shut-down or maintenance.

The pressure in the system against which the liquid has to be injected plays an important role in the pump selection since only positive displacement pumps[56], such as a piston or a plunger, would be capable of pumping against high pressures[53,91]. Other pump models such as centrifugal or diaphragm pumps, are only capable of pumping up to 150 psi (1 MPa). A piston pump can be used to pump against pressures as high as 2-3000 psi (14-20 MPa) although care should be taken to ensure that the pipelines can handle these high pressures. One of the disadvantages with positive displacement systems is that there is a certain amount of pulsation in the output; to overcome this, pulsation dampeners can be used. The selection of these pulsation dampeners and their installation is not difficult if the liquid to be pumped is at room temperature. When heated liquid injection systems are designed, the limited number of materials available for use as gaskets and seals for such systems make installation of pulsation dampeners for these systems prohibitively expensive[17].

If the injection port is situated at a low pressure zone, for example at the feed port or at a decompression zone, then other low pressure pumping devices such as centrifugal pumps or diaphragm pumps can be used, the advantage of these systems being that they deliver uniform non-pulsating flow. A diaphragm pump could be chosen if the liquid being handled is corrosive to pumping system, but such a system may be expensive if the diaphragm has to withstand elevated temperatures.

A drawback with a centrifugal pump is that the majority of the moving parts are exposed to the liquid; a serious limitation if the liquid is corrosive. Under these circumstances, careful selection of the material of construction is important.

2.4.2 PREBLENDING

When two or more components need to be introduced into a continuous process stream, a preblend of the components could be metered (Section 2.4.1) into the process stream. The product from a preblending stage is a uniform mixture (due to distributive mixing) of the different ingredients to be metered; this operation is often carried out in the "pellet or powder phase", i.e. the ingredients are not in a molten stage during this operation.

It is thought that preblending assists distributive mixing and this may be a significant benefit if the distributive mixing provided in the processing equipment is not sufficient[5]. The importance of preblending is increased if:

a) the metering of individual components is not accurate,

b) the flow of material in the processing equipment is plug flow, (hence not dampening any fluctuation in feed composition) and

c) if there are several components to be added to the process stream.

In cases (a) and (b), preblending can reduce fluctuations in input, and hence output, concentrations. In case (c), it could be prohibitively expensive to furnish weigh feeders for the accurate metering of each solid component, as is the case when additives are introduced into rubber in a continuous process.

There exist many simple and useful equipment designs for preblending, although, in general, there does not appear to have been any significant advances in this field in recent years[74].

2.4.3. COMPOUNDING

The compounding stage is when additives are <u>dispersed</u> into the polymer matrix. This operation is invariably performed in the melt phase. This stage results in a concentrated mixture of the additive and the polymer. Equipment used to obtain such solid dispersions in viscous polymers, while the polymer is in the melt phase, will be considered in this section. Compounding equipment should be capable of dispersing additives such as fillers, pigments, curing agents and stabilisers into a polymer matrix. A critical part in compounding most fillers is the wetting of the filler, and this is usually achieved by:

1) using high shear stresses since wetting is a high energy process[7],
2) using wetting agents which reduce the energy required for wetting of the filler thereby reducing the shear stress needed to wet the fillers.

The mixing intensity required would be dictated by the wetting properties of the polymer and the filler and by the demands of the application. When "difficult" fillers are to be incorporated, only high shear rate mixers with long mixing/residence times can be used if dispersion has to be "perfect"[109].

The compounded material can then either be used as a masterbatch or in its original concentration. The equipment used for compounding can be divided into batch and continuous compounding equipment. The batch compounding equipment includes an internal mixer[122,16,44] or a mill[8]. There are various machines available for continuous compounding and the basic design principles of the various machines are outlined in Section 2.3. The machinery under this category include: a single screw extruder (with attachments), a twin screw extruder and a ko-kneader.

2.4.4. Let-down

Once a masterbatch is prepared, it often needs to be let-down (and modified) to obtain the concentration of filler required in the product. This stage involves distributive mixing of the filler into the polymer since often more polymer would be added at this stage. The filler would have already been "dispersed" into the polymer at the compounding stage. The choice of equipment that can perform this function lies amongst: a mill, an internal mixer, and a single screw extruder. Although a twin screw extruder could perform this function, it is not often used for this processing stage due to its higher capital cost.

2.5 REACTOR OPTIONS FOR POLYMER MELT REACTIONS.

2.5.1 INTRODUCTION

It is expected that process flexibility would be an advantage during reactive processing since the required product could be produced at a range of throughputs. The flexibility, in this context, is defined as the independence between the amount of mixing and the mean residence time. This section is set out to assess the process flexibility of some continuous processing equipment in order to determine their suitability as the processing stage in a production of a reacted product. Single and twin screw extruders, ko-kneaders and cavity transfer mixers are considered here and process flexibility, in terms of an independence of throughput and mixing rate, is examined for these processes.

2.5.2 SINGLE SCREW EXTRUDERS[107,29,114,84]

The mixing action in a single screw extruder is expected to be related to the strain experienced by the polymer (Equation 2.8) which, in turn, is related to the rotational speed of the extruder. The throughput and the rate of mixing are interrelated in a single screw extruder for the following reasons.

1. Normally, these extruders are neither starve fed nor modular.
2. The rotational speed of the extruder also dictates the throughput.

The shear rate distribution is very broad in an extruder which implies that different elements of material would experience different shear and thermal histories.

Because of the broad shear rate distribution and the dependance of the rate of mixing on the mean residence time, this processing equipment was not chosen for reactive processing in this project.

2.5.3 TWIN SCREW EXTRUDERS [37,36,131,6,67,9]

The co-rotating twin screw extruders are usually designed on a modular structure. These are the type often used in reactive processing for the reasons outlined below. The design allows the inclusion of, for instance, additional kneading sections in the extruder train in order to achieve intensive mixing. The number of kneading blocks in the train allows the desired residence time and intensity of mixing to be achieved independently of throughput.

The counter rotating fully intermeshing twin screw extruders are well suited for processing low viscosity materials because of their positive conveying action although co-rotating twin screw extruders also display positive conveying action. This feature is exploited when twin screw extruders are used to effect polymerisation.

The one major disadvantage of the twin screw extruder, in the authors opinion, is the means by which it achieves the mixing[19]. High shear stresses are generated to disperse the agglomerates. However, high shear stresses also give rise to shear heat[14] and this shear heat generated in the polymer is not easily conveyed away from the polymer due to the poor thermal properties of organic materials[91]. If there are areas where localised heat is generated, this could lead to islands where the reaction rate is different from the polymer bulk[68]. Such considerations need to be borne in mind when using a twin screw extruder as a reactor. In spite of this perceived disadvantage, the improved mixing achieved in a twin screw extruder and its positive conveying characteristics have made it an attractive piece of equipment for reactive processing (Table 2.4).

2.5.4 KO-KNEADER

Not much literature is available that could demonstrate the process flexibility of a ko-kneader. Hence some of the comments made in this subsection are speculative for lack of literature to substantiate the predictions.

It is known[57, 58, 10, 23] that the output from a ko-kneader pulsates. This demands a dampening conveyor, such as a single screw extruder, to be assembled downstream of a ko-kneader. It is also known that the ko-kneader provides effective distributive mixing. Hence it is expected that it would be a good choice for reactive processing when the reactants are a polymer and a liquid. Since it has not been shown that there is positive conveyance in a ko-kneader, it is not expected to convey low viscosity liquids such as monomers; it is, therefore, not expected to be well suited for polymerisation systems (where the viscosity increases during the reaction mixture's passage through the reactor). Because of the positive conveyance in a twin screw extruder, a twin screw extruder is expected to show an advantage over the ko-kneader for the performance of polymerisation reactions.

2.5.5 CAVITY TRANSFER MIXER (CTM)

A cavity transfer mixer does not convey material - this requires it to be connected to a processing equipment that will convey. It is often connected to a single screw extruder. There are two ways in which a CTM can be arranged; it can either be connected directly to the extruder or it can be independently driven. The advantages and disadvantages of these two assemblies are given in the equipment development section. (Section 4.2).

In summary, the throughput and the rate of mixing are interrelated for CTMs directly driven by an extruder. However, for independently driven CTMs the throughput, (hence the mean residence time) and the rate of mixing, (hence the residence time distribution), could be independently controlled, a definite advantage when the equipment is being developed for reactive processing.

2.5.6 PROCESS SELECTION FOR VARIOUS MATERIALS

A summary of suitable process equipment for various feed stocks and product types is given in Table 2.3.

Table 2.3 Selection of the appropriate equipment for reactions.

Reactions	Processing equipment
Reactants : Solids and polymers. Product : Thermally mobile.	Batch: Mill (if air exposure is not undesirable) internal mixer. Continuous: twin screw extruder, perhaps a ko-kneader, a CTM if the solid can either be molten or dissolved.
Reactants : Solids and high viscosity liquids Product : Shear and/or thermally labile	Batch: Sigma blade mixer Continuous: Continuous sigma blade mixer
Reactants: Liquids and polymers Product : Thermally labile	Batch: mill Continuous: ko-kneader, twin screw extruder, independently driven CTM
Reactants : Low viscosity liquids Product : High viscosity liquids	Batch: RIM Continuous: Twin screw extruder.
Reactant : Polymer melts Product : Crosslinked (or quasi crosslinked) products	Batch: Mill, oven Continuous: fluidised bed, radiation.

2.6 REACTIONS IN CONTINUOUS POLYMER PROCESSING EQUIPMENT.

In this section, literature published on the use of continuous polymer processing equipment for reactions is reviewed.

2.6.1 INTRODUCTION

Polymerisation, and other reactions such as modification reactions, may be carried out in bulk, in solution or in dispersion/emulsion processes. Solution, dispersion and emulsion are popular processes as the much reduced viscosity makes fluid handling, mixing and heat transfer far easier. However, the extra costs of the continuous phase or the solvent handling and recovery have led to the development of improved bulk polymerisation methods. One such process is Reaction Injection Moulding (RIM) where the monomers are mixed and injected into a mould where polymerisation reaction takes place. However, as it is an intermittent process, it is not discussed any further here. Reactions in single screw extruders, twin screw extruders and cavity transfer mixers will be discussed in detail in the following sections.

2.6.2 REACTIONS IN SINGLE SCREW EXTRUDERS

Mixing in single screw extruders has been investigated, as discussed in Section 2.4.4. Reactions in single screw extruders have also been studied.

2.6.2.1 Mathematical predictions of the performance of a single screw extruder as a reactor.

The work referred to in this section is on the mathematical predictions on the possible use of a single screw extruder as a reactor. None of these authors actually performed experimental work to check their predictions and hence it is difficult to comment on the success of any of the modelling exercises.

Several authors have tried to build mathematical models [106, 26] to predict the behaviour of a single screw extruder as a reactor. Some of the more relevant pieces of work are discussed in this section.

Sebastian et al [106] used a model of two parallel plates to model a single screw extruder and to then predict its performance as a reactor. (Their rationale for using a model of parallel plates for a single screw extruder was that if the flight of an extruder screw were uncoiled, it would resemble parallel plates, if the sides of the flight were ignored. They argued that the sides of the flight can be ignored since the channel depth is much smaller then the pitch and hence the region between the two parallel plates is more significant than the edges.) They considered how viscosity may change for three different reaction types; random, step addition and chain addition. They concluded that devices that convey flow by means of pressure build up would be appropriate for a random polymerisation reactions since there would be only moderate change in viscosity; whereas the rapid viscosity increase and subsequent flow segregation in chain and step addition polymerisation would be more successfully handled in drag flow devices. (A similar model, ie.parallel plates, was also used by Lindt[38] to model flow of reactive liquids in twin screw extruders, Section 2.6.3.)

Elbirli and Lindt[38], attempted to develop the velocity profile in a single screw extruder when reactions with different reaction kinetics were attempted at a selection of extruder settings. Siadat et al[111] also attempted to model reaction in extruders. They assumed plug flow in a single screw extruder (not unjustifiably[12]) and considered a polycondensation reaction. They also investigated the heating effects corresponding to such reactions.

2.6.2.2 <u>The performance of a single screw extruder as a reactor.</u>

Some researchers have investigated the practical performance of a single screw extruder as a reactor, the more significant of these are discussed below. The effect of process parameters on the performance of a single screw extruder as a reactor were not examined by these researchers.

Sloman et al[112] and Fenner et al[41] have both reported on the use of a single screw extruder in the production of crosslinked polyethylene (PE) cables. The crosslinked polyethylene was produced by first grafting silane onto polyethylene, inside the extruder, and then reacting the grafted polymer with moisture, outside the extruder, to crosslink the polyethylene. BICC[117] also used a single screw extruder to graft silane onto PE and cured the grafted material in boiling water for 6 hrs.

Other reactions have also been attempted in an extruder, an example[110] of which is the sulphonation of EPDM. A patent is held by Badische Anilin & Soda Fabrik for a novel design of the screw to enable polymerisation reaction of ethylene to be carried out. It consisted of a hollow screw which allowed the recirculation of unreacted material. The patent claimed the production of homopolymers and copolymers of ethylene with molecular weights ranging from 1,000 to 200,000.

2.6.3 REACTIONS IN TWIN SCREW EXTRUDERS

Both the modelling work to predict the performance of a twin screw extruder as a reactor and the experimental work on its use as a reactor will be discussed in this section.

2.6.3.1 Predictions for the performance of a twin screw extruder as a reactor.

Mathematical models have been built to predict the performance of a twin screw extruder when used as a reactor. Some of the relevant pieces of work in this field are discussed in this section.

Lindt[38] analysed the flow of a reacting liquid between parallel plates. His justification for using this model was that flow in a shallow channel extruder can be modelled by parallel plates.

Jansson et al[59,] used a series of CSTRs to model the behaviour of a twin screw extruder. Anionic polymerisation reaction for Nylon 6 was modelled using this model. Some experimental work was carried out in a twin screw extruder which confirmed their predictions on the effect of increasing the rotational speed of the extruder on the molecular weight distribution. It was calculated that 56% savings, due to reduction in time and energy, could be made by this one stage process when compared with a two stage process and 26% savings could be made because of not having to reheat the mixture between the processing stages.

2.6.3.2. The performance of a twin screw extruder as a reactor.

The advantage of using a twin screw extruder as a reactor is the intense dispersive mixing, in addition to distributive mixing, that is achieved in this type of equipment[83]. This would imply that where reactions between solids and polymer melts need to be carried out, this type of equipment would be useful. The positive conveying feature of the twin screw extruder[130] is exploited when it is used to polymerise low molecular monomers into polymers[142]. Few standard designs of single screw extruders would be capable of conveying low viscosity liquids such as monomers.

Interest in the use of twin screw extruders for reactive processing has been intense in the past two decades[135]. In some cases, it has enabled the production of products previously not possible[52,43] when reactions and forming were carried out in different processing stages. For example amine grafting[3], that would unzip if heat treated afterwards, is now possible as the reactive processing stage can actually produce the end-usable product , thus avoiding subsequent heat treatment.

Table 2.4 summarises the most relevant work in the use of twin screw extruder for reactive processing.

Eise[36] explains ways of redesigning twin screw extruders to facilitate reactive processing. Redesigning of the modules[2] to obtain a better cleaning action has been one of the steps in this direction-"mixing elements are lens shaped and have a self wiping profile i.e. the tip of one element always wipes the flank of its partner"[125]. Another machinery improvement to accommodate reactive processing has been the better surface treatment, for example coating the surface with tungsten carbide[66], to improve the wear and corrosion resistance of the metal parts.

Table 2.4: Reactions attempted in a twin screw extruder.

Reaction	Comments
Polystyrene polymerisation[142]	Residence times between 2.5 to 20 mins were used to perform these reactions.
ABS polymerisation[143]	Chemical parameters were assessed in this work.
EP and PP polymerisation[144]	An intermeshing co-rotating self wiping twin screw extruder was used in this work.
Grafting Reaction Maleic Anhydride/EPDM[145]	Discussed the effect of different dienes on the grafting efficiency.
Polymerisation Polyurethane	The temperature was increased along the extruder to maintain a constant viscosity.
Polymerisation ABS[14]	Operating Conditions: Speeds of 15-30 rpm. Output of 0.3-1.7 kg/hr. Feed pressures of 150 psi. Shear rates of $50-300s^{-1}$.
Polyesters polymerisation[49]	The effect of process settings on the product quality was examined. A vacuum vented twin screw extruder was used with a mean residence time of 15-30 mins. L/D ratio was 37:1.
Polymerisation Nylon 6.[147]	Residence time of 2-3 min. Throughputs of 90-160 kg/hr.
Polymerisation Polymethyl methacrylate[116]	A counter rotating twin screw extruder used. A model of a series of CSTRs was shown to predict the experimentally observed trends but not their magnitudes.

2.6.4 REACTIONS IN A CAVITY TRANSFER MIXER

Gale[46], in 1988, presented the work done on the use of a CTM to graft silane onto polyethylene (PE). The grafted PE was subsequently crosslinked using moisture. The moisture curing of the grafted PE is carried out, in this work, in a heated water tank which is situated downstream of the CTM. Hence, the production of crosslinked polyethylene is a continuous process in such an operation. N.B. The level of crosslinking was taken to indicate the level of silane grafting and hence the level of reaction conversion for this reaction.

In Gale's[46] work, a mixture of peroxide, tin catalyst and silane was injected immediately upstream of a CTM. The CTM was directly connected to the extruder, i.e. an increase in the CTM speed was only obtained by an increase in the extruder speed, and hence the throughput. In addition to the extrudate samples, samples were collected from the bleed ports in the cavities of the CTM.

The variables examined were:-

1) the injection rate and
2) the screw speed.

Increasing the injection rate from 1.6 to 2.2% did not seem to significantly influence the level of crosslinking (measured by solvent extraction).

Increasing extruder speed (and the throughput and hence reducing the residence time) reduced the level of crosslinking. At 30 rpm, the level of crosslinking was 80%; at 105 rpm, the level of crosslinking dropped to 70%. By examining the results from the samples taken from the bleed ports, it was seen that the reaction progressed as the material went through the CTM. For example, with the extruder screw rotating at 60 rpm, at 1.6% injection, samples from bleed ports 1, 2 and 3 had 35%, 64% and 76% crosslinking. For similar conditions but with the extruder screw at 105 rpm, the samples had 10, 67 and 74% crosslinking. This indicates that increasing the mean residence time in the CTM had increased the reaction conversion.

2.6.5 THE EFFECT OF PROCESS PARAMETERS ON REACTIVE PROCESSING.

The majority of the effects quoted below are for the twin screw extruder as the reactive processing equipment: this is because the majority of the published literature and patents in the field of reactive processing are on the use of twin screw extruders as reactors. Other equipment is also reviewed where possible.

2.6.5.1. Effect of mean residence time on reactive processing.

Longer residence time in a twin screw extruder is expected to lead to better conversion; this was reported for the production of copolyesters[49] and Nylon[59]. Standard Oil Company[146] also noted that increasing residence time led to an increase in molecular weight. They found that increasing the mean residence time from 6 to 8.9 minutes increased the molecular weight of ABS from 58,300 to 152,300. This effect was also reported in Midland Silicones Ltd.[147] patent where a ko-kneader was used to graft silane onto polyethylene. This effect agreed with the results obtained for reactions performed in a CTM by Gale (Section 2.6.4).

2.6.5.2 Effect of residence time distribution (RTD) on reactive processing.

A valuable study was carried out by Stuber and Tirrell[116] to examine the influence of RTD on reactive processing. They reported, from experimental work, that RTD does have an influence on reactive processing. For the example they were studying, the polymerisation of methyl methacrylate, a broader RTD resulted in a broader molecular weight distribution of the polymer. (They also reported the influence of reaction progression on the RTD).

Standard Oil Corporation Company emphasised the importance of RTD on the product quality when Acrylonitrile/ Methacrylate[146] and ABS[143] were produced. They predicted that optimum length of residence time was required to ensure that reaction had progressed to a certain level. They postulated that if higher residence times (due to broad residence time distribution) were experienced by the rubber, overheating due to over-shearing or conduction from the barrel walls of the extruder, could lead to degradation reactions. Therefore, they emphasised the importance of narrow RTD in reactor design.

2.6.5.3 Effect of shear rate on reactive processing.

High shear rates have been traditionally recommended for reactive processing applications since shear rate was related to total strain which influences mixing in some equipment[83]. Shear rate has two effects that can influence reactive processing. One is its relationship with mixing; increasing shear rate improves mixing. The other is the shear heating effect which is represented by the equation below:

$$\text{Shear heating} \propto \text{shear stress} \times \text{shear strain} \qquad 2.14^{(14)}$$

$$\text{where shear stress} \propto \text{shear rate} \times \text{viscosity} \qquad 2.1^{(14)}$$

The anticipated improvement in mixing due to the increase in shear rate would suggest improved performance of a reactor as the shear rate was increased[83]. This would also be true of its effect due to shear heating. However, the effect of increased shear rate may not be advantageous, in practice, for two reasons.

(1) Shear heating above a certain level may damage

the polymer[143,146].

(2) Since there would be a shear rate distribution and hence a shear heating distribution, some pockets of material may be subjected to higher temperatures which could lead to non-uniform reaction conversion in the product.

There is therefore anticipated to be an optimum level of shear stress that should be exerted on the polymer.

2.6.5.4 Effect of temperature on reactive processing.

An increase in temperature is expected to increase conversion since most reactions need to overcome the activation energy to react. This is true even for exothermic reaction, where the initiation of the reaction is more rapid at higher temperatures. This has been confirmed by:

a) Stuber and Tirrell[116] for the production of polymethyl methacrylate in a twin screw extruder.

b) Badische, Anilin & Soda Fabrik Aktiengesselschet[9] for the production of polyethylene in a bored single screw extruder.

c) Jansson et al[59] in their mathematical prediction for a twin screw extruder.

d) Standard Oil Company [143,146] in the reactive processing of ABS and Acrylonitrile/methacrylate.

However, the majority of these researchers also state that temperature control is of great importance since excessive temperatures could lead to side reactions becoming significant. Thus, there is expected to be an optimum temperature for reactive processing.

2.6.5.5 Effect of feed pressure on reactive processing.

When gaseous monomers are introduced into an extruder, they are introduced under pressure. While Stuber and Tirrell [116] claim that this pressure would not have any effect on the product quality, they did not actually examine it. Whereas Standard Oil Company [143] studied this as a variable and concluded that increasing the feed pressure increases the reaction rate. Their reasoning for this effect was that as the feed pressure increased, the reactive liquid was given a greater opportunity to enter the voids.

2.7 EXPERIMENTAL OBSERVATIONS OF FLOW PATTERNS IN PROCESSING EQUIPMENT.

Researchers have used visual techniques to analyse flow in processing equipments. Some of the more significant pieces of work in this field are outlined below.

2.7.1 EXPERIMENTAL OBSERVATIONS OF FLOW PATTERNS IN A SINGLE SCREW EXTRUDER.

A number of researchers have studied the flow patterns or the velocity profiles in an extruder either by removing the polymer from the extruder screw or by photography [2,48,82].

Eccher and Valentinotti (1958)[35] were amongst the first to analyse the flow in a single screw extruder visually. They used polyisobutylene mixed with paraffin oil containing aluminium. They performed their experiments by rotating the transparent barrel and keeping the screw stationary. They noticed the presence of zero velocity and flow backwards at zones other than the screw surface even when there was an output. This contradicts with the findings by Mohr et al[81, 82]. This contradiction could be due to the definition of "flow backwards".

N.B. Eccher et al appear to define any flow where the angle of fluid travel is greater than 90° from the main direction of flow as flow backwards. However, Mohr et al[81, 82] defined flow backwards as any flow where the angle of travel is 180° from the main direction of flow.

Mohr et al[82] (1960) developed a model assuming that:

1. the viscosity of the fluid was constant at all points in the channel,
2. the boundary surfaces were flat,
3. the channel was very wide compared with the depth,
4. the barrel moved relative to the screw,
5. the leakage flow (flow through the clearance between the screw and the barrel) was negligible.

They predicted, from their analysis, that no material flows backwards in a single screw extruder, unless there was no flow. They carried out experiments, with corn syrup which is an isothermal Newtonian liquid, to test their predictions. The conclusions from the visual examination of the flow of a dye in a laboratory scale extruder confirmed their predictions; for all cases where there was an output, there was no region where there was backward flow. The conclusions drawn from this work are limited to constant fluid viscosity systems.

Mohr et al[81] (1961) then used hydroxyethyl cellulose in water, a non-Newtonian liquid, in a bid to understand flow of a non-Newtonian liquid in a single screw extruder. The flow appeared similar to that of the Newtonian liquid examined earlier[82]. They still only encountered zero velocity when there was no output.

2.7.2 EXPERIMENTAL OBSERVATIONS OF FLOW PATTERNS IN A CAVITY TRANSFER MIXER.

Gale[136] performed the first experiments on examining the flow patterns in a CTM. He introduced a dye into a cavity of a CTM and then examined the flow pattern of the dye as it progressed through the CTM. He had to assume that the dye flowed in a similar manner to the bulk. The flow diagrams can be seen in Rapra members report 97[136]. These diagrams illustrate the cutting and rotating action of the CTM that was expected from its design.

Lin[70] also carried out flow visualisation experiments whereby a dye was introduced into a CTM which was stopped and the flow patterns examined. Only some of the observations made on the micrographs could be predicted by the model (Section 2.9.3).

2.8 MATHEMATICAL MODELLING

The importance of understanding the effect of flow patterns and residence times on reactive processing is outlined in this section.

2.8.1. INTRODUCTION

Mathematical models have been devised to model and predict flow in physical systems. A model is valuable in predicting residence time distribution and is also useful in identifying the scale-up factors for process equipment. The kind of physical systems that have been modelled include continuous stirred tank reactors[64], trickle beds[21,62], semi-continuous/continuous stirred tank reactor[103], annular reactor[69], Kenic mixers (static mixer)[85], helically coiled tubular reactor[28,98], packed beds[22,88], series of CSTRs[126] and fluidised beds[89].

2.8.2 RESIDENCE TIME DISTRIBUTION (RTD).

2.8.2.1 Definition and uses of RTD.

Residence time distribution was defined by Levenspiel[68] through the following statement

"It is evident that elements of fluid taking different routes through a reactor may require different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution E, or the residence time distribution RTD of fluid."

The residence time distribution does not give a complete picture of how material flows within the reactor but gives the retention time of fluid in the reactor and as such is valuable information in determining the conversion in a reactor. The uses, limitations and the applications of RTD for reactor design are clearly reviewed by Danckwerts[30,31].

Some of the salient features from this paper are summarised below.

1. The residence time distribution can itself be used to predict the performance of a reaction if the reaction is first order and if it can be assumed that the rate constant of the reaction is constant throughout the reactor. This second condition would only be satisfied if there are no temperature gradients in the reactor.
2. If the reaction kinetics are not first order, the way the material flows through the reactor needs to be known since this would influence the reaction conversion.
3. Diffusion coefficients can be used to predict the residence time distributions quite accurately if the flow is laminar.

RTD obtained using impulse inputs were used by Abbi et al to determine the Dispersion Coefficients for packed beds[1]. RTD can also be used to model mixing[73] and to predict reactor performance[63,124,34].

2.8.2.2. Measurement of RTD.

RTD is determined by introducing a disturbance in the inlet stream and examining its effect on the outlet stream. The disturbance is introduced into the inlet stream either by a step input or by an impulse of an easily detectable trace. Bischoff[15] and Ostergaard et al[90] outline ways of disturbing the inlet stream with an imperfect pulse[68].

The outlet fluctuations are monitored using appropriate detectors. Hanley et al[50] discussed the use of electrical conductance to assess the outlet conditions. Others have used radioactive tracers to determine RTD[123]. The tracer can influence the RTD if the flow pattern of the tracer is different from that of the process fluid[97].

The RTD is usually analysed using statistical methods[47,78,92]. For example, Gibilaro et al[47] described means of analysing RTD data using frequency response data. Their analysis could evaluate the mean, variance, skewness and kurtosis (the forth moment). Michelsen[78] used least mean squares method to analyse RTD data with increased accuracy than was possible by using moments alone. Petho[92] described a way of using Laplace Transform to calculate the moments of the RTD.

2.9 MATHEMATICAL MODELLING OF PROCESSING EQUIPMENT.

A number of researchers have attempted to model the flow in processing equipment in an attempt to predict the performance of this equipment.

2.9.1 MATHEMATICAL MODELLING OF SINGLE SCREW EXTRUDERS.

Efforts to understand mixing in the single screw extruders have been intense. Mohr et al[82] studied the flow patterns in an extruder. From their theoretic analysis (their assumptions are listed in Section 2.7.1), they predicted, for both Newtonian and non-Newtonian liquids, that material does not flow backwards in a single screw extruder if there is any throughput. From their model, only at no throughput conditions would any material in a single screw extruder flow backwards. Their experimental work with both Newtonian and non-Newtonian[81] liquids agreed with the predictions.

Others have also attempted to build mathematical models. These models were mostly based on either numerical techniques or the strain relationship[80,12,35]. For example, Mitsoulis and Vlachopoulos[80] used finite element analysis to analyse flow and heat transfer equations whereas Bigg and Middleman[12] solved the dynamic flow equations, for both Newtonian and non-Newtonian fluids, to calculate the residence time distribution in a single screw extruder. Tadmor and Klein[120] have also attempted to model the several regions in an extruder such as the conveying section, the melting section and the metering section.

2.9.2 MATHEMATICAL MODELLING OF TWIN SCREW EXTRUDERS.

Mathematical models have been built to represent flow in twin screw extruders. Denson & Hwang[32] attempted to model the flow using a Newtonian liquid but did not confirm their predictions with experimental work. Szydlowski and White[118] used dynamic lubrication theory based on a power law shear viscosity model. They used FAN method (a modified finite element technique) to obtain the numerical solution for introducing power law behaviour. They had to handle power law behaviour because they wanted to examine the flow behaviour of non-Newtonian liquids. They were examining the flow of fluids in a modular intermeshing corotating twin screw extruder.

2.9.3 MATHEMATICAL MODELLING OF CAVITY TRANSFER MIXERS.

The earliest work to model the flow in a CTM was done by Bromilow and Hulme[18] of the Open University in 1986. In their two dimensional model, they model a CTM by two sets of "infinitely many, infinitely long cylindrical cavities separated by flat plates". Loss in curvature was considered acceptable if cavity diameter was significantly smaller than the CTM diameter. The upper set of cavities were moved relative to the lower row. They considered flow in one cavity and attempted to extrapolate from this to a whole array of cavities. They solved the equations of conservation of momentum and continuity, at instantaneous boundary conditions, using an adapted Galerkin finite element analysis. (Figure 2.5b p100)

In their second model, they essentially had similar setting to the first model but allowed the presence of a clearance between the upper and the lower cavities. They introduced the different boundary conditions and again solved the equations of continuity conservation of momentum using the Galerkin method (different boundary conditions were required to take into account the clearance between the top and the bottom row). As would be expected, the solution for this second model was similar to that of the first model as the clearance was made small. For both their models, they considered flow only under the following conditions.

i. A completely filled CTM.

ii. The material being processed was "an incompressible, isothermal, Newtonian fluid of negligible inertia".

They then used these models to qualitatively predict mixing in a CTM.

Limitations of this modelling exercise.

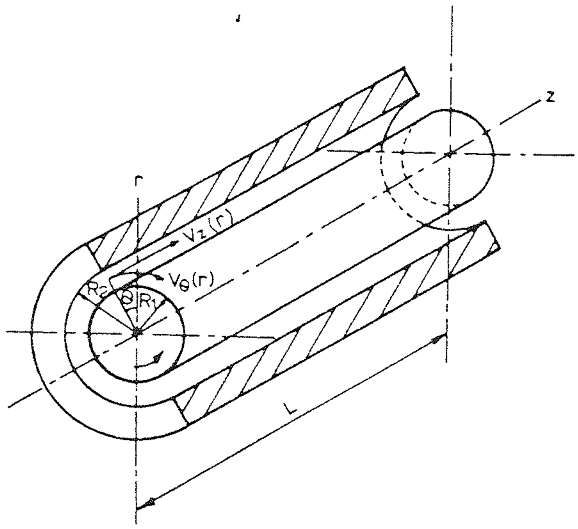
They did not examine the influence of design parameters such as cavity size and land length on the flow pattern in a CTM. They did not use the model to predict the residence time distributions in a CTM. They did not look at the influence of using polymer melts (instead of their ideal liquid) on either the flow patterns or the subsequent mixing. Both the models developed would encounter cases where the land on the bottom row is opposite the land on the top row. This is not possible in a "real" CTM design.

Lin[70] also attempted to model a CTM. He attempted to model the flow in a CTM when it was used in an injection moulding machine. The added complication of such an application is the linear axial motion of the CTM during the different stages of the injection cycle.
He chose the annular mixer model (Figure 2.5) in preference to the parallel plate model and the concentric cylinder mixer model because
i. of its good geometrical representation of the CTM
ii of its agreement with experimental results" (he does not comment on how well the other models' predictions agree with the experimental results).
iii. it allows flow fed by another pumping device (the other two models do not).

This model predicted that increased pressure drop across the annulus would be associated with :

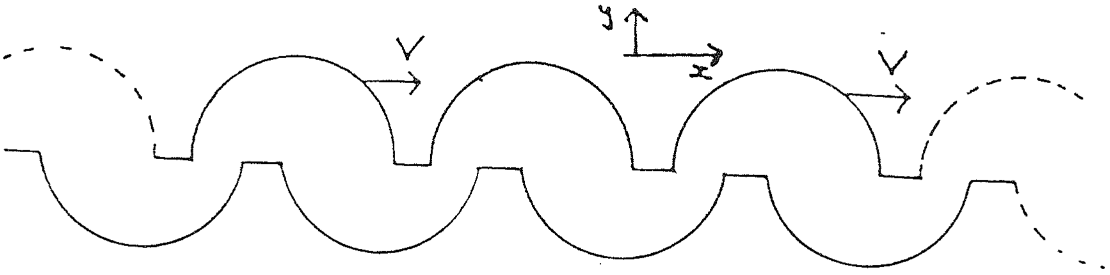
a) increased throughput,
b) increased melt viscosity,
c) increase in length of annulus and
d) decrease in clearance in the annulus.

Figure 2.5 An annular mixer model



Due to the linear axial motion of the CTM during the compression and decompression cycles, the land on the rotor is sometimes exactly opposite the land on the stator.

Figure 2.5b : The model used by the Open University.



the research study.

3. DEVELOPMENT OF PROJECT STRATEGY

3.1 OVERALL STRATEGY.

This section outlines the approach to the research study.

Although there was a commercial interest, from Rapra's view point, to investigate the CTM as a reactor, literature has been reviewed in order to assess the alternative processing pathways a potential processor may consider for use in polymer modification. This exercise (Chapter 2) was to ellucidate:

1) the market need for a CTM as a reactor (Section 3.3.2),
2) the market niches where a CTM would hold an advantage over other processing equipment (Section 3.3.2),
3) the possible application limitations of a CTM (Table 2.3).

At this stage, the reaction systems for study would be selected on the criteria listed below.

1) From an engineering aspect; it was preferred that two distinct reaction systems, one requiring a liquid reagent and the other a solid reagent, should be examined.
2) From the requirements of the market need; the selection of a reaction system using this criterion proved more difficult since it was observed that there were several niches in the market place where a CTM could be exploited.

The exact reaction systems selected for study should preferably satisfy both the engineering and the market place selection criteria mentioned above.

The overall strategy of this research project involved:

1) a literature survey to establish the need for developing a CTM as a reactor (Chapter 2) ,
2) an assessment of a CTM as a reactor for solid-polymer reactions (Section 6.4.1.1),
3) an examination of a CTM as a reactor for liquid-polymer reactions (Section 6.4.1.2 & 6.4.2.2),
4) an investigation of batch techniques for effecting reactions (Section 6.2),
5) the marketing of a project to further investigate the performance of a CTM as a reactor (Section 3.3),
6) an investigation of the process parameters that influence flow in a CTM using residence time distribution (Section 6.5).

A work plan for the Project is given below:

for [illegible] the

1st year	2nd year	3rd year
Literature survey to establish value of this research	Mathematical modelling to form a background for the kind of models that could be used for the CTM.	
Establish the feasibility of the CTM as a reactor; a considerable amount of redesign and construction.	This period of time was also used to examine the flexibility of a CTM as a reactor.	
	During the design and building of new equipment, made opportunities to gain hands-on experience with other processing equipment.	
	Marketing of a research project This took 6 months to complete from the start of the marketing campaign to the launch of the group project.	Continue with the residence time distribution and modelling work. Also commence writing up of the Thesis.

3.2 EXPERIMENTAL PLAN.

This brief section outlines the reasons for selecting the reactions in this project.

3.2.1 CHEMICAL REACTION SELECTION.

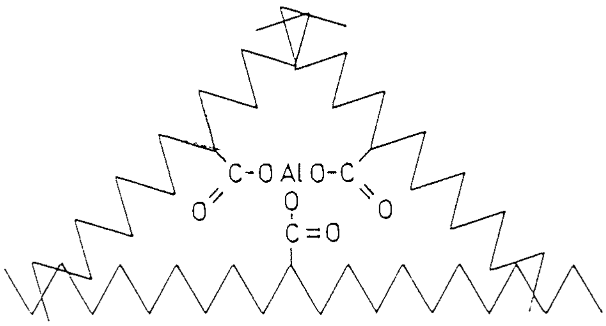
In this project two main types of chemical reactions were studied, namely:

(i) neutralisation,
(ii) grafting.

The selection of both grafting and neutralisation reactions for study in this project is intended to emphasise the interest in the CTM as a reactor across a range of marketable polymer products.

(i) A neutralisation reaction is one whereby a neutralising salt, containing a metal ion, is reacted with an acid functional polymer to bond the metal salt onto the polymer. This can lead to the quasi-crosslinking of the polymer chains (refer to Figure 3.1)

Figure 3.1 Quasi-crosslinking of a polymer.



The choice of a neutralisation reaction was made because the product (a metal salt bound to a polymer) of some of the neutralisation reactions can be a polymer bound reagent such as a polymer bound catalyst. Polymer bound catalysts are considered as speciality polymers with a high cost : tonne ratio.

(ii) A grafting reaction is one in which a monomer (of the required chemical structure) is chemically grafted onto an appropriate polymer (refer to Figure 3.2). The grafting reaction is commonly carried out on bulk-tonnage polymers to produce polymers with added value due to improvements in their application potential. This market appeal arises from the improved properties of the grafted product. The sales of a grafted product would, in most instances, be lower than their parent bulk-tonnage polymers.

Figure 3.2 Monomer grafted onto a polymer.

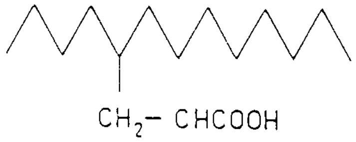


Table 3.1 The added value due to modification of the polymer (1989 estimates).

Polymer	Cost
PE	£ 700 per tonne
Grafted PE	£1400 per tonne

3.2.2 REACTOR SELECTION.

These above mentioned reactions were to be attempted in the melt phase. Interest would be primarily in continuous melt reactor design development. This would involve the development of a CTM (the reasons for its selection are given in Section 3.3.2) to enable efficient incorporation of the reagents into the reactor system.

It was anticipated that reactions would also be attempted in other processing equipment to:

1) gain an insight into alternative processing techniques,

2) enable a practical comparison of a reaction in a continuous system to one in a batch system,

3) gain an understanding of how changes in polymer rheology due to reaction are accommodated by different designs of reactors.

The batch reactors examined included a two roll mill, an oven and a sigma blade mixer. A two roll mill was anticipated to be useful for incorporating polymers with solids or liquids. The reaction could either be completed on the mill or the material could be heated in an oven, perhaps under a nitrogen blanket.

A sigma blade mixer was anticipated to be useful in performing reactions between high viscosity liquids and solids or liquids. The reactions could be completed whilst the material was still in the mixer or could be completed in an oven.

3.2.3 PRODUCT CHARACTERISATION.

The reaction conversion was to be assessed analytically. The product was characterised by the chemists at Rapra and full details of the analysis will not be discussed in this thesis. However, the analytical techniques used for product analysis are briefly outlined below.

The products of the neutralisation reaction were tested for insolubility since the proportion of insolubles is an indication of pseudo-crosslinking and thus of the extent of this reaction. The product from grafting reaction was also tested for insolubility to assess the presence of side reactions such as crosslinking.

Infra-red absorption (or transmission) spectra were also used to characterise the product. Since different chemical bonds absorb energy at different levels, and hence at different wavelengths, it is possible to quantify the extent of conversion using IR absorption spectra.

Although it was appreciated that the reason for performing these reactions was to enhance product properties, product property characterisation was considered outside the scope of this project.

3.2.4 FLOW AND RESIDENCE TIME DISTRIBUTION IN A REACTOR.

Since one of the objectives of the Project was to characterise the performance of a CTM as a reactor; it was reasoned that knowledge of the flow in a CTM would assist in the understanding of the relevant processes. It was considered inappropriate for this project to study the details of the flow pattern. However, one consequence of the flow pattern, the residence time distribution, was considered important to the performance of the reactor. The relevance of residence time distribution (RTD) to reactor performance and design is clearly discussed by Levenspiel[68]; salient features are outlined below.

1) A broad RTD results in a lack of uniformity in the reaction time and consequently to a non-uniformity in the product's appearance and properties.
2) For a reaction with first order reaction kinetics, conversion can be calculated with the knowledge of RTD.
3) A mathematical model based on RTD data can be used to model the pattern of movement of reactants through the reactor. This working model may then be used to predict levels of conversion for reactions of known reaction kinetics.
4) The model may also be useful in identifying scale-up factors for the reactor.

3.2.5 PROCESS PARAMETERS INFLUENCING RTD.

Residence Time Distribution was to be studied for a CTM under a range of process conditions. An understanding of the influence of the process parameters on the RTD would enable the process conditions to be predicted to obtain the required RTD. The technique to be adopted was to introduce a tracer impulse (a dye) immediately upstream of the CTM. The extrudate samples were analysed for dye concentration. The curve of concentration against time (normalised so that the area under the curve was unity) is the residence time distribution.

The parameters that were expected to influence the RTD are:

1) the CTM rotational speed,
2) the throughput,
3) the geometry of a CTM such as the number and size of cavities,
4) the polymer melt rheology.

It was expected that only the first two parameters, the CTM rotational speed and the throughput, would be examined in this project. The last two parameters, of the melt rheology and the CTM geometry, were expected to be outside the time scope of this project.

An attempt was to be made, within the time constraints of the Project, to develop a working mathematical model to model the flow in a CTM. The RTD data were to be used to correlate the model parameters with process variables. This preliminary model was anticipated to be the first step in the development of a more sophisticated model, which would be outside the scope of the Project, but which would:

1) predict the flow and reactor behaviour of CTMs,
2) enable scale-up of CTMs.

3.3. MARKETING THE REACTIVE PROCESSING PROJECT.

3.3.1 INTRODUCTION

The reasons for "marketing" the project have already been outlined in Section 1.4. But before the project could be marketed, two important points had to be clarified:

i. the interest in reactive processing and

ii. the market niche for a CTM as a reactor.

The extensive literature published in the field of reactive processing (discussed in Chapter 2) confirmed the use of processing equipment as reactors as a growth area.

The market niche for a CTM as a reactor is outlined below.

3.3.2 THE NEED FOR AN EFFICIENT LOW SHEAR RATE REACTOR.

The processing equipment used to perform reactions in polymeric systems are either (i) batch, (ii) continuous or (iii) semi-continuous.

(i) The batch operations commonly employed to effect reactions use:

a) a mill,

b) an internal mixer,

c) a press.

(ii) The continuous operations that are employed in reactive processing use:

a) a single screw extruder,

b) a twin screw extruder,

c) a mixer such as a CTM,

d) a ko-kneader.

(iii) The major semi-continuous processing technique that has recently received much attention is reaction injection moulding (RIM) technology.

The continuous processing equipment used for reactive processing are discussed in the literature survey but this section outlines reasons why the combination of a single screw extruder (for conveying) with a CTM (for reacting) was chosen for this research project.

A significant advantage of a low shear rate mixer in its use as a reactor lies in the low energy input through shear heating that would be imparted to the polymer melt.

<u>N.B.</u>

Since shear stress = $(\text{shear rate})^n$ x viscosity ... 3.1

and shear heating $\propto$ shear rate x shear stress 3.2

In any flowing system, there exists a shear field[14]. If the shear-rate distribution is non-uniform, a portion of material will experience higher levels of shear stress than the average shear stress. These portions of polymer melt would reach a higher temperature (due to shear heating) and hence may behave as hot spots where the reaction rate is different from that of the bulk (Equation 3.3).

$$\frac{d(\ln k)}{dT} = \frac{\Delta H_R}{RT^2} \qquad 3.3$$

$$X_A = \frac{Cp\Delta T}{-\Delta H_R} \qquad 3.4$$

So by choosing equipment that would exert only a low shear stress, the maximum sheer stress experienced by the material is also lowered. This is why a CTM, which is a low shear rate mixer, was selected for study as a polymer melt reactor in this project.

3.3.3 MARKETING OF THE PROJECT.

3.3.3.1 Introduction

The marketing strategy to develop and launch a group sponsored project to develop industrially attractive technology is discussed in this section. The research project was marketed for the following reasons.

1) To verify the validity of the technical content of the project; if the project received industrial acceptance and attracted industrial investment, it would be indicative of the technical soundness and commercial exploitability of the ideas marketed.
2) To obtain financial backing for the development of the project.
3) To examine whether any guidelines could be established on the marketing of a research project.

It was recognised that the marketing strategy for developing a research project differed from many of the typical marketing strategies outlined in the industrial marketing literature. In order to enable comparison with the marketing of a research project, marketing strategies used for three different product types, namely a perishable product (Section 3.3.3.2), an automobile (Section 3.3.3.3) and a testing facility (Section 3.3.3.4), are discussed briefly. These strategies are discussed under the following headings:

- i) knowledge of the market place and the market gap,
    - a) demand for the product
    - b) the targeted customer for the product
- ii) the pricing policy,
- iii) test marketing,
- iv) publicity/promotion/sales.

3.3.3.2 Marketing concepts applicable for a perishable product[128,101,115].

3.3.3.2.1 Market place and its knowledge.

Consider a typical perishable product such as a confectionery bar. The high demand for confectionery of all types suggest that the market for a confectionery bar exists. As in the other cases to be considered, a major parameter determining the success of the product would be the manufacturer's perception of the gap in the market. Having identified and assessed the gap in the market, the product and its promotional image would need to be developed with this gap in mind.

3.3.3.2.2 The pricing policy.

A particular characteristic of the purchase of a perishable product is that it is not subject to significant premeditation and often the person wanting the product (and hence interested in the product's quality, specification, etc.) and the person providing the finance for the purchase are one and the same. Thus the price has to be set at a level to attract this one person.

3.3.3.2.3 Test marketing

Test marketing is a very critical part in the development of a perishable product. Test marketing of a consumable product may, for instance, be carried out in private homes with an invited group attending a "tasting session". The opinion of the tasters is taken into account if modifications are to be made to the product. The appeal of the name and the packaging of the product may also be assessed through such panels.

3.3.3.2.4 Publicity/promotion/sales

Advertising is the main means of informing the public of the launch of a new product. Advertising is an effective means of promoting a low cost, high sales item such as a confectionery bar for the following reasons:

a) the product is of such low cost that direct personal selling is not economical,

b) the customers are remote from the manufacturers and hence cannot be contacted individually,

c) the time and/or space available in media advertising is sufficient to let the client know enough about the product to encourage its purchase,

d) it is a means of creating the desired image for a product.

The sale of a confectionery bar is typically off the retail counter. The promotion is the most important part of the marketing campaign since it needs to overcome customer loyalty to other products; the publicity needs to have brought the product to the potential customer's attention and the packaging and promotional display needs to catch the eye and generate the appropriate image. It is unlikely that the retailer will specifically promote or recommend the product.

3.3.3.3 Marketing concepts applicable for an automobile.

128,101,115

3.3.3.3.1 Market place and its knowledge.

As for the perishable product, the identification of the gap in the market is critical and determines the market sector that is targeted. The obvious differences between a confectionery bar and motor car are the price and the premeditation that would precede the purchase. Furthermore, the motor car will differ in that although a basic model may be produced, specific extras and/or novel facilities may be available at extra cost to give more choice to the potential client. Which extras would most tempt the potential customer to part with the maximum amount of money can be established only with a sound market knowledge. People may be prepared to pay a "lot more" for the "little extras", and this would be exploited by the automobile manufacturers.

3.3.3.3.2 The pricing policy.

The price of an automobile and the market that would be targeted are closely related. The customer may be an individual with a definite financial ceiling or the purchaser may be a corporate organisation seeking a fleet of company cars and not necessarily having a similarly rigid budget. The price may also sometimes be seen as a prestige symbol and could then be used to indicate the quality of the product.

3.3.3.3.3 Test marketing.

Test marketing is only carried out so far as to establish the performance of the car. Usually, by the time the car has been manufactured, only very minor modifications could be made to the automobile; the results of the road tests would decide whether to launch the product or not.

3.3.3.3.4 Publicity/promotion/sales.

The performance data of a car (from road tests) are published in the specialist magazines and are used for promotion together with media advertising and promotion events such as motor shows. Advertisement is often used to build the appropriate image for a product, which can then dictate its value. Advertising also acts as an after-sales confidence booster for the clients[128] and ensures that they return to buy the same make of car year after year.

The retailers are used for stocking, selling and servicing the car, and play an important role in enabling the client to test drive a car before purchase. A retailer may provide incentives for purchasing from his stock by providing special discounts.

3.3.3.4. Industrial marketing of a testing facility.[128,101,115]

3.3.3.4.1 Market place and its knowledge.

The market need strongly dictates the facilities that should be provided by a testing facility. The decision to be taken by someone intending to enter or expand into this market would be to assess the advantages of either being a specialist in one instrumentation or being able to provide an overall service. Such a decision should only be taken with a thorough understanding of the market place so that the targeted customers require what is being provided by the service.

3.3.3.4.2 The pricing policy.

In this context, this service is costed according to the value of the service, and this cost is a reflection of the time and expertise required to perform the task. Unlike for the other products, an opportunist establishment may have a range of price tags for the same service depending on whether it is, for the customer, essential, useful or interesting. The urgency with which the results are required could also influence the "value" of the service.

3.3.3.4.3 Test marketing

As in the other examples, test marketing needs to be carried out before the capital expenditure is made since this expenditure would determine the range of testing services provided. Once a commitment on the capital expenditure has been made, the other area of test marketing would be in attempting to assess new markets for the testing facilities already available.

3.3.3.4.4 Publicity/promotion/sales.

Unlike the products discussed previously, the publicity related to the launch of a new test facility should be targeted. It could be advertised through specialist technical publications, direct mail shots and promotional exhibitions. The publicity of a service through exhibitions could be prohibitively expensive for the smaller companies; if the facility is intended to attract customers amongst the larger companies, then a promotion at a technical or trade exhibition may be worthwhile. Any accreditation of the service by a recognised authority would be an advantage during such promotional activities. The financial transaction usually takes place after the client is invoiced; unlike for cars, no credit is usually provided and there is a time delay between receiving the work and receiving the payment.

3.3.3.5 Marketing reactive processing research .

The main reasons for marketing the Reactive Processing Project were:

i. to raise funds for the research project,

ii. to test the validity of the technical ideas put forward in the work programme,

iii. to possibly establish ground rules for marketing research projects.

The research project involved developing technology for reacting polymer systems with an aim to increasing the polymer's value by improving its properties.

In developing the marketing approach, it may be useful to compare similarities between this "product" and those previously discussed.

3.3.3.5.1 Knowledge of the market place and the gap in the market.

The knowledge of the market place was just as important in launching and developing a research project as it would be for all the other situations mentioned earlier. The market pull for a research project is more complicated than for the other "products" discussed earlier because of the speculative nature of research. Since the cost of research is increasing whilst the probability of inventing a new polymer is decreasing, co-operative research ventures have become more attractive.

N.B. For example, the cost of a scientist or an engineer working on a project escalated by 53% between 1971 - 1976.[27]

The need for research, in general, is illustrated by the concern of both industry and government towards the lack or drop off in innovative research. A significant proportion of R and D money is devoted to either defensive research (to satisfy legislation) or short term research (<3 years.) It is the finance allocated to short term projects which is of interest when examining the market for a research project.

The technical programme of the project and the market need for this project have been discussed already (Section 3.3.2). What will be discussed next is the market pull for such a research project and how the research programme was tailored to suit the market demand.

Knowledge of the gap in the market place was essential to enable:

(a) determination of the technical content of the project,
(b) determination of the target areas,
(c) determination of the pricing policy,
(d) promotion of the project.

In this case, as for all the other marketing examples given, the perception of the gap and the means of targeting the market determines (a) the product and (b) the marketing techniques to be used to develop the appropriate image. In the context of the research project, the project was developed because of the perceived need for the appropriate research to be carried out. It was unlikely that the "customers" would view this project as essential. Therefore, as for the previously discussed examples, the designed "product" would be competing for its funds with other products (research projects); these competing projects not necessarily being in the same technical field.

3.3.3.5.1.1 Determining the technical content.

For a research project to be attractive to a range of companies, the following criteria need to be satisfied.

a) The research matter must be of relevance to a range of companies.

b) It needs to be selectively targeted.

c) It must be commercially exploitable and this merit should be emphasised to the clients,

d) An appropriate marketing approach must be used.

The following processes and associated product types were identified as being of potential interest to customers:

i) production of a speciality rubber e.g. catalysts,

ii) production of a grafted product using a bulk polymer,

iii) production of blends and alloys.

It is known that careful selection of the monomer for grafting could lead to property improvements in the product. The kind of property improvements that have been documented include increased impact strength, improved filler intake, improved high temperature performance and many others [206,207]. The value of a polymer can increase by two-fold because of the property improvement. To maximise this commercial attractiveness, the added value should be achieved at a minimal cost. In this context, continuous melt reactions compete favourably with the traditional solution or emulsion techniques.

For these and other reasons, grafting reaction was the chosen growth area for exploitation in this project. The project was aimed towards developing "enabling" technology which could be used for a range of grafting reactions.

The actual grafting reaction to be investigated was selected after test marketing these fundamental ideas.

3.3.3.5.2 Target areas.

The target areas for marketing the project were determined by the selection of the reaction system to be studied. The target areas were then perceived as follows.

a) Large multi-national companies who already perform extensive R and D in-house and would like to explore the possibility of using a CTM as a reactor at a reasonably low cost to each company. These companies may already be using other equipment for reactive processing. (It emerged in fact that this category of companies would contribute to approximately 60% of the sponsoring group members.)

b) Smaller companies who do not have an extensive in-house R & D commitment but are aware of the advantages of cooperative research. This group may not be involved in any in-house reactive processing activities but may be prepared to invest relatively small sums of money outside their companies to receive potentially valuable information. (It emerged that this group would make up to 40% of the group sponsors.)

c) The companies that actually manufacture polyolefins in large quantities and are interested in any new applications for them or any means of increasing its market value. This sector overlaps significantly with group (a) since most of the bulk polymer manufacturers are multi-national companies with high turnovers. The project was not necessarily targeted to this group but it was found that this sector was greatly interested in sponsoring the proposed research.

d) The companies licensed to sell CTMs may be interested in optimising its design and in new applications for the mixer. (This was thought to be a great catchment sector but in fact it emerged that not a single sponsoring company belongs to this sector. This could be because the licensees of CTM are more interested in selling other machinery and for these companies, sales of CTM are not the mainstream interest area; their investment would lie in developing their machinery, not in CTM development.)

3.3.3.5.3 The pricing policy.

One of the major differences between marketing a perishable product and a research project would be the difference in the financing of the project. For a project, a technical person would scrutinise the technical content of the project but then would have to convince a manager, more interested in financial rewards than the technical merits of the project. This need for the project to be appealing to two people, viewing the project from two entirely different angles, needs to be borne in mind if a marketing campaign is to be successful.

The choice of whether the project was to be targeted to the bulk tonnage polymer manufacturers or the speciality polymer manufacturers influenced the pricing policy. There are only few speciality polymer manufacturers (because of the lower (tonnage) demand). However, the cost of these polymers is higher than the bulk-tonnage polymers. Consequently, if the project were targeted to the speciality polymer manufacturers, only a few companies would sponsor and the cost for each company would be high. Since this project was targeted to the bulk tonnage producers, it could appeal to several companies and the fees per company could be kept low.[141] The fees for individual company was kept low (£ 2-3000) to prevent the sponsoring companies facing problems with justifying the expenditure. If the fees for joining the group were comparatively high (£15-30,000), it is expected that the time lapse between the marketing and the launch of the project would be longer.

3.3.3.5.4 Test marketing.

In the context of the project, the quality of the product is the quality of the project programme, and this is a very important factor governing the success of a research project.[101] To fine-tune the work programme to suit the requirements of the market place, ideas for the work programme were test marketed. The Rapra staff involved in the project attended a conference in Stuttgart, West Germany organised by Polymer Processing Society, (with a bias towards reactive processing).

A face to face survey was carried out in order to assess the response to the ideas developed for the project.

Questions in the survey.

1) Is their company a Rapra member? Yes/No.
Informs us if they have any background information about Rapra and its ability to set up group projects.

2) Have they heard of reactive processing? Yes/No.
Yes: What kind of reaction systems would their company be interested in.
No: Describe reactive processing and its advantages over traditional means of carrying out reactions.
Ask them then what reaction system they would be interested in.

Assess their response to establish:

a) the reaction system that would be of industrial interest,
b) a contact for future correspondence (if they seem interested in joining the group project).

Appraisal of the feedback at the Conference was positive (13% of the group members were contacts established at the Conference). This led the organisers to believe it prudent to continue with the marketing campaign.

During test marketing, the emphasis was on the project plan rather than the image of the project. The image of the project was created by the professional handling of enquiries and by the literature produced. The literature was produced to appeal to the technologically advancing companies but this aspect, the literature production, was not test marketed. The literature was produced by Rapra, experienced at producing technical literature. However, for a perishable product, it would be essential that the image, the packaging, the perception of product quality were test marketed since they all play a more significant role in the marketing of a perishable good.

3.3.3.5.5 Promotion.

Publicising the launch of a project is useful in stimulating interest in the project in industrial circles; the scientific press was used to achieve this. It was also useful that the companies had "heard" about the project before they received further information at a later stage. Advertising as a means of publicity, although useful for marketing perishables, is not useful for relaying technical information. This is because the time and space available in advertising are not sufficient to convey the content and context of a technical project.[115]

The information regarding the project was relayed to the target companies mainly by direct mailing of leaflets outlining the project.

The direct mailing technique was successful. This success was attributed to the following practices:

i) The companies to be informed about the project were carefully selected. This meant that most of the companies who may have been interested in the project were informed about its launch.

ii) The literature was not sent to companies but to people who would be responsible for deciding on the membership of the project.[101] The cost of reaching a recipient by this technique is greater than if a press advertisement were placed but direct mailing is thought to make a more favourable impact on the client.

When the companies responded to the mailshot leaflet, attempts were made to clarify their perceived needs through telephone conversations.

a) Are they Rapra members? Yes/No.
Informs the organisers of the background information the client might have on Rapra.

b) Have they used Rapra before? Yes/No.
If yes:- Which departments have they used previously?
This gives an indication of their perception of Rapra and the company's interests.

If no:- Explain to them Rapra's activities and especially Rapra's ability to organise group projects.

c) Have they heard of the reactive processing project? Yes/No.

d) Have they received the leaflet? Yes/No.

leading to

e) Are they interested? Yes/No/Do not know.

Yes: Send them the project plan and the enrollment form. (Appendix H)

No: What would they be interested in? - to form ideas for future projects.

Do not know: Explain what the project is all about so that they can decide on its relevance to their interests.

f) If interested: Invite them to an introductory meeting and provide them with the enrollment form.

As a result of this publicity, Rapra enjoyed peripheral advantages too, in that it was to increase its membership: 13% of the group members joined Rapra in 1988 as a result of their involvement in the project and this number was likely to double during 1989.

3.3.3.5.6 The "sale".

Unlike in the marketing of the testing facilities where the performance and the range of equipment that is available is the selling feature; for the marketing of a research project, the project plan and the ability to implement these ideas are the selling feature. The detailed project plan had to be drawn up for approval by both the technical staff and their managers, before any financing was made available for research.

Once the prospectuses were circulated, the industrial representatives had to hand:

a) an insight into the approach that was to be taken during the project and
b) an outline of the work programme.

To follow this through, two information meetings were organised. The aim of the meetings was to

1) present the work programme,
2) clarify any queries regarding the programme,
3) gain pointers on the immediate work plan.

The above exercise was invaluable in establishing the Group. To a certain extent, because the companies had an input into formulating the final project plan, it was easier for them to justify involvement in the project.

The work programme which was finally drawn up was complementary to the objectives set out for the PhD Project.

3.3.3.5.7 The project plan.

The sponsoring group expressed an interest in developing a working model to rationalise the flow pattern in a Cavity Transfer Mixer. The kind of model that was to be tested consists of either a series of Continuous Stirred Tank Reactors (CSTR) or a network of CSTRs. The idea of a series of CSTRs was to be tested initially (being the simpler of the two models, refer to Section 6.5.2). The residence time distribution (RTD) was to be used to aid in the comparison. If a series of CSTRs model was found not to be a satisfactory model, a network of CSTRs could be tested. Other modifications could be made to the model to accommodate the experimentally observed trends.

Chemical engineering parameters were to be examined to assess their influence on RTD. The knowledge of their influence on flow may help to build a better or a more comprehensive model.

The parameters that were to be studied include:

1) the mean residence time,
2) the RTD,
3) the melt rheology,
4) the reactor performance relationship.

The programme for the PhD also examined the residence time distribution of one EPDM of known rheological properties, the influence of two process parameters on the residence time distribution and the CTM reactor performance for certain reactions.

3.3.4 CONCLUSIONS.

3.3.4.1 Marketing.

The success of the marketing campaign, which lasted for five months (from when the conference was attended to the date of the last information meeting), will be assessed below.

25% of the companies contacted regarding the project, responded to the leaflet. At the initial stage of contact, not all of them were even aware of reactive processing. Out of all the companies contacted, only 4% (of the group) were unable to sponsor co-operative research and this decision seemed to have been made as a corporate decision. However, 17% of the companies who responded to the marketing campaign actually joined the group project (which is a higher level of recruitment than in any other project launched at Rapra). It is also the largest group project presently running at Rapra (there are approximately 16 current group projects at Rapra) which is a good indication of the marketing campaign's success.

3.3.4.2 Technical.

The technical content of the project is complementary to the technical content for the PhD. The challenge was in the formulation of a technical programme which was acceptable to companies with a broad range of interests. This could only be done with a reasonable knowledge of the market place and its requirements.

The technical content of the Group sponsored project was determined by the marketing exercise. However, the technical content of the PhD project was not influenced by the marketing exercise.

THE EQUIPMENT SELECTION AND DEVELOPMENT

4.1 INTRODUCTION

Since the development of the processing equipment is a significant part of this research project, a section is devoted to this subject.

In outline, the perceived need of the developed equipment required a polymer melt conveying section (probably a single screw extruder), a reactive reagent metering stage followed by a reaction stage. This latter stage would, because of the wider interests of the Project, be a cavity transfer mixer. It was perceived as a requirement of the study that the feed rate and the mixing rate could be independently set, thus independent drives for both the stages were required.

The selections of the single screw feed extruder and the crosshead extruder were made on the basis of availability and upon the throughput range and the materials to be studied. Details of this equipment are given in the equipment schedule (Section 4.3).

The selection and development of the equipment is discussed under the following headings:

1) the drive selection for the CTM,
2) the metering system and its modifications and
3) the equipment modification to enable residence time distribution studies.

Their pertinence to reactive processing will be clarified and emphasised as necessary.

4.2 DRIVE SELECTION FOR THE CTM.

During the initial stages of the Project, a choice was available:

1) connect the CTM to the extruder screw (Figure 4.1),

2) have an independent drive for the CTM which would be arranged at a crosshead to the feed extruder (Figure 4.2).

The advantages and disadvantages of the two systems were examined so a rational decision could be made; these are explained below.

4.2.1 CONNECTING THE CTM DIRECTLY TO AN EXTRUDER SCREW.

The advantages of a CTM fitted to an extruder are:

1) space saving,
2) decreased capital expenditure.

The serious disadvantage of fitting the CTM to the extruder is that it reduces the process flexibility due to the direct dependence of mixing rate on the throughput.

Figure 4.1 : Equipment arrangement depicting a CTM connected directly to an extruder.

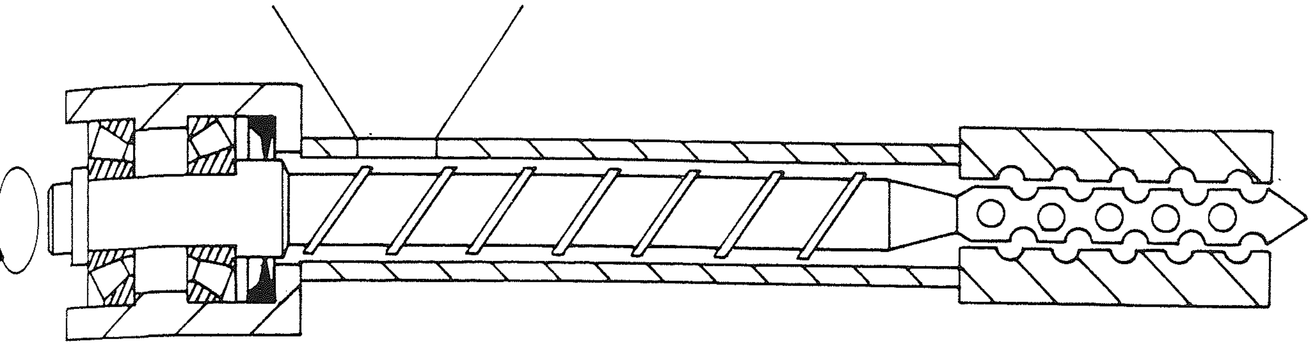
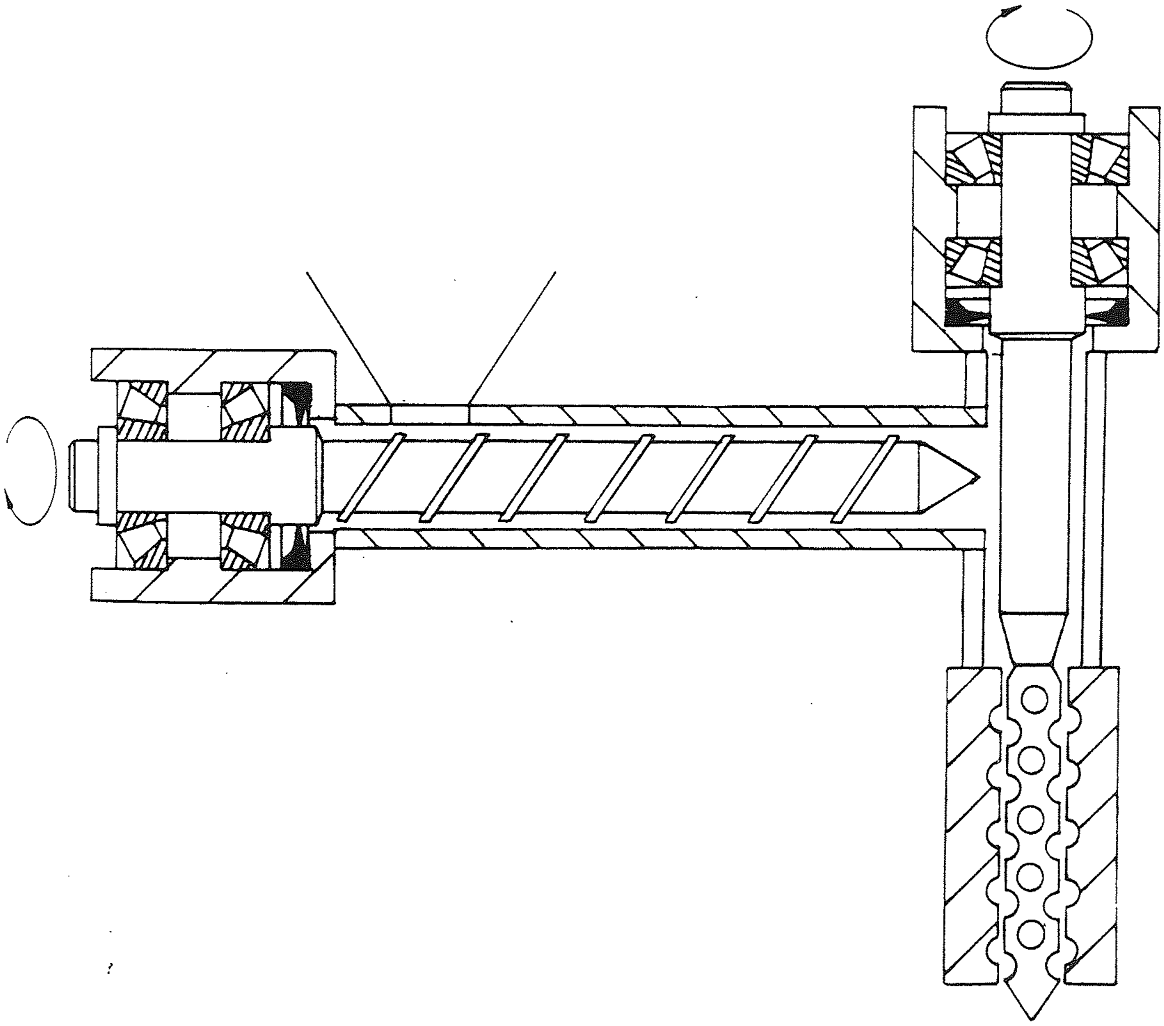


Figure 4.2 : A crosshead arrangement with a CTM connected to an independently driven crosshead.



4.2.2 INDEPENDENTLY DRIVEN CTM.

The perceived advantages of an independently controlled CTM are listed below.

1) Greater flexibility i.e. the ability to alter the degree of mixing independently of throughput. Throughput would be controlled by the feed extruder and the rate of mixing by the crosshead.

2) The independent CTM drive could have more power; high viscosity materials produced within the reactor could be processed. This would infer the use of a low power drive to convey the material, and a higher power drive for reacting and conveying the product.

3) Information gained from this arrangement would be relevant for the cases where the CTM is fixed directly to the extruder.

In this project, space was not at a premium thus the selection of a crosshead arrangement caused no problems. The extra cost as shown in Table 4.1 below could be of significant concern in the industrial environment but for this project, the need for flexibility led to the selection of the crosshead arrangement.

Table 4.1: The cost comparison between a dependently and independently driven CTM

Dependently driven system		£25,000
Feed extruder	£16,000	
Attached CTM	£ 9,000	
Independently driven system		£41,000
Feed extruder	£16,000	
Crosshead extruder	£16,000	
CTM	£ 9,000	

The costs are for a 1 inch extruder and an appropriately designed 1 inch CTM (1987 quotes).

4.3 EQUIPMENT SCHEDULE.

Arrangement as in Figure 4.2.

Feed extruder Figure 4.4

Two start square pitch screw

The L:D ratio = 12

The diameter = 1 inch

Compression ratio = 1.9

Throughput range = 0-6 kg/hr (the upper limit depending on material)

The power of the drive = 1.25 hp (0.9 KW)

Constant torque motor

Speed range = 0-130 rpm.

The CTM Figure 4.5

Number of cavities = 27

The volume of the CTM = 135 cm^3

Power of the drive = 1 hp (0.75 KW)

Constant torque motor

Speed range = 0-166 rpm

Arrangement as shown in Figure 4.3

Feed extruder 1 Figure 4.4

Double start square pitch screw

The L:D ratio = 12

The diameter = 1 inch

Compression ratio = 1.9

Throughput range = 0-6 kg/hr (the upper limit depending on material)

The power of the drive = 1.25 hp (0.9 KW)

Constant torque drive

Speed range = 0-130 rpm.

Figure 4.3 : The modified equipment design where the crosshead consists of an extruder screw and then a CTM. Liquid was injected immediately upstream of the CTM.

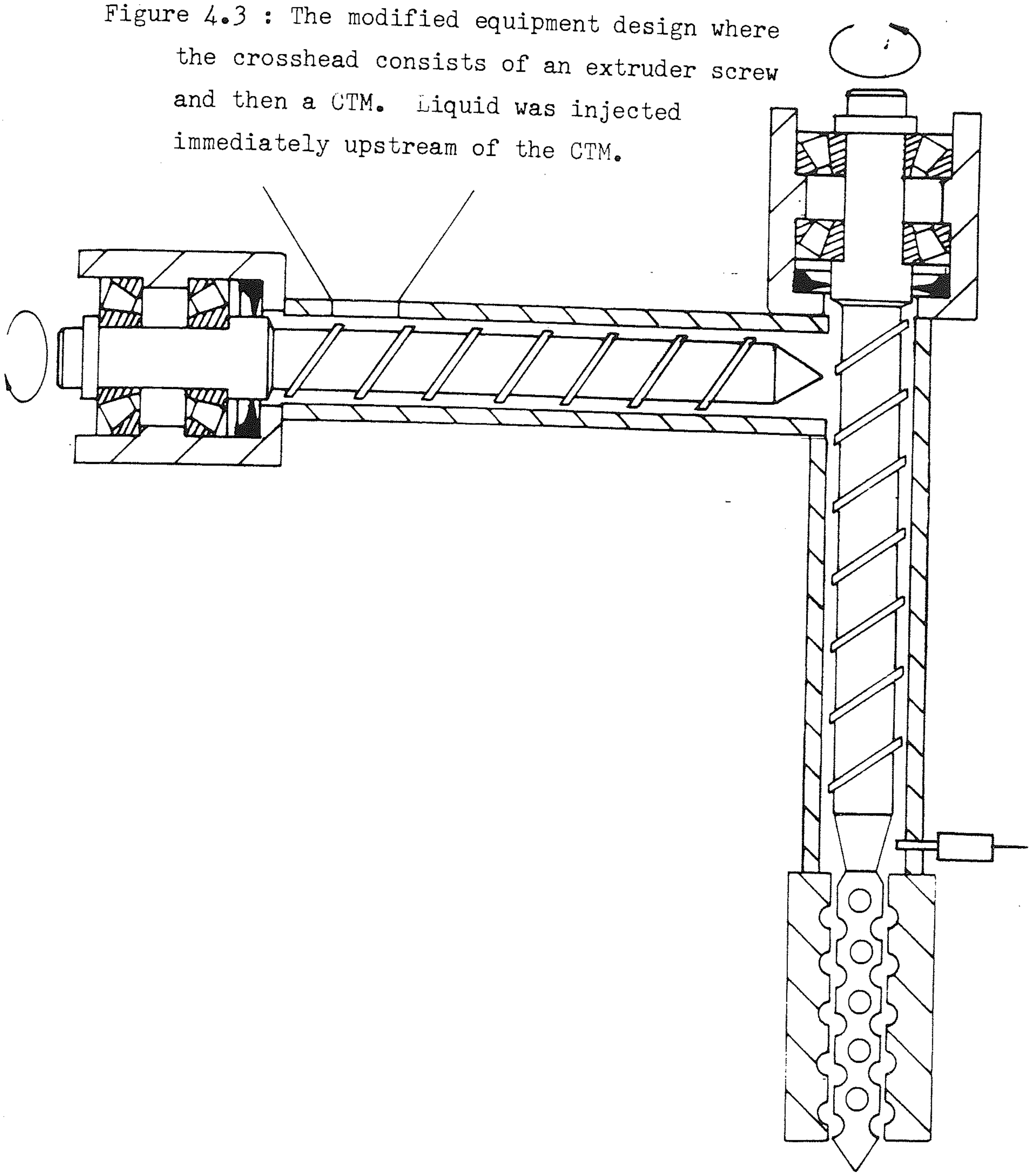


Figure 4.4 : A drawing of the feed extruder 1.

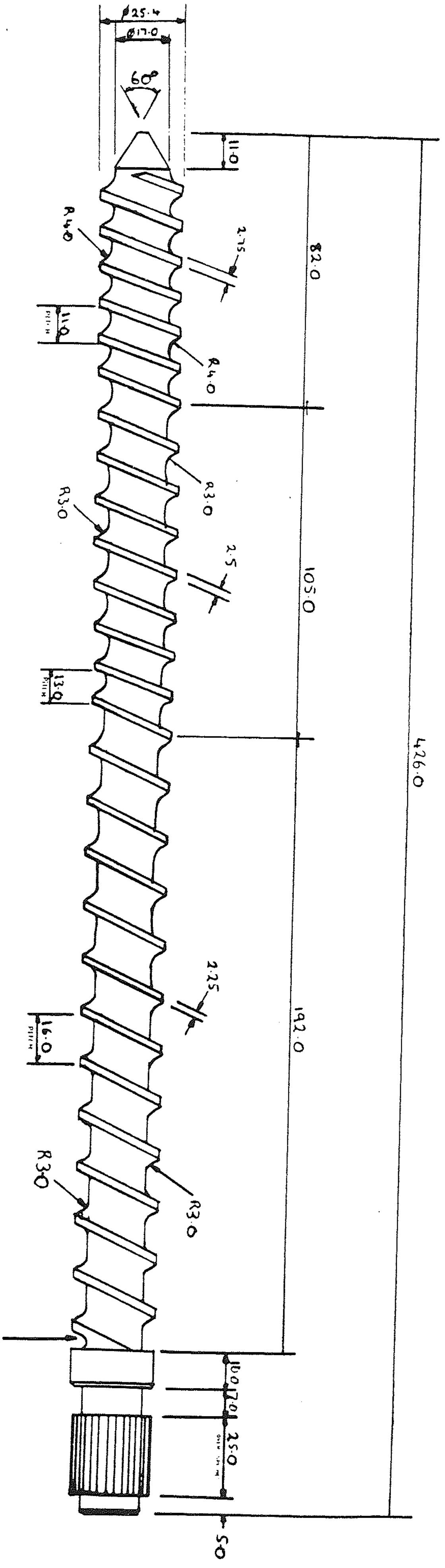
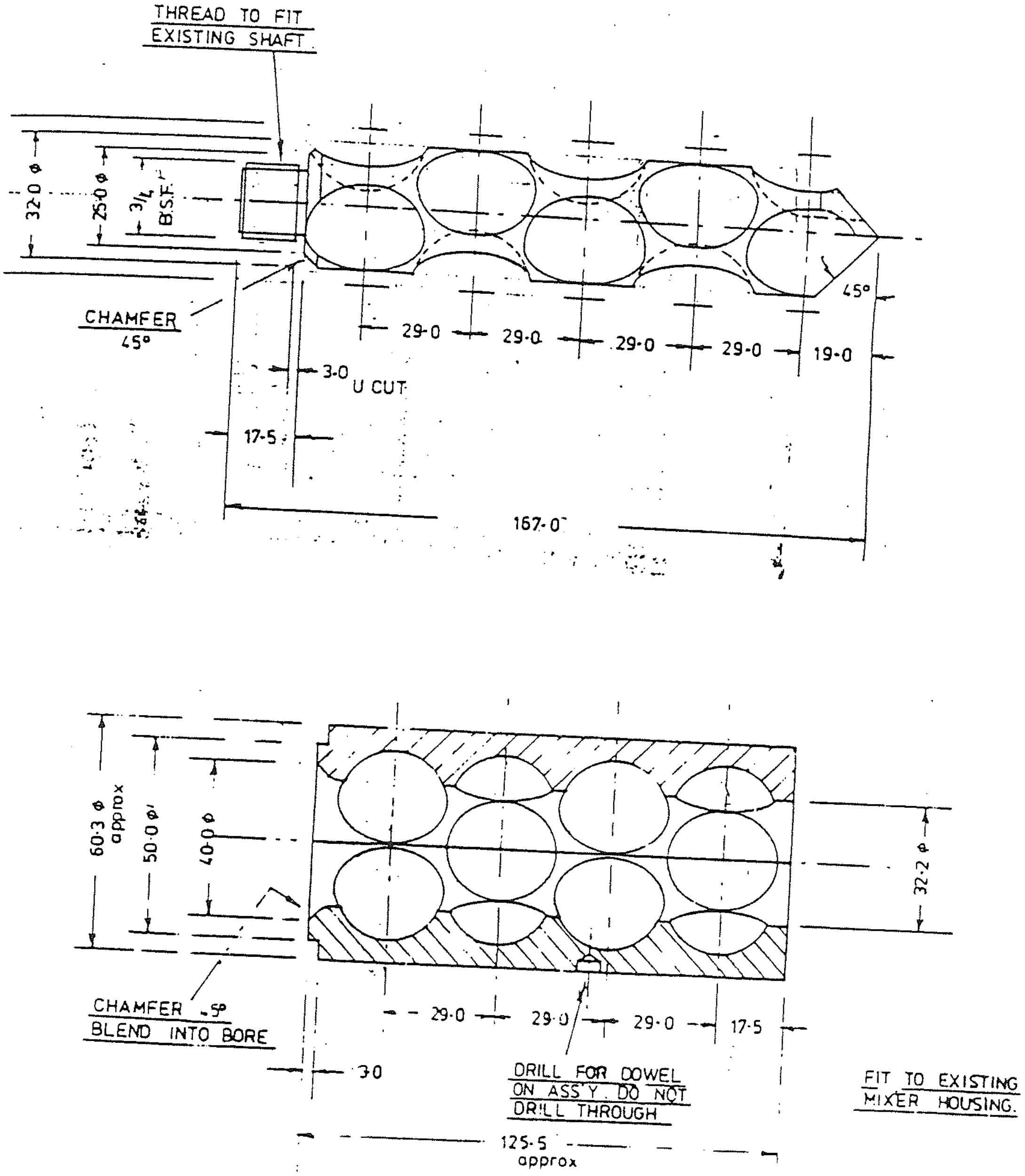


Figure 4.5 : The drawing of the CTM used during the initial trials.



The feed extruder 2 Figure 4.6

Single start square pitch screw

The L:D ratio = 20:1

The diameter = 0.8 inch

Throughput range = 0-6 kg/hr (the upper limit depending on material)

The power of the drive = 2.5 KW

Constant torque drive

Speed range = 0-200 rpm

The crosshead extruder Figure 4.7

Single start square pitch screw

The L:D ratio = 6

The Diameter = 1 inch

Constant channel depth

Throughput range = 0-6 kg/hr (the upper limit depending on material)

The power of the drive = 4.5 hp (3.36 KW)

Speed range = 0-150 rpm

CTMs

55C Figure 4.8

No of cavities = 55

Volume of the CTM = 22.4 cm^3

Figure 4.6 : The drawing of the feed extruder 2.

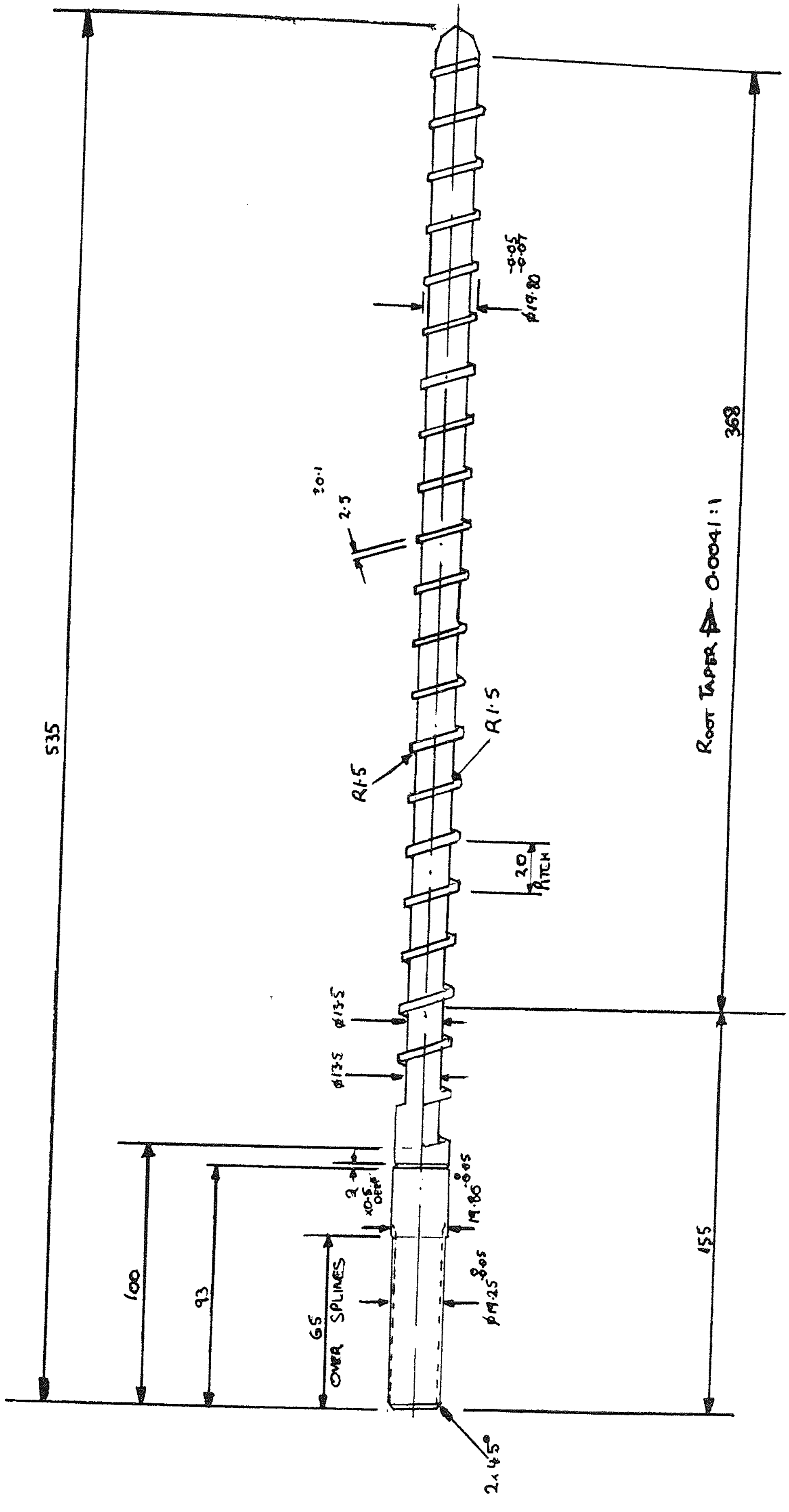


Figure 4.7 : A drawing of the crosshead extruder screw.

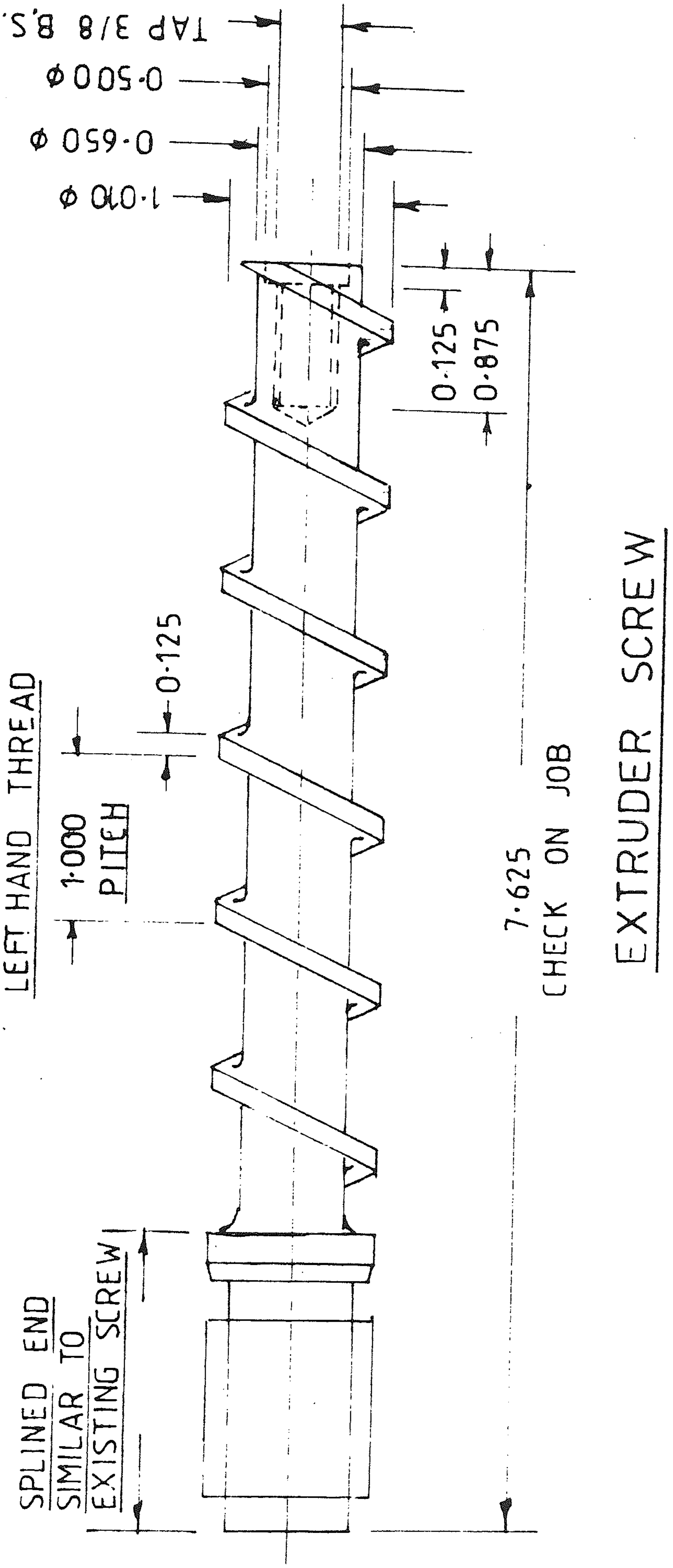
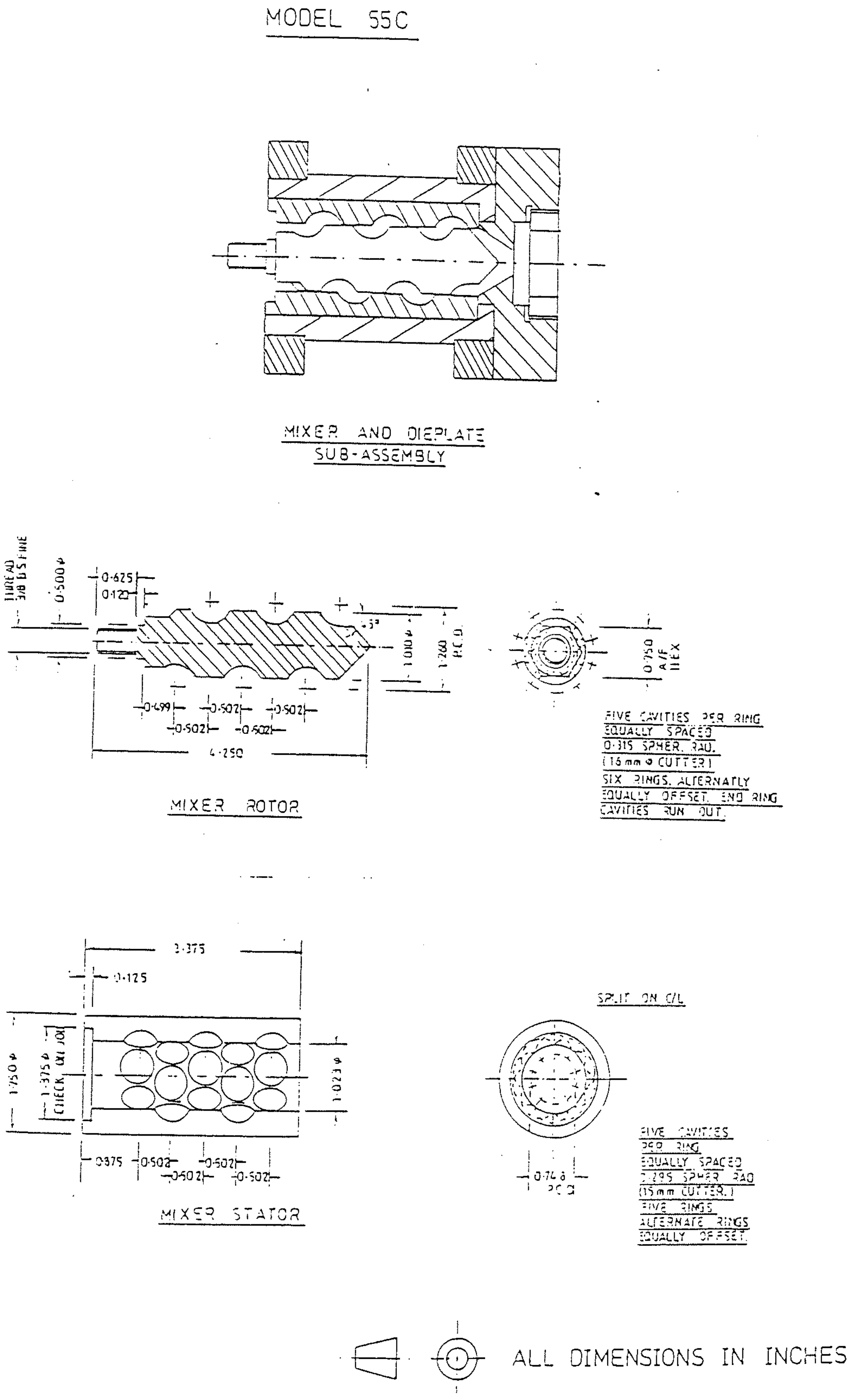


Figure 4.8 : A drawing of the 55C CTM.



55L Figure 4.9

No of cavities = 55

Volume of the CTM = 53.2 cm^3

110C Figure 4.10

No of cavities = 110

Volume of the CTM = 43.6 cm^3

4.4 SELECTION AND DESIGN OF CTMS.

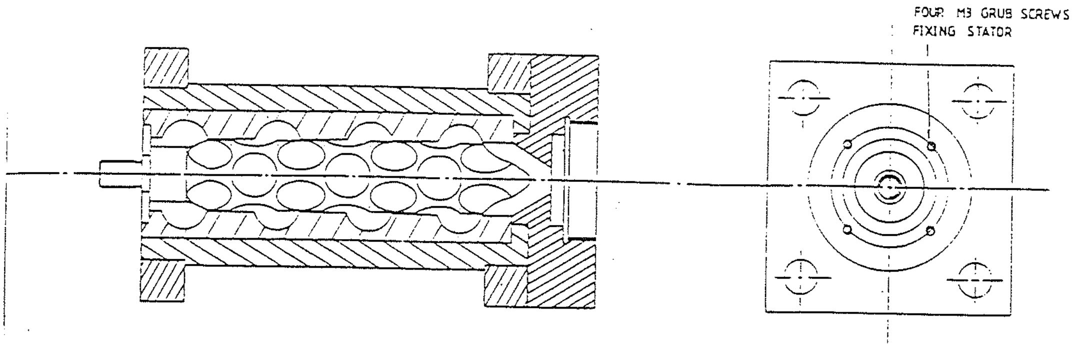
In the earlier experiments, with the quasi-crosslinking neutralisation experiments, a CTM (Figure 4.5) available at Rapra was used. Three CTMs were subsequently designed to enable the study of the influence of the cavity geometry on the flow inside a CTM. The parameters altered in the design were the number and size of the cavities. Consequently, the volume of the CTM was also altered. The details of the CTMs, referred to as 55C, 55L and 110C CTMs are given in Section 4.3 (Figures 4.8, 4.9 and 4.10 respectively).

All the CTMs and injectors were made of stainless steel 316L and the CTMs were nitrided to give the product better corrosion and abrasion resistance.

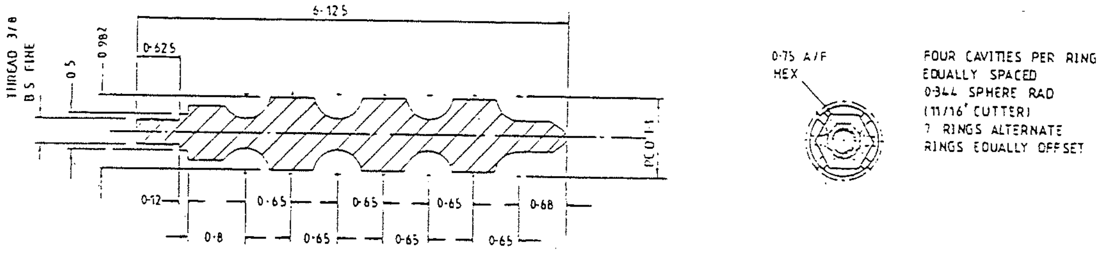
The flow inside a CTM could be analysed using residence time distribution; residence time distribution is used to model flow inside mixers and reactors (refer to Section 2.8.2.1). Such models could be used (using standard

Figure 4.9 : A drawing of the 55L CTM.

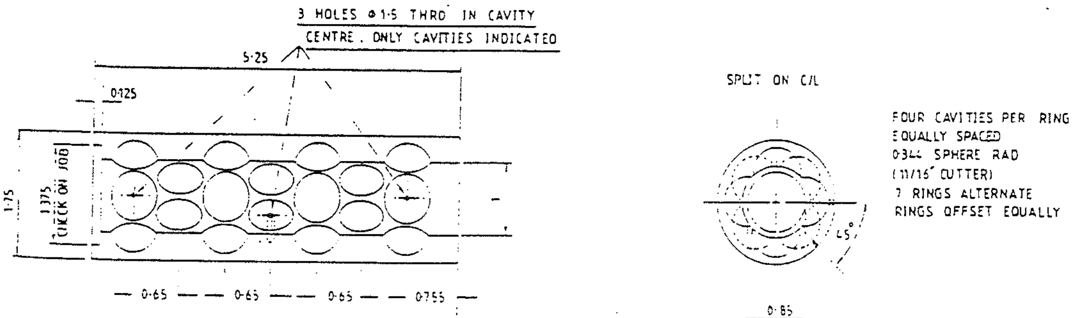
MODEL 55L



MIXER AND DIEPLATE SUB-ASSEMBLY



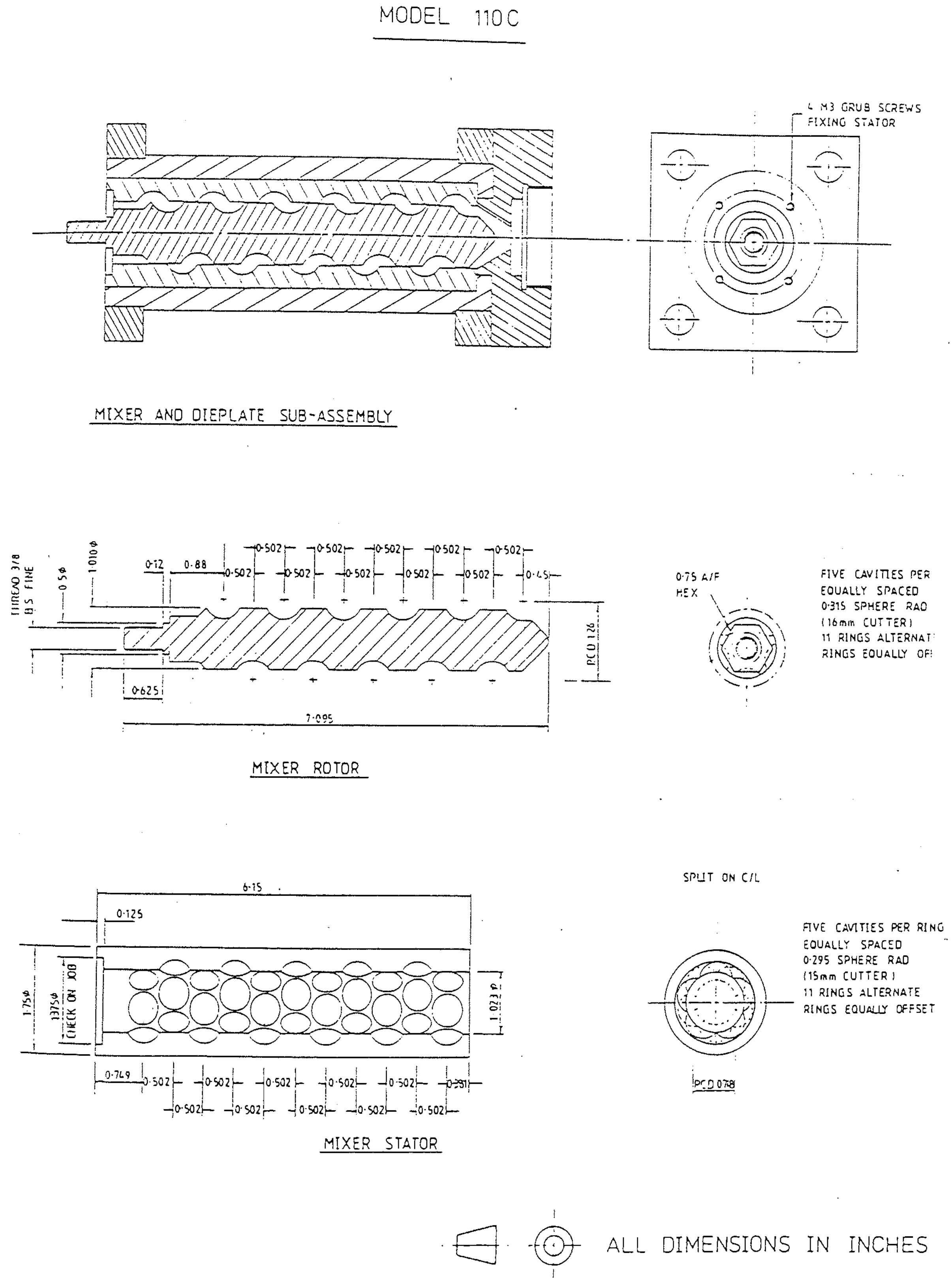
MIXER ROTOR



MIXER STATOR

ALL DIMENSIONS IN INCHES

Figure 4.10 : A drawing of the 110C CTM.



chemical engineering principles) to predict the reactor's performance during reactive processing.

By comparing the RTDs for the 55C and 55L CTMs, the influence of the cavity size on the flow in a CTM can be examined. Likewise a comparison of the RTDs for the 110C CTM and the 55C CTM, could ellucidate the influence of the number of cavities on the flow in the CTM. A comparison between the 55L and the 110C CTMs is expected to provide similar mean residence times for given process conditions, and would indicate the influence of size and number of cavities on the flow inside of a CTM.

4.5 METERING SYSTEM.

The equipment was set up to attempt neutralisation and grafting reactions. The neutralisation reactions involved reaction between an acid functional polymeric material and an alkaline reactant. In this project, grafting reactions usually involved non-functional polyolefinic materials and acid functional monomers, the monomers being grafted onto the polymeric backbone. This required the metering of solids and liquids into the polymer melt stream.

4.5.1 SOLIDS METERING SYSTEM.

The neutralisation reaction attempted required the metering of solids. A particulate neutralising reactant (of approximately 0.5 mm diameter) and an acid functional polymeric material in strip form (Section 5.3.1) were both introduced at the hopper. The strips of 15 mm x 2 mm were hand fed into the extruder while the particulate reactant was fed using the vibrating tray feeder. This selection of solid metering device was based more on availability than on desirability. The equipment to choose, if cost were no restriction, would have been a screw feeder (Table 2.2).

The vibrating tray feeder was fixed to the extruder. The feed rate of the particulate material leaving the tray was calibrated beforehand by collecting and weighing samples over timed intervals. It was noticed that the feed rate from the vibrating tray was not steady. This could have been due to the vibrations of the extruder interfering with the vibrating tray, resulting in unsteady feed rate. The feed rate of the polymeric strips was also not steady since the particulate materials appeared to "lubricate" the extruder screw and prevented the drawing in of the strips by the screw at a steady rate.

These problems could have been solved in different ways. The particulate material, when molten or taken into solution, could have been introduced into the polymer melt using the liquid metering system.

The particulate material could be mixed with the polymer (for example on a mill); this material could be made into strips and introduced into the hopper. This route could be undesirable if the reactants would react on the mill. However, it was decided that the CTM was not the equipment to use to process shear labile high viscosity materials such as those that are produced by the neutralisation reaction under consideration. This led to resolving ways of metering liquids. This metering technique could also enable injection of solids either by dissolving them in a suitable solvent or by melting the solid and then metering the solution.

4.5.2 LIQUID METERING SYSTEM.

A liquid metering system was selected to introduce liquid reagents immediately upstream of the CTM. Liquid was to be introduced at this stage to confine the reaction to within the CTM.

4.5.2.1. Pump selection.

The pressure immediately upstream of the CTM was high (sometimes as high as 1000 psi). A pump had to be selected which would deliver liquid at such pressures. Since the outlet pressure had to be high, neither a centrifugal pump nor a diaphragm pump could be used. Hence a plunger pump was selected for this application. A pulsation dampener could have been introduced in line but this option was not taken due to the prohibitive cost, (pump £1500, pump + pulsation dampener £2800; 1986 prices). During operation, no significant pulsation in the injection line was noticed and it was thought that the connecting pipework (between the pump and the extruder) possibly acted as a pulsation dampener.

A plunger pump is a positive displacement pump and is capable of developing high pressures[17]. The pressures that can be developed are related to the plunger diameter. The pump selected for use in this work could generate pressures of up to 3000 psi. This ensured that at normal process conditions, the pump was capable of delivering the liquids into the process stream.

However, it was noted that, as the process pressure against which the pump was pumping increased, the pumping efficiency decreased. This strong influence of the process conditions on the injection rate was why the injection rate needed to be measured "in situ" and could not be deduced from the pump setting.

4.5.2.1.1 Priming of the pump.

Initially, a reservoir connected to the pump (at atmospheric pressure) was placed below the pump, assuming that the pump would suck the liquid up to the pump. However, this was not successful. The possible reasons why the pump did not work with the liquid level below the pump were:

a) the pump was not primed (there was not enough positive suction head),

b) the pump could not seal the air in the cylinder.
N.B. This was why air locks need to be avoided when conveying liquids. It has been noticed that whenever airlocks were present, liquid injection was

disrupted.

To overcome these problems, a siphon system was set up. A reservoir of liquid was kept above the injection level and the pump was primed. The weight loss of the reservoir was used to determine the injection rate. This was successful, but the start up times were excessive (sometimes in hours). In this context, start-up times were defined as the time elapsed before attaining steady injection. Any air in the injection system could lead to an air lock and consequently cause disrupted injection.

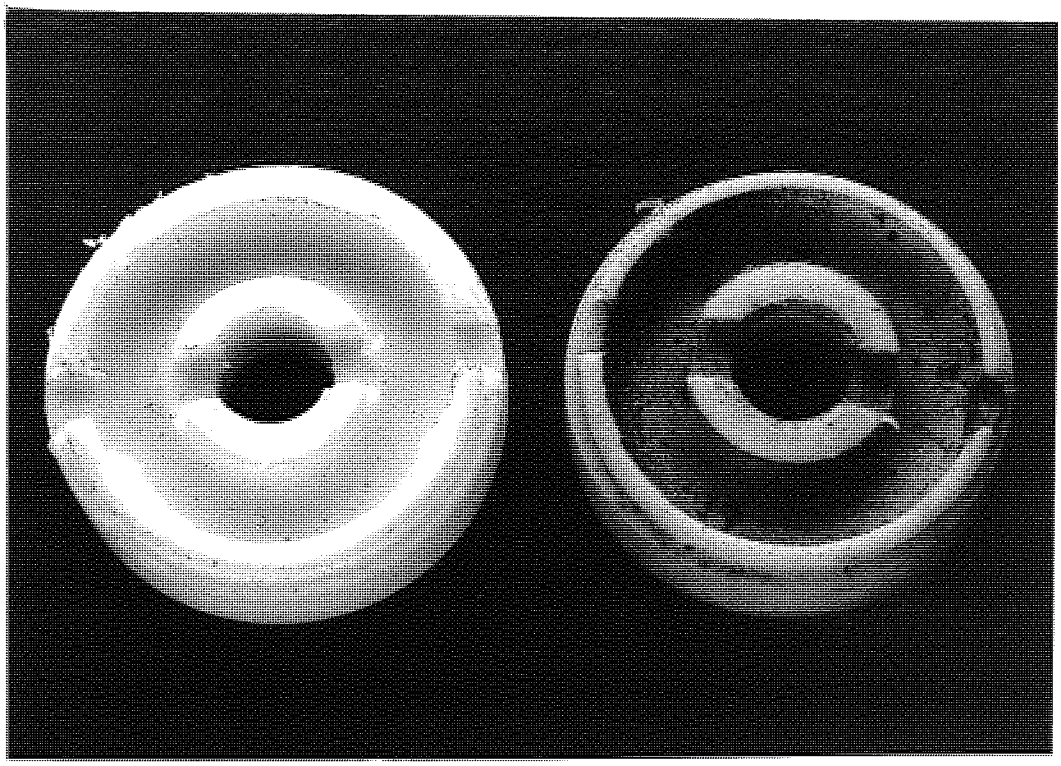
Air in the line, in a siphon system, was very slow to clear using this system. To remedy this problem, the reservoir was pressurised to a sufficiently high pressure to ensure that the line could be vented to clear any air. Nitrogen was used as the pressuring gas since it would also provide an inert blanket to avoid unwanted reactions in the reservoir. Start-up times were reduced to 15 minutes, following this improvement in design.

4.5.2.1.2 Materials of construction for the pump.

All the pipework and connections that were in contact with the injection liquid were made of either stainless steel or PTFE. Where connections were not available in these materials, disposable parts made of polymeric materials were used. Assembly parts made of polymeric materials (or coatings) were preferentially used wherever possible since metal salts are known to degrade peroxide (and are used as catalysts for this reason)[105]. The acid is also very corrosive[91], and so mild steel would not survive under such conditions for long; even if it did, rust, as debris, would get incorporated into the product.

The material selection for the pump parts was also stringent. The corrosive nature of the acid is such that special seals, made of PTFE or Viton, had to be used. Even these were periodically damaged and had to be replaced (Figure 4.11).

Figure 4.11: A photograph comparing a new seal with a damaged seal



4.5.2.1 Operational trouble-shooting for injection pump.

The following problems were encountered and overcome in the operation of the pump.

1. The liquid leaked from behind the seals - this was an indication that the seals were damaged. Replacement of seals resolved this problem.

2. No pressure was being generated but no liquid was leaking from behind the seals. Debris (due to corrosion or reaction of the liquid being injected) may have blocked the non-return valve. Replacement of the non-return valves resolved this problem.

4.5.2.3 Design modification to the injection system to accommodate reactant entry into a CTM.

To incorporate the liquid reactant injection system into the process train, the liquid metering assembly needed to fulfil a number of functions.

4.5.2.3.1 Ensure that injection was possible.

In order to establish a technique for the injection of a liquid into a process stream, injection of a non-reacting liquid was initially attempted. A non-reacting liquid was selected at this stage to avoid the complication of reaction. Table 4.2 indicates the operating problems encountered in such a system and the steps taken to remedy them.

Table 4.2: Guidelines to steady injection of unreactive liquids

Observation	Consequence	Cause	Remedy
Unsteady weight loss	Unsteady injection of liquid	Injector not flush with the barrel wall	Remount the injector correctly
No pressure build-up and no weight loss	No liquid injection	The non-return valves on the pump are not working	Replace the non-return valves
Injection pressure is high before weight loss is observed	Injector does not open until high pressures	Injector opening pressure is high	Reduce the injector opening pressure
No weight loss of liquid even at high pressures	No liquid injection	The injector had opened too far and is blocked with rubber	Clean and adjust the injector. Tighten the injector spring.

The injector opening pressure can be increased by:

(1) increasing the stiffness of the spring,
(2) increasing the length of the spring,
(3) tightening the valve further.

The converse is true for decreasing the injector opening pressure.

4.5.2.4 Ensure operation with reactive liquids.

Once the technique for the injection of unreactive liquids was satisfactory, the injection of slow reacting liquids, containing chemicals such as oleic acid was attempted. Following the guidelines outlined in Table 4.2, there were no further problems with oleic acid injection (Appendix D).

However when injection with more reactive liquid mixtures containing chemicals such as acrylic acid was attempted (Appendix D), it was found that it was necessary to maintain more precise control on the processing parameters to enable steady injection.

Some of the problems encountered whilst injecting homopolymerisable liquid mixtures, such as acrylic acid and peroxide, will be outlined in this section.

When reactive liquid mixtures were being injected, the injector blocked with the polymerised product. This could have been due to the heat transmitting to the injector leading to the reaction of the injecting liquid whilst it was still in the injector. Once the reaction in the injector started, it would be auto-accelerating.

The possible reasons for premature reaction were:

1) the overheating of the injector,
2) the long retention time in the injector.

Initiation of the polymerisation reaction within the injector would reduce the flow of the injection liquid and hence increase the retention time of liquid in the injector. This premature and undesirable reaction needed to be prevented if steady injection of homopolymerisable liquid was to be obtained. The equipment modifications undertaken to enable the continuous injection of homopolymerisable liquids are described in this subsection.

4.5.2.4.1 Cooling of the injector.

If the injector were kept at a low temperature, the reaction in the injector would be slower and may even stop. In an attempt to achieve this objective, a thermally insulating layer of ceramic fibre paper was placed

(1) between the processing equipment and the injector, and

(2) between the reactor CTM and the processing equipment.

This in itself was not sufficient to maintain a low enough temperature and injection of a mixture of acrylic acid and peroxide attempted with this set up led to an injector blocked with polymerised material. This happened even when an injector with a smaller hold-up volume was used (Section 4.5.2.4.2).

This indicated that the injector needed to be cooled further. A cooling jacket was considered for this purpose. The choice had to be made between a liquid and a gaseous cooling medium. A liquid, such as water, would be a more efficient cooling medium than a gas, such as air, because of its higher heat transfer coefficient[91].

heat transfer coefficient for water/water system

- 200-250 Btu/ft^2 hr °F

heat transfer coefficient for water/air system

- 5-20 Btu/ft^2 hr °F

However, since the cooling jacket needs to be dismantled quickly and frequently, to make the water cooling arrangement leakproof would have been more difficult, hence an air cooling jacket was selected. Initially this did not cool the injector sufficiently when the hole available for air to enter the jacket was small. This resulted in the liquid polymerising in the injector. This hole was widened (so, enough cooling gas could be introduced into the cooling jacket).

4.5.2.4.2 Reduction of the retention time.

To reduce the possibility of the reactive mixture of acrylic acid and peroxide reacting prematurely in the injector, the retention time in the injector needed to be reduced. The approach was to reduce the volume of the injector; Figures 4.12a and b, illustrate the difference. The internal volume of the larger injector is 7.15 ml and

Figure 4.12a : The original valve injector.

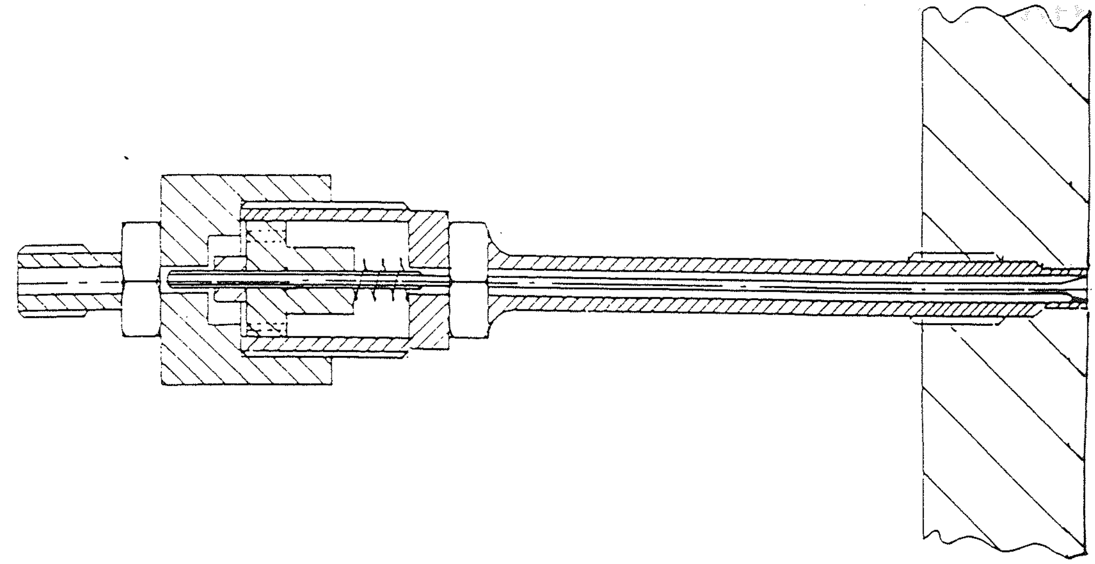
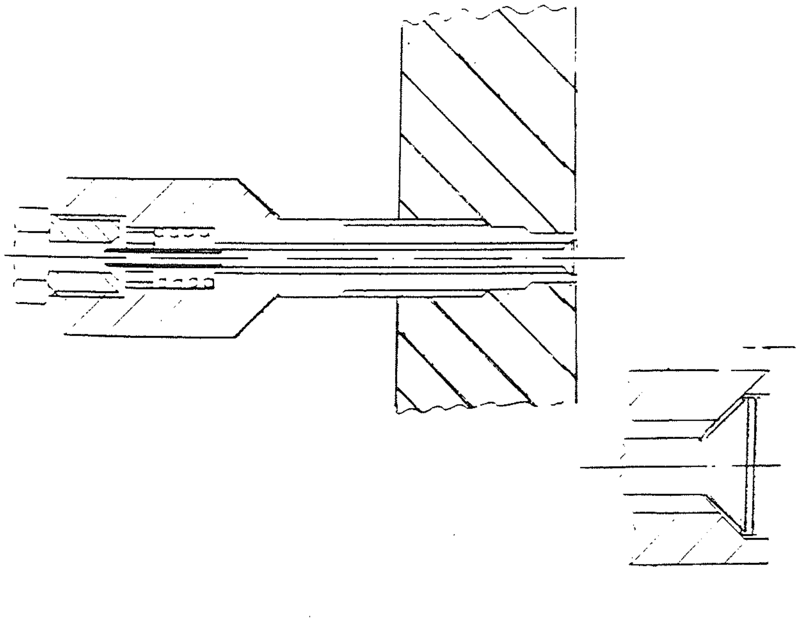


Figure 4.12b : The low volume valve injector.



VALVE NOT TO OPEN BEYOND TOP OF INJECTOR STEM.
(MOVEMENT OF 0·2 TO 0·3mm SHOULD BE SUFFICENT)

that of the small injector is 3.27 ml. 55% reduction in volume was achieved by this alteration in design, with a corresponding reduction in retention time.

The pressurised entry to the pump also enabled quick start-up of injection and further reduced the retention time in the injector.

4.5.2.5 <u>The operational arrangement.</u>

To prevent the polymerisation of the reactive liquid in the injector, the problem was tackled by:

1) keeping the injector cool,
2) reducing the retention time and
3) pressurising the liquid entry to the metering pump.

Liquid metering using the smaller volume injector, an air cooling jacket and pressurised introduction of liquid to the pump enabled successful and steady injection of reactive liquids.

The operating instruction for start up are given in Section 4.5.2.6.

4.5.2.6 The start-up procedure used for injection of reactive liquids.

The injection system was tested for leaks before each run using a relatively innocuous liquid such as xylene. Once the system was operational, the reactive liquid of interest was introduced into the system.

4.5.2.6.1 Test run

Reference to Figure 4.13 may assist in understanding this start up schedule. (The letters refer to those given in Figure 4.13). Xylene was introduced into an appropriate container (A) and that container was placed into the pressure vessel (B) which was on a balance (C). A pressure line was connected to the pressure vessel; the vessel was pressurised with N2 (D). The reservoir of xylene and the pump were connected with a nylon tubing (E) that could be replaced easily and frequently. The outlet from the pump was connected to PTFE lined steel tubing (F) capable of withstanding high pressures. A 'T' joint was made in the high pressure side of the pump to connect a pressure gauge (G). The outlet pipe (H) of the pump, which would in operation be connected to the injectors, was left open to the atmosphere during start-up.

The pressure vessel was pressurised to approximately 20 psi. When xylene emerged from the open end of the tube (H), it was inferred that all the air in the process line had been expelled and the pressure was released from the pressure vessel, to stop the wasteful flow of liquids.

The open end of the tubing (H) was then connected to the injector (as in Figure 4.14). The extruders, first the crosshead and then the feed extruder, were turned on (the hopper was maintained full). This would initiate the flow of polymer melt in the equipment. The pressure vessel was again pressurised and the pump turned on.

After about 5 minutes, the pressure would start to increase in the high pressure side of the assembly. This was due to the pump pressurising the outlet stream. When the pressure reached the opening pressure for the injector (dependent on the injector set-up), the injector valve would open and the pressure would drop. After 5-10 minutes of pressure fluctuation, the pressure would settle down. This, accompanied by weight loss of the pressure vessel, was an indication that the injector valve was constantly open.

A successful test run with xylene ensures that:

1) The pump is operational, i.e. the seals and non-return valves are in good enough condition to generate the required injection pressures.
2) The injection line is without leaks. (This is useful since when reactive liquids are being injected, leaks can be more hazardous than with xylene).

Figure 4.13 : An injector set-up during start-up, when the process line is not connected to the injector.

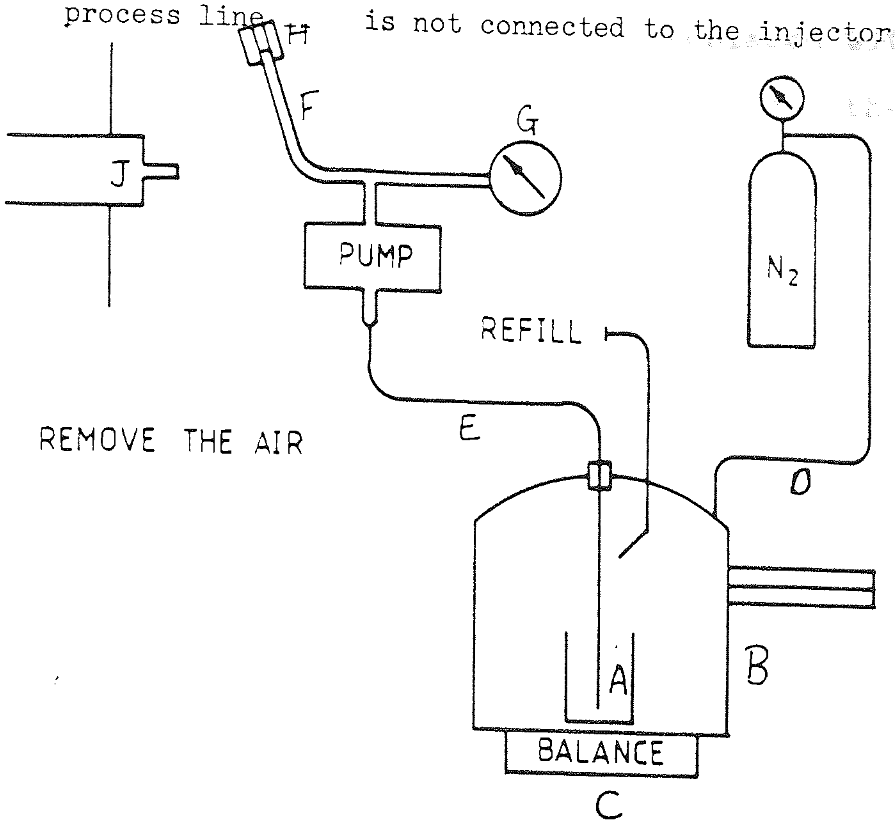
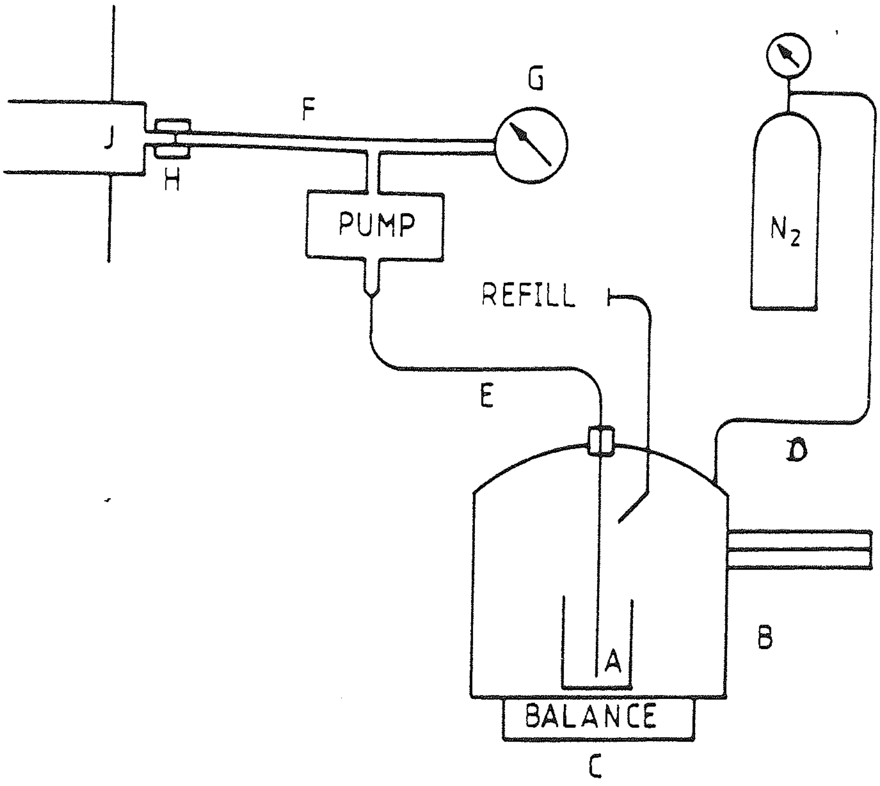


Figure 4.14 : The injector set-up during steady state injection.



4.5.2.6.2 Reactive liquid

Xylene in the previous trial was replaced with the reactive liquid. To achieve this transfer, the container containing xylene (A in Figure 4.13), was removed from the pressure vessel. The line (H) was disconnected from the injector. The pressure vessel was pressurised without any liquid in the pressure vessel; this would push all of the xylene out of the injection line and fill the line with nitrogen. This was done to avoid the possible dilution of the reactive liquids to be introduced later.

The procedure for the test run would be repeated again, but this time with the reactive liquid.

The injection rate was controlled by both the stroke length of the pump and the injector valve set-up.

4.6 MODIFICATIONS TO THE INJECTION SYSTEM FOR RESIDENCE TIME DISTRIBUTION STUDIES.

Residence time distribution data were to be obtained to gain an understanding of the flow pattern in the CTM. Two practical options were open for experimental determination of the RTD in the CTM. Firstly, the RTD in the CTM itself could be determined by injecting a dye immediately upstream of the CTM. Secondly, two RTDs could be obtained; one for the extruder system without the CTM and one with the CTM attached. The RTD in the CTM could thus be deduced from the comparison. If this RTD determination method were selected, the dye (in pellet form) could be introduced in the hopper and the dye concentration on the extrudate analysed.

The first method was selected because of the reduced experimentation and its inherent error involved. The introduction of the dye immediately upstream of the CTM (where the process pressure is high) posed injection problems. The dye used in this project was 5wt% ferric acetyl acetonate in xylene.

The first attempt at introducing a dye at the injection port upstream of the CTM was to inject a measured amount of dye, using a syringe. The syringe had to be carefully selected since the seals on some of the pistons were not capable of sealing at high pressures. For example, when the syringe as shown in Figure 4.15 was used, the syringe leaked but did not inject. The syringe of the type shown in Figure 4.16 injected with greater success. This syringe (as in Figure 4.16) was used in several experiments and yielded reliable results.

However, even the syringe with a vacuum seal and Luer lock still leaked at the seal and the introduction of exactly 1 ml. of dye was not possible. One run was done where the dye left in the syringe, dye that had leaked and the dye in the samples were all accounted for and it was shown that less than 1/2 ml. of dye was injected into the rubber. Not surprisingly, both this method and the

Figure 4.15 : A disposable syringe.

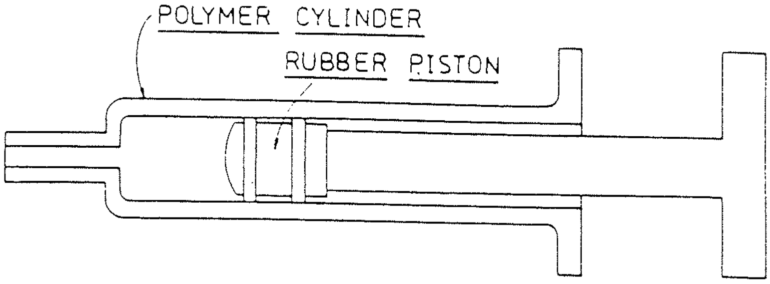
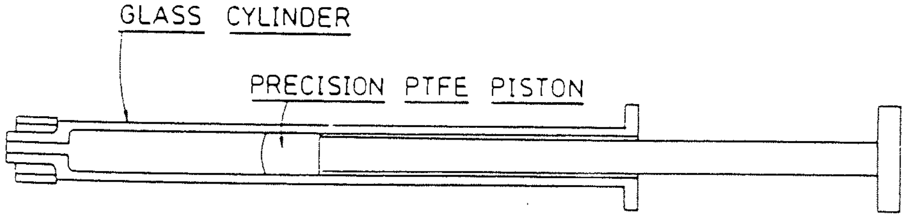


Figure 4.16 : A Luer lock syringe.



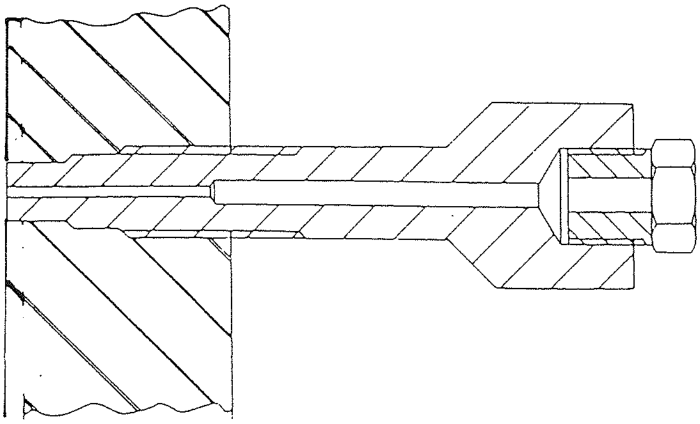
improved method, discussed in the next paragraph, gave similar results since they both depend on the same principle (Section 6.5.1).

The design was modified further so that a nitrogen cylinder was connected to an injector so that the required pressure would be available to open the injector. The dye was introduced into the injector and the required pressure was used to open the injector and introduce the dye into the polymer melt stream.

The extrudate samples were taken, at timed intervals, after the dye was introduced into the polymer melt. The concentration of the extrudate samples were assessed by visually comparing the samples against standards of known concentrations. The samples' concentration was then plotted against time elapsed since the introduction of dye and were adjusted so that the area under the curve was unity (i.e. the curve was normalised). These normalised concentration values are called exit age distributions and this exit age distribution plotted against time axis yields the residence time distribution curve.

Even the design of the injector had to be optimised to ensure reliability in results. The design of the first injector used is shown in Figure 4.17. The narrow stem

Figure 4.17: A plain injector.



and the connections were filled with the dye and the injector was then connected to a gas cylinder. The gas cylinder was regulated by a high pressure regulator so that 3000 psi could be obtained from the regulator. However, in most experiments, pressures of less than 1000 psi were used. With the injector shown in Figure 4.17, when the pressure was high enough to inject the dye, the gas from the cylinder entered the melt stream at such a velocity that almost all the rubber in the CTM was blown out.

To overcome this problem, a non-return valve was used to inject the dye. The design of this injector is shown in Figure 4.12(a and b). The valve at the exit controlled the flow of dye and prevented the high speed entry of gas into the polymer melt stream which would disrupt the flow of polymer melt in the CTM. This injector was used in the subsequent experiments to determine the residence time distribution. In some experiments, exactly 1 ml. of the dye was placed in the injector and the pressure applied (for five seconds) to inject the dye. In these experiments, the amount of liquid left in the injector was taken into account. This showed conclusively that all the dye was accountable i.e. dye was not flowing upstream of a CTM. In the subsequent experiments the injector was filled with dye and the pressure applied for 5 seconds to introduce the dye. The advantage of the second experimental technique (totally filling the injector), was that the extruder did not have to be turned off, nor the injector dismantled, between runs. Not stopping the extruders ascertained that identical extruder speed settings were maintained, and hence eliminated errors due to possible variations in speed of the drive. However, this error could be more easily eliminated by measuring the extruder speed with a tachometer. The extruder speed was checked with tachometer in most experiments.

2.6.1 THE START UP FOR AN RTD EXPERIMENT.

A high pressure line was connected to the gas cylinder. This pipe line was capable of withstanding 3000 psi. The required amount of dye was introduced into the injector and the injector connected upstream of the CTM. The high pressure line was connected to the injector.

The extruders (first the crosshead extruder and then the feed extruder) were started and the system was allowed to reach steady state. A steady temperature and pressure upstream of CTM was taken to indicate that the process had reached steady state.

The valve of the cylinder was then opened, to reach the process pressure on the injector. Once the injector opened, it was left open for 5 seconds to ensure that enough dye had entered the CTM. The samples, at timed intervals, were taken after the 5 seconds period had elapsed. These samples were then put in labelled bags and compared with standards of known concentrations.

The throughput at the process settings was also measured.

The rotational speed of the extruders was measured with a hand held tachometer.

4.7 DISCUSSION

4.7.1 INTRODUCTION

The details of the experimental work and selection and development of equipment are given in Sections 4.1 to 4.6. This section attempts to summarise these details.

4.7.2 THE INFLUENCE OF CTM GEOMETRY AND PROCESS VARIABLES ON RTD.

Three CTMs were designed and built so that the influence of design parameters and process variables on residence time distribution could be assessed. The design variables that could be examined in future projects would be the size and number of cavities. In this project, the RTD variation due to the following parameters have been examined.

1. The CTM rotational speed.
2. The feed extruder speed.

The influence of the CTM geometry and polymer melt rheology on RTD and reactive processing have not been covered here but are recommended for future work.

It was found that:

1) increasing the CTM speed marginally narrowed the RTD,
2) increasing the throughput (feed extruder speed) narrowed the RTD.

4.7.3 NEUTRALISATION REACTIONS.

Two different types of neutralisation reactions were attempted during this project: between solids and polymers, and between liquids and polymers. The neutralisation reactions between solids and polymers resulted in quasi crosslinked products whereas those between liquids and polymers had products that were thermally labile.

4.7.3.1 Neutralisation reactions between solids and polymers.

In the experiments initially carried out of the neutralisation reaction between solids (alkaline metal salts) and polymers, the CTM shown in Figure 4.5 was used. This was useful in obtaining a working knowledge of a CTM. All the four systems tested with quasi crosslinked product displayed similar processing difficulties; some of these are summarised below.

The two reactants, the polymeric reagent in strip form and the particulate material in powder form, were introduced at the hopper of the feed extruder. The strips were hand fed and the powder was fed using a previously calibrated vibrating tray feeder. Feed problems were encountered with the metering of both of these materials.

1) The vibrations from the extruder interfered with the vibrating tray feeder and upset the steady flow of powder.

2) The powder on the extruder screw appeared to inhibit the gripping of the polymeric strips. This led to further fluctuations in the throughput.

One other method attempted to ensure constant ratio of reactants and constant throughputs was to mix the two ingredients together (on a mill), make strips out of the mixture and feed these strips into the extruder. This was not successful since reaction occurred within the ram extruder which was used to form the strips.

The viscosity increase due to this neutralisation reaction was significant (Appendix E). Prior art[105] predicts that quasi crosslinking is a direct result of this reaction. Quasi-crosslinked bonds can be broken down at high shear stresses, thus this product behaves like a crosslinked or cured product at low shear stress but starts to flow when the bonds are broken at high shear stress. However, if the bonds are broken down, the reaction has been reversed. So, a high shear rate mixer, which would make the product flow, would also reverse the reaction. The CTM could not be used since it was not capable of processing such high viscosity thermally non-labile systems. An operational option to overcome this problem could be to mix the two reactants together in a CTM and then to react them outside. However, since this technology is already established, this path was not pursued.

4.7.3.2 Neutralisation reactions between liquids and polymers.

Introduction of liquid reagent has been successfully performed. A neutralisation reaction was successfully performed under this category where the product was thermally labile (Section 6.4.1.2).

In order to avoid problems in solid reactant metering, it was proposed to take the solid into solution and then to inject this solution upstream of the CTM. Although the solid introduction for the neutralisation reaction using the liquid injection system was not attempted, solids, in solution, were injected into a CTM to graft (Section 4.5.2).

4.7.4 GRAFTING REACTIONS.

The majority of the effort on the grafting reactions during the Project was on the liquid and polymer reaction system. However, the feasibility of heated injection (for injection of solids in liquid phase) was examined.

4.7.4.1 Grafting reactions between a solid and polymer where the solid is injected into polymers with a heated injection system.

When the liquid metering pump was purchased, it was foreseen that injection of heated liquids may be required. To satisfy this potential requirement, the pump was equipped with an oil heating jacket. To enable injection of heated liquids, an injection line was designed with an oil heating jacket. The reservoir of liquid in the pressure vessel was also then heated using an electric band-heater which was controlled by a PID temperature controller dictated by a thermocouple in the reservoir. This equipment set-up was able to handle liquids that would recrystallise under laboratory condition at 38°C.

N.B. It appeared as if liquids were recrystallising at a higher temperature in the injection line than in a beaker in a laboratory. This could possibly be due to an increase in nucleation sites in the process line compared to a beaker which would have a smooth glass surface. It was not possible to verify this explanation since it is impossible to measure the exact temperature in the process line.

4.7.4.2 Grafting reactions between liquids and polymers.

The majority of the grafting reactions studied entailed the mixing and reacting of a liquid reactant with a polymer melt. This required the development of a system for the introduction of liquids upstream of the CTM. To this end, a plunger pump was selected to enable injection of liquids against the high pressures encountered at the injection stage. The injection rate is determined by the stroke length and plunger diameter in such a pump. The plunger diameter was already set at 3mm in the selected pump. The stroke frequency was also set at 151 strokes/min. The stroke length could be varied between 0 and 20mm. The possibility of purchasing a pulsation dampener was investigated but this accessory in itself would have cost as much as the pump. On a cost basis, the pulsation dampener was not purchased. However, in the final assembly, no significant pulsation was observed.

This observation was confirmed by a steady injection pressure. This could be because:

1) the pipework and the connections by the pressure gauge and the injector acted as "pulsation dampeners",
2) the high frequency of plunger action may not have created noticeable pulsation.

The assembly of the injection system had to be "right" to obtain steady injection. The injector had to be set so that the opening pressure of the injector was similar to the process pressure upstream of the CTM (which was measured using a Dynisco PT460E pressure transducer). The opening pressure of the injector was controlled by the stiffness of the spring (Figure 4.12) and the length of the spring.

Once the injector was set up flush against the barrel wall and there were no air locks in the injection line, steady injection was possible. Once the steady state was reached and the required injection rate (controlled by the stroke length and measured by weight loss) was obtained, samples of the extrudate were taken.

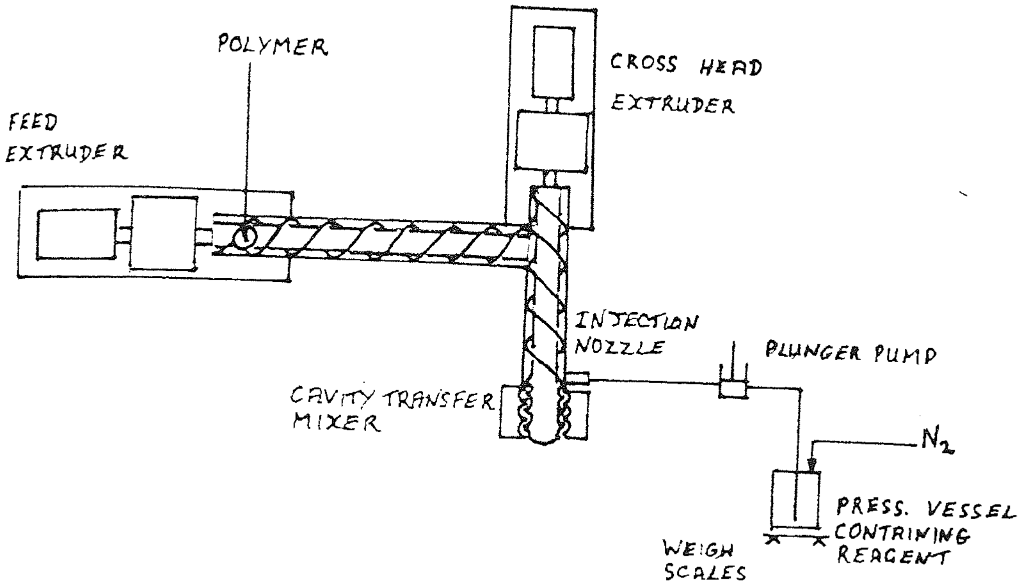
4.7.4.2.1 Homopolymerisable liquid injection.

The liquid injection assembly described in Section 4.7.4.2 was useful when injecting liquids which do not homopolymerise such as oleic acid, di-butyl maleate, bis-tributyl tin oxide. However, the injector under normal operating conditions got too hot and the liquid stayed in the injector for too long and liquids such as acrylic acid would homopolymerise. To alleviate this problem:

1) the injector was thermally insulated from the extruder using ceramic fibre paper,
2) the injector was air cooled and
3) the volume of the injector (and hence the retention time) was reduced by 50%.

Injection of homopolymerisable liquids such as a mixture of acrylic acid and peroxide was then possible.

The equipment layout developed during this project is shown below.



5. EXPERIMENTAL TECHNIQUE

5.1 INTRODUCTION

This section is set out to describe the experimental techniques adopted in this project.

5.2 MEASUREMENTS OF PROCESS VARIABLES.

Various measurements were taken routinely as part of the experimental work. The measured values are given in the Appendix D. What is discussed in Sections 5.2 - 5.6 is the way these and other measurements were taken.

5.2.1 THROUGHPUT

The throughput of the polymer was measured by weighing samples of extrudate collected over timed intervals. At least two readings were taken before a value was quoted. It was checked that the two readings did not vary by more than 4% and if this criterion was satisfied, the average value was quoted. If the values did fall outside the 4% error margin, more readings were taken to establish the more representative value.

5.2.2 ROTATIONAL SPEED OF THE EXTRUDER.

The speed of rotation of the extruder screws was measured using a hand-held tachometer. The speed was recorded when the tachometer registered a steady (± 1 rpm) reading.

5.2.3 PRESSURE.

Pressure readings were taken immediately upstream of the CTM using a pressure transducer (Dynisco PT460E). A cyclic fluctuation (refer to Section 6.3.1.4) was noticed in this pressure and a mean value or a range of values were quoted as appropriate.

5.2.4 TEMPERATURE.

Temperature measurements are very important in gaining an insight into the way the process behaves. With the extruder set up, temperature measurements were taken:

1) upstream of the CTM, using a thermocouple situated flush against the barrel wall,
2) of the extrudate, using a hand-held digital thermometer,
3) of the rotor and the stator, using a hand-held digital thermometer.

When ovens were used, the temperature of the oven was recorded as the temperature registered by a thermometer installed to read the internal air temperature of the oven.

When a sigma blade mixer was heated using the steam jacket, the steam pressure was noted and the temperature corresponding to this pressure was recorded. The actual material temperature would be a function of several other factors such as the exotherm of the reaction, surface area to volume ratio of the reactor and the specific heat of the reaction mixture.

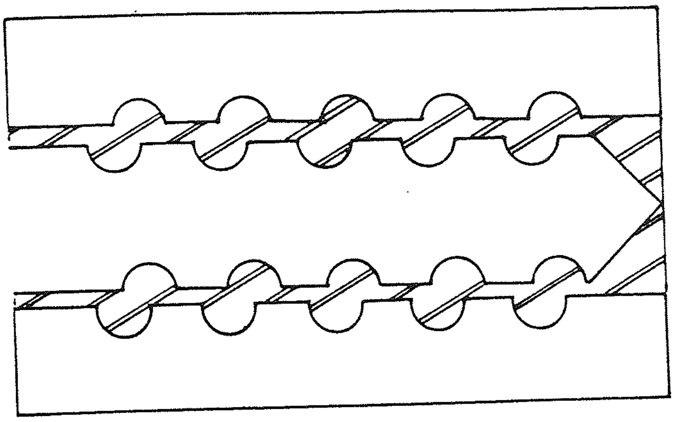
5.2.5 INJECTION RATE.

Measurement of the weight of liquid introduced into a batch operation, such as a mill or a sigma blade mixer, was relatively straightforward. The amount of liquid required in the batch was weighed and added to the rest of the mixture. When introducing a liquid into a continuous stream, the injection rate had to be continuously monitored. This was done by placing a reservoir of the liquid to be injected on a balance; the weight loss observed using a balance was, during steady state, recorded as the injection rate.

5.3 MEASUREMENT OF THE VOLUME OF A CTM.

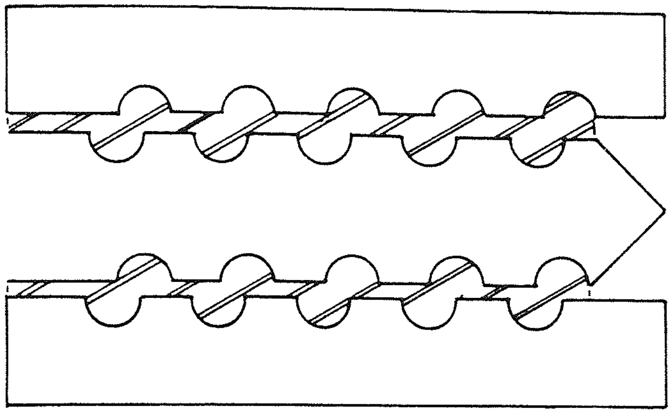
Knowing the effective volume of a CTM is necessary; for a given throughput, it influences the mean residence time in a CTM. This volume was measured initially by filling the CTM with propanol. However, this measurement included segments in the CTM which were not active when using the CTM as a reactor or when the RTD was determined (Figure 5.1).

Figure 5.1: A cross-sectional view of a CTM; the hashed segment represents the total volume inside the CTM.



So, the next method used was to fill the zones which were part of the "active volume" with putty (Figure 5.2). By knowing the weight of putty required to fill the active volume of the CTM and the putty's specific gravity (which in this case was 2.2 g/cc.), the active volume of a CTM could be calculated.

Figure 5.2: A cross-sectional view of a CTM; the hashed segment represents the volume of the CTM that was represented in the RTD experiments



5.4 COLOUR STANDARDS AND CODING OF EXTRUDATE SAMPLES.

The colour concentration of the samples of the extrudate obtained from the RTD experiments had to be evaluated. A colour meter, made by Minolta, was assessed for this purpose. It was found that the readings obtained using this meter were strongly dependent on the surface of the extrudate exposed to the meter. Since the extrudate samples were irregular, by changing the way the sample was placed in the "attachment", different readings were obtained (Appendix D). The samples could be taken into solution and the iron concentration of the solution could be analysed using u/v absorption. U/v absorption technique would have been a time consuming way to assess the colour concentration of all the RTD samples; for each RTD run, approximately forty samples were taken.

The extrudate samples were compared visually with colour standards (made of known concentrations of dye). Some of the coloured extrudate samples were analysed using u/v absorption to check that the visual comparison was not incorrect. This verified that visual comparison of colour was an effective and efficient way to colour code polymeric extrudate samples with non-uniform surfaces.

5.5 DATA ON THE RHEOLOGICAL BEHAVIOUR OF POLYMER BASED MATERIALS.

The flow behaviour or the rheological behaviour of the material to be processed influences the processing characteristics significantly. An example would be the influence of the polymer melt viscosity on the throughput in a single screw extruder, as given in Equation 2.3. The measurements of the rheological behaviour of polymeric materials, used in this project, were:

1) Capillary rheometer data,
2) Monsanto traces and
3) Mooney viscosity.

Details of how the different measurements are taken are amply discussed by Rauwandaal.[99]

5.6 HALF LIFE OF A PEROXIDE.

Information on the half lives of peroxides at different temperatures in a given solvent are supplied by peroxide manufacturers. However, it is known that the concentration and the matrix composition can influence the half life of a peroxide (the half life of a peroxide is not similar to that of a radioactive material; half life of a peroxide is dependent on its concentration). Hence, the half life of cumene hydroperoxide in Keltan 720 (511.82g of Keltan 720 and 87.74g of 70% pure cumene hydroperoxide mixture) was determined. To this end, curing curves using the Monsanto rheometer 100 were obtained and used to calculate the half life of the peroxide in this polymer (Appendix F).

This was an empirical means of determining the half life of a peroxide.

5.7 EQUIPMENT

5.7.1 EXTRUDER.

The way the extruders were set up will be first explained. The majority of the connections were bolted together so that the assembly could be easily dismantled. The rotation of the crosshead extruder was always started before the feed extruder. This was to ensure that material was conveyed away from the crosshead and the build-up of pressure at the crosshead was avoided.

The extruders and the CTM were cleaned regularly. The polymer was removed from the CTM and extruders (by heating) and the surfaces were polished using polishing cream and hand drill. This maintained the equipment in a reasonably clean state. This was especially important when the process material was altered, to avoid contamination of the new stream with the material previously used.

5.7.2 MILL.

Milling is a standard operation where material is introduced between two rolls and a band is made of the polymer. In this project, milling was used in two areas; firstly in the production of colour standards for the RTD tests and secondly as a batch reactor. Either a liquid or a solid reagent could be added to the band. Usually, the foreign material would break up the area of the band where the liquid or solid was added. During the addition of the liquid or the solid, care was taken so that the band did not totally disintegrate. While making the colour standards, even greater care had to be taken so that the grease from the bearings of the mill did not enter the band and alter the colour of the polymer.

5.7.3 SIGMA BLADE MIXER.

The operation of a sigma blade mixer was fairly straightforward. All the ingredients to be mixed (or reacted) were put into the mixer. If the mixture needed to be heated, the steam jacket was turned on. The mixer was then turned on. At the end of the batch time, the mixture was removed.

The sigma blade mixer was cleaned using a solvent such as xylene or propanol. It was not an easy piece of equipment to clean due to the small clearances between the blade and the vessel.

5.7.4 OVEN

In this project a vacuum oven was used to:

1) heat,
2) react or
3) dry.

Usually, the first two stages could be grouped together where material was heated to react. If the presence of oxygen could cause side reactions to occur, the oven was purged with nitrogen for the first five minutes of the heating cycle. The oven was then sealed.

Even when the material was to be dried, the oven would be purged with nitrogen if undesirable reaction could occur due to the presence of oxygen.

5.8 MATERIAL PREPARATION.

Thermoplastics are usually available in pellet form. Pellets can be easily fed into an extruder by the use of a hopper. Elastomers are not as easy to handle; some are also available in pellet form but this is restricted to only a few elastomers which can be pelletised. If the elastomer is too "sticky", pelletising the rubber is impractical and useless since they stick together again. So these elastomers are supplied in bales (25 kgs.). In this project, when small pieces of rubber cut out of the bale were fed into the extruder, unacceptable throughput fluctuations were noticed. This problem was overcome by feeding stripped rubber.

5.8.1 THE PREPARATION OF THE STRIPS OF RUBBER.

Firstly, pieces of rubber from the bale were milled and a band formed. Gradually the nip of the roller was reduced until the thickness of the sheet was approximately 2 to 3mm. The band, in sheeted form, was then rolled together and put into a heated ram extruder. Vacuum of twenty five mm Hg was created inside the ram extruder, to improve heat transfer to the rubber. The roll of rubber was left in the extruder for at least 25 minutes. After that period, the vacuum in the ram extruder was released and pressure was exerted on the ram to produce the extrudate. This extrudate was either stored on a reel (if the rubber was not too sticky and was not going to stick to itself) or was protected in folded paper (to prevent it sticking to itself).

The strips were then fed into the feed port in the extruder and led to a steady throughput rate (only ± 4% fluctuation in throughput).

5.9 SAFETY PRECAUTIONS.

There were several situations that required careful assessment of the hazards involved. The handling of noxious chemicals such as acrylic acid, methacrylic acid, cadmium oxide and maleic anhydride required stringent precautions to be taken.

Whilst handling acrylic acid, methacrylic acid and maleic anhydride at low temperatures and pressures, safety glasses and safety shoes were worn. When handling cadmium oxide, a one-piece overall and a face shield were worn and were immediately disposed of afterwards.

Whilst handling any materials at high pressures, as was the case during liquid injection, face shields were worn.

Industrial quality rubber gloves were worn when handling any noxious liquids. High pressure injection of peroxides was avoided once the hazards inherent to such an operation were brought to our notice by people with experience in handling peroxides.

6. SUMMARY: OBSERVATIONS AND TREATMENT OF RESULTS

6.1 INTRODUCTION

The results from the experimental programme are presented in Appendix D; this section brings together the major trends observed.

6.2 REACTIONS CARRIED OUT IN BATCH EQUIPMENT.

Several batch reactions were carried out to allow subjective comparison between the performance of batch and continuous (CTM) processes. The reactions on batch equipment were performed to completion.

6.2.1 MILL.

The reactions performed on a mill are listed below:-

Table 6.1 : A list of reactions attempted on a mill

Polymer	Additive	Reaction type
Vamac G	Aluminium isopropoxide	Neutralisation
Krynac 211	Calcium hydride	Neutralisation
Vamac G	Magnesium ethoxide	Neutralisation
EPDM	Maleic anhydride	Grafting
EPDM	Methacrylic acid	Grafting

These experiments were useful in illustrating the advantage of performing certain reactions on a mill in preference to a CTM; an example would be where the viscosity increases during reaction were significant, i.e. some of the neutralisation type reactions.

The first three reactions listed in Table 6.1 are neutralisation reactions and it was noticed in these experiments that the product had a higher viscosity than the unmodified polymer (Appendix E). These reactions were not easily performed in a continuous process but a mill, with its flexibility to handle materials of a range of high viscosities could cope with these products.

N.B. A mill could only be used for this reaction since the presence of air enveloping the reaction mixture was not detrimental to the reaction.

The fourth and the fifth reactions listed in Table 6.1 were grafting reactions where maleic anhydride was grafted onto EPDM, Keltan 720. It was noticed that the viscosity increase due to this reaction was not significant (Appendix E).

These reactions on a mill (and also sigma blade mixer Section 6.2.2) were useful in illustrating the rheological changes that could take place during reaction.

6.2.1.1 Additives to reduce the crosslinking in the grafted product made on the mill.

As observed in Section 6.4.2.2.6 , crosslinking was prevalent in products when grafting was attempted, for example on EP. It was thought possible that addition of another polymer, such as HDPE or butyl rubber, may offset this side reaction by reducing the concentration of the crosslinkable polymer in the reaction mixture. As can be seen in Appendix D, the effect of additives was not clear from the results and this avenue was not explored further.

6.2.2 SIGMA BLADE MIXER.

A sigma blade mixer was tested in order to investigate its application in certain reactions. It was, as was expected from the literature survey (Table 2.2), used for reacting high viscosity liquid rubbers with solids and low viscosity liquids (viscosity of HC434 at 25 °C, a liquid rubber = 2.50p, viscosity of H_2O at 20 °C, an additive in this context = 1.00cp).

Table 6.2: The reactions attempted in a sigma blade mixer.

polymer	neutralising reagent
HC434	Calcium oxide
HC434	Magnesium ethoxide
CTBNX 13	Cadmium oxide

All reactions tested in this category were neutralisation reactions. All the products from these reactions showed an increase in viscosity evident from the flow properties of the product compared to that of the unmodified polymers. For example, the reactants (e.g. HC434) flowed at room temperature (appeared like golden syrup) and flowed more easily at higher (40 °C) temperatures; the reacted product did not flow either at room temperature or even at 40° C.

6.3. EXTRUDER ARRANGEMENT.

The effect of process parameters on the operation during steady state and unsteady state conditions will be discussed in this section.

6.3.1 STEADY STATE.

The adopted crosshead arrangement consisted of a feed extruder and an independently driven CTM at 90° to the feed extruder. This was later modified to have a larger drive on the crosshead and to have a liquid injection port upstream of the CTM.

6.3.1.1. The effect of process conditions on throughput.

It can be seen in Figure 6.1 that, for the equipment set-up used in this project, the throughput is strongly dependent on the feed extruder speed for a given polymer.

In Figure 6.2, it can be seen that the crosshead extruder also influences the throughput but not as significantly as the feed extruder speed does. The effect of crosshead extruder speed on the throughput was comparatively small; a 100% increase in feed extruder speed led to a 100% increase in throughput whereas a 100% increase in crosshead extruder speed led to a 10 to 15% increase in throughput. Such low dependence of throughput on the

Figure 6.1 : The effect of feed extruder speed on throughput (PE).

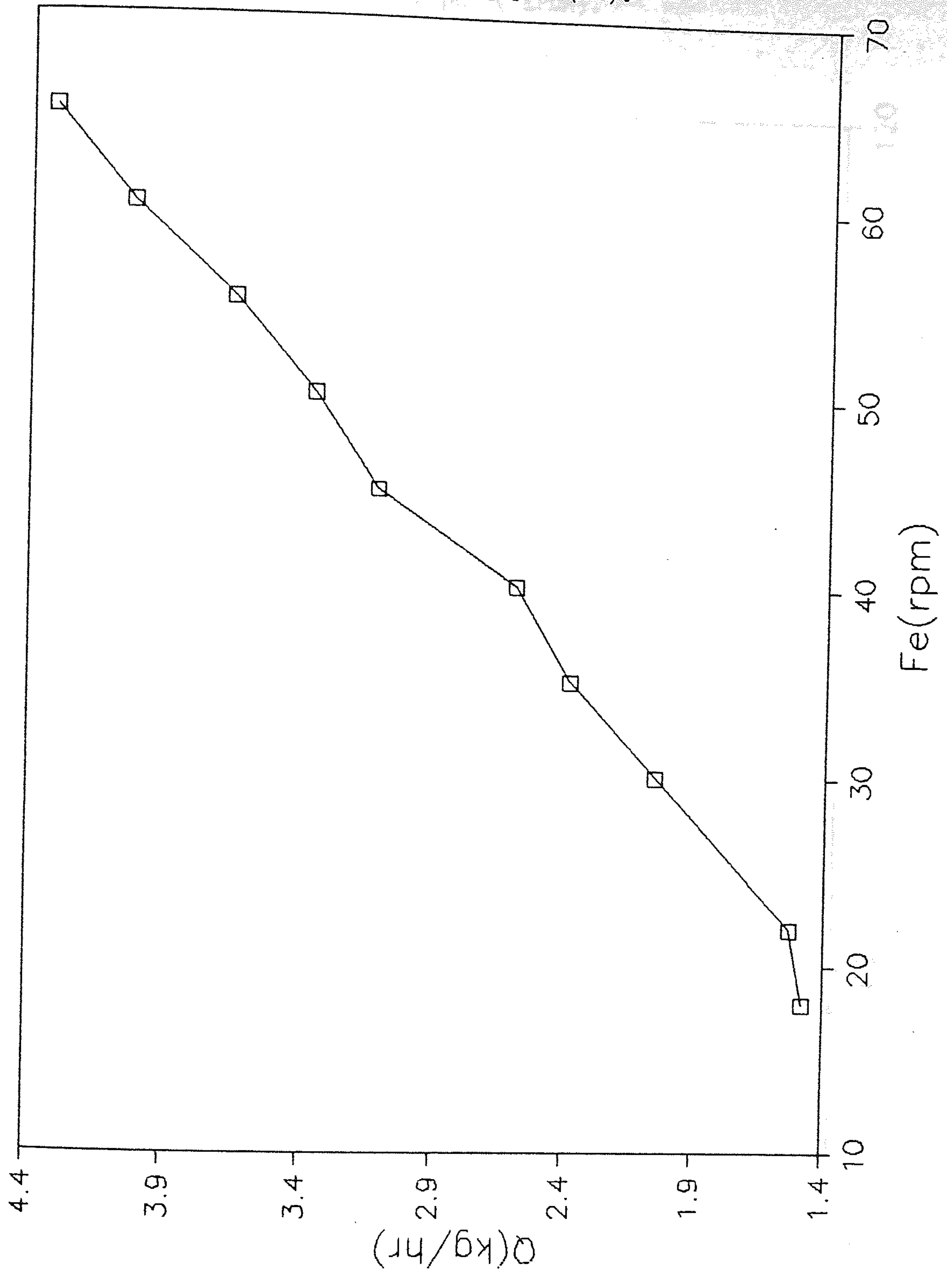
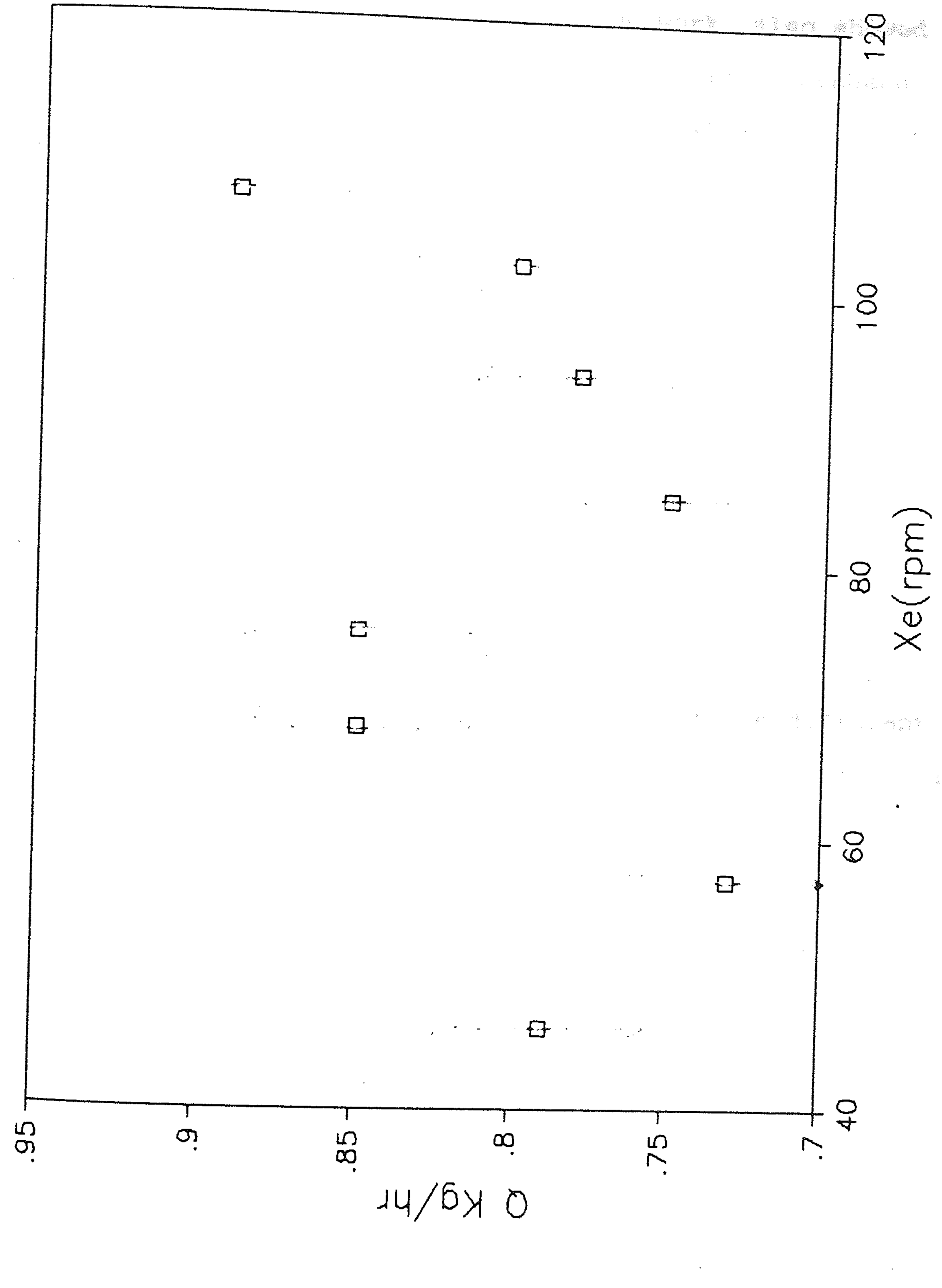


Figure 6.2 : The effect of crosshead extruder speed on the throughput (EPDM).



crosshead extruder speed leads to a near independent control of throughput and the rate of mixing.

N.B. The residence time distribution work also showed (Section 6.5.1.1.2.1) that the change in crosshead extruder speed does not significantly alter the mean residence time but does influence the standard deviation of the residence time distribution.

6.3.1.2 The effect of CTM geometry on throughput.

The influence of CTM geometry on the process is examined in this section. It was anticipated that although the different designs of CTMs may provide different resistances to flow, leading to a different pressure upstream of the CTM, it would be the feed extruder speed that would determine the throughput. The throughput readings are given in Table 6.3 for the three different designs of CTMs. (The crosshead extruder speed was set at 40 rpm. The material being processed was Vamac G.)

Table 6.3 : The effect of CTM geometry on throughput.

(Arrangement as shown in Figure 4.3).

CTM	Fe rpm	Q kg/hr.
55C	20	0.9
55L	20	0.6
110C	20	0.8
55C	38	1.3
55L	38	1.5
110C	38	1.3

The data from the Table 6.3 showed the anticipated effect; for a given feed extruder and crosshead extruder speed, the influence of CTM geometry on the throughput was only 5% to 25%. It appears as if the influence of the geometry is less significant when the cavity geometry is the same, as is the case for 55C and 110C CTMs. The larger variation appears when the cavity geometry is dissimilar, as is the case for 110C and 55L CTMs. The data in Table 6.3 are shown in Figure 6.3. It appears, from the limited data used in this comparison, that there is greater variability of throughputs at the lower feed extruder speed than at higher feed extruder speed. This could be explained by the extruder speed variation data presented in Appendix B. If, at both feed extruder speeds, the speed variation of the extruder screw were ± 1 rpm, this speed variation would make a greater influence on the lower throughput than the higher throughput measurement.

6.3.1.3 The effect of polymer rheology on throughput.

The effect of the polymer rheology on throughput was also examined. To this end, the throughput was measured for two polymers, at similar process setting (besides the fluctuations which were outside the control of the operator). Two polymers were chosen which are known to have different viscosities:

Keltan 720 Mooney viscosity ML(1+4) at 125°C = 63

Vamac G, Mooney viscosity ML(1+4) at 100°C = 16 ± 3

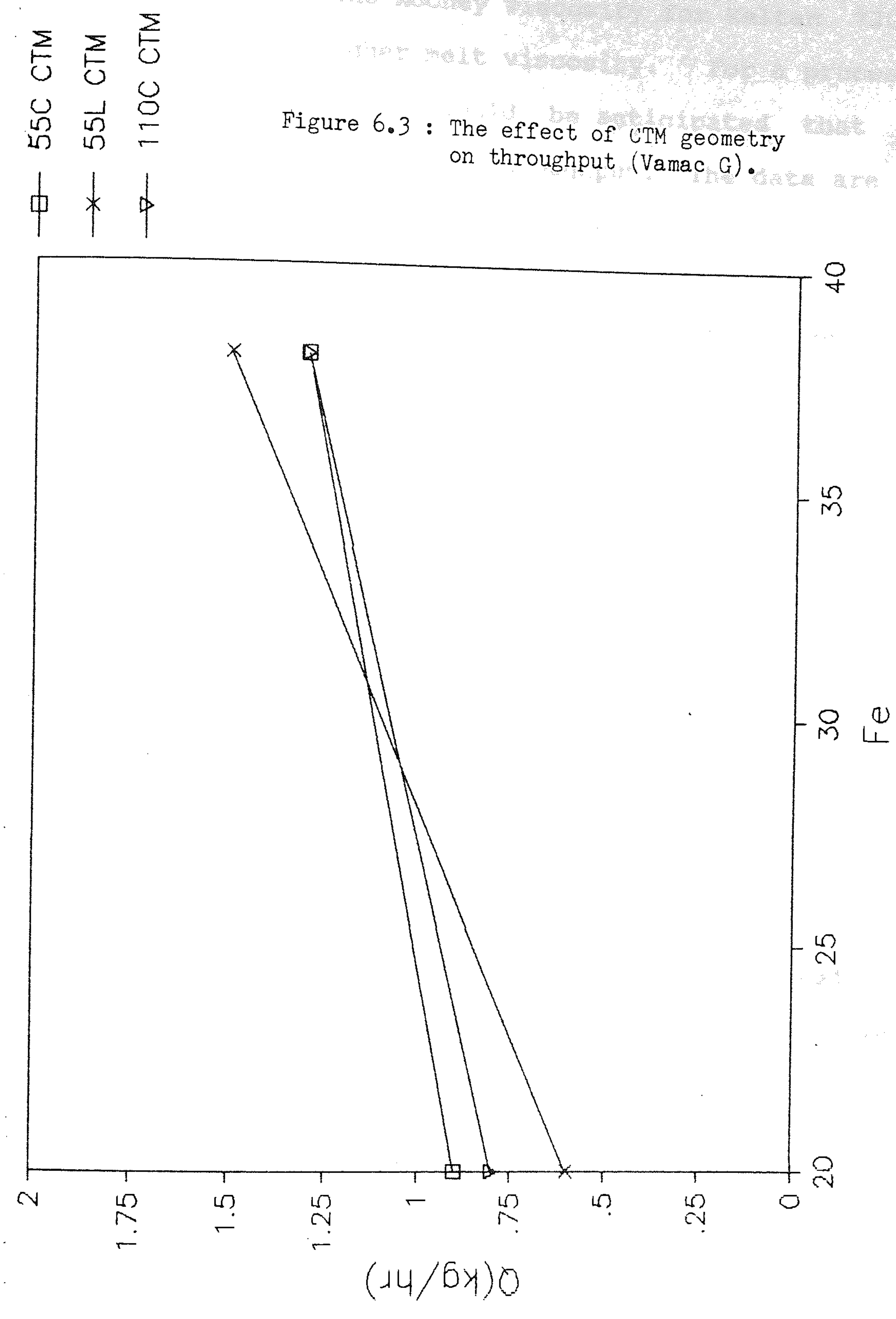


Figure 6.3 : The effect of CTM geometry on throughput (Vamac G).

The higher value for the Mooney viscosity for Keltan 720 shows that it has a higher melt viscosity. For a process which is power limited, it would be anticipated that Keltan 720 would have a lower throughput. The data are presented below to verify this statement.

Table 6.4: The influence of polymer melt viscosity on the throughput; Xe = 60 rpm (Figure 6.4), (Arrangement as shown in Figure 4.3).

Polymer	Fe rpm	Q kg/hr
Keltan 720	20	0.44
Vamac G	20	1.23
Keltan 720	38	0.85
Vamac G	38	2.41

As expected, Vamac G has a higher throughput than Keltan 720, for a given process setting.

6.3.1.4 Steady state fluctuations.

Pressure fluctuation upstream of the CTM was observed during steady state operation of the equipment as shown in Figure 6.5.

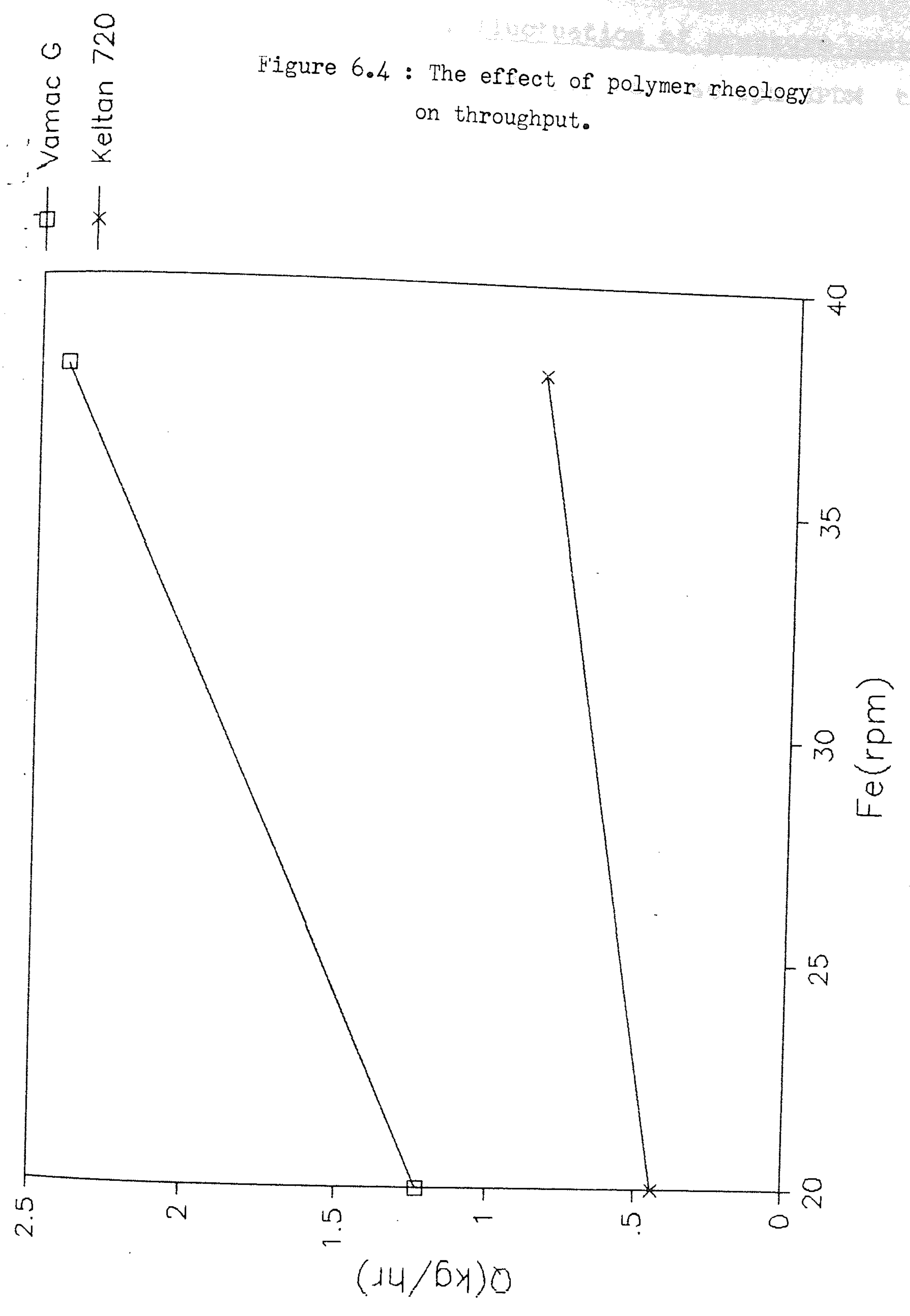
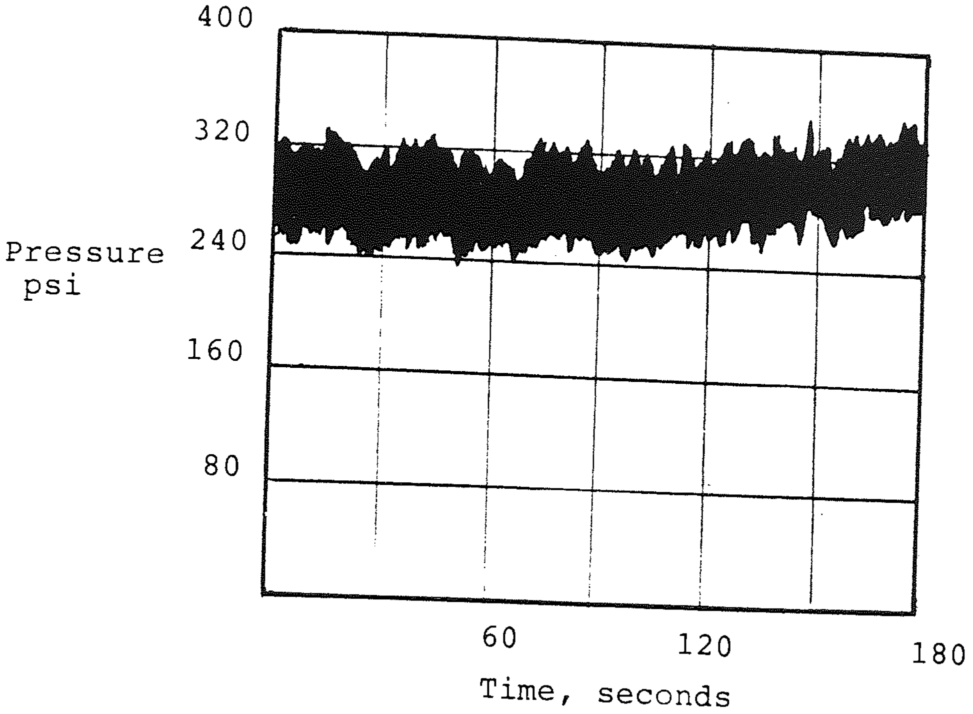


Figure 6.4 : The effect of polymer rheology on throughput.

Figure 6.5 : The regular fluctuation of pressure upstream of the CTM (110C CTM Fe = 20 rpm, Xe = 66 rpm EPDM type, Total 657).



To examine the causes of the fluctuating pressure, the pressure fluctuations were examined over an enlarged timescale. The chart recorder plots of some of these experiments are given in Figures 6.6, 6.7 and 6.8.

Figure 6.6 : The cyclic fluctuation of pressure upstream of the CTM (Material: EPDM type, Total 657, 110C CTM, Fe = 20 rpm Xe = 66 rpm).

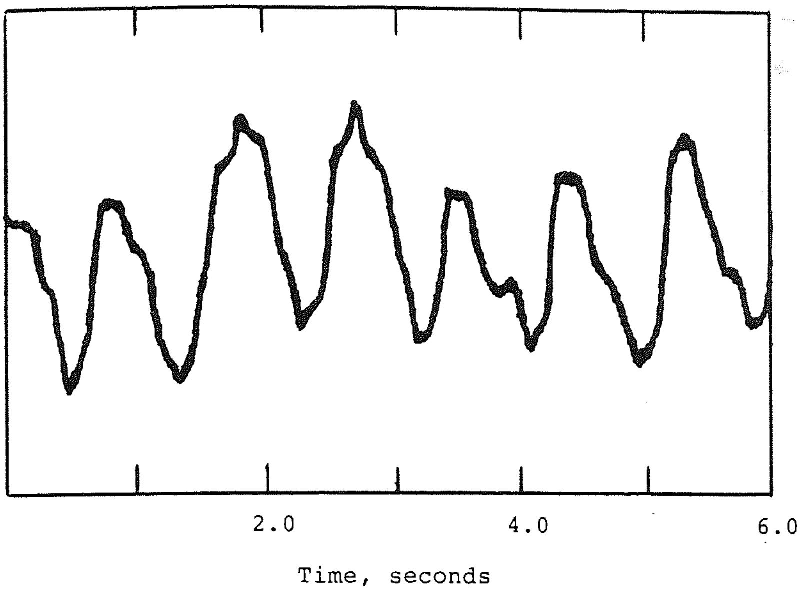


Figure 6.7 : The cyclic nature of the pressure fluctuation upstream of the CTM (Material: EPDM type, Total 657, 110C CTM, Fe = 20 rpm Xe = 86 rpm).

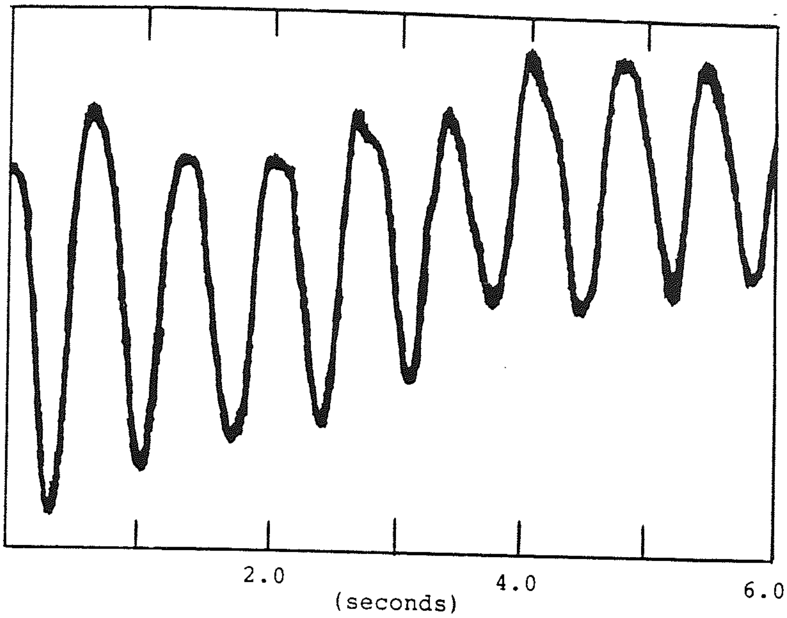


Figure 6.8: The cyclic nature of the pressure fluctuation upstream of the CTM (Material: EPDM type, Total 657, 110C CTM, Fe = 20 rpm Xe = 95 rpm).

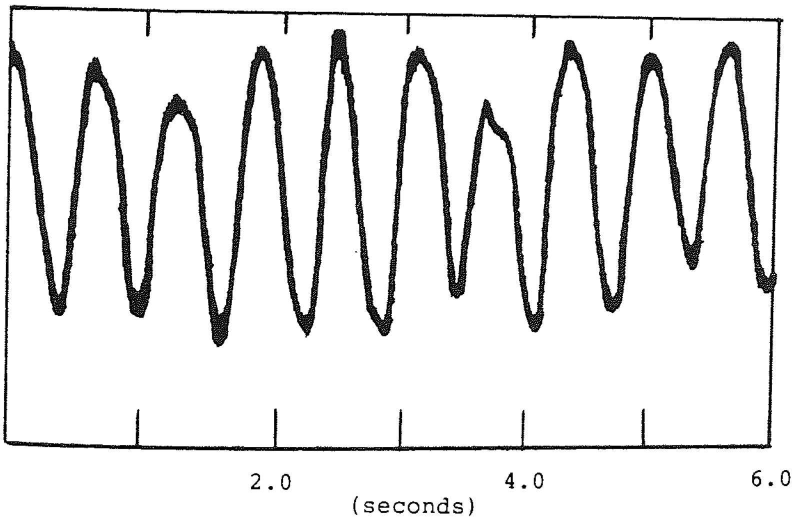


Table 6.5: The relationship between the pressure fluctuation and the crosshead extruder speed

(cpm = cycles per minute;

cps = cycles per second)

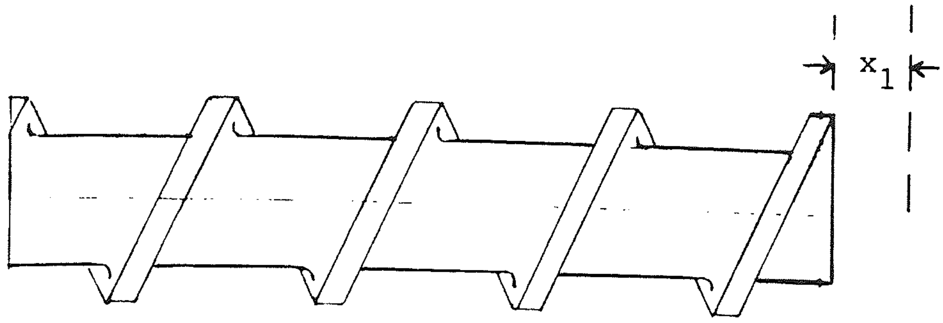
Xe	No.of cycles in 15 seconds	cps	cpm
66	17	1.13	68
86	22	1.47	88
95	25	1.67	100

There is a clear relationship between the frequency of the pressure fluctuation and the speed of revolution of the crosshead extruder. This could be explained by:-

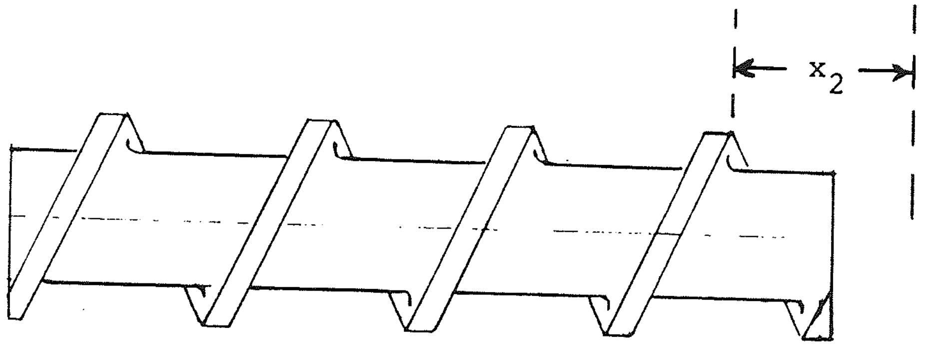
1) the conveying of material by the flight,
2) the variation in distance between the flight and the transducer (see Figures 6.9 and 6.10).

The position of the flight relative to the transducer as the extruder screw revolves. (Figures 6.9 & 6.10)

At t = 0: Figure 6.9



Half a revolution later: Figure 6.10



Where X1 = 14mm

and X2 = 27mm

Further information on this effect could be obtained by a systematic study of the effect of pressure variation with distance from the end of the extruder screw. This was not considered appropriate for this project.

6.3.2 UNSTEADY STATE.

During start up, an unsteady state behaviour relating the pressure upstream of the CTM and the temperature of the extrudate was observed. This effect can be seen in Figures 6.11 and 6.12.

A sequence of events as described below may explain this behaviour. When the extruders and the CTM are stationary, the polymer is primarily heated by the oil heating jacket and the electric band heater from the outside of the barrel and the stator respectively. Both heaters were thermostatically controlled. There is no ideal means of heating a polymer that is inherently a thermal insulator (thermal conductivity of PE = 0.33 W/m °C compared to 51.9 W/m °C for carbon steel). When the extruders and the CTM start to rotate, it is expected that shear heat would be imparted to the polymer. As time progresses, the temperature of the extrudate would increase until it reaches steady state. The steady state temperature is expected to be dependent on the throughput and the shear rate. The shear rate, in turn, is expected to be related to the CTM geometry and its rotation speed.

As the temperature of the polymer melt increases, its viscosity would decrease. The decrease in the pressure upstream of the CTM is expected to reflect this decrease

gure 6.11 : A trace showing the unsteady state prevalent during the start-up of a CTM.
(Polymer = EPDM; CTM = 110C; Fe = 40 rpm; Xe = 66 rpm).

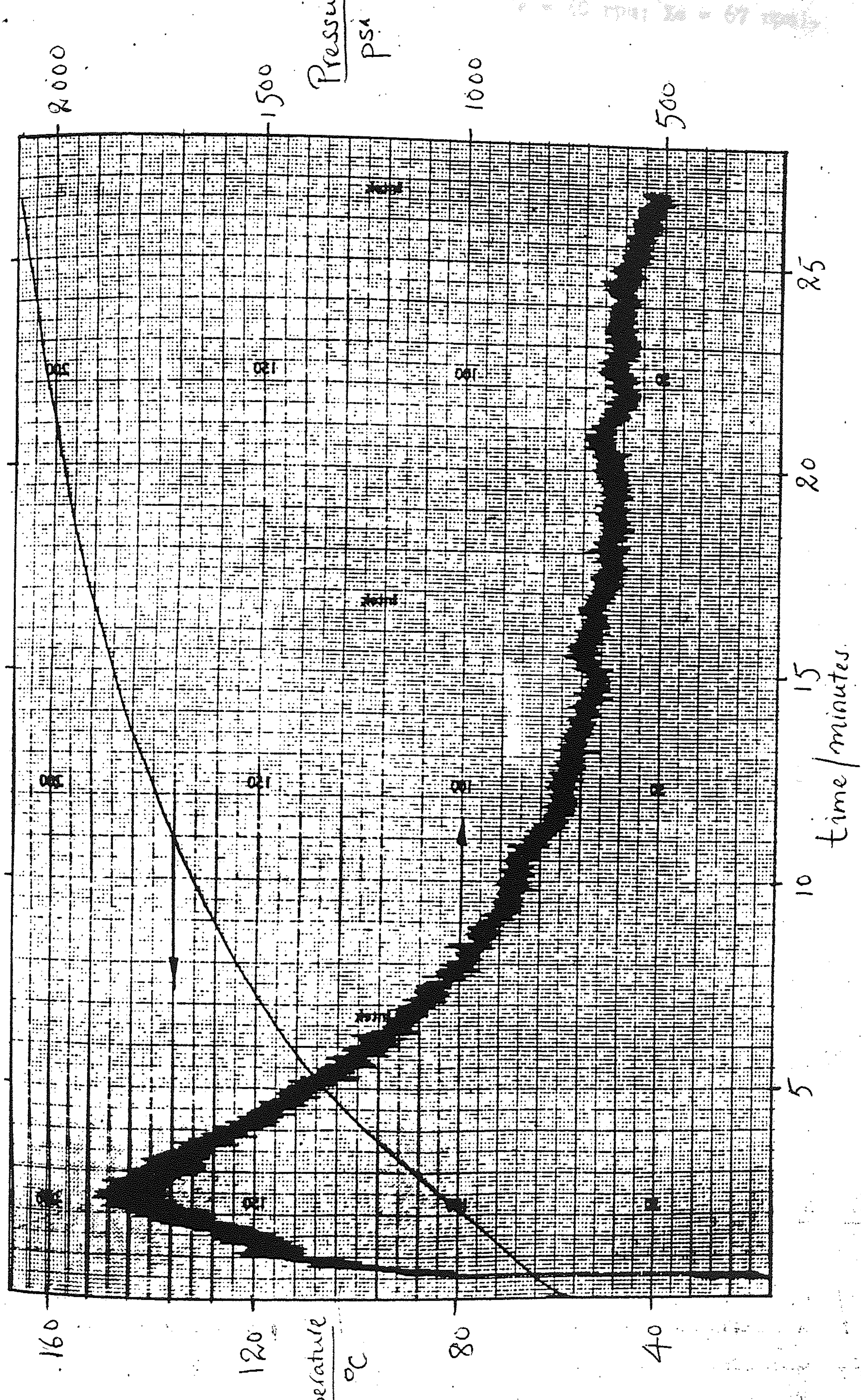
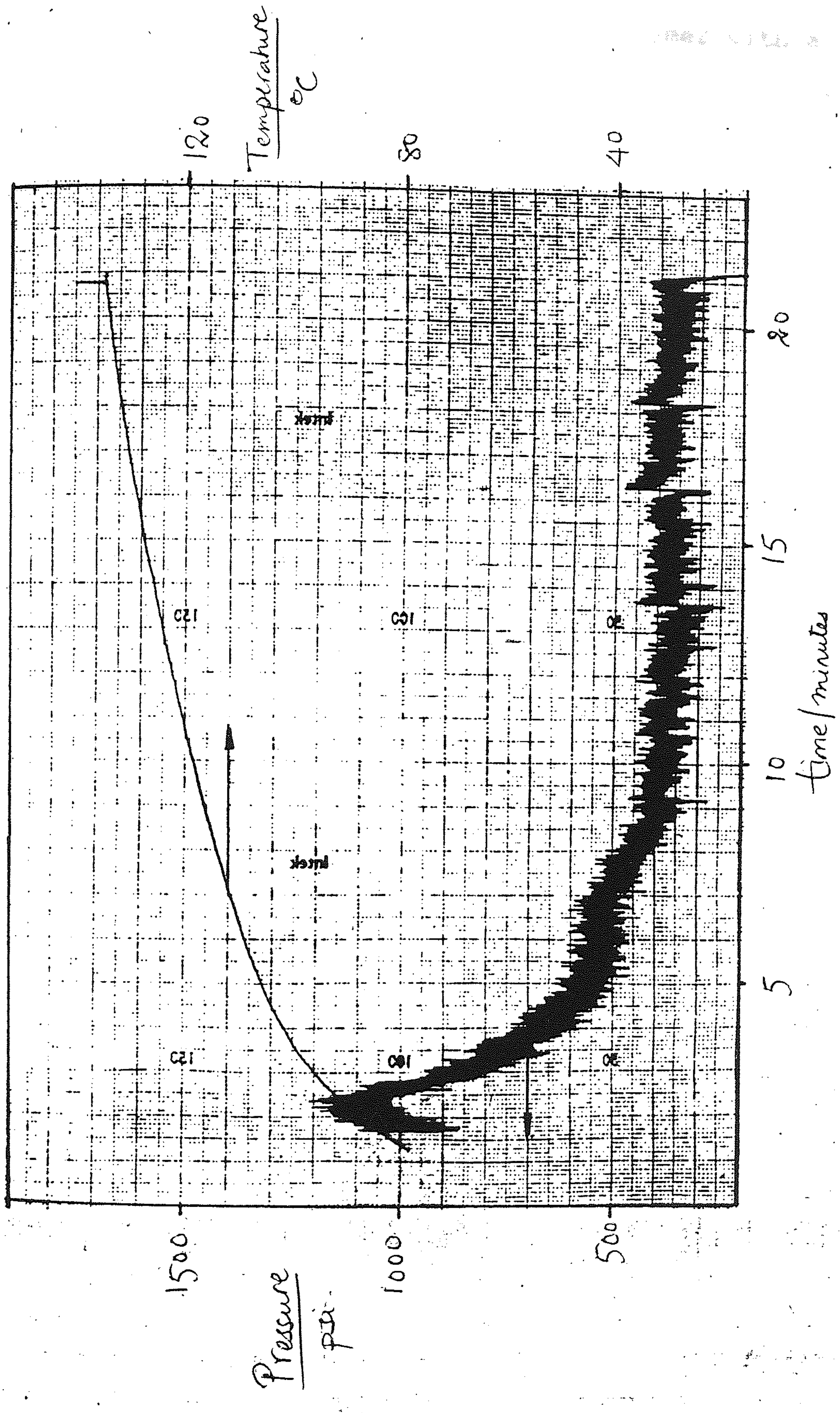


Figure 6.12 : A trace showing the unsteady state behaviour prevalent during the start-up of a CTM. (polymer = EPDM; CTM = 55L ; Fe = 40 rpm; Xe = 67 rpm).



in the polymer melt viscosity. It is anticipated that if two polymers with different polymer melt viscosities were processed with a given CTM, the polymer with a lower viscosity would have a lower pressure upstream of the CTM.

All the experiments, besides those described in this subsection, were carried out at steady state so as to obtain representative and reproducible data.

6.4 REACTIONS CARRIED OUT ON A CONTINUOUS PROCESS USING A CTM.

The reactions carried out in a CTM are discussed in this subsection. These are the neutralisation and the grafting reactions.

6.4.1 NEUTRALISATION REACTION.

The neutralisation reactions attempted in this project were either between solids and polymers or between liquids and polymers.

6.4.1.1 Neutralisation reactions between solids and polymers.

Four neutralisation reaction systems of this type were attempted in a CTM. These are listed below:-

1) Vamac and aluminium isopropoxide
2) Carboxylated nitrile rubber and aluminium isopropoxide
3) Carboxylated nitrile rubber and magnesium ethoxide
4) Vamac and magnesium ethoxide

For all of these reacting systems, it was observed that the CTM seized at the point at which or before which acceptable conversion had been achieved. These problems were exacerbated by the difficulties encountered in metering of the raw materials, i.e. the neutralising powder and the rubber which was in the form of strips.

Table 6.6 : The effect of neutralisation reaction on processing

Polymer	Neutralising Agent	CTM speed/rpm		CTM T/°C	Code Number
		before	after		
Vamac	Al.isopropoxide	25	0	160-170	2711851
Vamac	Al.isopropoxide	25	0	200-210	2711852
Vamac	Al.isopropoxide	30	0	150	2811851
XNBR	Al.isopropoxide	30	0	200	1812851
XNBR	Al.isopropoxide	30	0	190	1912851
XNBR	Al.isopropoxide	30	10	235	1912852
XNBR	Al.isopropoxide	30	1	170	1501861
XNBR	Mg.ethoxide	25	10	170	1601861
XNBR	Mg.ethoxide	25	4-5	190	1601862

Since the CTM speed dropped significantly, or seized, when the reaction product was formed in the CTM (Table 6.6), it was concluded that the CTM was not the appropriate equipment for such reactions.

However, because the CTM exhibits such highly efficient mixing characteristics, it was proposed that the CTM could be used as a mixer for the reaction ingredients, the polymer then being removed from the CTM before reaction progressed too far for the CTM to seize. The reaction could then proceed to completion in a secondary system outside the CTM (i.e. a mill or an oven). This avenue was explored. However, the use of an oven or a mill after the

CTM did not appear to act as an effective reactor as judged by the insolubility data in Table 6.7. In fact, some of the data seem to indicate the degradation of the polymer during this heating stage. Further work, which was not considered appropriate in the current study, would need to be done in order to confirm this observation and to identify trends in performance.

Table 6.7 : The effect of oven and mill heating on neutralisation reactions.

Mode of heating	Temp.of of heater (°C)	Comments	Insolubility before (%)	Insolubility after (%)
Mill	40	2 passes	(67)	40
Mill	50	1 pass	36	41
Mill	60	1 pass	31	84
Mill	70	1 pass	60	63
Oven	150	1 min.	9.5	9.5
Oven	150	2 min.	9.5	6
Oven	150	3 min.	9.5	2
Oven	200	1 min.	8.5	3.5
Oven	200	3 min.	8.5	3.5
Oven	240	1 min.	6.5	0.5
Oven	240	2 min.	6.5	1.5
Oven	240	3 min.	6.5	1.5

N.B. The reaction conversion (Table 6.7) is related to the product insolubility since quasi-crosslinked materials would be insoluble in the same way that crosslinked materials are[105]. Reproducibility of the insolubility data is given in Appendix B.

A demonstration of this effect of the increase in viscosity is shown, at least for one of these systems, by the viscosity increase due to reaction. (The capillary rheometer data for Vamac G and for the aluminium salt of

Vamac G are given in Appendix E). It is evident from this data that, at low shear rates (as anticipated in a CTM), the aluminium salt of Vamac has a higher apparent viscosity.

6.4.1.2 Neutralisation reaction between liquids and polymer.

Neutralisation reaction between bis-tributyl tin oxide (a liquid) and polystyrene allyl alcohol was attempted as part of this project. Attempts were made to increase the level of neutralisation of the product and to examine the effect of process temperature on the reaction conversion.

6.4.1.2.1 The effect of temperature on neutralisation reactions.

It would be expected, from kinetic theory, that increasing the temperature of a reaction mixture would increase the rate of reaction, and hence the reaction conversion. This would only be true if the reaction kinetics are the rate determining step, i.e. if:

1) the reaction kinetics are slow,
2) the reactant concentration is high.

The expressions used to describe the level of tin in the product and the conversion are given below.

$$\text{level of tin} = \frac{\text{weight of tin on the product}}{\text{weight of product}} \times 100 \qquad 6.1$$

$$\text{conversion (\%)} = \frac{\text{weight of tin on the polymer}}{\text{weight of liquid injected}} \times 100 \qquad 6.2$$

N.B. Tin is substituted by the monomer when Equation 6.1 and Equation 6.2 are used to calculate the level of grafting.

Table 6.8 : The effect of temperature on reactor performance for neutralisation of polystyrene allyl alcohol and bis-tributyl tin oxide.

Code	Q kg/hr	liquid injected %	Tctm °C	Textr °C	Level of tin %	Conversion %
2605883	0.93	9.4	120	110	8.0	75
2605882	0.91	10	150	138	7.3	73

Kinetic data for the melt reactions considered in this study are not readily available and consequently, it is not possible to be certain of the rate determining step. There is limited evidence from the data (presented in Table 6.8) for the neutralisation of tin with polystyrene based polymer, that increased temperature did not raise the reaction rate. This suggests that the concentration of the neutralising liquid may be the rate controlling factor for the reaction conditions studied.

6.4.1.2.2 Ways of increasing the level of neutralisation.

When tin (bis-tributyl tin oxide) was neutralised with polystyrene allyl alcohol, it was found that increasing the injection rate increased the amount of tin that was bound to the polymer. (This amount is referred to as the "level of tin" in the product). The level of tin that is bound onto the polymer is a significant parameter because of its influence on the calculation of the conversion, as defined by Equation 6.2.

Table 6.9 : Ways of varying the level of tin.

Code	Injection rate g/hr.	Q kg/hr.	liquid in the product %	n inj rate %	Tctm °C	Level of tin OHg → Sn %	Conversion %
2605883	87	1.02	8.5	8.5	120	8.0	75
2605884	138	1.3 (2605883 + liquid)	18	11	120	17.1	87
2705882	138	0.79	17.5	17.5	120	24.4	100

(55L CTM was used in these experiments.)

The data presented in Table 6.9 above are clarified below.

The sample coded 2605883 was made with unmodified polymer in the extruder and 8.5% of tin compound injected into the polymer.

To make sample 2605884, the sample 2605883 from the previous run was introduced into the extruder (2605883 already had 8.5% tin compound) and a further 11% of tin compound was injected into the polymer stream.

Sample 2705882 however, was made by injecting 17.5% of tin compound directly into unmodified polymer.

What may be seen in Table 6.9 is that similar levels of tin in the product can either be obtained by injecting high levels of liquids in one shot or by injecting lower levels but in two stages. Two stage injection may, in some cases, overcome the problem of slippage due to injection of large quantities of low viscosity liquids into polymer melt. Slippage was not a problem during the experiments described in this section.

Since the purpose of these experiments was to examine the feasibility of a two shot technique, the fact that greater conversion was obtained with a one shot method (Sample 2705882) compared to the two shot method (Sample 2605884) is noted, but is not examined further in this thesis.

6.4.2 GRAFTING REACTIONS.

Work was carried out on grafting reactions between solids and polymers and between liquids and polymers, this latter combination being the majority of the work. The results of variation in processing parameters on these reactions are described in this section.

6.4.2.1 Grafting reactions between solids and polymers.

One set of experiments to test the feasibility of heated injection was performed, but not enough data were available to analyse it. All that can be said is that the possibility of heated injection has been established.

6.4.2.2 Grafting reactions between liquids and polymers.

The liquid injections carried out in this category were:-

Oleic acid and peroxide (TBPEH or cumene hydroperoxide)
Oleic acid
Peroxide
Acrylic acid
Acrylic acid and peroxide
Dibutyl maleate and peroxide
Maleic anhydride and peroxide in solution (heated injection).

Although injection of 70% cumene hydroperoxide in cumene (as made available by suppliers) was attempted in the early experiments, it was discontinued owing to the hazardous nature of injection of this (potentially explosive) material at high pressure.

Some of the major trends observed in the experimental work on grafting are outlined below.

6.4.2.2.1 The effect of temperature on grafting.

Similar effects of temperature on the reaction conversion, as described in Section 6.3.1.2.1 were evident for grafting of dibutyl maleate onto EP rubber. The data relevant to the grafting reaction are presented in Table 6.10 given below.

N.B. A mixture of 10 parts of dibutyl maleate and 1 part of dicumyl peroxide was injected into EP rubber (C0054).

Table 6.10 : The effect of temperature on grafting di-butyl maleate onto EP rubber

Code	Q Kg/hr	liquid injected %	Tctm °C	Textr °C	Conversion %
0203881	0.50	22	70	150	90
0203882	0.50	24	150	230-240	90

The results in Table 6.10 reveal that, for the reaction system under study, the temperature at which the CTM was set did not influence the product composition.

The possible temperature distribution in the CTM was not examined although it is appreciated that it would be the actual temperature distribution in the reactor that is crucial in determining the performance of the reactor[116,129,59,143].

Examination of the Tables 6.8 and 6.10 reveal a potentially important difference. For the tin neutralisation reaction (Table 6.8), when the CTM was set at 150°C, the temperature of the extrudate was measured to be 138°C. Whereas, for the grafting reaction (Table 6.10), when the CTM was again set at 150°C, the extrudate temperature was measured to be 230 to 240°C. Two possible explanations for this difference are outlined below:-

a. The grafting reaction may be more exothermic and hence could generate more heat during the reaction leading to a greater temperature rise (assuming that the two polymers have similar specific heat capacities[91]).

b. The difference in extrudate temperature could be due to the difference in the viscosities of the two polymers; the EP rubber, C0054, is more viscous than polystyrene allyl alcohol (Appendix E). Hence, shear heating would be more significant for EP rubber than for the polystyrene allyl alcohol.

It is not possible, from the work done in this project, to say which of the two explanations is valid. If more grafting reaction work were carried, with the same monomer but with a different polymer (so the second polymer had a similar chemical structure but had a different melt viscosity), the results from such experiments may cast light on which of the two factors outlined above is more significant.

6.4.2.2.2 The effect of liquid injection rate on flow behaviour.

Increasing the injection rate of the liquid led to surging in the polymer flow. This is seen from comparing runs 0602871 and 0602872 (Appendix D) where the injection rate was increased from 2.3 g/min to 2.8 g/min. Surging was observed while making the product 0602872, during the run with a higher level of injection.

A possible explanation for this could be that if more liquid is added than can be mixed quickly into the polymer matrix, then the liquid would lubricate the metal surface and would hinder the "conveying" of the polymer. This would lead to surging in the output. This phenomenon of slippage leading to surging, is also encountered if oil migrates from a polymer during processing and lubricates the extruder surfaces.

6.4.2.2.3 The effect of injection rate on grafting.

It was observed for the neutralisation reaction (Section 6.4.1.2.2), that at the low reactant levels utilised in this study, the reactant concentration influenced the reaction conversion. This was also observed for the grafting of dibutyl maleate onto EP rubber (Table 6.11).

Table 6.11 : The effect of injection rate on grafting.

Code	Q kg/hr	Liquid injected %	Tctm ^{0}C	reaction conversion %
0303882	1.11	8.0	150	54
0303883	1.11	11.5	150	69

Increasing the injection rate and keeping all the other process parameters constant appeared to increase the level of reaction. The effect of injection rate, at higher reactant level, was not considered in this study; it is recognised that at high levels of liquid reactant, slippage may occur and make the data interpretation more difficult.

Gale[46] presented data on silane grafting in a CTM that show that increasing the injection rate would increase the level of reaction for this reaction also.

This effect is thought to be demonstrated if the availability of the monomer is the rate determining stage in the progress of the reaction. This could be the case either if the mass transfer is not efficient or if the mass transfer is efficient but the reaction is not progressing to completion because of the shortage of one of the reactants.

6.4.2.2.4 The effect of CTM rotational speed on grafting.
The effect of CTM rotational speed on the grafting of oleic acid onto Keltan 720, a type of EPDM (with cumene hydroperoxide as the initiator), can be seen by comparing the results in Table 6.12.

Table 6.12 : The effect of crosshead extruder speed on grafting.

Code	CTM rotational speed (crosshead extruder speed) rpm	level of grafting %	Crosslinking %
2901871	20	17	50
2901873	40	17	50
2901872	60	16	50

N.B. The feed extruder speed was set at 20 rpm and the injection rate of oleic acid was 2g/min.

It is seen from the data in Table 6.12 that, for this reaction system, the crosshead extruder speed does not noticeably influence the product composition. This should not be taken as a general rule since the influence of the crosshead extruder speed is expected to be dependent on whether mass transfer is the rate determining step for the given reaction system.

6.4.2.2.5 Effect of feed extruder speed and mean residence time on grafting.

It was expected, from kinetic theory, that increasing the mean residence time in a reactor would increase reaction conversion. This trend was evidenced during the di-butyl maleate grafting onto EP rubber.

Table 6.13 : The effect of feed extruder speed (and mean residence time) on reactor performance.

Code	Fe rpm	Q kg/hr	$\bar{t}$ s	Injectn. rate %	Textr. °C	Conversion %
0303881	40	0.84	182	10.4	214	80
0303882	60	1.11	139	10.0	249	54

The CTM used was the 55L CTM with a measured internal volume of 53.2 ml. The temperature of the CTM was set at 150°C. The $\bar{t}$ was calculated by dividing the volume of the CTM by the volumetric throughput (assuming the melt density of the polymer to be 800 kg/m^3).

Eventhough the temperature in the reactor was higher at the higher feed extruder speed (which would increase the rate of the reaction), the product made at a lower feed extruder speed had a higher conversion. This would indicate that it is the mean residence time, not the reactor temperature, that is the important factor influencing conversion of this reaction in this reactor.

Gale[46] also observed this effect when he was examining the grafting of silane onto polyethylene in a CTM. The way he examined this parameter was by taking samples from different cavities in the CTM.

The significance of this effect on the reaction of interest is expected to depend on the rate determining step of the reaction. Hence, the validity of this effect for each reaction of interest needs to be tested.

An increase in the feed extruder speed appears to influence the process conditions quite markedly; some of these effects are described below:-

(i) The throughput increases and consequently the mean residence time decreases.

(ii) The extrudate temperature increases; this indicates that an increase in the throughput leads to a higher shear rate in a CTM. This is predictable if the flow in a CTM is compared to that in an annulus [14, 70]. Another explanation is that since more material is passing through the reactor, even though the reaction conversion is lower at the higher throughput, there is more heat of reaction generated at the higher feed extruder speed; this would also result in a higher extrudate temperature.

6.4.2.2.6 The level of crosslinking in the product.

The level of crosslinking was measured by examining the level of insolubles in the product.

Crosslinking was observed in several experiments when either oleic acid or acrylic acid was injected into a polymer of EPDM type. In a grafting reaction, crosslinking is an undesirable side reaction whereby the polymer chains are linked together, often with the monomer that is grafted onto the polymer. The presence of crosslinking in the product of such a reaction is evidence of reaction proceeding in the reactor, albeit an undesirable side reaction.

An example illustrating this behaviour is the product made from a mixture of 93.5g of cumene hydroperoxide and 300g of oleic acid injected into Keltan 720 (0602871); the intention was to graft oleic acid onto Keltan 720. The product did contain 16% grafting but also contained 50% crosslinking.

6.5 THE RESIDENCE TIME DISTRIBUTION (RTD) IN A CAVITY TRANSFER MIXER.

In a bid to gain an insight into the influence of process parameters on the flow pattern in a CTM, residence time distribution has been measured. This section presents the experimental observations and an attempt to predict the RTD in a CTM through the development of a mathematical model.

6.5.1 EXPERIMENTAL OBSERVATION OF RTD.

The influence of certain key process variables on residence time distribution in a CTM have been studied.

The variables examined under this category were:
1) the rotational speed of the feed extruder,
2) the CTM rotational speed.

Other parameters, such as the polymer rheology, which could influence the RTD were outside the scope of this project and have been recommended for future work.

Consistent with the neutralisation and grafting reactions, these experiments were carried out without a die in position so that the RTD data could be directly related to the reaction experiments. The absence of a die reduced the pressure upstream of the CTM and eased the injection of tracer dye and hence increased the reliability of the tracer experiments.

Table 6.14 : The process conditions used during RTD experiments.

Code	CTM	Fe rpm	Xe rpm	Q kg/hr	$\bar{t}$ s	σ s	P psi	Emax s^{-1}	N *
A	55C	20	60	(0.57)	114	34		0.0149	11
J	55C	20	40	(0.43)	149	43		0.0093	12
G	55C	20	70	(0.59)	110	21		0.0235	27
T	55C	20	40	(0.53)	122	45		0.0086	7
S	55C	20	60	(0.50)	130	34		0.0144	14
V	55C	20	70	(0.44)	146	33		0.0132	20
Z	55C	20	60	(0.46)	140	35		0.0107	16
H	55C	38	70	(0.95)	68	19		0.0244	13
K	55C	38	40	(1.09)	59	28		0.0128	4
W	55C	38	40	(1.40)	46	29		0.0158	2
Y	55C	38	70	(1.22)	53	23		0.0204	5
Ph1	55C	30	46	0.79	103	29	700 to 800	0.0153	12
Ph2	55C	30	57	0.73	109	31	450 to 550	0.0186	12
Ph3	55C	30	68	0.81	87	28	350 to 500	0.0165	9
Ph4	55C	30	75	0.83	97	30	300 to 450	0.0160	10
Ph5	55C	30	85	0.75	94	27	200 to 250	0.0192	12
Ph6	55C	30	94	0.77	93	23	200 to 300	0.0249	16
Ph7	55C	30	102	0.79	93	28	200 to 300	0.0204	11
Ph8	55C	30	107	0.84	83	22	150 to 250	0.0232	14
4	110C	20	40	(0.61)	206	35		0.0108	35
7	55L	20	40	(0.70)	218	59		0.0079	14
17	55C	20	40	(0.49)	131	23		0.0188	32
2	110C	20	60	(0.60)	209	42		0.01165	25
8	55L	20	60	(0.89)	173	45		0.0079	15
14	55C	20	60	(0.49)	133	20		0.0178	44

N.B. The throughput values quoted in brackets throughout this section are not measured but are calculated using the equation given below.

$$Q = \frac{3600 \times VCTM \times \rho}{\bar{t}} \qquad 6.\ 3$$

The density of the polymer melt was taken from technical literature to be 800 kg/m^3.

* $N = \bar{t}^2 / \sigma^2$

A chart to show the significance of the different parameters referred to in RTD studies

Parameter	Practical definition; units	Its process and flow significance
CTM	The CTM used during the given experimental run	Since the different CTMs designed have different geometries, they were expected to show different flow patterns and hence have different RTDs.
Fe	The rotational speed of the feed extruder; rpm	This was expected to determine the throughput of the system and for a given CTM and polymer, the mean residence time.
Xe	The rotational speed of the crosshead extruder; rpm	An increase in the rotational speed of the crosshead extruder and hence the CTM was expected to improve mixing and also influence RTD.
Q	Throughput; kg/hr	The throughput was expected to be influenced by the feed extruder speed, for a given polymer.
$\bar{t}$	Mean residence time; s	Mean residence time was calculated from the RTD and was defined as the time by when half the material introduced at t = 0 has exited the vessel.
σ	Standard deviation; s	Standard deviation was calculated from the RTD; it is the square root of the second moment about the mean. It is a measure of the spread of the distribution.
E	Exit age distribution as defined in Equation 6.4; s^{-1}	Exit age distribution information can be used to:- 1) construct working mathematical models 2) for certain reactions, predict the reactor performance.
E_{max}	The maximum value of the exit age distribution; s^{-1}	An increase in this value is taken to indicate a narrowing of the RTD.

$$E = \frac{C_i}{\Sigma\, C_i dt_i} \qquad 6.4$$

where C_i = concentration of dye in the extrudate at time t_i

dt_i = time interval over which the extrudate sample was taken

The reproducibility of RTD data was important to validate the observed trends. To this end, some experiments were duplicated and compared.

Table 6.15 : The reproducibility of RTD data.

Code	Fe rpm	Xe rpm	$\bar{t}$ s	σ s	Emax s^{-1}	Q kg/hr
J	20	40	149	43	0.0093	(0.43)
T	20	40	122	45	0.0086	(0.53)
A	20	60	114	34	0.0149	(0.57)
S	20	60	130	34	0.0144	(0.50)
Z	20	60	140	35	0.0107	(0.46)
G	20	70	110	21	0.0235	(0.59)
V	20	70	146	33	0.0132	(0.44)

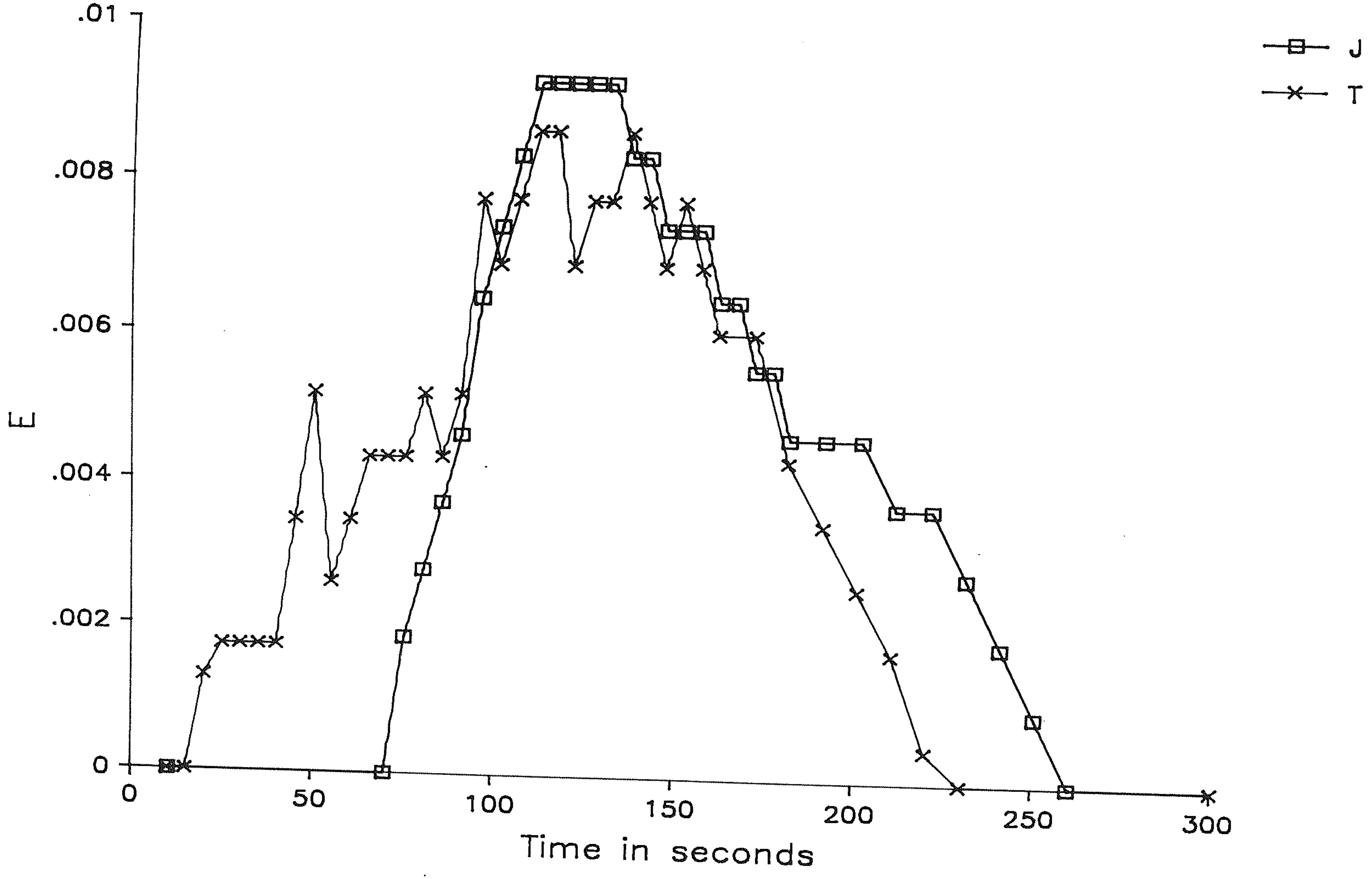
The Table 6.15 and the Figures 6.13, 6.14 show that the RTD experiments were reasonably reproducible with variability of ± 10% in $\bar{t}$, though a larger variability in Emax was observed. The standard deviation of the residence time around the mean shows excellent reproducibility. The following observations can be made regarding the reproducibility of RTD data.

1) Figures 6.13, 6.14 show that the curves for Codes [J and T] are similar as are [A, S and Z].

2) For similar process settings, the mean residence time ($\bar{t}$) had not changed within ± 10%.

3) The σ values also had not changed within ± 1s for any given set of process conditions (except for [G and V]). It must be borne in mind that the mean residence times for G

Figure 6.13 : The RTD traces showing the reproducibility of the experiments (Fe = 20 rpm; Xe = 40 rpm)



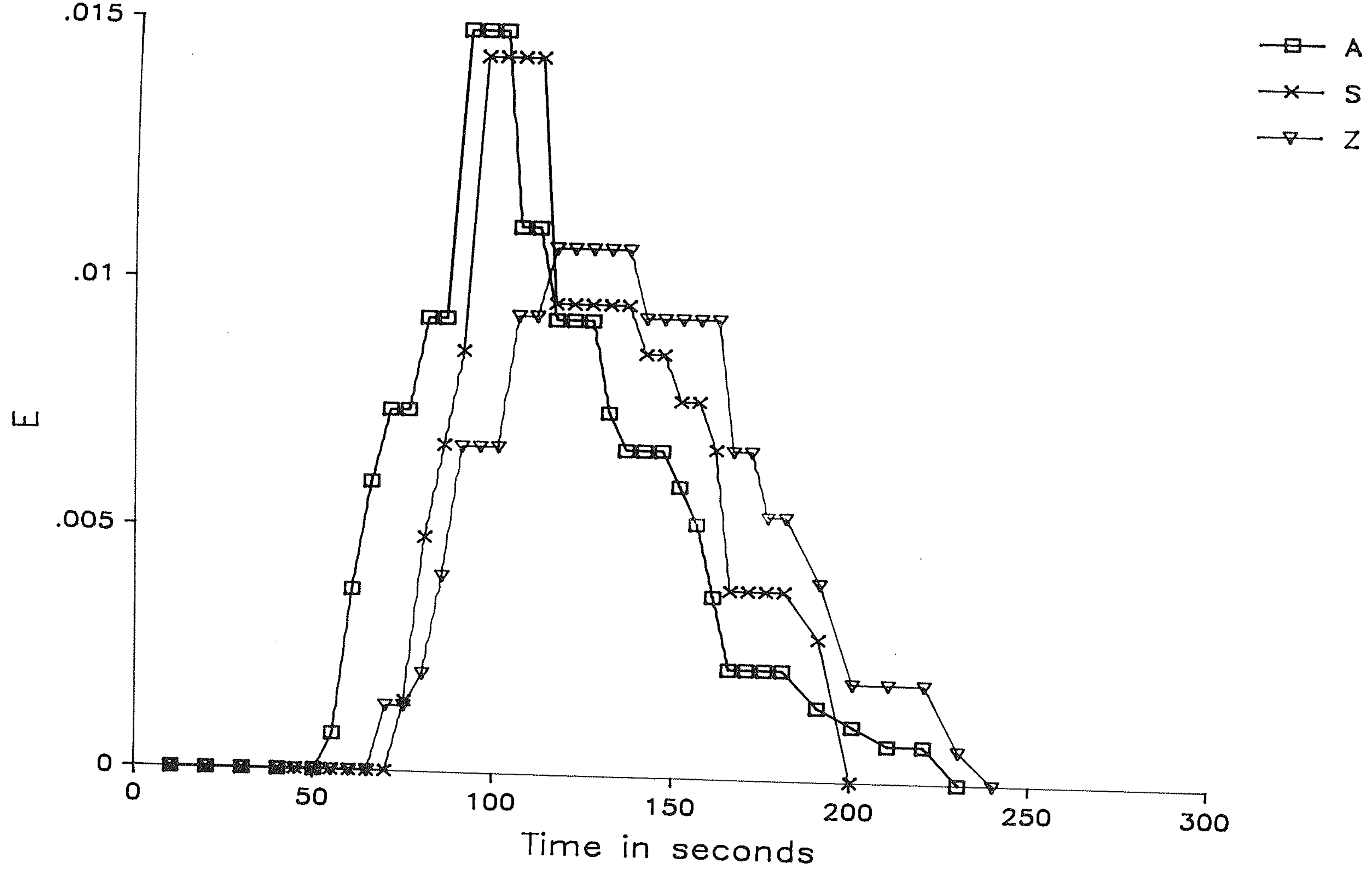


Figure 6.14 : RTD traces showing the reproducibility of the RTD experiments (Fe=20 rpm; Xe = 60 rpm).

and V are significantly different and this could contribute to the variation in standard deviation. The difference in $\bar{t}$ for G and V could be due to the feed extruder speed deviating from 20rpm for the two experiments (in these initial experiments, the screw speeds were not measured using a tachometer).

6.5.1.1 The effect of the process and design parameters on RTD.

The effect of some process parameters (such as the feed extruder speed and the rotational speed of the CTM) are individually assessed in this section.

6.5.1.1.1 The effect of the feed extruder speed on RTD.

To examine the effect of the feed extruder speed on flow inside a CTM, some data obtained for the 55C CTM are abstracted from Table 6.14.

Table 6.16: The effect of feed extruder speed on RTD.

Code	Fe rpm	Xe rpm	$\bar{t}$ s	σ s	Emax s^{-1}	Q kg/hr
T	20	40	122	45	0.0086	(0.53)
K	38	40	59	28	0.0128	(1.09)
V	20	70	146	33	0.013	(0.44)
Y	38	70	53	23	0.020	(1.22)

There are several important trends to be observed from the Table 6.16. (This RTD information can also be seen in Figures 6.15 and 6.16).

1) An increase in the feed extruder speed leads to a decrease in mean residence time. This is a reflection of the increased throughput at increased feed extruder speeds. The effect of feed extruder speed on the throughput can also be seen in Figure 6.1.

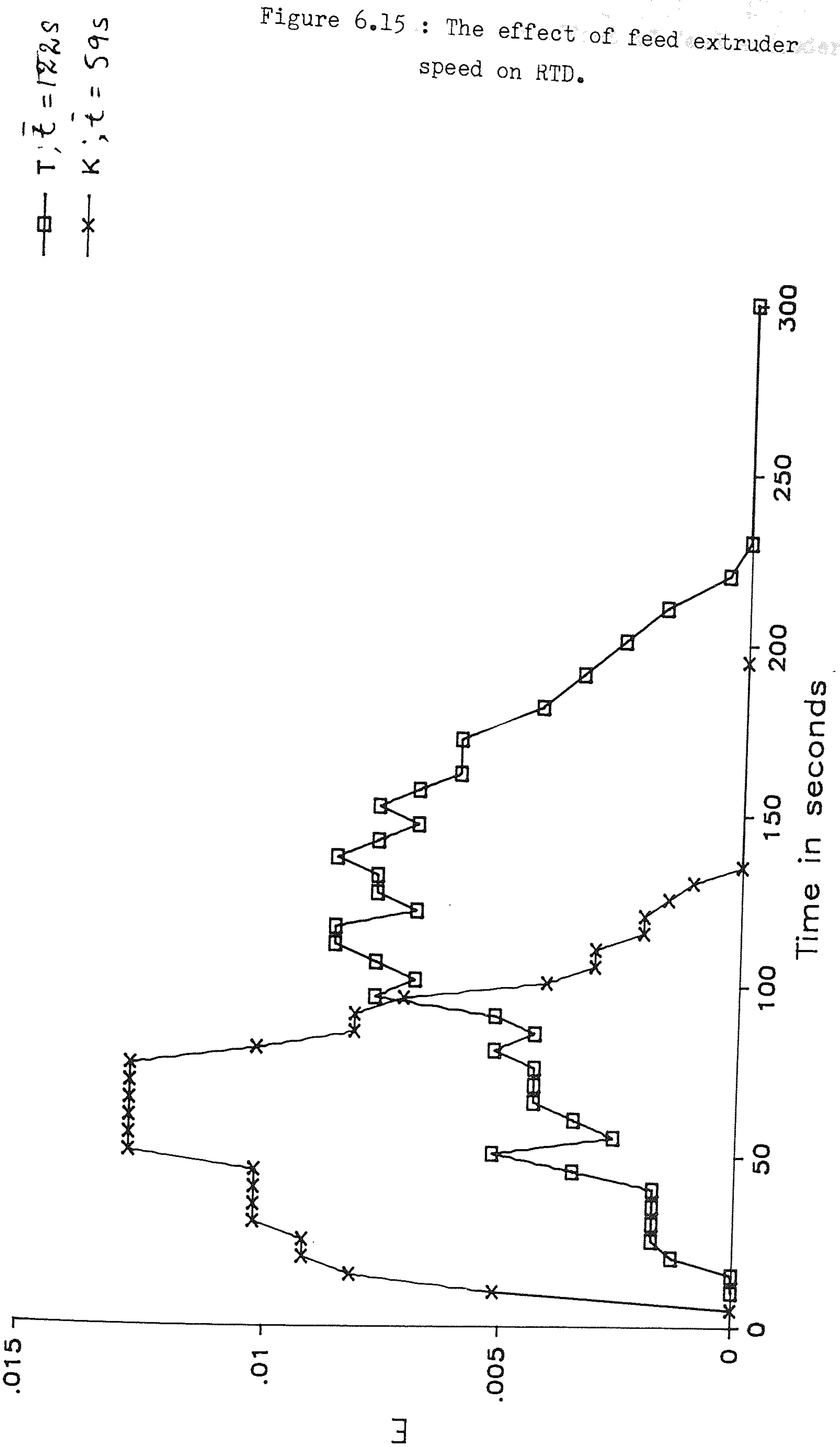


Figure 6.15 : The effect of feed extruder speed on RTD.

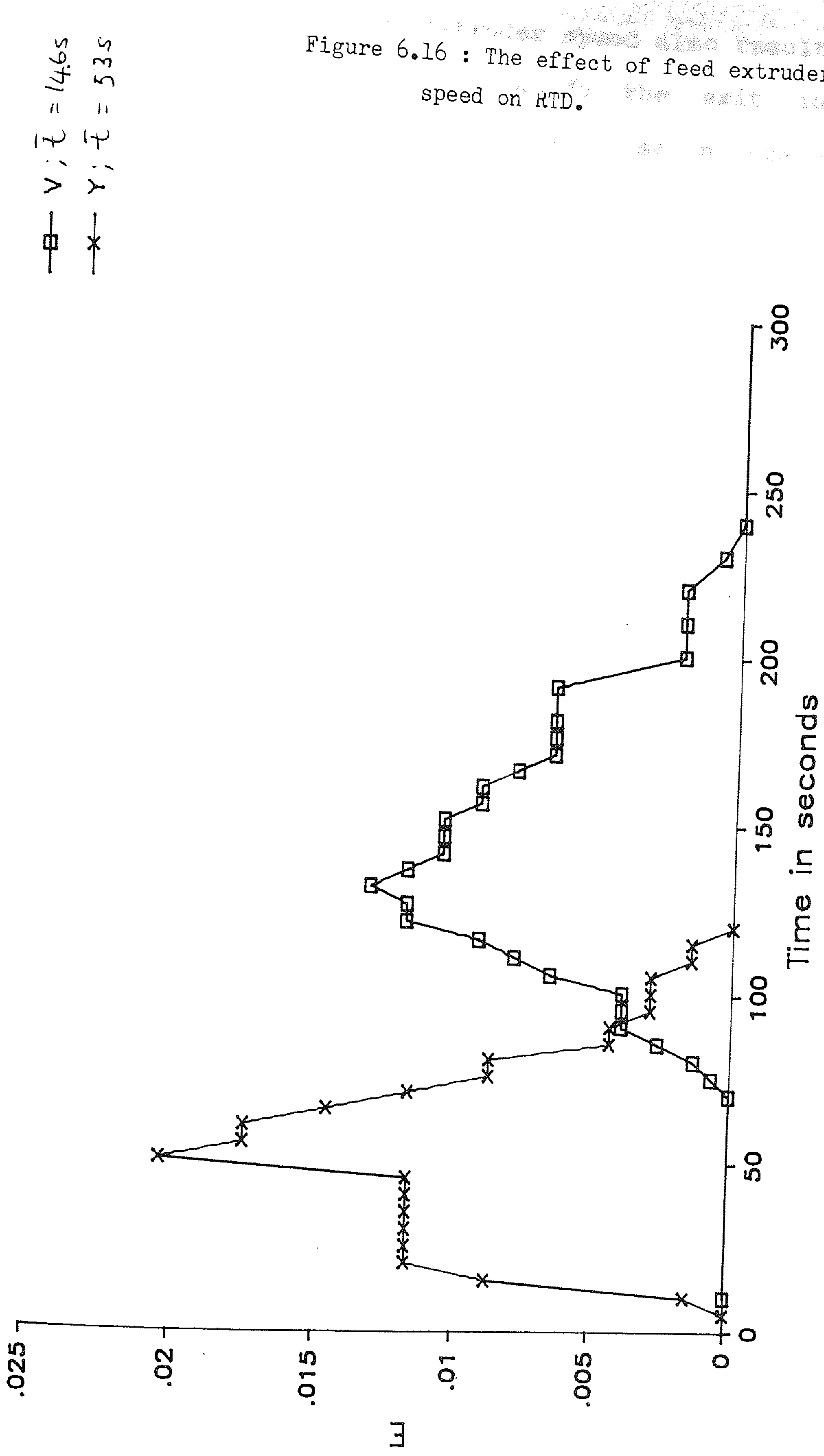


Figure 6.16 : The effect of feed extruder speed on RTD.

2) An increase in feed extruder speed also results in an increase in maximum value for the exit age distribution (Emax) and a decrease in standard deviation (σ). These trends indicate the narrowing of the RTD. This trend of increasing feed extruder speed leading to a narrowing RTD is clearly seen in Figures 6.15 and 6.16.

6.5.1.1.2 The effect of crosshead extruder speed.

The crosshead extruder, in the adopted arrangement, was connected to the CTM. Hence the crosshead extruder speed would control the CTM rotational speed. This was considered an important variable since, for a given CTM, the rotational speed of the CTM controls the rate of mixing. Hence the influence of this parameter on the process conditions and the RTD was examined; these effects are examined in this section.

6.5.1.1.2.1 The effect of crosshead extruder speed on the process conditions.

The influence of the crosshead extruder speed on the process conditions is examined initially; data relevant to this effect are given in Table 6.17.

Table 6.17 : The effect of crosshead extruder speed on the process conditions.

Code	Fe rpm	Xe rpm	Q kg/hr	$\bar{t}$ s	P psi	Comments
Ph1	30	46	0.79	103	700 to 800	↑
Ph2	30	57	0.73	109	450 to 550	55C CTM EPDM
Ph3	30	68	0.81	87	350 to 500	
Ph4	30	75	0.83	97	300 to 450	
Ph5	30	85	0.75	94	200 to 250	
Ph6	30	94	0.77	93	200 to 300	
Ph7	30	102	0.79	93	200 to 300	
Ph8	30	107	0.84	83	150 to 250	↓
4	20	40	(0.61)	206		110C CTM EPDM
2	20	60	(0.60)	209		
7	20	40	(0.70)	218		55L CTM & EPDM
8	20	60	(0.89)	173		
17	20	40	(0.49)	132		55C CTM & EPDM
14	20	60	(0.49)	133		
80	40	58	1.28	76	150 to 250	110C CTM & PP
81	40	68	1.25	100	100 to 200	
82	40	88	1.23	90	100 to 200	
83	40	97	1.20	91	100 to 150	↓

The trends apparent from the data in Table 6.17 are discussed below.

a) The upstream pressure

The pressure upstream of the CTM drops as the crosshead extruder speed increases; this is evident from runs Ph1 to Ph8 and runs 80 to 83. One possible explanation for this is the increase in shear heating in the CTM (due to the higher shear rate at a higher crosshead extruder speed) resulting in a decrease in viscosity of the polymer melt (refer to Appendix E). This would lead to a lower pressure requirement for a similar level of throughput. The two sets of data with two different polymers show a similar trend.

b) Throughput

For the majority of the examples cited in the Table 6.17, the crosshead extruder speed influences the throughput, but this effect is not as significant as that of the feed extruder speed on the throughput. This effect can also be seen for EPDM in Figure 6.17 where the increase in crosshead extruder speed is seen to increase the throughput. This trend is reversed for the PP experiments, the runs 80 to 84, as seen in Figure 6.18. A possible reason why the two polymers behave in such a different manner may be because of the significant difference in viscosity between the two polymers (Appendix E). For the material with a higher melt

Figure 6.17 : The effect of crosshead extruder speed on the throughput (EPDM)

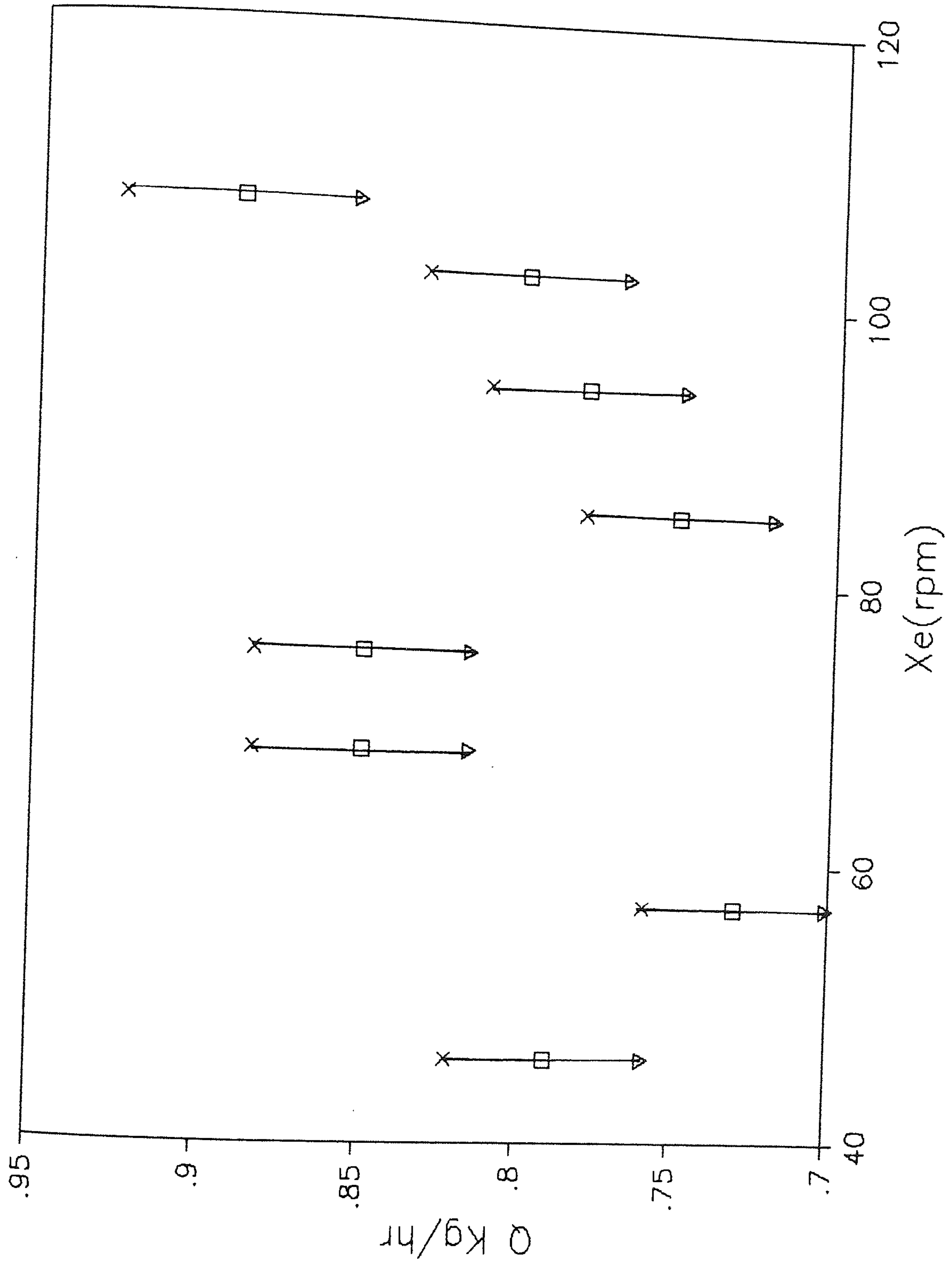
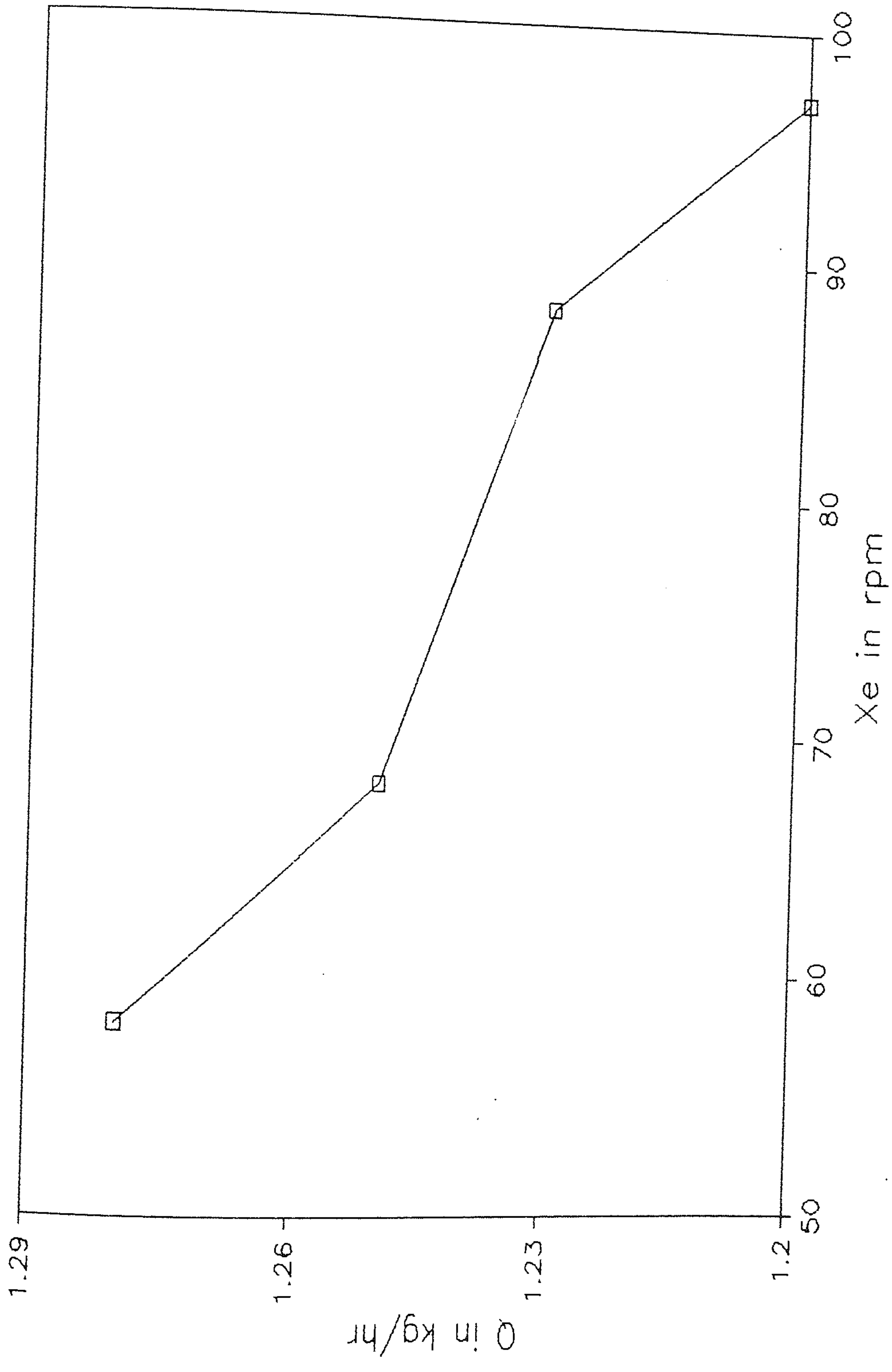


Figure 6.18 : The effect of crosshead extruder speed on throughput (PP)



viscosity, the polymer melt is conveyed more efficiently at higher crosshead extruder speeds; for the material with a lower melt viscosity, the increase in crosshead extruder speed leads to a lower melt viscosity (due to increased shear rate) and the polymer melt may not convey as easily. This would indicate that there is an "optimum" value for melt viscosity for extruder conveying.

The effect of crosshead extruder speed on the throughput is examined further in the following paragraphs.

(i) An increase in the feed extruder speed from 20 rpm to 38 rpm led to a drop of 38% in the mean residence time (Section 6.5.1.1.1). An increase in the crosshead extruder speed from 40 rpm to 120 rpm led to a drop in the mean residence time of 21% out of which 15.5% drop was obtained from 40 rpm to 72 rpm. This implies that when the crosshead extruder speed is "low" (the actual speed is expected to be dependent on the feed extruder speed), the crosshead extruder speed still influences the throughput; however, as the crosshead extruder speed increases, the screw behind the CTM gets starve fed and the throughput is dependent more and more on the feed extruder speed.

(ii) There is a significant scatter in the throughput as seen in Figure 6.17. This is explained by the fluctuation in both the feed and crosshead extruder speeds (Appendix B). A fluctuation of ± 1 in the feed extruder speed and ± 2 in the crosshead extruder speed has been observed and could contribute to the scatter observed in the Figure 6.17.

6.5.1.1.2.2 The effect of crosshead extruder speed on RTD.

There were two schools of thought on how the crosshead extruder speed may influence the residence time distribution. These are outlined below:

a) There is literature[116] published by Stuber and Tirrell that states "improved mixing (i.e. more flow divisions) would lead to a broader RTD." Although the investigators did not experimentally measure the RTD, they inferred that their statement was valid because of data on polymerisation reactions attempted in a twin screw extruder. They observed that, increasing the speed of rotation of a co-rotating twin screw extruder resulted in a polymer (product of the polymerisation reaction in the extruder) with a broader molecular weight distribution;

this effect was attributed to the broader RTD that they expected because of the better mixing at the higher rotational speed of the extruder. If this theory were valid for a CTM, it would be expected that increasing the rotational speed of the CTM would broaden the RTD.

b) If, increasing the rotational speed of a CTM led to the polymer melt stream passing through more cavities for a given mean residence time; it would be expected, from the model of a series of CSTRs, that increasing the rotational speed of a CTM would narrow the RTD.

Since the two "theories" predict opposite behaviours, it was not possible to anticipate the effect of crosshead extruder speed on the RTD. The experimentally observed trends could indicate which model was more valid for a CTM.

To this end, the effect of crosshead extruder speed on the RTD was examined in this project.

Table 6.18 : The effect of crosshead extruder speed on RTD.

Code	Xe rpm	$\bar{t}$ s	σ s	Emax s^{-1}	σ/Q hr s/kg	Emax/Q 3600/kg	Fe rpm
Ph1	46	103	29	0.0153	36.71	0.0104	30
Ph2	57	109	31	0.0186	42.47	0.0255	30
Ph3	68	87	28	0.0165	34.57	0.0204	30
Ph4	75	97	30	0.0160	34.48	0.0193	30
Ph5	85	94	27	0.0192	36.00	0.0256	30
Ph6	94	93	23	0.0249	29.87	0.0323	30
Ph7	102	93	28	0.0204	35.44	0.0258	30
Ph8	107	83	22	0.0232	26.19	0.0276	30
4	40	206	35	0.0108	57.38	0.0177	20
2	60	218	42	0.0117	70.00	0.0194	20
7	40	132	59	0.0079	84.29	0.0113	20
8	60	209	45	0.0079	50.56	0.0089	20
17	40	173	23	0.0188	46.94	0.0384	20
14	60	133	20	0.0178	40.82	0.0363	20

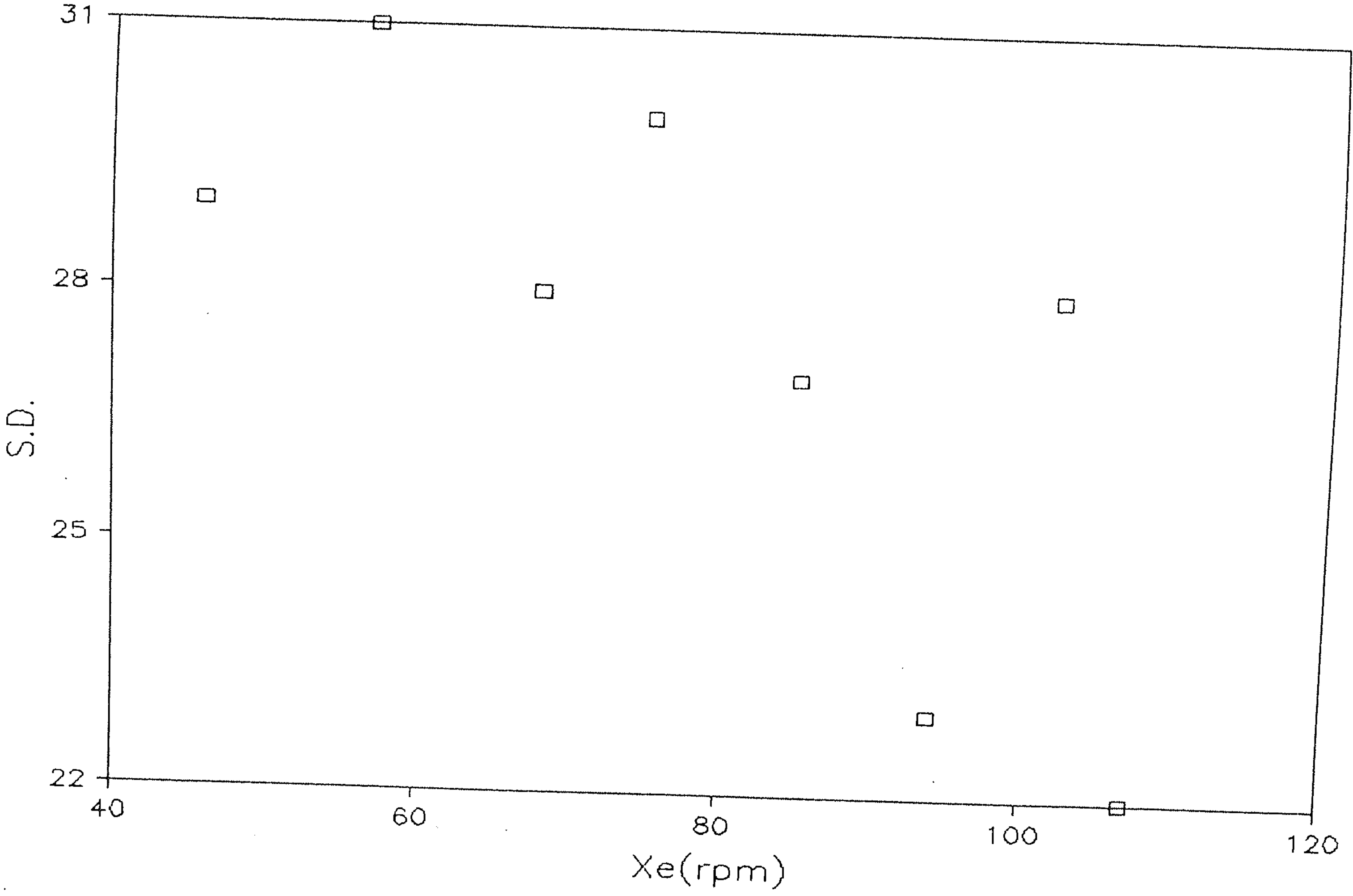
N.B. 1: An increase in Emax/Q represents a narrower RTD, and vice versa.

2: A decrease in σ/Q also represents a narrower RTD, and vice versa.

Figure 6.19 shows a plot of standard deviation against the Xe for the experiments coded Ph1 to Ph8. This figure shows that increasing the crosshead extruder speed narrows the RTD. This trend is also evident from Table 6.18 for Codes [7 & 8] and [17 & 14]; this trend is not seen for Codes [4 & 2].

Figure 6.19 does not take into account any changes in throughput for the different experiments. It has already been shown (Section 6.5.1.1.1) that the throughput has a significant effect on the RTD. So, Figure 6.20 was plotted with σ/Q versus the crosshead extruder speed (to take into account the throughput

Figure 6.19 : The effect of crosshead extruder speed on the standard deviation about the mean residence time.



variation). Figure 6.20 also shows that increasing Xe results in a lower σ/Q, which implies that increasing the crosshead extruder speed does narrow the RTD, even accounting for differences in throughput.

This same effect can also be seen in Figure 6.21 by plotting Emax/Q versus the crosshead extruder speed. This plot shows an increasing Emax/Q for increasing Xe, which also reinforces the view that the residence time distribution narrows as the crosshead extruder speed increases.

Since the RTD narrows for increasing CTM rotational speeds, as could be explained from a model of a series of CSTRs, a model of a series of CSTRs is recommended to model flow in a CTM.

6.5.2 PREDICTION OF THE RESIDENCE TIME DISTRIBUTION.

In order to assist in the design and scale-up of CTM reactors it was thought useful to attempt to model the behaviour of such a reactor. The first step in such a model is the development of a prediction of the RTD. An

Figure 6.20 : The effect of crosshead extruder speed on S.D./Q.

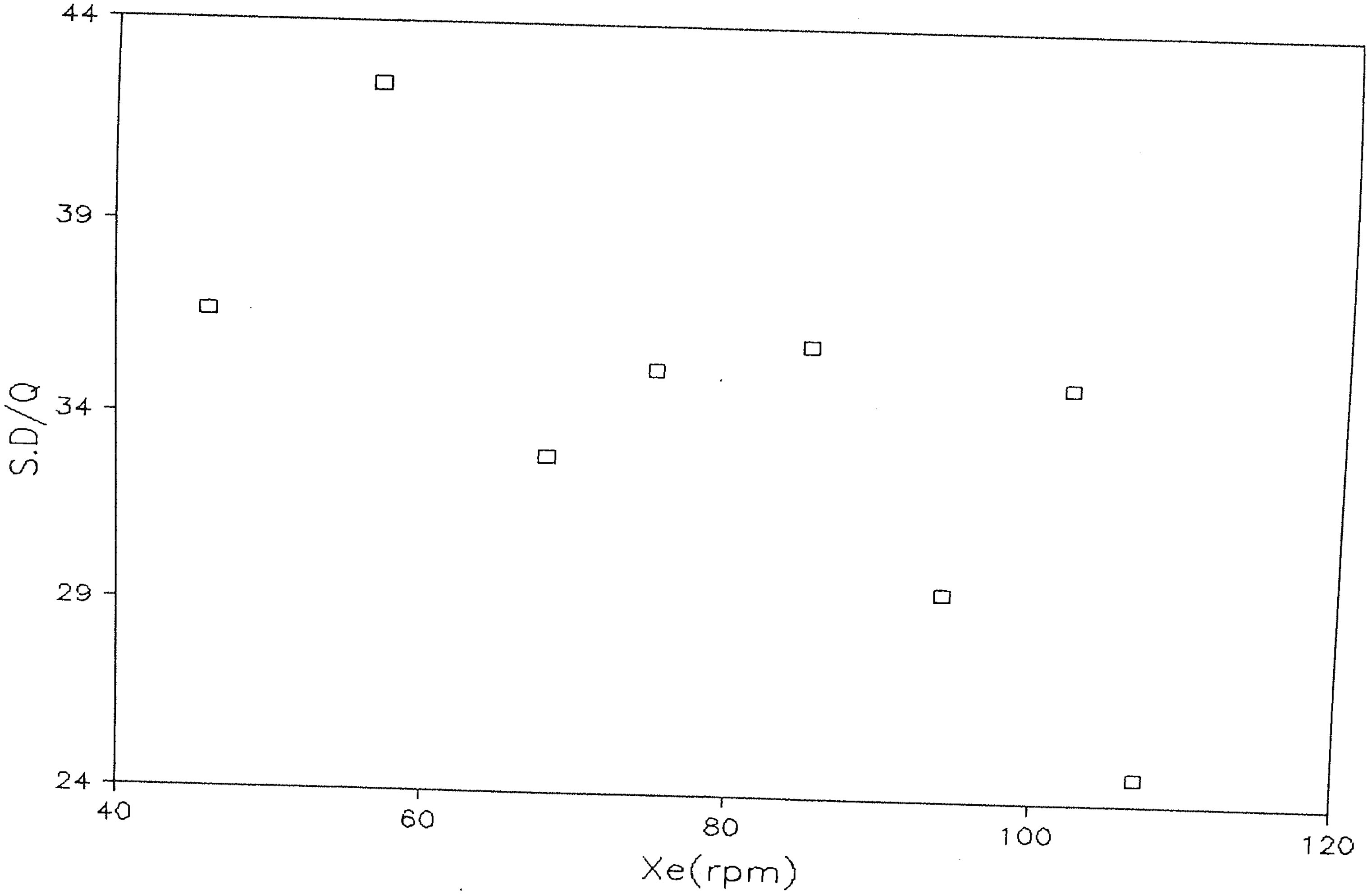
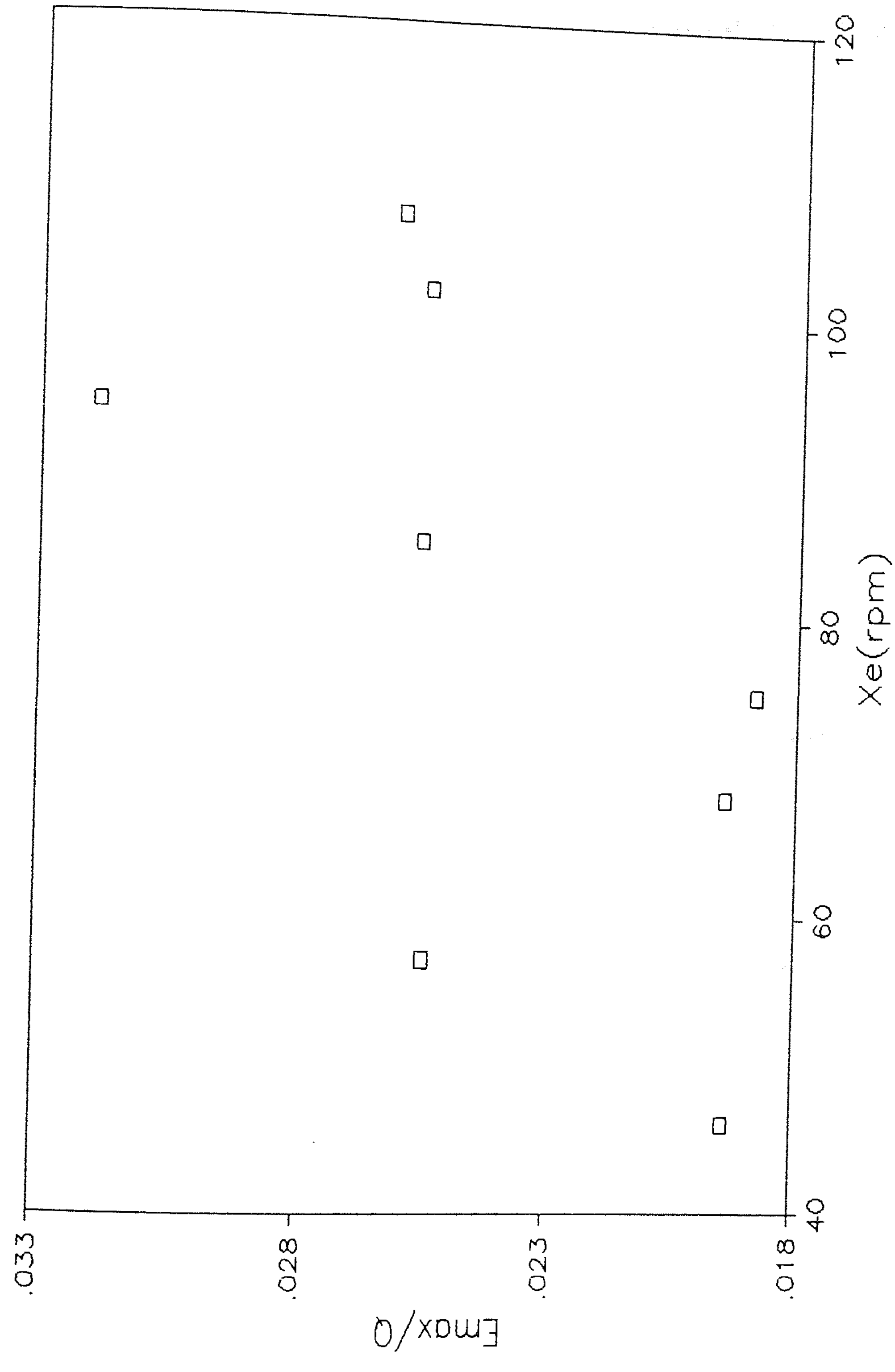


Figure 6.21 : The effect of crosshead extruder speed on Emax/Q.

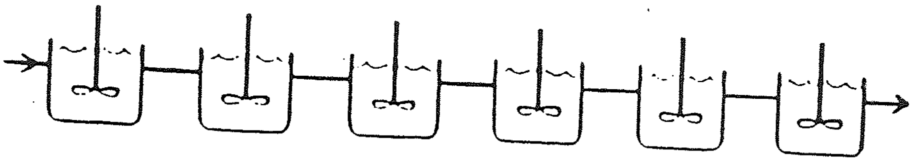


attempt to develop such a predictive model is described here.

6.5.2.1 The Mathematical Model.

A model consisting of a series of continuously stirred tank reactors (CSTRs), as shown in Figure 6.22, is used in this comparison. The reason for the selection of this model is given in Section 6.5.1.1.2 but will be outlined again here. It is known that if a model of a series of CSTRs were valid, the increase in crosshead extruder speed would lead to a narrower RTD, whereas if the theory that increasing the mixing would broaden the RTD were valid, the Model of a series of CSTRS would not be valid. To examine if the Model would be valid for a CTM, the effect of the CTM rotational speed on RTD was examined (Section 6.5.1.1.2.2). It was found that the increase in the rotational speed of the CTM did lead to a narrower RTD; this implied that the model of a series of CSTRs could be used for a CTM.

Figure 6.22: A schematic view of a series of CSTRs.



The residence time distribution of such a system is given by Equation 6.15, the derivation of which is given in Appendix C.

$$E = \frac{N^N t^{N-1}}{(\bar{t})^N (N-1)!} e^{-Nt/\bar{t}} \qquad 6.15$$

The variables in this model are:

a) the mean residence time, $\bar{t}$ (Figure 6.23)

b) the number of cavities, N (Figure 6.24)

6.5.2.2 Comparison between the mathematical model and the experimental RTD.

The effect of process and design parameters on RTD have already been discussed in Section 6.5.1.1. In this section, the experimentally observed trends will be compared with those predicted by a model of a series of CSTRs.

6.5.2.2.1 The predicted effect of feed extruder speed on RTD.

As discussed in Section 6.5.1.1.1, the feed extruder speed influences the throughput and hence the mean residence time. So when a comparison was to be made between the experimental observation of the influence of feed extruder speed on RTD and that predicted by the Model, the parameter to be examined in the Model was the mean residence time. Figure 6.23 presents the mathematically predicted RTD trend for changing the mean residence time.

Figure 6.2.3: The effect of varying $\bar{t}$ on RTD as predicted by a model of a series of CSTRs.

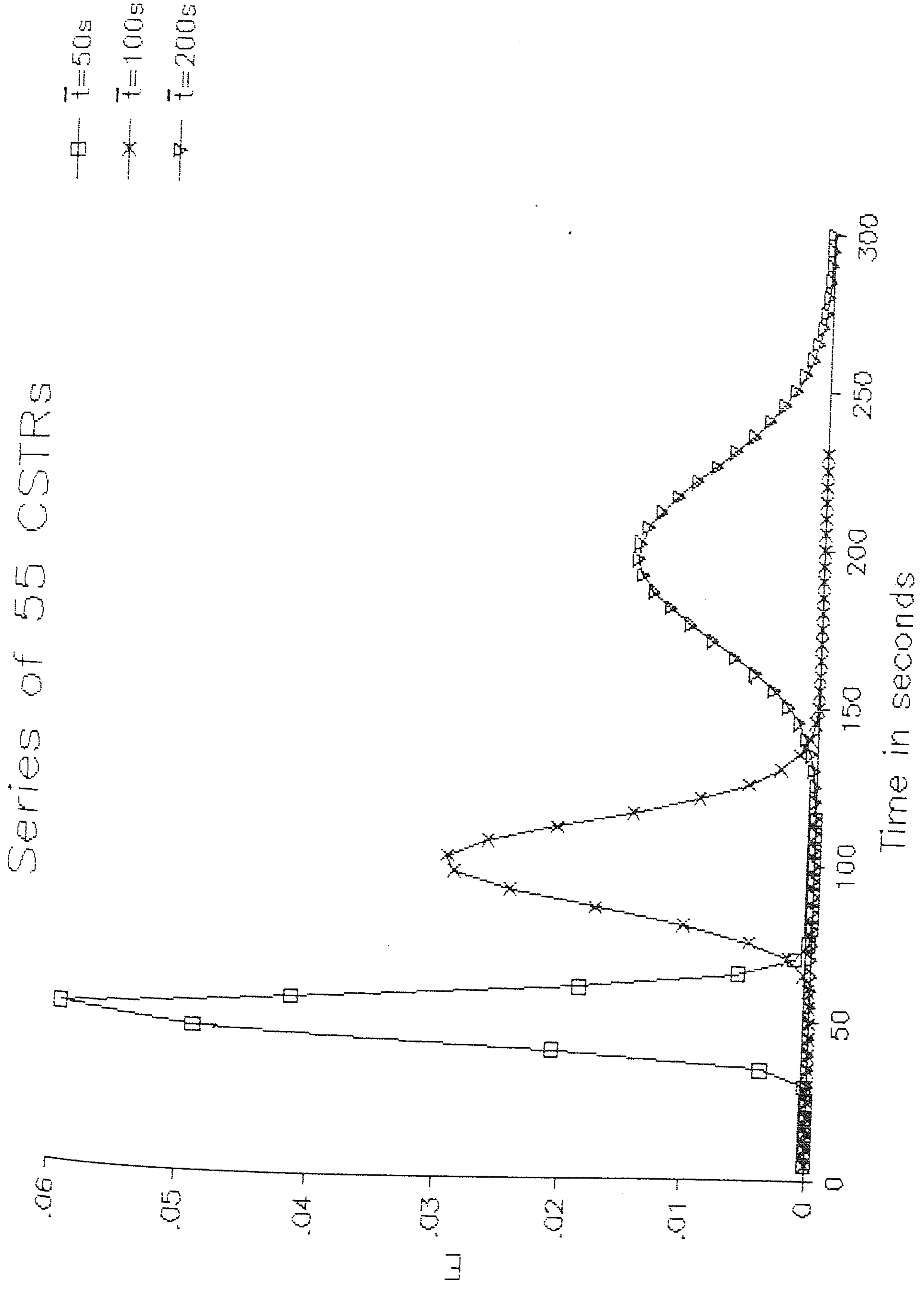
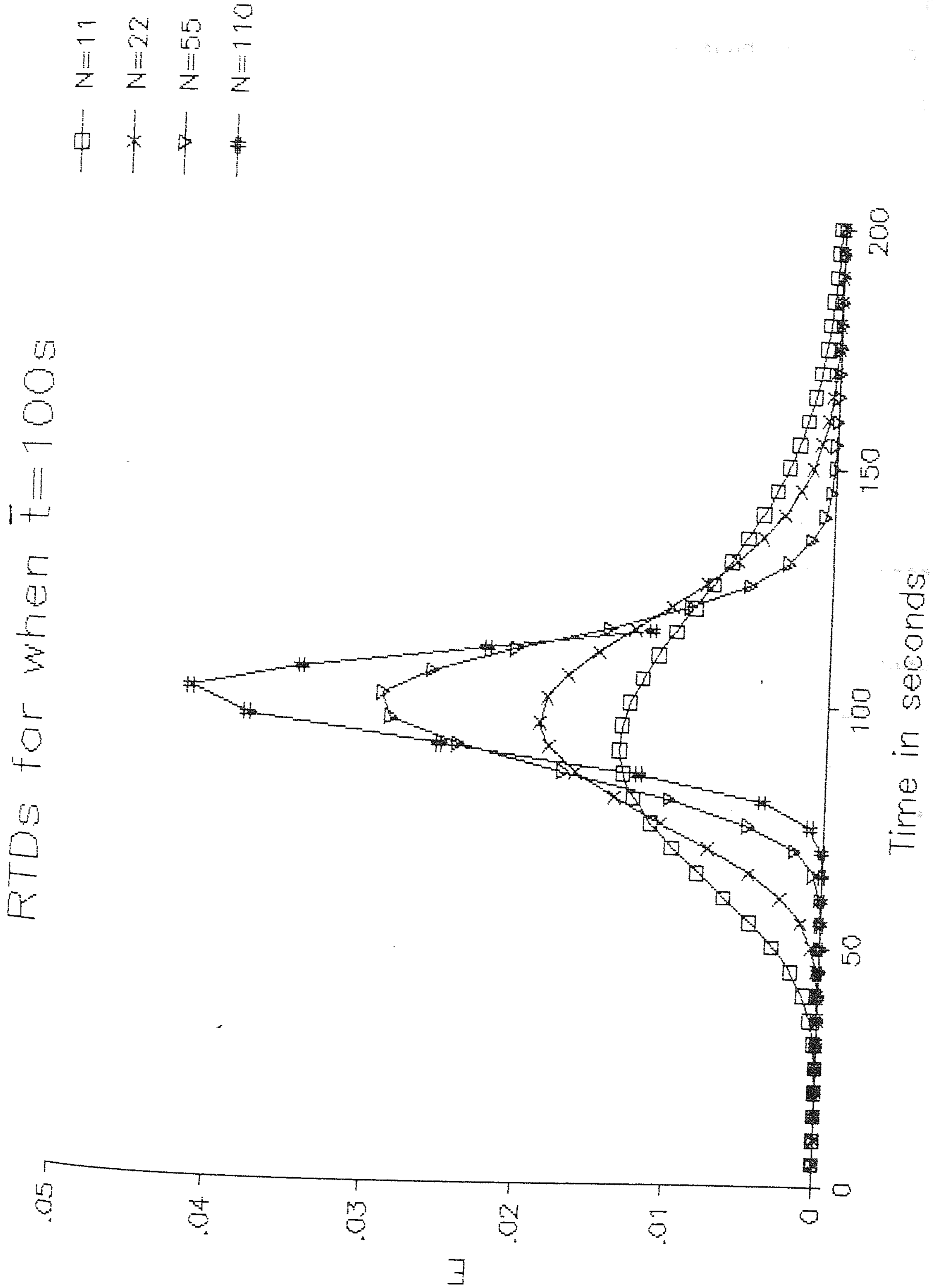


Figure 6.24 : The effect of changing the number of tanks (in a series of CSTRs) on RTD.



It was apparent from the experimental work that increasing the feed extruder speed narrowed the RTD. This was also predicted by the Mathematical Model. The Model, without any stream splitting or backmixing, was able to predict this trend but not the magnitude of this trend. The magnitude of the effect was not considered during this comparison although it is expected that such information would be valuable. A more thorough model would have to be developed, which would take into account the polymer rheology, before the actual magnitude of the experimentally observed effects could be predicted. This work is recommended for future work.

6.5.2.2.2 The predicted effect of the number of cavities on RTD.

According to the Mathematical Model, increasing the number of tanks in series without changing the mean residence time is expected to narrow the RTD, as seen in Figure 6.24. This, in practical CTM design, is achieved when the number of cavities are increased without increasing the total volume of the CTM.

The number of tanks predicted by the model does not correspond to the number of cavities in a CTM, as seen in Table 6.14. However, it would be anticipated that, for a given mean residence time and cavity geometry, increasing the number of cavities in a CTM would narrow the RTD.

Correlation between the experimental RTD trends and those predicted from the mathematical model

Variable	Experimental	Model
increase the feed extruder speed	increase in throughput, decrease in mean residence time, narrowing of RTD	the model also predicts the narrowing of the RTD
increase in crosshead extruder speed	a slight increase in the throughput and a corresponding decrease in the mean residence time, narrows RTD, decreases the pressure upstream of CTM	if an increase in number of cavities could be taken to represent an increase in the cross-head extruder speed; the model predicts a narrowing of the RTD.

7. DISCUSSION

7.1 INTRODUCTION

The major sections of this project were:

i. the redesign of (available) continuous polymer processing equipment to accommodate reactant introduction,

ii. the determination of the feasibility of using a cavity transfer mixer (CTM) as a reactor for a variety of melt phase reactions,

iii. the effect of independent process variables on CTM operation and performance,

iv. the marketing of a research project to progress further study into the use of a CTM as a reactor.

The redesign of the equipment is described and discussed in Chapter 4, the marketing of the research project is discussed in Section 3.3. Only points ii. and iii. from the list above are discussed together in this section. Firstly, the reactions that can be effected in a CTM are discussed. Systems that do not lend themselves to reactive processing within a CTM are also identified. Comparison of the operation of a CTM for grafting is made with a batch reactor system for the same reaction. The operational flexibility of the evolved design is examined alongside the influence of various process parameters on the performance of reactive processing within a CTM (with reference to, for instance, the residence time distribution).

7.2 REACTIONS THAT CAN BE PERFORMED IN A CTM.

A CTM has been used in this project to chemically modify polymers. A piece of processing equipment can be best used to perform those reactions where the conditions provided by the equipment are those that are desirable for the reaction. Hence a CTM would be best used to perform those reactions which take advantage of the conditions (listed below) that are provided in the CTM. The reputed features of a CTM that could be exploited to perform continuous polymer melt reactions are discussed below.

1. Good interfacial contact between the different reagents is achieved in a CTM; this is a desirable feature since improved mass transfer between the reagents can be achieved. This could be useful especially for fast reactions where the rate determining step of the reaction would be the mass transfer stage.

2. Thermal homogenisation of the mixture is achieved due to the distributive mixing in the CTM. In a CTM, the material flow is reoriented and redistributed. This redistribution of the flow would lead to the thermal homogenisation of the reaction mixture. Thermal homogenisation prevents the formation of hot spots in the reaction matrix; hot spots are undesirable since these could provide "islands" where the reaction conversion is different from the matrix. Such non-uniform reaction conversion could lead to a non-uniform product.

3. As a CTM is a closed vessel, the reaction mixture can be maintained under a controlled environment. For example, if a comparison is drawn between a CTM and a two roll mill, a polymer matrix on a two roll mill would be exposed to the open "uncontrolled " environment of the plant. If the reaction attempted on a two roll mill would suffer a side reaction with oxygen, it would be almost impossible to eliminate oxygen from the reaction environment. Another advantage of a CTM reactor being a closed system is that when hazardous and irritant chemicals are to be handled, the concentrations of such chemicals could be minimised in the work space.

4. A CTM achieves its distributive mixing by redistributing the streams. The design of the CTM is such that the material is not made to flow through tight clearances. Since the material flows only through larger clearances, the shear rate is kept low. This is an advantage for a couple of reasons. Firstly, if shear sensitive materials, such as polystyrene are processed on twin screw extruders, well known as high shear rate mixers, the polymer would suffer chain scission; this could be undesirable in some cases. Secondly, since high shear rates lead to high shear stresses which result in shear heating, high shear rate mixers may not be desirable reactors for high viscosity materials in some instances because of the shear heating that would be experienced by the polymer.

7.3 REACTIONS THAT CANNOT BE PERFORMED IN A CTM.

As in any other type of processing equipment, reactants cannot be processed in a CTM if either the reactants or the products are not mobile under the processing conditions. An example of this is discussed in this subsection.

It has been abundantly clear from the experimental work that the reactions which result in a significant increase in viscosity are not amenable to reactive processing in a CTM. This is especially true if the reaction product is not thermally labile but is only shear labile. This means that the product does not display thermoplastic behaviour but behaves like a thermoset material. This would mean that increasing the CTM temperature would not lead to a decrease in viscosity, and hence would not encourage flow (Appendix E). This was true for some of the neutralisation reactions attempted in this project, where the reaction led to a quasi-crosslinked product which was only shear-labile. For this product, it is predicted that even a high shear rate reactor would not have been effective since at high shear rates, the quasi-crosslinked product would flow (Appendix E) but only because the bonds have been broken; this implies that the reaction reverses under high shear stress. So, if the reaction product is quasi-crosslinked, it is anticipated that the reaction could not be performed inside most continuous processing equipment.

What can be done is that the reagents could be mixed together in a processing equipment and then the reaction could proceed outside the equipment. It is reasoned that even when this product was made on a mill (Section D 2.2.1.), while it was passing through the nip of the mill, the reaction was reversed.

When the neutralisation of liquid rubbers was attempted in a sigma blade mixer, it was noticed that when the mixer stopped rotating, the viscosity of the product increased (Appendix D 2.3). This viscosity of the material with the mixer stationary cannot be measured, since it was not possible to measure the viscosity of a material at zero shear rate with the equipment available at Rapra. And if the material is shear sensitive, the shear rate applied to measure the viscosity would actually alter the viscosity of the material. It is for reactions like these that the batch processes, such as a sigma blade mixer, were useful. They enabled an understanding to be gained into the flow behaviour of reaction products that could not have been obtained easily from any measurement or testing.

7.4 OPERATIONAL FLEXIBILITY.

The design of the reactive processing system, incorporating a CTM, allowed significant flexibility both in the systems processed and in the process parameters to which they were subjected. The following sections outline

1. the systems studied and
2. the process variables of the designed system.

The process variables assessed in this section are:

a. the throughput and the mean residence time,
b. the rate of mixing and the residence time distribution,
c. the reaction temperature,
d. the reagent composition and
e. the injection rate.

7.4.1. THE SYSTEMS STUDIED.

The flexibility of the injection system was such that a variety of liquids could be injected into the polymer melt. A liquid injection assembly, as described in Section 4.5.2., was used in this project with the following liquids.

oleic acid
acrylic acid
di-butyl maleate
bis-tributyl tin oxide
maleic anhydride " in solution"

The variety of liquids that could be injected using the adopted arrangement, illustrates the flexibility of

1. the injection system as a means of introducing low viscosity liquids into a polymer melt and
2. the CTM for mixing such a range of liquids (of varying viscosities) with a range of polymer melts at a variety of ratios.

Such flexibility allows the CTM reactor to be used for performing a range of reactions using different polymer and monomer combinations. In this way, the product having a range of desired properties could be manufactured. In addition to the flexibility in mixing low viscosity and high viscosity liquids in a range of ratios, the evolved equipment arrangement allowed independent variation of a number of process parameters.

7.4.2 THE PROCESS VARIABLES OF THE EVOLVED EQUIPMENT FOR REACTIVE PROCESSING.

The significance of the process variables available in the equipment set up designed in this project, to reactive processing, is discussed in this subsection.

7.4.2.1. The mean residence time.

It has been shown that the feed extruder speed strongly influences the throughput (Section 6.3.1.1.) and that, for a given CTM volume and polymer rheology, the throughput determines the mean residence time (Section 6..5.1.1.1). It was shown in Section 6.4.2.2.5, atleast for one reaction system, that the mean residence time was an important factor influencing the [illegible] performance.

7.4.2.2. The residence time distribution.

It has previously been suggested (ref 140) that the rotational speed of the CTM influences the rate of mixing. The results from this project have shown that it also influences the RTD (Section 6.5.1.1.2.2).

The scant data available, for one reaction system (Section 6.4.2.2.4), on the influence of crosshead extruder speed on a reactor CTM performance indicate that changing the CTM speed does not influence the CTM performance. For example, increasing the crosshead extruder speed from 20 rpm to 60 rpm did not influence the performance (refer to Table 6.12). However, there are other design parameters that could influence the RTD such as the cavity transfer mixer geometry and the polymer melt rheology. These parameters should be examined for the individual reaction system of interest to examine the correlation between the RTD and reactor CTM performance.

It would not be valid to generalise between one reaction system and another since the influence of the rate of mixing on the reactor performance is expected to be dependent on

i. the reaction kinetics and

ii. the mass transfer stages involved (the viscosity of the reaction mixture).

These have not been examined in this project.

7.4.2.3. The reaction temperature.

The CTM and the extruders could be set to operate at different temperatures in the adopted arrangement. "For practically all elementary reactions"[68], temperature plays a significant role in reaction kinetics. Hence, if reaction kinetics were the rate determining step, increasing the reactor temperature would improve the reactor performance. However, this parameter would need to be examined for each reaction system of interest since the reaction kinetics of the chosen reaction system would play a deciding role in how this parameter influences the reactor performance.

7.4.2.4. The reagent composition.

When mixtures of two reagents (for example a monomer and peroxide) were to be injected into a polymer melt stream, the composition of the mixture to be injected could be easily altered. The influence of this parameter has not been assessed in this project but it is anticipated that it could be an important process variable for some reaction systems.

7.4.2.5. The injection rate.

Since the stroke frequency and the plunger diameter are set for a given pump, the injection rate could be altered by adjusting the stroke length of the plunger pump; in this project (Section 6.4.1.2.2 and Section 6.4.2.2.3.), this variable has been shown to strongly influence the reactor performance.

The required levels of liquid could be obtained in the outlet stream by introducing the reactant liquid either in one shot or in two shots (Table 6.9). The two shot technique could be exploited if the level of liquid required in the product is high. This is because at high liquid injection rates, slippage has been shown to occur, which then leads to surging of the output stream. When this is the case, the liquid level could be dropped and the required level of liquid could be introduced in two stages.

N.B. The exact level of liquid which would lead to surging is expected to be dependent on

a. the solubility between the polymer melt and the low viscosity liquid and

b. the process conditions.

7.5 COMPARISON OF CTM PERFORMANCE WITH BATCH REACTOR FOR POLYMER GRATING REACTION.

Advantages of a CTM as a reactor have been discussed in general terms in Section 7.2. An example is quoted here from this project to illustrate one of the advantages. When grafting reactions were attempted on a mill between a polymer (EPDM rubber) and liquid (oleic acid), the incorporation of the liquid reagents (Appendix D 3.2.3.) was a time consuming and labour intensive process; it had to be done in two stages. One reagent, the peroxide, had to be added to the polymer; this first step once took as long as four hours to make 900 g of this mixture. This mixture had to be placed in an oven overnight. The following day, another reagent, the monomer was added to a portion of this mixture. This new mixture with both the peroxide and the monomer had to be heated, to react, in an oven which was previously purged with nitrogen. So, to make approximately 150 g of grafted product, it took two days and seven man-hours. Compared to this, once the liquid injection system had been developed, it was possible to produce about one kilogramme per hour of the grafted material using a CTM (Appendix D.3.1.1.).

Another instance where use of CTM proved to be an advantage was when grafting of maleic anhydride onto a polymer was attempted. When this reaction was attempted on a mill (Appendix D 2.4.2.), the milling process had to be interrupted due to operator discomfort, since maleic anhydride is a severe irritant. Even wearing safety glasses and dust mask, it was not possible to work on a two roll mill with maleic anhydride as an additive for more than five minutes at a time. When the maleic anhydride was injected into a CTM, the experiments were performed for two consecutive days, for seven hours per day (Section 4.7.4.1.), without any interruptions due to operator discomfort.

In summary, the closed injection system of a CTM was an advantage whilst handling hazardous or irritant materials.

8. CONCLUSIONS

8.1 INTRODUCTION

The important achievements of this project are as follows.

1. A cavity transfer mixer (CTM) assembly has been developed to successfully perform grafting (and some neutralisation) reactions in high viscosity systems.
2. The performance limitations of a CTM reactor have been assessed.
3. A study of the flow characterisation of a CTM has been initiated using residence time distribution (RTD).
4. A research project which would further investigate the characteristics and viability of the CTM as a reactor has been set up.

All these stages have been successfully accomplished during this project. Progress in these different aspects of the Project will be summarised below.

8.2 DEVELOPMENT OF A CTM TO PERFORM REACTIONS.

Selected available polymer processing equipment (in this case a CTM and extruders) has been modified to incorporate changes to the equipment layout to enable precisely controlled introduction of reagents into the polymer melt stream. Initial study generated useful guidelines for setting up the process assembly so as to attain the required processing conditions for a given reaction system . For example, the injector would be set to open at a similar pressure to the process pressure upstream of the CTM. This led to steady injection; the reasons why steady injection was obtained under these conditions are explained in Chapter 4.

Operational expertise was gained during the development stage with the result that trouble shooting was faster and more effective. For example, if there was a leak from behind the seals, the reason for the fault was quickly diagnosed to be damaged seals and operational experience gained enabled the system to be back on stream within twenty four hours.

8.3 LIMITATIONS OF A CTM REACTOR.

Two types of reactions with products of distinctly different flow properties were attempted in the CTM. It has been shown that the CTM is not an effective design for a reactor if the product has a high viscosity and is only shear labile i.e. if the product is quasi-crosslinked. It is postulated that no continuous processing equipment could be used to perform such a reaction.

On the other hand, where the product is not quasi-crosslinked and has a viscosity not significantly different from that of the reactant polymer, a CTM is well designed to perform the reactions. This indicates that a CTM can be an efficient reactor if its ability to generate interfacial area and maintain thermal homogeneity is exploited.

8.4 CHARACTERISATION OF A CTM IN TERMS OF RTD.

It was anticipated, even during the very early stages of the Project, that the design of a CTM, the process conditions and the polymer rheology, would all influence the flow pattern in a CTM. One of the three parameters mentioned above have been examined in this project. The method selected for studying the flow behaviour was residence time distribution. A simple mathematical model (consisting of a series of a CSTRs) was used to predict RTD trends. The mathematically predicted trends were also exhibited in the experimentally measured residence time distributions. The magnitude of the trends was not predicted by the mathematical model. The influence of polymer rheology on RTD could not have been assessed using this model.

8.5 MARKETING OF THE RESEARCH PROJECT.

A research project to further characterise a CTM as a reactor was set up and marketed as part of this PhD Project. This was successfully executed in that it resulted in the launching of the biggest group project to run at Rapra.

Besides the financial rewards due to the sponsorship, the Group Project confirmed that the work proposed in the work programme (Appendix H) was technically sound and was of commercial value.

There are several ideas that could be followed up and hypotheses that need testing. Some of these are outlined in the Recommendations for Future Work (Chapter 9). The majority of these ideas are presently being examined as part of the Group Sponsored Project at Rapra Technology Ltd., Shawbury, Shropshire, U.K..

9. RECOMMENDATIONS FOR FUTURE WORK

9.1 INTRODUCTION

As discussed in Section 4, the main achievement of this project is in the operational knowledge gained of a CTM used as a reactor. Limited knowledge of polymer melt reactions and batch reactors has also been gained.

There are several avenues that were unexplored due to time restrictions. Some of these ideas for the future progress of the work will be outlined in this section. The majority of these ideas are being examined by a team at Rapra as part of the Group Sponsored Project set up as a result of the marketing exercise, described in Section 3.3, which was an integral part of this project.

9.2 THE INFLUENCE OF PROCESS PARAMETERS ON REACTOR PERFORMANCE AND RTD.

The design of the extruder and CTM set-up in this project is such that several process parameters are available as variables. Their influence on both the RTD and the reactor performance need to be studied to gain a thorough understanding of the mechanisms governing the optimal use of a CTM reactor. The influence of some of these variables that need to be examined are given below.

9.2.1 CTM GEOMETRY.

The design of the CTM geometry is expected to influence the residence time distribution . Its influence on the reactor performance for a given mean residence time is expected to be worth examining. This may cast light on the influence of the mode of mixing on the reactor performance.

9.2.2 CROSSHEAD EXTRUDER SPEED (CTM ROTATIONAL SPEED).

Again the influence of the CTM rotational speed on the process conditions and the RTD have been discussed in Section 6.5.1.1.2; its influence on reaction has been observed for one reaction system in Section 6.4.2.2.4. The influence of CTM rotational speed on a range of polymer melts and monomers is expected to ellucidate the inter-relationship between reaction conversion, reaction kinetics and mass transfer steps.

9.2.3 FEED EXTRUDER SPEED.

This parameter has been found to strongly influence both the mean residence time and the residence time distribution (Section 6.5.1.1.1). Its influence on reactor performance was observed, for one reaction, in Section 6.4.2.2.5.. However, the influence of the feed extruder speed on the reactor performance, and further studies on its influence on RTD, would be a valuable parameter for examination since such information could be used to formulate scale-up laws.

9.2.4 THE POLYMER MELT RHEOLOGY.

The polymer melt rheology has been shown to influence the throughput (Section 6.3.1.3.). Its influence on RTD may give information on the flow patterns of material in a CTM and should be studied if only for this reason.

A change in polymer melt rheology may lead to changes in the conditions in a reactor that may then influence its performance as a reactor. Some of the possible ways this variable may influence the process conditions in the reactor are given below.

i. The temperature regime in the reactor is expected to be dependent on the polymer rheology (Section 6.4.2.2.1).

ii. The misciibility of the low viscosity reactant in a polymer melt will vary with flow properties.

iii. The mass transfer during reaction would change due to the viscosity of the reaction mixture changing.

The work recommended for the future development on the mathematical model is given below.

9.3 MATHEMATICAL MODELLING.

In this PhD Project, a simple flow model consisting of a series of CSTRs has been used. This model correctly predicted the experimentally observed trends in RTD but has not been used to predict their magnitude. An improved model may be aimed at the prediction of the magnitude of the trends. Some suggestions for modifications to the model are given below.

1. A series of CSTRs with backmixing where the backmixing ratio is related to relevant process and design parameters, for example the CTM geometry and the crosshead extruder speed.
2. A network of CSTRs with split streams.
3. A network of CSTRS with backmixing.
4. A series or a network of CSTRs with tanks of varying sizes.

9.4 AIM FOR FUTURE RESEARCH PROGRAMS.

Once a mathematical model has been constructed that would incorporate the possible effects of polymer rheology and can predict for a range of polymer systems and CTMs

a. the RTD trends and

b. the reaction conversion

it can be concluded that the model does successfully predict the behaviour of a CTM reactor.

It is at this stage that "the model" could be used to design CTMs and specify process conditions to obtain a given conversion for an untested reaction system of known reaction kinetics and flow properties.

NOMENCLATURE

Notations

Units are given in the text for where they are omitted in the list below.

A,K	Constants
μ	dynamic Viscosity Nsm^{-2}
$\dot{\gamma} = dv/dx$	shear rate s^{-1}
R	shear stress Nm^{-2}
N_{RE}	Reynolds number
ρ	Density of fluid kgm^{-3}
L	Length (metering) m
D	Diameter m
g	tip clearance mm
t	time
$\bar{t}$	mean residence time
N	speed rpm
k	rate constant
Q	throughput kg/hr
h	channel depth
S	surface area
Cos α & Cos β	directional cosines
r	striation thickness
f( )	function of
E	Exit age distribution s^{-1}
B,G	reactants
e, b, g	no of moles of E, B & G
C	concentration
v	velocity ms^{-1}
$\lambda_{1,2,3}$	locations of maximum shear rate
Ø	helix angle
N	Number of tanks

subscripts t = tip e.g. $\dot{\gamma}_t$ or Dt

c = cure

m = mixing

t = tangential

i = initial

max	maximum
h	head
v	volumetric
f	final
$\partial x/\partial y$	total strain
V	volume
V_a	active volume
$\bar{\gamma}$	average total shear
e	tip width mm
Rapra	Rapra Technology Limited, the sponsoring organisation
CTM	Cavity Transfer Mixer
RIM	Reaction Injection Moulding
CSTR	Continuous Stirred Tank Reactor
Fe	Feed extruder
Xe	Crosshead extruder

REFERENCES

1. Abbi Y.P., Gunn D.J., Trans.Inst.Chem.Eng.,p.225-31, Vol.54, 1976.
2. Anon. Modern Plastics, p.22, April 1984.
3. Anon, Modern Plastics International, April 17(4) p.4 1987.
4. Atherton W.H., Conveying Machinery, The Technical Press Ltd., London, 1937.
5. Baker Perkins Chemical Machinery "Hydispenser" Wet mixing of creams and pastes over a wide range of viscosities, Technical literature.
6. Baker Perkins Chemical Machinery, "Polycon continuous reactors". Technical literature.
7. Barr, Chung, SPE journal, p.71, 22, No.5, 1966.
8. Bernhardt E.C. "Processing of Thermoplastic Materials" Reinhold Publishing Corp. N.Y. Plastics Engineering Services, 1959.
9. Berstoff Technische Information, "Berstoff High Performance twin screw extruder compounding plant type 2E/2E-A in two stage design". Technical literature.
10. Bhatnapar A., Brontman L.J. 38th Annual Conference, Reinforced Plastics/Composites Inst. The Society of the Plastics Ind., Session 8-E, Feb.7-11 1983.
11. Biesenberger J.A., Gogos C.G., Polymer Engineering and Science. Mid. Sept. 20(13) 1980.
12. Bigg D., Middleman S., Ind.Eng.Chem.Fund., p.66-71, Vol.13, No.1, 1974.
13. Bigio, Boyd, Erwin, Gailus, Polymer Engineering & Sci. Vol.25, No.5, 1985.
14. Bird R.B., Steward W.E. and Lightfoot E.N., "Transport Phenomena" John Wiley & Sons Ltd., New York, 1960.
15. Bischoff K.B., Can.J.of Chem.Eng., p.129, June 1963.
16. Blow C.M., "Rubber Technology and Manufacture", Butterworth, London, 1971.
17. Bran and Luebber, Metering and Proportioning, Technical literature.
18. Bromilow T.M. & Hulme A.T., " Towards a mathematical model of the Cavity Transfer Mixer", Rapra Technology, October 1986.
19. Bolen W.R., Colwell, R.E., SPE j., p.24, Aug. 1958.
20. Booy M.L., SPE Trans. Vol.3, No.3, July 1963.
21. Buffham & Rathor, Trans. I.Chem.E, Vol.56, 1978.
22. Buffham B.A., Gibilaro L.G., Chem.Eng.Sci., p.1399-1871, Vol.23, 1968.
23. Buss-kneader lines for continuous mixing, kneading, compounding, trade literature.
24. Carley and McKelvey, Ind.& Eng.Chem. Vol.45, No.5, May 1953.
25. Ceresa R.J., "Block and Graft Copolymerisation", Vol.1 Published by John Wiley and Sons, 1984.
26. Chella J.M. Ottino R., Chem.Reactn.Eng. p.567-70.
27. Chemical Engineer, Sep. 15, 1978.
28. Cleland F.A., Wilhelm R.H., A.I.Chem.E.J., p.489-497 Dec. 1956.
29. Colwell & Nickolls, Ind.& Eng.Chem., p.84-843, Vol.51, No.7, July 1959.
30. Danckwerts P.V., Chem.Eng.Sci. p.93-102, Vol.81,

1958.

31. Danckwerts P.V., Chem.Eng.Sci. p.1-18, Vol.2, No.1, Feb., 1953.
32. Denson G.D., Hwang Jr.B.K., Polym.Eng.& Sci. Vol.20, No.14, Sep.1980.
33. Dettaven E.S., Ind.& Eng.Chem. p.813-6, Vol.51, No.7, July 1959.
34. Domnesteam R., Chem.Eng.Sci., p.2260-1, Vol.28, 1973.
35. Eccher & Valentinotti, Ind.& Chem.Eng., p.829-836, Vol.153, No.5, May 1958.
36. Eise K., Plastics Compounding, p.44, Jan/Feb. 1986.
37. Eise K., Advances in Polymer Technology, Vol.3, No.2, p.113, 1985.
38. Elbirli B., Lindt J.T. Polym. Proc.Eng., p.109-130 1 (2) 1983-4.
39. Erwin L., Polym.Eng.& Sci., p.572-576, Vol.18, No.7, 1978.
40. Evans C.W., "Powdered and Particulate Rubber Technology", Applied Science Publishers Ltd., London, 1978.
41. Fenner & Robinson, Plastics & Rubber proc.& appl., p.305-313, 3, 1983.
42. Flynn S.R., Pitture & Vernice, 8.
43. Frund Jr., Z.N. Plastics Compounding, Sep/Oct p.24 1986.
44. Funt, "Mixing of Rubbers", Rapra, Shrewsbury, 1972.
45. Gale, G.M. Plastics & Rubber Proc.& Appl. 2, p.347-352, 1982.
46. Gale G.M., Applied Organometallic Chemistry, 1988.
47. Gibilaro L.G., Stevens M.D., Woldram S.P., Chem.Eng. Sci., p.1394-1396, Vol.33 1978.
48. Gogos, Maxwell, Polymer Engineering and Science, Vol.6, No.4, Oct. 1966.
49. Gouinlock E.V., Marciniak H.W., Shatz W.H., Quinn E.J., Hindersinn R.R., J. of App. Polymer Science 12, 1968.
50. Hanley & Mischke, Ind.Eng.Fund, Vol.17, No.1, 1978
51 Hermann H.Eise K., Polymer Engineering and Science, Vol. 4, No2, Jan 1978.
52. Hohfeld R.W. Plastics World, August, 1985
53. Holland F.A., Fluid Flow for Chemical Engineers, Edward Arnold (Publishers) Ltd. London 1973.
54. Hudson W.G., "Conveyors and Related Equipment", John Wiley & Sons, New York, 1944.
55. Illing G., Modern Plastics Aug. 1969.
56. Ivek Precision Liquid metering systems, trade literature.
57. Jakopin S. Advances in Polymer Technology, Vol.3 p.365-381, No.4, 1982.
58. Jakopin S., Franz P., Plastics Southern Africa p.32-46, April 1984.
59. Jansson L.P.B.M.., Schaart B.J., Smith J.M., Polymer Extrusion II. 15.1-15.5.
60. Jepson C.H., Ind.& Eng.Chem. Vol.45, No.5, May 1953.
61. K-Tron Soder: trade literature.
62. Kan K.M., Greenfield P.F., A.I.Chem.E.J, 123, Vol.29, No.1, Jan.1983.

63. Kattan A., Adler R.J., Chem.Eng.Sci., p.1013-28, Vol.27, 1972.

64. Klein, David & Villermaux, Ind.Eng.Chem., Vol 3, No 2, 1973.

65. Kosel U.M., Plastics & Polymers, Oct. 1971.

66. Kreisker K., Plastics Technology, p.75-79, Sep.1985.

67. Leistritz:Extrusionstechnik, "The multi-extrusion system for mixing, kneading and strand extrusion 2SE GG + GL". Technical literature.

68. Levenspiel, O., "Chemical Reaction Engineering", John Wiley & Sons, 1972.

69. Lin.S.W., Chem.Eng.Sci. Vol.35, p.1477-1488, 1980.

70. Lin S.Y.,Plastics and Rubber Processing and Application 8 (1987),133-145

71. Lin. S.V., Bevis, Plastics and Rubber Processing and Applications, Vol.7, No.1, 1987.

72. Maddock, B.H., SPE Journal, p.983-4, Nov.1959.

73. Mao K.W., Toor H.L., A.I.Chem.E J., p.49-52, Vol.16, No.1, Jan. 1970.

74. Mathews G., "Polymer Mixing Technology", Approved Science Publishers, London, 1982.

75. McKelvey, Bernhardt, SPE Journal, p.22-43, Vol.10, No.3, March 1954.

76. Menges G., and Lehnen J.P., Plastverarbeiter 21, No.5 XXII 1-8, 1970.

77. Ed. by Merril A.M., "Machinery and Equipment for Rubber and Plastics", Bill Brothers Publishing Corporation, Compiled by the Rubber World, 1963.

78. Michelson, M.L., Chem.Eng.J. p.171-9, 4 1972.

79. Mitchell J.R., Chemical Engineering Deskbook, p.93 Issue Oct., 1978.

80. Mitsoulis Vlachopoulos, Advances in Polymer Technology, Vol 4, No.2, p.107, 1984.

81. Mohr, Clapp & Starr, SPE Trans.,p.113-120, Vol.1, No.3, July 1961.

82. Mohr, Squires, Starr, SPE j., Vol.16, p.1015, Sep. 1960.

83. Motoyoshi M., Japan Plastics Age, p.39-44, July/August 1982.

84. Narkis & Ram, Polymer Engineering & Science, p.24-25, Vol.7, No.1, Jan. 67.

85. Nauman E.B., The Can.J.of Chem.Eng. p.136-140 Vol.60, Feb. 1982.

86. Ng. K.Y.& Erwin L. 37th Antec of the SPE, 1979 25: 241

87. Nichols R., and Khera F., Plastics & Rubber Weekly, 25th August, 1984.

88. Orth P., Schugerl K., Chem.Eng.Sci. p.497-507, Vol.27, 1972.

89. Ostergaard K., Michelsen M.L., Can.J.of Chem.Eng., p.107-112, Vol.47, April 1969.

90. Ostergaard K., Michelson M.L., Chem.Eng.Sci., p.588-592, Vol.25, 1970.

91. Perry R.H., and Chilton C.H., "Chemical Engineers' Handbook" McGraw Hill Kogakushen Ltd., Tokyo, 1973.

92. Petho, A., Chem.Eng.Sci. p.807-810, Vol.23, 1969.

93. Plascams, Rapra Technology, U.K.

94. Plastic-color Proportioning Unit, Trade literature.
95. Potente H., Kunststoffe p.439-441, 75, 7, 1985.
96. Potente H. Paper 17, Polymer Extrusion II, PRI, London 11-13 Sept. 1985.
97. Potente H., Lappe H., Plastics & Rubber Proc.& Appl., p.135-140, 6, No.2, 1986.
98. Ranade V.R., Ulbrecht J.J., Chem.Eng.Comm. p.165-176, Vol.8, 1981.
99. Rauwandaal C., "Polymer Extrusion" Hanser Publishers, N.Y., 1986.
100. Rauwandaal C.J. Polymer Engineering and Science, November 1981, Vol 21, No 16.
101. Raymond E.& Corey, "Industrial Marketing Cases & Concepts", Prentice Hall Inc 1983.
102. Rim Y.S., Davison J.A., Nudenberg W., U.S. Patent 4316971, 1982.
103. Roth, Basaram, Seagrave, Ind.Eng.Chem.Fund. Vol.18, No.4, 1979.
104. Schmidt M.J., Castro J.M., Polymer Engineering and Science June 25(9) 1985.
105. Scott, K.W., MSc thesis, "Synthesis and Characterisation of polymer support catalysts and wetting agents," University of Lancaster, 1987.
106. Sebastian D.H., Biesenberger J.A. SPE 41st Antec p.121, May 1983.
107. Sevens, E.T., "Rheology of Polymers." Reinhold Publishing Co., p.106-113, 1962.
108. Severini F., Tarazzani C., La Chimica e L'industria May 59(5) 1977.
109. Sheldon R.P., "Composite Polymeric Materials" Applied Science Publications, London, New York, 1982.
110. Siadat B., Lundberg R.D., Lenz. R.W., Polym.Eng.& Sci., p.330-334, Vol.20, 8, May 1980.
111. Siadat B., Malone M., Middleman S. Polymer Eng.& Sci., Vol.19, No.11, Aug. 1979.
112. Sloman, Williamson, Electrical Review Int.,p.45-48, Vol.205, No.9, 7th Sep.1979.
113. Spencer R.S., Wiley R.M., J. Colloid Science, 6; 113; 1951.
114. Squires P.H., SPE j., Vol.14, No.5, p.24, 1958.
115. Stanton William J., "Fundamentals of Marketing", McGraw Hill 1984.
116. Stuber N.P., Tirrell M., Polymer Process Engineering 3 (1 and 2) 71, 1985.
117. Swarbrick P., Green W.J., Maillefer C., U.S. BI 4117 195, 1982.
118. Szydlowski W. & White J.L., J. of non-Newtonian fluid mechanics, 28, p.29-46, 1988.
119. Tadmor, Duvdevani, Klein, Polymer Engineering & Science, p.198-217 July, 1967.
120. Tadmor Z and Klein I., "Engineering Principles of Plasticating Extrusion", Van Nostrand Reinhold Company, New York, 1970.
121. Thomson F.T. Chemical Engineering Desk top Issue p.77-87, October 30, 1978.
122. Thorn A.D., Thermoplastic Elastomers - A review of current information, published by Rapra Technology,

U.K., 1980.
123. Todd D.B., Polymer Engineering & Science, Vol.15, No.6, June, 1975.
124. Turner J.C.R., Chem.Eng.Sci., p.549-57, Vol.26, 1971.
125. Wall D. " A review of cable compounding using a co-rotating twin screw extruder", International meet on power and communication cable technology.
126. Weinstein H., Adler R.J., Chem.Eng.Sci. p.65-75, Vol.22, 1967.
127. Whelan T., and Craft J., "Injection moulding of plastics materials". The Polytechnic of North London, 1986.
128. Wilmshurst J., "The fundamentals and practice of marketing", Heinemann, 1983.
129. Wisseroth K., Trieschmann R.H., Mohr H., Scholl R., U.S. Patent 3503944, 1970.
130. Wood. R., Plastics & Rubber Inst., p. 207-210, Vol.4, No.5, Sep/Oct.1979.
131. Wyrough and Loser Inc., "Extruder Mixing"
132. Private Communication with Werner and Pfeiderer.
133. Private Communication with Buss Hamilton.
134. Private Communication with Francis Shaw.
135. Private Communication with Rapra.
136. Rapra Technology Limited CTR 104.
137. Rapra's Members Report 16
138. Rapra's Members Report 45
139. Rapra's Members Report 46
140. Rapra Technology Limited CTR 99.
141. Rapra Technology Limited, internal document, 1988.
142. U.S. Patent 3536 680 1970.
143. U.S. Patent 4463 137, 1984.
144. Sutter H., Penker R., U.S. Patent 4058 654, 1977.
145. Caywood Jr.S.W., U.S. Patent 3884882, 1975.
146. U.S. Patent 4410659, 1983.
147. US Patent 3646155 1972.
148. U.S. Patent No.3642964, 1972.
149. Vibra Screw Inc. - Is your bulk material: stored discharged, metered, mixed weighed sized. Trade literature.
150. Lappe H., & Potente H., p.108-111, Antec '84.
151. Adur A.M., Flynn S.R., SPE Antec 87.
152. Brydson J.A., "Flow Properties of Polymer Melts", 2nd Edition, George Goodwin, London, 1981.
153. Ed.by King A., and Wentworth V.H., "Raw Materials for Electric Cables", Ernest Benn Limited, London, 1954.
154. Ed. by Whelan A., and Craft J.L., "Developments in PVC Production and Processing, 1".

APPENDIX A

LIST OF ABBREVIATIONS AND TRADENAMES

Abbreviations

ABS	Acrylonitrile butadiene styrene copolymers
PE	Polyethylene
EPR	Ethylene propylene copolymers
PC	Polycarbonate
PVdf	Poly(vinylidene fluoride)
TPU	Thermoplastic polyurethanes
PET	Poly(ethylene terphthalate)
PPO	Poly(phenylene oxide)
PBT	Poly(butylene teraphthalate)
PSU	Sulphone polymers
PMMA	Poly(methly methacrylate)
PTFE	Polytetrafluoroethylene
PVC	Poly(vinyl chloride)
PEEK	Polyether ether ketone
SAN	Styrene acrylonitrile polymer
LLDPE	Linear low density polyethylene
PP	Polypropylene
CaO	Calcium oxide
NBR	Nitrile Rubber
PS	Polystyrene
EPDM	Ethylene propylene diene terpolymer

Tradenames

Krynac 211	Carboxylated nitrile rubber
N33 C50	Nitrile rubber
T657	EPDM
K720	EPDM
C0054	EPR
Vamac G	A functional terpolymer
Viton	A fluorinated elastomer

APPENDIX B

a. Fluctuations of extruder speeds

With the extruder set-up used, there was a fluctuation in the screw speeds and hence the throughput during "steady state". This is illustrated by the following data.

When the feed extruder was set at 38 rpm, the measured speed was, on average, 34.5 rpm. Tachometer readings are listed below.

Time (min)	Tachometer reading (rpm)
0	35
0.5	34
1.5	34
2.5	35
3.5	35
4.5	34
5.5	35

These data represent a ±1 rpm error in the feed extruder speed.

Similar readings for when the crosshead extruder speed was set at 40 rpm are given below.

Time (min)	Tachometer reading (rpm)
0	38
1	36
2	38
3	38
4	38
5	39

These data represent a ±2 rpm error in the crosshead extruder speed.

These fluctuations resulted in a variation in throughput. Data relevant to this effect are presented in the table below.

Time (min)	Throughput (kg/hr)
1	1.31
2	1.25
3	1.31
4	1.28

This represents a ±3% variation in throughput.

Greater variations were noticed during start-up but during steady state, a ±4% variation was taken to be acceptable.

b. Variability in insolubility test

The percentage insolubles in an aluminium salt of K220 (XNBR) was measured. Two samples were taken from a batch to test the reproducibility of the analytical technique.

Sample	% insoluble
1	96.9
2	95.2

Therefore the data on the percentage insoluble can be taken to be within ±1% error.

APPENDIX C

A series of continuously stirred tank reactors (CSTRs).

The Equation 6.5 (quoted below) was used in this thesis to estimate the residence time distribution (RTD) of a series of CSTRs.

$$E(t) = \frac{N^N t^{N-1}}{\bar{t}^N (N-1)} \quad e^{\frac{-Nt}{\bar{t}}} \qquad 6.5$$

where E = exit age distribution
N = number of tanks in series
$\bar{t}$ = mean residence time of the series of tanks
t = time

This can be derived, as shown below.
Consider 1 CSTR

$$E(t) = e^{-Nt/\bar{t}} \qquad C1$$

where $\frac{\bar{t}}{N}$ = mean residence time for one tank

$$\text{Laplace of a function} = \int_0^\infty e^{-st} f(t)\,dt \qquad C2$$

For the exit age distribution of one tank:

$$\text{Laplace transform} = \int_0^\infty e^{-st} \cdot e^{-Nt/\bar{t}}\,dt \qquad C3$$

$$\int_0^\infty e^{-(s + \frac{N}{\bar{t}})t}\,dt \qquad C4$$

$$= \left[- \frac{e^{-(s + \frac{N}{\bar{t}})t}}{(s + \frac{N}{\bar{t}})} \right]_0^\infty \qquad \begin{matrix} C4 \\ C5 \end{matrix}$$

Laplace transform for the E(t) for one tank $= \dfrac{1}{S + \frac{N}{\bar{t}}}$ C6

Laplace transform for the E(t) for N tanks $= \dfrac{1}{(S + \frac{N}{\bar{t}})^N}$ C7

$$\therefore \quad E(t) \text{ for N tanks } = \frac{N^N . t^{N-1}}{\bar{t}^N (N-1)} \quad e^{-Nt/\bar{t}} \qquad \text{C8}$$

Which is the same equation as 6. 5 used in the thesis.

APPENDIX D

D.1 INTRODUCTION

Different reactions were attempted as part of this Project. They can be divided into those between:

1) solids and polymers,
and 2) liquids and polymers.

D.2 REACTIONS BETWEEN SOLIDS AND POLYMERS

Reaction between solids and polymers that were attempted in this project are discussed in this section. These reactions can be divided into those carried out in a CTM, a mill or in solution.

D.2.1 REACTIONS BETWEEN SOLIDS AND POLYMERS ATTEMPTED IN A CTM

The reactions attempted in a CTM between particulate reactants and polymers are described below. The polymer was in strip form in all the experiments summarised in this sub-section unless otherwise stated.

D.2.1.1 Reaction: aluminium isopropoxide and Vamac G. Nov '85

The aluminium salt had to be ground down and was then fed using a vibrating tray.

Process conditions.

Fe = 20 rpm

Throughput of Aluminium salt = 150 to 180 g/hr

When the CTM was at 160°C - reaction was not completed; with the CTM at 200°C - reaction went to completion. When operating the CTM at 200°C, the CTM seized.

The above experiment was repeated (F_e = 20 rpm), the temperature was dropped to 150°C to see if the high temperature, used in the above mentioned experiment, was detrimental to the process operation. The CTM seized again. It had reacted better at 200°C. A pocket of gas produced during this experiment was released through the die.

So, it appears as if at low temperatures, this reaction does not progress as far as it does at higher temperatures; this is not unexpected.

Jan '86
Process Condition

Speed F_e = 30 rpm CTM = 105 rpm
Temperatures F_e = 50°C CTM = 120°C
Power consumption F_e = 0.3 KW hr/kg CTM = 0.35 KW hr/kg
Throughput of rubber = 1.7 kg/hr.
of aluminium salt = 150 g/hr.
Arrangement as shown in Figure 4.2 was used.
The reaction was found not to have gone to completion, according to the solubility test.

Process Condition

Speed F_e = 30 rpm CTM = 102-110 rpm
Temperature F_e = 50°C CTM = 150°C
Power consumption F_e = 0.46 KW hr/kg CTM = 0.74 KW hr/kg
Throughput of rubber = 0.9 kg/hr
of aluminium salt = 180 g/hr
The pressure upstream of the CTM = 500 psi.
Arrangement as shown in Figure 4.2 was used
The product has 27% insoluble material; insolubility being a result of this neutralisation reaction.

Process Condition

Speed F_e = 30 rpm CTM = 100-106 rpm
Temperature F_e = 50°C CTM = 150°C
Power consumption F_e = 0.34 KW hr/kg CTM = 0.34 KW hr/kg
Throughput of rubber = 1.4 kg/hr
of aluminium salt = 720 g/hr
The pressure upstream of the CTM was 950 psi.
Arrangement as shown in Figure 4.2 was used.
Product insolubility was 47%.

This product was heated in an oven at 120°C for three hours, and the insolubility of the product was found to be approx. 40%.

Process Condition

Speed F_e = 30 rpm CTM = 100 rpm
Temperature F_e = 50°C CTM = 150°C
Power consumption F_e = 0.37 KW hr/kg CTM = 0.57 KW hr/kg
Throughput of rubber = 0.85 kg/hr
of aluminium salt = 170 g/hr
The pressure upstream of the CTM was 1000 psi.
Arrangement as shown in Figure 4.2 was used.

The product insolubility was 24%.

Feb '86

Process Condition

Speed F_e = 20 rpm CTM = 100 rpm
Temperature F_e = 50°C CTM = 190°C
Power consumption F_e = 0.2 KW hr/kg CTM = 1 KW hr/kg
Throughput of rubber = 500 g/hr
of aluminium salt = 145 g/hr

The extrudate temperature was 200°C; the pressure upstream of the CTM was 1000 psi.
Arrangement as shown in Figure 4.2 was used.

The product insolubility was 17%.

Process Condition

Speed F_e = 20 rpm CTM = 100 rpm
Temperature F_e = 100°C CTM = 190°C
Power consumption F_e = 0.67 KW hr/kg CTM = 1.42 KW hr/kg
Throughput of rubber = 370 g/hr.
of aluminium salt = 60 g/hr

The pressure upstream of the CTM was 250 to 500 psi.
Arrangement as shown in Figure 4.2 was used.

The product insolubility was found to be 16%.

Assessment of heat treatment downstream of a CTM to complete the neutralisation reaction

The effect of post heating of the reactive mixture was examined. Samples for heat treatment were prepared in an extruder.

Arrangement as shown in Figure 4.2 was used in this experiment.

March '86

Process Condition

Speed F_e = 20 rpm CTM = 100 rpm

Temperature F_e = 50°C CTM = 120°C

Throughput of rubber = 720 g/hr.

of aluminium salt = 85 g/hr

This sample was taken and passed through a heated 2 roll mill (to be referred to as a mill).

The sample taken which had passed through a heated (150°C) mill stuck to the roller. Therefore further samples were taken with the product passing through the mill at lower temperatures.

Mill temperature °C	No. of Passes	% Insoluble Before Milling	% Insoluble after Milling
40	2	67	40
50	1	36	41
60	1	31	84
70	1	60	63
150	2	20	23

The effect of residence time, at elevated temperatures, on reaction conversion

Oven Temperature/°C	Time Span/min	% Insolubility
150	0	9.5
150	1	9.5
150	2	6
150	3	2
200	0	8.5
200	1	3.5
200	3	3.5
240	0	6.5
240	1	0.5
240	2	1.5
240	3	1.5

Observations on aluminium isopropoxide and Va_mac G reaction.

1) It was possible to perform this reaction in a CTM. However once the reaction had progressed to a certain (as yet undefiend) level, the CTM would seize. One explanation for this behaviour could be high viscosity of the quasi-crosslinked product which was only shear labile.
2) The possibility of using the CTM as a mixer with a heated reactor downstream of the CTM could have been further explored, if such a study were of commercial interest. The preliminary experiments carried out in this Project were not successful in demonstrating any useful trends.

D.2.1.2 Reaction: Carboxylated nitrile rubber and aluminium isopropoxide

Dec '85

Mooney viscosity of the aluminium salt of carboxylated nitrile rubber (Krynac 110C) made at Rapra, could not be measured, even at a temperature of 170°C.

Process Condition

Speed	F_e = 25 rpm	CTM = 30 rpm
temperature	F_e = 50°C	CTM = 200°C

Vapour was released from the CTM during this experiment (which was probably isopropanol). This indicated that reaction was taking place in the CTM, the CTM speed fell to 0 rpm. Arrangement as shown in Figure 4.2 was used during these experiments.

Process Condition

The only process parameter altered, compared to the previous run, was the CTM temperature.

CTM temperature = 190°C	CTM speed fell to 0 rpm.
CTM temperature = 235°C	CTM slowed down.

IR spectrum of the product showed that reaction had gone to completion.

The product burnt when the polymer feed was not steady but otherwise, the extrudate did not appear burnt but had reacted.

Jan '86

Process Condition

Speed F_e = 30 rpm CTM = 30 rpm
Temperature F_e = 50°C CTM = 170°C

When the material had reacted in the CTM, the CTM speed of rotation fell to 1 rpm.

D.2.1.3 Reaction: Carboxylated nitrile rubber and magnesium ethoxide

Arrangement as shown in Figure 4.2 was used.

Jan'86

A) Process Condition

Speed F_e = 20 rpm CTM = 25 rpm
Temperature F_e = 50°C CTM = 170°C

When the material in the CTM had reacted, the speed fell to 10 rpm.

B) Process Condition

Speed F_e = 20 rpm CTM = 25 rpm
Temperature F_e = 50°C CTM = 190°C

When the material in the CTM had reacted, the speed fell to 5 rpm.

The product from condition (B) had reacted further than the product made from condition (A). For both (A) and (B), the throughput of rubber was 1 kg/hr and that of Magnesium ethoxide was 120 g/hr.

D.2.1.4 Reaction: Vamac G and magnesium ethoxide

March '86

Process Condition

Speed F_e = 20 rpm CTM = 90 rpm
Temperature F_e = 100°C CTM = 190°C

The CTM speed fell to zero when the material in it started to react.

D.2.2 Reactions carried out on a mill

A mill was used to incorporate reactants into polymers. These reactants could either be liquids or solids. Only reactions where oxygen in the air does not interfere with the desirable reaction should be performed on the mill. Some reactions have been attempted on a mill, as part of the research programme to gain an insight into changes in material properties due to reaction progression.

D.2.2.1 Reaction: Vamac G and aluminium isopropoxide

March '86

113.0 g of Aluminium salt was added to 1730 g of Vamac G. It took two hours to prepare a homogeneously reacted product.

D.2.2.2 Reaction: Krynac 211 and CaH_2

May '86

Krynac 211	222.93 g
CaH_2	11.83 g
Distilled Water	10 ml

This mixture was milled and coded 1605861. Both the flow properties of the product and the IR indicated that reaction was complete .

D.2.2.3 Reaction: Vamac G and magnesium ethoxide April '86

1143.3 g of Vamac and 138.5 g of magnesium salt were mixed together on a mill. The insolubility of the product was 46%.

D.2.2.4 Reaction: EPDM and maleic anhydride October '86

EPDM Keltan 720 (K720)	869.88 g
Cumene hydroperoxide	104.70 g

These ingredients were mixed on a mill and heated for 4.5 hours in an oven set at 70°C.

To 163.6 g of the above mixture (of K720 and peroxide) 12.8 g of maleic anhydride was added.

This mixture with maleic anhydride was heated at 120°C for 2 hours in an oven previously purged with nitrogen.

D.2.3 Reactions in a sigma blade mixer

A Sigma blade mixer (sometimes referred to as a Universal Mixer in the literature) was used to mix either solids or liquids into high viscosity liquid polymers . The mixer used in these experiments had a steam jacket to enable the heating of the reaction mixture. Being a batch process, the reaction was performed to completion.

D.2.3.1 Reaction: Calcium oxide and carboxyl terminated polybutadiene

April '86

HC434	502.20 g
Calcium oxide (CaO)	9.35 g
H_2O	10.8 ml

The materials were mixed for approximately 1.5 hours.

June '86

HC434	1202.22 g
CaO	20.89 g
H_2O	20 ml

The ingredients were mixed in a sigma blade mixer with the steam jacket on (steam pressure was 25 psi which corresponds to 115°C) for 4 hours. It was observed that the mixing action was better when the mixer had 1.2 kg of fluid than 0.5 kg.

D.2.3.2 Reaction: Carboxyl terminated polybutadiene and magnesium ethoxide

June '86

HC434	1060.44 g
Magnesium ethoxide	36.55 g
Ethanol	6 ml

These ingredients were mixed for 17 hours in a sigma blade mixer heated by a steam jacket (steam pressure = 25 psi, steam temperature = 115°C).

April '86

HC434	1001 g
Magnesium ethoxide	35.62 g

The ingredients were mixed for 7 hours.

D.2.3.3 Reaction: CTBNX 13 and CdO

May '86

CTBNX 13	1020.00 g
CdO	80.02 g

The ingredients were mixed for 6 hours in a Sigma blade mixer which was heated by a steam jacket (steam pressure at 25 psi, which corresponds to 115°C).

D.2.3.4 Reaction: CTBNX 13 and CaO

August '86

CTBNX 13	1102.50 g
CaO	38.38 g
H_2O	22.52 g

These ingredients were mixed in a sigma blade mixer without any steam heating. The mixing time was 4.5 hours. The mixture was dry; emulsions were made (as described below) to render the product more useful as a wetting agent for fillers.

September '86

Emulsion 1

CTBNX 13	1108.16 g
CaO	24.37 g
H_2O	28.20 g

These ingredients were mixed in a sigma blade mixer for 6.5 hours.

Emulsion 2

CTBNX 13	1449.06 g
CaO	25.21 g
H_2O	814.7 g

Emulsion 3

CTBNX 13	1260.96 g
H_2O	708.93 g
CaO	21.94 g
Trichloroethane	1849.43 g

D.2.4 Solution reactions

Some reaction experiments were carried out in solution since this method of reaction is often used in the polymer industry.

D.2.4.1 Reaction: Solution grafting of sodium onto nitrile rubber

Jan '86

The nitrile rubber used was N33 C50. Sodium was to be grafted onto the nitrile rubber. The rubber was taken into solution, the solvent used was toluene. Slow distillation of the solution was initiated. Sodium isoproponol in isoproponol was slowly introduced into this solution. The rate at which the sodium salt was introduced was important since the NBR could precipitate, if enough care was not taken.

The solution was distilled and after the reaction had completed (viscosity increased significantly), the solution was poured into trays and the solvent evaporated off in a vacuum oven.

For the above experiment, the reaction mixture contained

NBR	22.90	
Toluene (Analar)	2000	ml
Sodium isoproponol	11.54	g
Isoproponol	100	ml

D.3 POLYMERS AND LIQUIDS

Under this category the reactions carried out can be divided into those in a CTM, a mill or in solution.

D.3.1 Reactions in a CTM

Initially the reactions attempted in the CTM where a liquid reagent was reacted with a polymer melt will be explained. The first few experiments led to modification in design; these results are not used in the summary of results due to the learning process leading to unreliable readings.

D.3.1.1 Injection of oleic acid into a polymer

Polymer in the extruder was K720.

Oct '86
Process Condition

Speed	F_e = 20 rpm	X_e = 60 rpm
Temperature	F_e = 70°C	X_e = 70°C

The stroke length of the pump was set at 1.74 mm which, if the pump was injecting to its full capacity would inject 110 ml/hr. A die with 3 strips was used so that the output could be reintroduced into the extruder. The throughput was 0.8 kg/hr. This material was coded 1310861. A reservoir of liquid was used to feed the pump. However, no injection took place during this experiment due to the excessive air locks in the injection line.

Process Condition

Speed	F_e = 20 rpm	X_e = 60 rpm
Temperature	F_e = 70°C	X_e = 170°C CTM 120°C

The stroke length was 3.48.

Throughput of (K720 + oleic acid + cumene hydroperoxide) 1310861 was 0.67 kg/hr.
The reservoir system was still used and found not to be reliable. A float was placed on the reservoir to calculate the injection rate. This mode of measuring the injection rate was also found not to be satisfactory.

Injection of cumene hydroperoxide into K720 (EPDM)
Oct '86

Pump was set at 4 mm, injector was opening at 300 to 350 psi. Injection was possible but was not easily monitored using the level drop of the float technique.

The pipeline was rearranged with a PTFE lined tubing for the high pressure side to minimise the possible degradation of peroxide.

Injection of liquid was attempted again using the level drop measurements. The importance of the injector setting was assessed.

Injection of oleic acid into EPDM K720

Dec '86

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C; CTM = 200°C
Injection pressure = 250 psi
Three strip die was used.
Injection rate = 210 g/hr.
The stroke length was set at 6 mm.
Sample was coded 1612861.

Injection of cumene hydroperoxide into K720

January '87

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C; CTM = 70°C
Pump setting = 4.0 m
Injection rate = 2.7 g/min
Injection pressure = 300 psi

Arrangement was used as shown in Figure 4.3. Surging of the throughput was noticed.

Injection of cumene hydroperoxide into K720

Process Condition

Speed F_e = 20 rpm X_e = 20 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 70°C
No die was present
Injection pressure = 380 to 280 psi
Pump setting = 3.5 mm
Sample was coded 0901871.

Injection of oleic acid into a previously prepared mixture of K720 and cumene hydroperoxide

Jan '87

The mixture coded 0901871 was introduced into the extruder. 2 g/min of oleic acid was injected into this mixture. The feed extruder was 20 rpm. No die was present during these experiments.
The injection pressure was 250 psi.
The CTM was at 150°C; the extruders were set at 70°C.

Sample	X_e rpm	% Grafting	% Crosslinking
2901871	20	16.7	50
2901872	60	17	50
2901873	40	16	50

Injection of cumene hydroperoxide into K720

Feb '87

Code 0302861 F_e = 20 rpm X_e = 20 rpm
Injection rate = 2.5 g/min
Injection pressure = 250 to 300 psi
Pump setting 3.0 mm

Code 0302862 F_e = 20 rpm X_e = 20 rpm
Throughput 480 g/hr
Injection rate = 1.6-1.8 g/min
Injection pressure = 250 to 300 psi
Pump setting 2.5 mm

This injection was carried out for 5.5 hours and when the CTM was stripped, no obvious crosslinking was observed.

Injection of cumene hydroperoxide and oleic acid into K720

Liquid for injection 93.45 g of Cumene hydroperoxide
+ 300 g of oleic acid.

Process Condition

Speed F_e = 20 rpm X_e = 20 rpm
Temperature F_e = 70°C X_e = 70°C;CTM = 130°C
Pump setting = 3.4 mm
Injection rate = 2.3 g/min
Injection pressure = 250 to 400 psi
Throughput = 740 g/hr

The product had 16% grafting and 50% crosslinking.

The sample was coded 0602871.

Injection of cumene hydroperoxide and oleic acid into K720

Liquid for injection was made up of 93.45 g of the peroxide and 300 g of oleic acid.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C;CTM = 130°C
Throughput of rubber = 710 g/hr
Pump setting = 2.8 mm
Injection rate = 2.5 g/min
Injection pressure = 300 to 1200 psi
Surging was noticed.
This sample was coded 0602872.

D.3.1.2 Injection of acrylic acid into a mixture of EPDM and TBPEH

July '87

A mixture was made of 1 kg of K720 and 1 g of TBPEH on a mill. The extruders and the CTM were filled with this mixture.

Process Condition

Speed F_e = 20 rpm X_e = 40 rpm
Temperature F_e = 70°C X_e = 70°C;CTM = 150°C
Polymer throughput = 0.80 kg/hr.

August '87

A new injection system was introduced. A pressurised vessel was to be used to introduce the liquid to the pump.

Injection of acrylic acid into K720 and peroxide

Throughput = 0.9 kg/hr
Injection rate = 0.8 g/min

Steady injection was obtained.
The sample was coded 0708871.

D.3.1.1 Injection of Acrylic acid and peroxide into K720 August '87

55C CTM was used in all of the following experiments unless stated otherwise.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Throughput rate = 0.5 kg/hr
Injection rate = 0.4 to 0.5 g/min

Steady injection was possible.
The sample was coded 1108871.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 150°C
Throughput rate = 1.15 kg/hr
Injection rate = 90 g/hr
Injection pressure was 100 psi
This sample was coded 2108871.

Injection of acrylic acid into K720 and peroxide
September '87

The old injector was used. A mixture used was made of 99.9% EPDM and 0.1% peroxide.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 70°C
Throughput rate = 0.86 kg/hr
Injection rate = 80 g/hr
This sample was coded 0409871.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 100°C
Throughput rate = 0.93 kg/hr
Injection rate = 90 g/hr
This sample was coded 0409872 .

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 150°C
Throughput rate = 1.06 kg/hr
Injection rate = 100 g/hr
This sample was coded 0409873 .

Injection of a mixture of acrylic acid and peroxide into K720

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 120°C
Throughput rate = 0.80 kg/hr
Injection rate = 110 g/hr
Injection pressure was 400 psi
This sample was coded 0809871.

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm
Temperature F_e = 70°C X_e = 70°C CTM = 180°C
Throughput rate = 0.89 kg/hr
Injection rate = 100 g/hr
Injection pressure was 400 psi
This sample was coded 0809872.

The injector blocked during operation in all these experiments where a mixture of acrylic acid and peroxide was injected.

November '87

The old injector was used to inject 100 parts of acrylic acid and 0.5 parts of TBPEH. The injector was blocked after a short span of operation. When the old injector was used for injecting 100 parts of acrylic acid and 0.1 parts of TBPEH with the CTM heated to 175°C, the injector was blocked again.

The new injector was used to inject 100 parts of acrylic acid and 0.05 parts of TBPEH. However, it also got blocked.

Injection of acrylic acid and TBPEH into T657

Jan '88

Air was blown over the injector to cool it. When the CTM was at 70°C, without the air to cool the injector, the outside of the injector was measured to be at 50°C; with the air cooling the injector, the injector was measured to be at 28°C. The injector was set at 3 mm, the injection rate was 2.8 to 3.0 g/min at a pressure of 200-300 psi. However, the injector was blocked. The sample taken before the injector blocked was coded 2901881.

The hole in the cooling jacket was widened so that more air could go into the jacket to cool the injector further.

Injection of Acrylic acid and TBPEH into T657

Feb '88

55L CTM and the injector with a small internal volume with air cooling, were used during this experiment.

The improved cooling jacket was being used. When the CTM temperature was 80°C, the injector, with the cooling, was at 22°C.

F_e was set at 20 rpm and was checked to be at 18 rpm:
X_e was set at 40 rpm, the CTM temperature was at 105°C, and the injection rate was 2 g/minute.
Sample 0502881 was collected under these conditions.

F_e was set at 20 rpm and was checked to be at 18 rpm.
X_e was set at 60 rpm and was checked to be at 56 rpm.
CTM was set at 105°C, injection rate was 1.7 to 2 g/min.
Sample 0502882 was collected when the throughput was 0.60 kg/hr.

F_e was set at 20 rpm and was checked to be at 18 rpm.
X_e was set at 60 rpm and was checked to be at 56 rpm.
CTM was set at 120°C and the extrudate temperature was 155°C.
Injection rate was 1.8 to 2 g/min. Sample 0502883 was collected when the throughput was 0.6 kg/hr.

The injector did not block during this experiment.

Injection of di-butyl maleate and dicumyl peroxide into EP rubber (C0054)

March '88

55L CTM was used during this experiment.
The new injector with air cooling was used.

A mixture of 10 parts of dibutyl maleate and 1 part of dicumyl peroxide mixture was to be injected.

F_e was set at 20 rpm and was checked to be at 19 to 20 rpm.
X_e was set at 70 rpm and was checked to be at 67 to 69 rpm.
CTM was set at 70°C, the injection rate was 1.8 g/minute at 300 psi. The throughput (of rubber) was 0.50 kg/hr and the extrudate temperature was 150°C. Sample 0203881 was collected under these conditions.

F_e was set at 20 rpm and was checked to be at 19 to 20 rpm.
X_e was set at 100 rpm and was checked to be at 94 rpm.
Injection rate was 2 g/minute at 300 psi.
The throughput (of rubber) was 0.50 kg/hr and the extrudate temperature was at 230 to 240°C when the CTM was set at 150°C. Sample 0203882 was collected under these conditions.

F_e was set at 40 rpm and was checked to be at 34 rpm.
X_e was set at 100 rpm and was checked to be at 95 rpm.
Throughput at these settings was 630 g/hr (when CTM was at 70°C). The injection rate, with the injector set at 2.0 mm, was 1.4 to 1.5 g/min.

The injector opened at about 200 psi and was adjusted so it would open 0.36 mm. The extrudate temperature was 214°C with the CTM set at 150°C. This sample was coded 0303881 and was found to have 80% conversion.

F_e was set at 60 rpm and was checked to be at 50 rpm.
X_e was set at 100 rpm and was checked to be at 95 rpm.

CTM was set at 150°C, and the extrudate temperature was 249°C. The injection rate was 1.75 to 1.85 g/min and the rubber throughput was 1.11 kg/hr. The rest of the equipment set up was as it was for sample 0303881. This sample was coded 0303882 and was found to have 54% conversion.

F_e was set at 60 rpm and was checked to be at 50 rpm
X_e was set at 100 rpm and was checked to be at 95 rpm
The injection rate was now 130 g/hr (2.2 g/min).
The throughput was 1.13 kg/hr.

CTM temperature was set at 150°C and the extrudate temperature was 242°C to 251°C. This sample was coded 0303883 and was found to have 69% conversion.

The jar containing the injecting liquid was refilled during the injection and this operation of refilling the jar was successful.

Injection of bis-tributyl tin oxide into polystyrene allyl alcohol
May '88

Polystyrene allyl alcohol was granulated into a fine powder and fed into an extruder using a vibrating tray feeder. The vibrating tray was used as the independent feeder; bis-tributyl tin oxide was injected just upstream of the CTM. The extruder was kept at 120°C.

55L CTM was used in the experiments described below.

The crosshead extruder speed was set at 90 rpm and was measured to be at 87 rpm.

When the throughput (rubber + liquid) = 1.02 kg/hr
Injection rate = 1.8-2 g/minute
Internal pressure was 32 psi
CTM was set at 120°C
Extrudate temperature was 109 to 116°C.
The sample was coded 2605881.
The reaction conversion was 76%.

When the throughput (rubber + polymer) = 1.0 kg/hr
Injection rate = 1.4, 1.5, 1.6, g/minute
Pump was set at 3 mm
CTM was set at 150°C
Extrudate temperature was 138°C.
Injection pressure was 150 psi
and the internal pressure was 30 psi
The sample taken was coded 2605882.
The reaction conversion was 73%.

When the throughput (rubber + liquid) = 1.02 kg/hr
Injection rate = 1.45 g/minute
Pump was set at 2.9 mm
CTM was set at 120°C
and the extrudate temperature was 116°C.
The sample taken was coded 2605883.
The reaction conversion was 75%.

The other process parameters were similar to that prevalant whilst taking samples 2605881 and 2605882.

When the throughput (rubber and liquid) was 0.9 kg/hr
Injection rate = 1.7 g/minute
CTM was set at 120°C
Extrudate temperature was 115 to 116°C.
Injection pressure was 170 psi and
the internal pressure was 30 psi.
The sample taken was coded 2705881.

When the throughput (rubber and liquid) was 0.8 kg/hr
Injection rate = 2.3 g/minute
CTM was set at 120°C
Injection pressure was 150 to 200 psi and
the internal pressure was 30 psi.
The sample taken was coded 2705882.

The reaction conversion was 100%.

The above sample of 2605883 was placed into the extruder using a vibrating tray and more tin compound was injected into this mixture.

When the throughput of 2605883 was 1.3 kg/hr
Liquid injection rate = 2.3 g/minute
CTM was set at 120°C
Extrudate temperature was 116°C
Injection pressure was 150 psi and
the internal pressure was 30 psi.
The sample taken was coded 2605884.
The reaction conversion was 90%.

D.3.2 REACTION BETWEEN POLYMERS AND LIQUIDS CARRIED OUT ON A MILL

Grafting reactions attempted between liquid reagents and polymers are described in this section. These are mostly either oleic acid grafting reactions or methacrylic acid grafting reaction.

D.3.2.1 Reaction: EP and oleic acid

May '86

EP rubber	188.2 g
Cumene hydroperoxide	21.0 g
Oleic acid	39.7 g

This mixture was heated in an oven at 120°C for 2 hours. This mixture was coded 2805861.

D.3.2.2 Reaction: EP blended with butyl rubber and oleic acid

EP rubber	51.0 g
Butyl rubber	52.5 g

This was blended on a mill. To this, 5.8 g of cumene hydroperoxide was added on a mill. The material was heated in an oven overnight at 70°C. To this mixture, 10.8 g of oleic acid was added, again on a mill. This final mixture was heated in an oven at 120°C for 2 hours, the oven previously purged with nitrogen. This product was coded 3005861.

Reaction: EP blended with high density polyethylene and oleic acid

June '86

EP	42.2 g
HDPE Vistalon	43.4 g

These ingredients were blended on a mill. To this 4.7 g of cumene hydroperoxide was added. This mixture, with the peroxide, was heated in an oven at 70°C overnight. 8.9 g of oleic acid was added to this heated mixture which was then again heated in an oven at 120°C for 2 hours, the oven having been previously purged out with nitrogen. This sample was coded 0306861.

	Description	% insoluble after 6 days	% insoluble after 14 days
EP + HDPE		57	55
1804861		39	36
0306861	EP + HDPE + oleic acid	47	49
3005861	EP + butyl rubber + oleic acid	14	1

Reaction: EPDM and oleic acid

October '86

EPDM Keltan 720	869.9 g
Cumene hydroperoxide	104.7 g

These were mixed on a mill and heated in an oven set at 70°C for 4.50 hrs.

To 101.1 g of the above mixture,
22.9 g of oleic acid was added.

This mixture was then heated to 120°C for 2 hours in an oven previously purged with nitrogen.

D.3.2.3 Reaction: EP and methacrylic acid

April '86

EP (C0054)	297.8 g
Cumene hydroperoxide	33.3 g

These two ingredients were mixed on a mill which was set at 50°C. It took 4 hours to achieve a homogeneous mixture. This mixture was left overnight in an oven set at 70°C.

To this mixture, 19.2 g of methacrylic acid was added on a mill. During this stage, the mill was kept at room temperature. This mixture was heated to 120°C for 2 hours in a sealed oven previously purged with nitrogen.

D.3.2.4 Reaction: Polystyrene (PS) and methacrylic acid

April '86

Polystyrene was plasticised using cumene hydroperoxide

PS	20.04
Cumene hydroperoxide	6.5

These were mixed in a beaker (to plasticise PS) and then milled.

This mixture was left overnight in an oven at 70°C. To this mixture, 4.1 g of methacrylic acid was added. This mixture was then heated to 120°C in an oven previously purged with nitrogen. Some grafting had taken place as seen by the IR spectrum. This compound was coded 2504861.

May 1986

More of the similar material (as 2504861) was made using 273.5 g of PS, 82.2 g of cumene hydroperoxide and 25 g of methacrylic acid. This compound was coded 0605861. 0.29 g mole of acid was grafted on 300 g of 0605861.

D.3.3 SOLUTION EXPERIMENTS BETWEEN SOLIDS AND POLYMERS

Experiments to examine the grafting kinetics of methacrylic acid onto EPDMs were performed. The peroxide used was tertiary butyl per-2 ethyl hexanoate (TBPEH). The EPDM tested was Keltan 720; the diene group on this EPDM was dicyclopentadiene.

A. The mixture was set at 90°C.
The mixture contained:
500 ml toluene
50.06 g of EPDM
0.045 g of TBPEH in 50 ml toluene
7.5 of methacrylic acid in 50 ml toluene

B. The mixture was heated to 92°C.
The mixture contained :
500 ml toluene
49.76 g of EPDM K720
0.051 g of TBPEH in 50 ml toluene
10.051 of methacrylic acid

C. The mixture was heated to 70°C.
The mixture contained:
500 ml toluene
50.016 g of EPDM K720
0.06 g of TBPEH in 50 ml THF
7.47 methacrylic acid in 50 ml THF

D. The mixture was kept at 70°C
The mixture contained:
500 ml THF
49.872 g methacrylic acid in 50 ml of THF
0.052 g of TBPEH in 50 ml of THF

Samples A and B were analysed and grafting of methacrylic acid onto EPDM was noticed.

D.4 RTD

To establish the procedure for determining the residence time distribution, the following experiments were performed.

Nov '88

Attempts were made to inject a solution of dye using a hypodermic needle into the polymer melt but this was not possible with the 3 strip die downstream of the CTM. When the die was removed, injection of the dye was possible. Following RTD experiments were carried out without a die downstream of the CTM.

RTD Experiments without a die

Nov '86

A - $F_e = 20$ rpm $X_e = 60$ rpm
C - $F_e = 20$ rpm $X_e = 40$ rpm
D - $F_e = 20$ rpm $X_e = 80$ rom
E - $F_e = 20$ rpm $X_e = 20$ rpm

Attempted to describe the RTD curve using:

1) The time lapse between when the first signs of the die appeared and the peak level.
2) The time lapse between when the peak level of dye and the last sign of dye appeared.

December '86

A colour meter made by Minolta was examined to assess its usefulness in measuring colour concentration in rubber. It was found that it was not a reliable means of measuring dye levels in rubber.

A sample of the data obtained using the Minolta colour meter on granular samples of rubber is given below.

Sample	Attempt	Y	x	y
1	1	17.97	0.3258	0.3339
	2	16.84	0.3266	0.3339
	3	18.16	0.3254	0.3332
2	1	16.37	0.3420	0.3541
	2	16.23	0.3390	0.3500
	3	16.33	0.3394	0.3510
3	1	15.98	0.3503	0.3626
	2	15.86	0.3522	0.3646
	3	17.48	0.3464	0.3587
4	1	18.06	0.3587	0.3709
	2	18.08	0.3600	0.3727
	3	19.84	0.3607	0.3733
5	1	18.49	0.3634	0.3739
	2	19.39	0.3657	0.3765
	3	16.70	0.3685	0.3783
6	1	18.60	0.3677	0.3754
	2	17.83	0.3698	0.3785
	3	17.84	0.3687	0.3774
7	1	15.53	0.3874	0.3877
	2	15.92	0.3890	0.3880
	3	14.99	0.3866	0.3871
8	1	15.95	0.3986	0.3945
	2	15.94	0.3974	0.3937
	3	15.87	0.3801	0.3785
9	1	16.62	0.4027	0.3963
	2	15.28	0.4005	0.3932
	3	17.07	0.4046	0.3970

The variables Y, x and y describe the co-ordinates describing the colour. The variation in these values for the same sample demonstrates that a Minolta colour meter was not useful for quantifying colour in rubber samples obtained during RTD runs.

An RTD run was carried out without a CTM. This was to assess if any material was flowing backwards from the CTM. All the dye appeared in the outlet in the first 10 seconds.

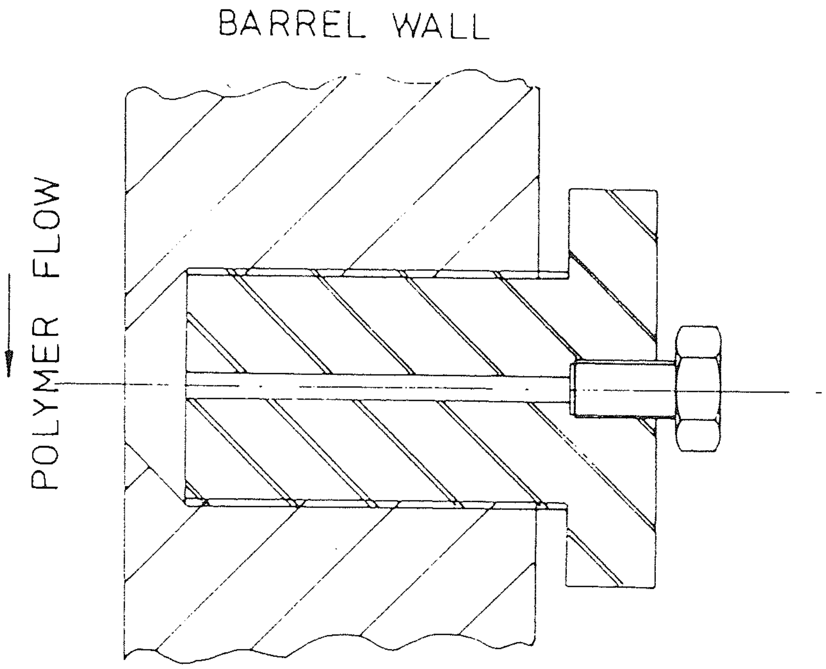
Another RTD with:

F_e = 38 rpm and X_e = 60 rpm.

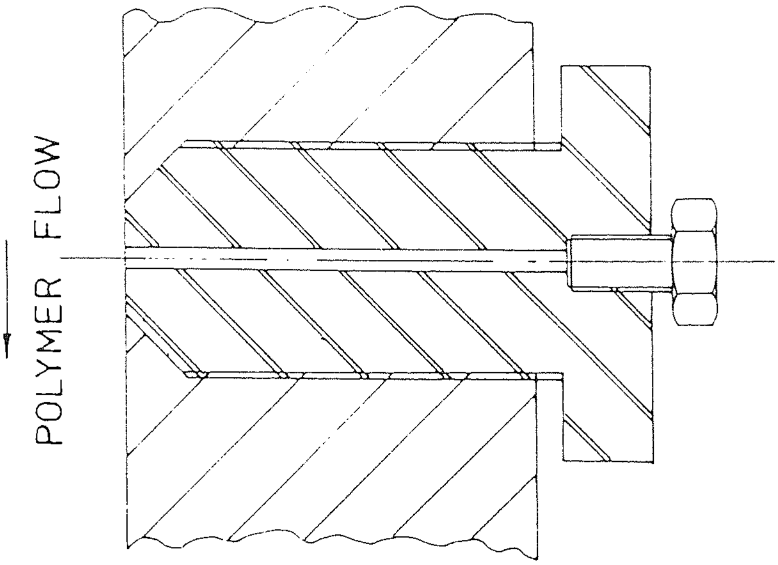
The throughput at this setting was 1.38 kg/hr.

The injection port for injection dye during RTD was modified so that the port comes flush with the wall of the extruder.

D.1 Before



D.2 The improved Design



BARREL WALL

The pressure upstream of the CTM was measured using a pressure transducer.

Without a die	500 psi
With a 3 strip die	800 to 1200 psi

Jan '87

RTDs were obtained with K720; the temperatures of all zones were set at 70°C.

Series G	F_e = 20 rpm and	X_e = 70 rpm
Series H	F_e = 38 rpm and	X_e = 70 rpm
Series J	F_e = 20 rpm and	X_e = 40 rpm
Series K	F_e = 38 rpm and	X_e = 40 rpm

RTDs with K720

Feb '87

Series	F_e rpm	X_e rpm	CTM
T	20-22	40	55C
S	20-22	60	55C
V	20-22	70	55C
W	38	40	55C
X	38	60	55C
Y	38	70	55C
Z	20-22	60	55C
2	20	60	110C
4	20	40	110C

Some of the standards were analysed by IR for confirmation.

May '87

More RTD work was done with K720 and with the 55L CTM.

Series 7 F_e = 20-22 rpm X_e = 40 rpm
Series 8 F_e = 20-22 rpm X_e = 60 rpm

Sep '87

RTD to account for all of the dye

Series AA: The dye was injected into a CTM and all the traces of dye, in the injector and inside the CTM, were retained to account for all of the dye.

F_e = 20-22 rpm X_e = 60 rpm
Throughput = 0.80 kg/hr

All the dye was accounted for:

0.45 ml of the dye entered the CTM
0.55 ml left in the syringe

Oct '87

A new experimental procedure for the RTD work was designed. High pressure gas from a cylinder was used to push the dye into the CTM.

This design modification was used in the RTD work to follow.

RTD for the 55C CTM with the injector opening 0.17 mm

The injector was only opened for approximately 1 second. As soon as dye started to enter the CTM, the nitrogen pressure was reduced.

Series	F_e rpm	X_e rpm	Throughput kg/hr
14	20	60	0.94
17	20	40	0.91

It was noticed that the pressure had to be applied for longer (5 seconds) time periods to ensure that enough dye entered the CTM. In the experiments to follow, the gas pressure was kept on for 5 seconds.

RTD of EP C0054

March '88

An attempt was made to inject 1 ml of dye, into EP with the F_e set at 40 and checked at 34, X_e set at 100 and checked at 97 rpm. The CTM temperature was set at 150°C and the extrudate temperature was 220°C. However the dye could not be seen in the extrudate (because EP C0054 was green) and hence the experiment was ignored.

RTD runs with K720 with 55C

	Q	F_e		X_e		P
	kg/hr	rpm		rpm		psi
		Set	Measured	Set	Measured	
Ph1	0.79	33	30	48	46	700 to 800
Ph2	0.73	33	30	60	57	450 to 550
Ph3	0.85	33	30	70	68	350 to 500
Ph4	0.85	35	30	80	75	300 to 450
Ph5	0.75	33	30	90	85	200 to 200
Ph6	0.78	34	30	100	94	200 to 300
Ph7	0.80	33	30	110	102	200 to 300
Ph8	0.89	34	30	116	107	150 to 250

GENERAL

Some experiments were attempted with the different equipment set-ups used.

Arrangement

The crosshead arrangement, with the CTM on the crosshead was arranged. This experiment was carried out with SBR rubber to examine if there were any obvious faults with the assembly. A rod die was present during these experiments and the extruders were set at 50°C.

SBR rubber was cut into strips and it was found that the shape and size of the rubber were critical in avoiding feed problems.

The assembly was tested using polyethylene; the throughput to feed extruder speed relationship for the equipment set-up shown in Figure 4.2 is given below:

Speed of Extruder rpm	Q kg/hr
18	1.48
22	1.53
30	2.05
35	2.38
40	2.59
45	3.12
50	3.36
55	3.66
60	4.03
65	4.32

The effect of crosshead extruder speed on throughput

Vamac G was used in these experiments.

F_e rpm	X_e rpm	Q kg/hr
20	2	leak at the crosshead
20	8	leak at the crosshead
20	10	1.30
20	10	1.24
20	20	1.29
20	30	1.31
20	40	1.29
20	50	1.30
20	60	1.33
20	70	1.29
20	80	1.34

Throughput for Vamac G No die present.

F_e rpm	X_e rpm	Q kg/hr
20	40	1.20
20	60	1.23
20	70	1.25
20	70	1.19
38	40	2.37
38	40	2.36
38	60	2.41
38	70	2.34

Throughput for K720 No die present.

F_e rpm	X_e rpm	Q kg/hr
20	20	0.41
20	40	0.44
20	60	0.44
20	70	0.43
38	20	0.97
38	40	0.90
38	60	0.85
38	70	0.92

Effect of feed form on throughput; polymer used was K720; the extruders were set at 70°C, and the CTM was set at 200°C.

F_e rpm	X_e rpm	Q kg/hr	Material Form
20	20	0.49	Strip
20	60	0.63	Strip
20	20	0.42	Granules
20	60	0.50	Granules

The volume of the 55L CTM is 67 ml and of 110C CTM is 58 ml when filled with proponal. This volume was measured again to include only the regions that are used, i.e. excluding the entry and exit zones. This measurement gives the volume of 53.2 ml for 55L CTM and 43.6 ml for 110C CTM.

<u>The throughput measurements for 55L CTM with K720</u>

F_e rpm	X_e rpm	Q kg/hr
20	40	0.480
20	40	0.657
20	40	0.627
20	40	0.450
20	40	0.676
20	60	0.867
20	60	0.921
20	60	0.732
20	60	0.732
20	70	0.731
20	70	0.873
20	70	0.776
20	70	0.776
38	40	1.496
38	40	1.567
38	40	1.567
38	60	1.631
38	60	1.361
38	60	1.361
38	70	1.475
38	70	1.454
38	70	1.454

The throughput measurements with the 110C CTM and Keltan 720

F_e rpm	X_e rpm	Q kg/hr
20	40	0.90
20	40	0.79
20	40	0.69
20	60	1.00
20	60	0.76
20	60	0.97
20	70	0.99
38	40	1.87
38	40	1.36
38	40	1.13
38	60	0.91
38	60	1.35
38	60	1.50
38	60	1.38
38	70	1.0

The throughput measurements with the 55C CTM and Keltan 720

F_e rpm	X_e rpm	Q kg/hr
20	40	0.91
20	40	0.93
20	40	0.46
20	60	0.87
20	60	0.58
20	60	0.47
20	70	0.88
20	70	0.60
20	70	0.45
38	40	1.30
38	40	1.30

F_e rpm	X_e rpm	Q kg/hr
38	40	1.80
38	60	1.38
38	60	1.51
38	60	0.82
38	70	1.37
38	70	1.01
38	70	1.84

General Background

The liquid loss due to pump injection was calibrated using white spirit. But this kind of calibration was found not to be reliable.

Liquid tested was oleic acid.

Stroke length mm	Measured Q ml/hr	Q from calibration ml/hr
0.8	27	10.5
0.8	22	18
0.8		
6.0	300	350
6.0	280	335

From the limited data presented above, it appears as if the calibration was more accurate for high injection rates than for low injection rates.

A syphon was used instead of the reservoir.

Stroke length mm	Injection pressure psi	Injection rate kg/hr
5.0	100	0.288
5.0	800	0.150
5.0	800 to 600	0.372
6.5	700 to 200	0.180
6.5	800	0.138

Still testing the injector setting. Polymer entered the injection during this test run.

Injection of xylene into K720 was attempted with a tight injector so that injector did not open further than the lip of the injector.

Stroke length mm	Injection pressure psi	Injection rate kg/hr
5.0	350 to 600	0.180
5.0	500 to 650	0.050 Didn't open
5.0	500 to 600	0.114
5.0	300 to 650	0.084
5.0	600 to 400	0.228
6.0	800 to 700	0.036

Polymer did not enter the injector.

Injection of xylene into K720

Dec '86

Process Condition

Speed F_e = 20 rpm X_e = 60 rpm

Temperature F_e = 70°C X_e = 70°C CTM 70°C

Another injection of xylene into K720 with the rounded hexagonal piece. All the experiments previously carried out were with the hexagonal piece. All the extruders were set at 70°C.

Stroke length mm	Injection pressure psi	Injection rate of Xylene kg/hr
5.0	650 to 550	0.114
5.0	650 to 550	0.120
6.0	650 to 600	0.186
6.0	520 to 650	0.138
6.0	580 to 650	0.174
6.0	580 to 680	0.180

Injection of xylene into EPDM (T657)
Jan '87

Process condition

Speed F_e = 20 rpm X_e = 40 rpm
Temperature F_e = 70°C X_e = 70°C CTM 70°C

The stroke length of the plunger pump was set at 7.7 mm.

This experiment was trying to establish during start-up the relationship between the injection rate and pressure .

Jan '88

Injection rate g/min	Injection Pressure psi
3.4	150
1.0	200 to 300
1.0	150 to 200
2.5	150
3.15	150
3.15	250 to 200
1.35	200

Dec '86

Determination of the half life of the Cumene hydroperoxide into K720

Milled 511.82 g of K720 and 87.74 g of 70% pure cumene hydroperoxide together.

It took three hours to achieve a homogeneous mixture; the sample was coded 1012801.

Monsanto traces were used to determine the half life of the peroxide, in a polymer matrix, at different temperatures.

Temperature °C	Half life minutes
150	18
160	17
165	12
165	12
170	6
180	3
190	1
193	1
195	1
200	1

The half lives quoted in technical literature for cumene hydroperoxide in chlorobenzene using differential thermal analysis (DTA) are listed below

Temperature °C	Half life minutes
140	1380
150	600
160	330
170	144
180	66
188	60
215	10
220	7
225	5
230	4
255	1

There is an obvious difference in the half lives quoted in the literature and the measured values. The measured half lives listed in the table are always lower than those quoted in literature. This implies that any reaction times estimated would be on the safe side in that if the half lives quoted in the literature are used to calculate the number of half lives spent by an initiator in a reactor, the actual number of half lives the initiator spends in the reactor will be greater. This provides a safety margin in design; hence it was concluded that the half lives quoted in literature could be used during reactor design.

APPENDIX E : FLOW PROPERTIES OF SOME POLYMERS.

In this appendix, the rheological data used in this thesis is collated. The information in the Table below was taken from trade literature.

Product	Rheological data.
polystyrene allyl alcohol RJ 100	8 x 10^4 cps at 120C.
Vamac G	ML(1+4) at 100 C= 16 + 3
Keltan 720	ML(1+4) at 125 C = 63
Dutral C0054	ML(1+4) at 100 C = 43.

The specific gravities of some of these polymers are listed below.

Polymer	Specific gravity
Vamac G	1.03
Keltan 720	0.86

The capillary rheometer data for Vamac G and an aluminium salt of Vamac G are given in Figures E1 and E2 respectively. Both the Figures show the pseudoplastic behaviour inherant to polymer melts but the aluminium salt of Vamac G has a melt viscosity that is more strongly dependent on shear rate than Vamac G. And the viscosity of the aluminium salt at low shear rates is higher than that of Vamac G. These features demonstrate the quasi-crosslinking in the aluminium salt.

Figure E1 : The viscosity of Vamac G as a function of shear rate at 70 C.

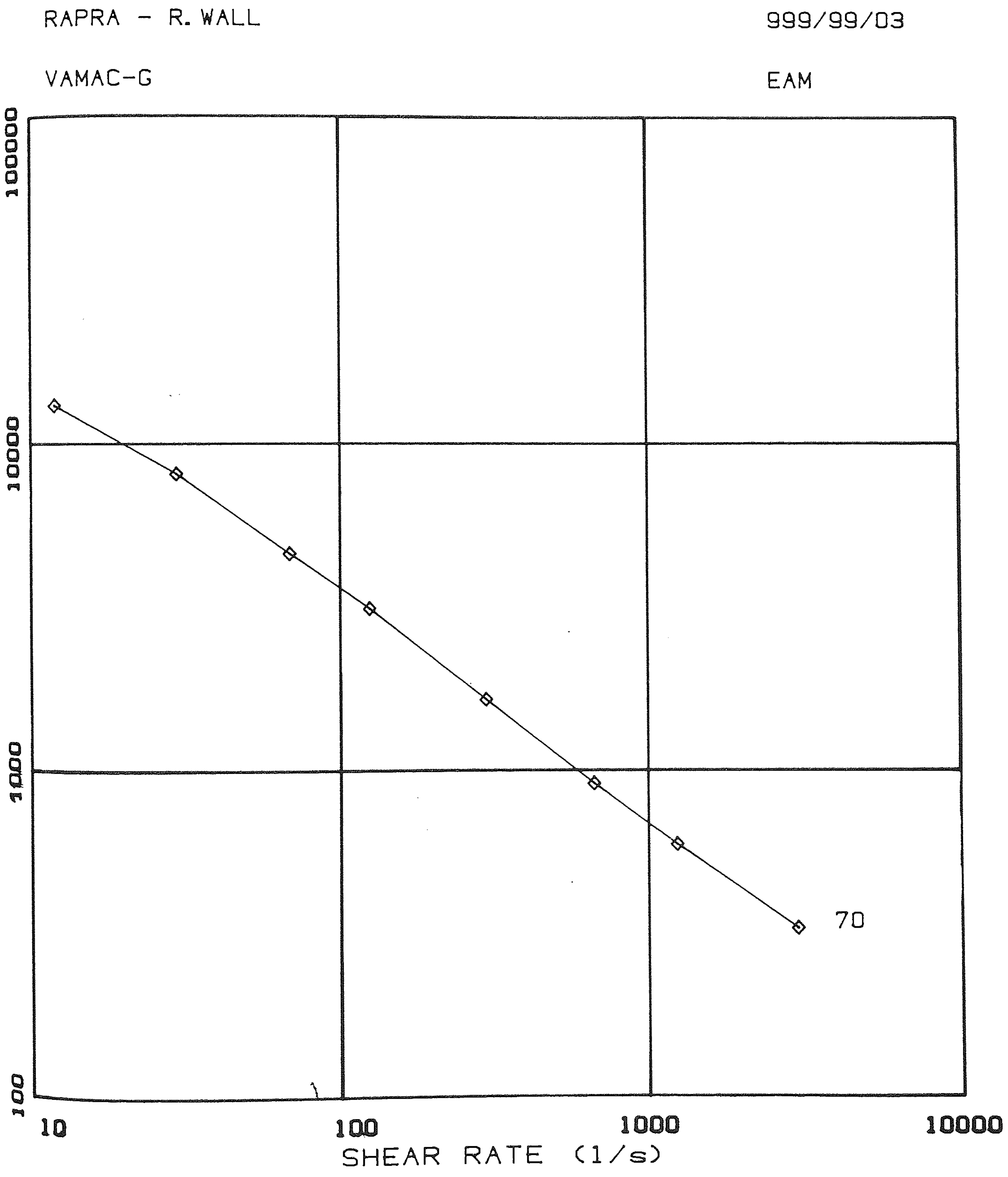


Figure E2 : The apparent viscosity of the aluminium salt of Vamac G as a function of shear rate.

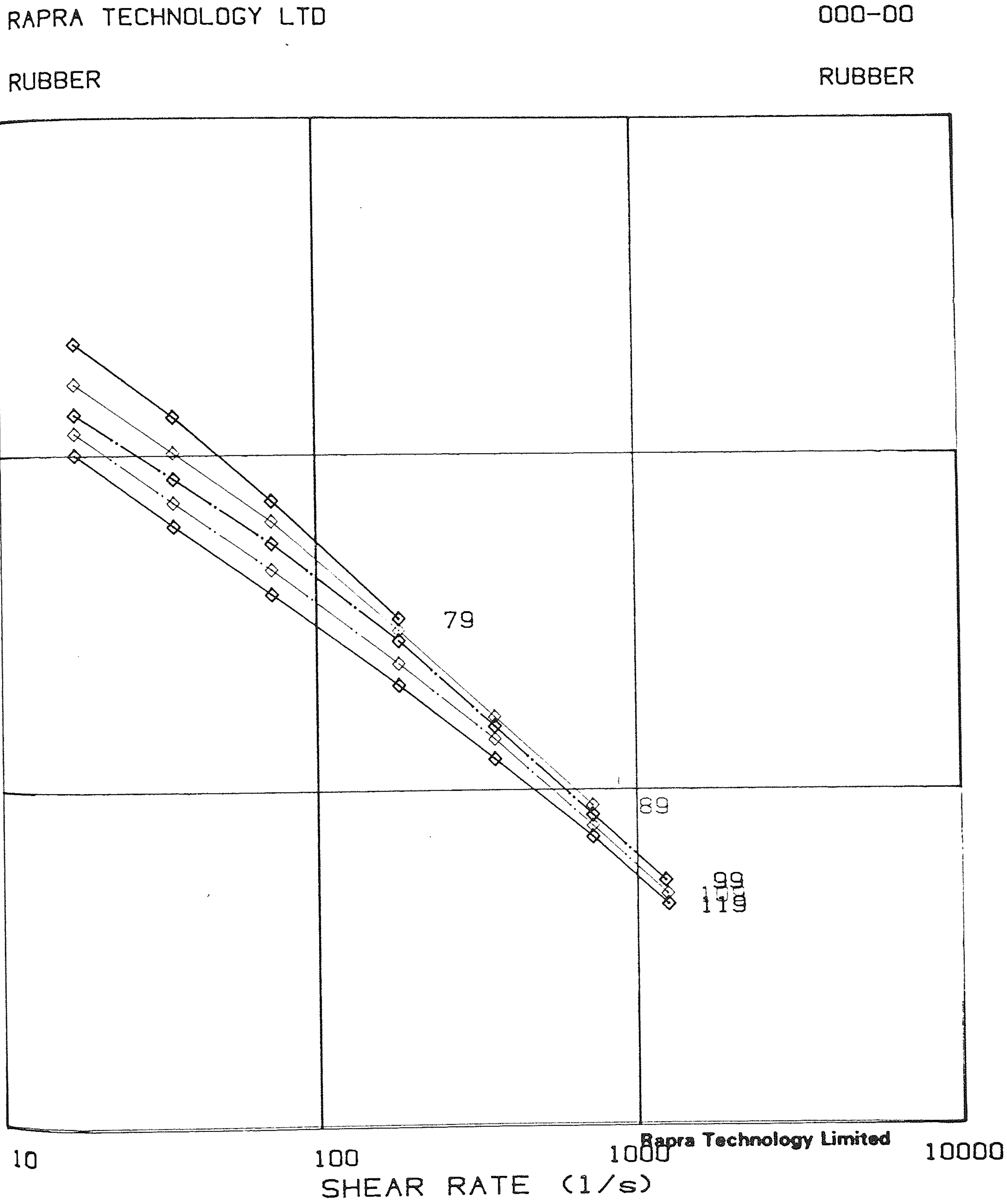


Figure E3 : The apparent viscosity of Keltan 720 as a function of shear rate.

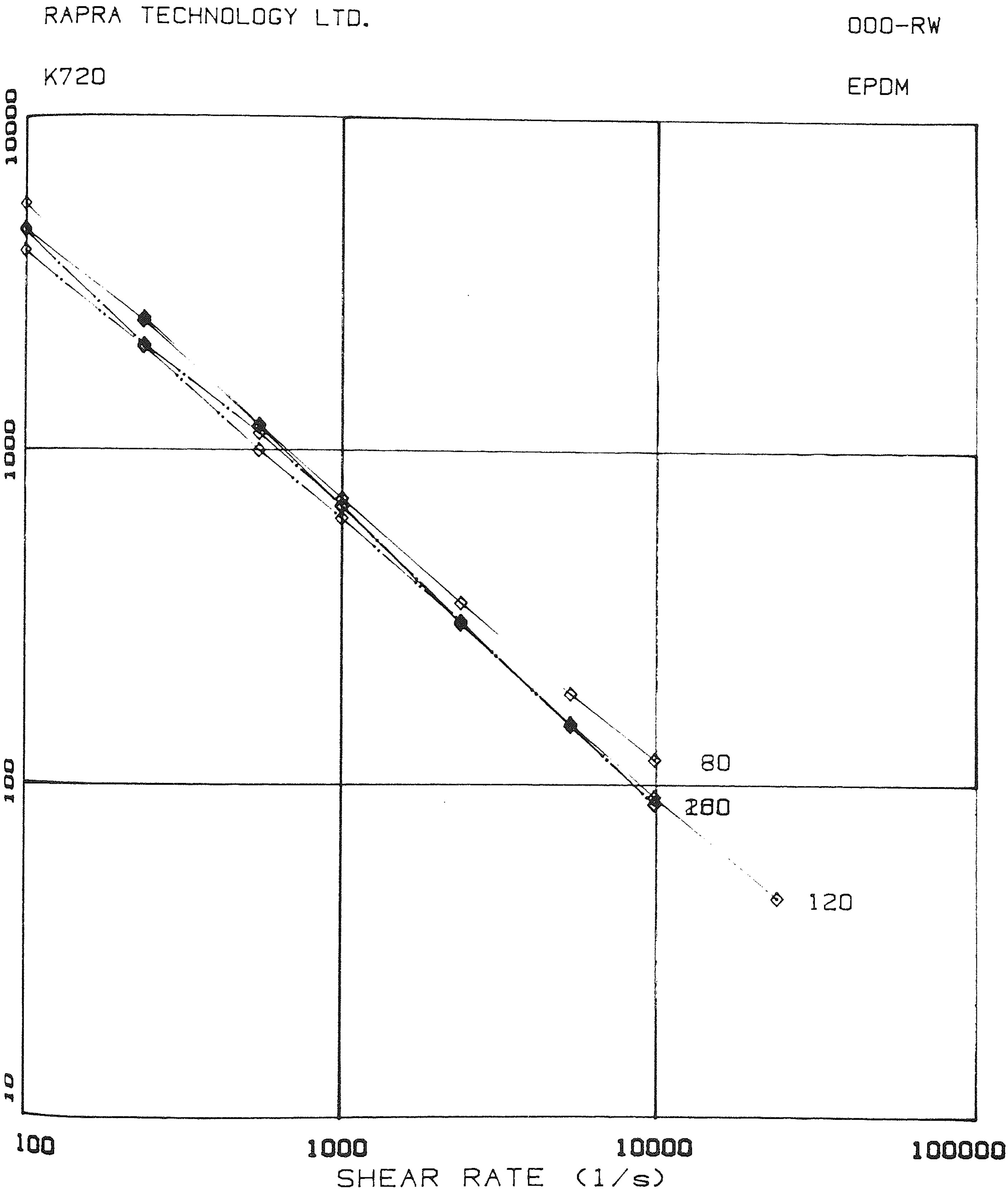
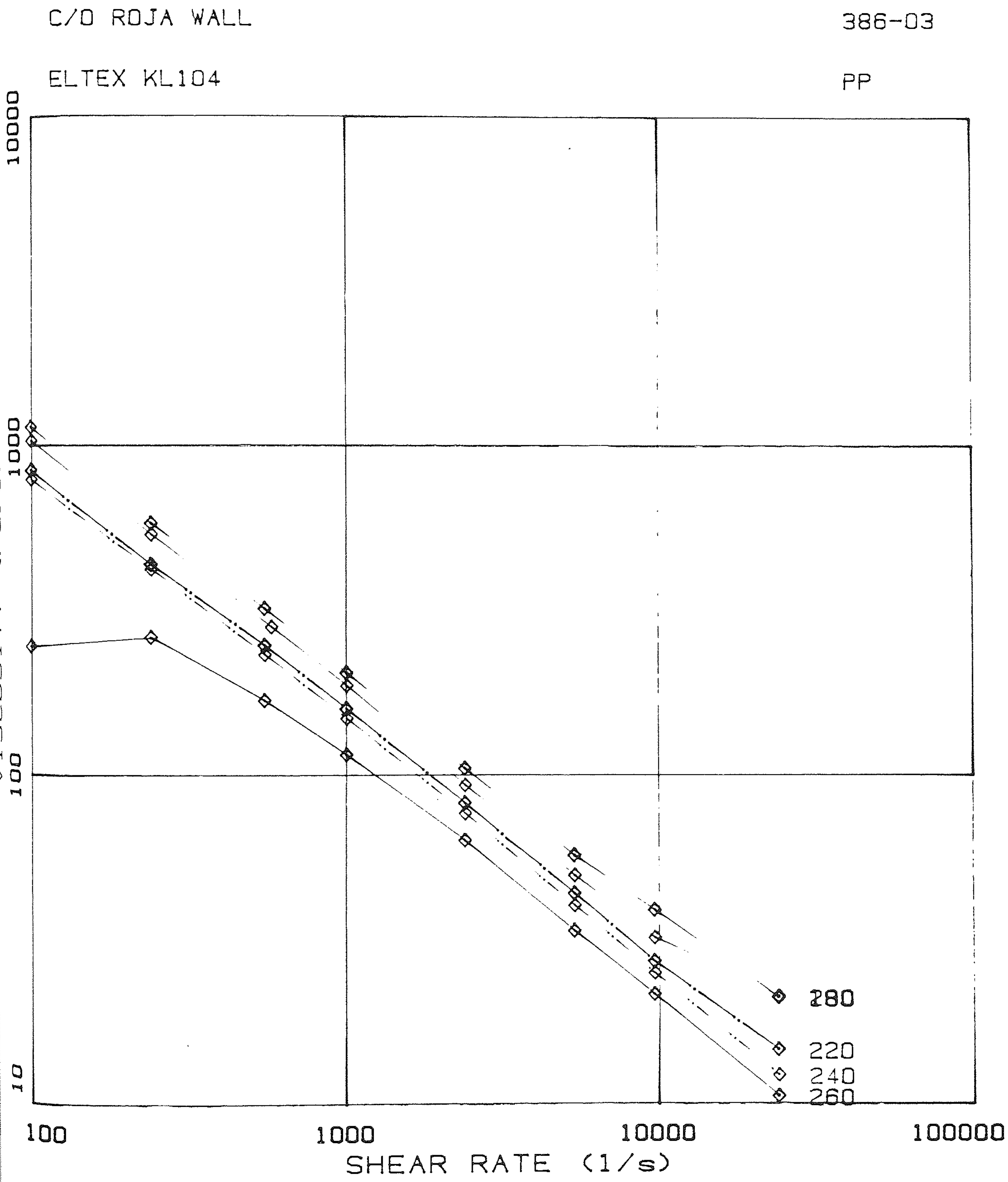


Figure E4 : The apparent viscosity of Eltex KL 104 (PP) as a function of shear rate.



APPENDIX F

Measurement of Peroxide Half Lifes

It is known that the matrix into which the peroxide is introduced influences its half life. To examine how important this effect may be, the half life of cumene hydroperoxide was examined at different temperatures (between 150 to 200°C), in Keltan 720. The method used is outlined in Bulletin PRC-10 published by Hercules Peroxides. The method used compensates for sample heat-up time. The half life was estimated using the procedure described in the bulletin and which is outlined below:-

1) A Monsanto oscillating disk rheometer (ODR) trace was obtained for the "curing" mixture at the required temperature.

2) The $\log_{10} \Delta$ torque (torque infinity - torque) at time t was plotted versus time t. The gradient of this plot (m) was measured.

3) The half life ($t1_{/2}$) was calculated from

the equation below:

$$t1_{/2} = \frac{-0.301}{m} \qquad \text{F1}$$

The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 150°C

Table F1

Temperature =150°C

time/minutes	delta T	log$_{10}$ delta T
64	0	
60	.25	-.602060
50	1.5	.1760913
55	.75	-.124939
45	2	.3010300
41	2.5	.3979400
37.5	3	.4771213
30.5	4	.6020600
33.5	3.5	.5440680
27	4.5	.6532125
21	5.5	.7403627
24	5	.6989700
18.5	6	.7781513
15.5	6.5	.8129134
13.5	7	.8450980
11	7.5	.8750613
9	8	.9030900
7	8.5	.9294189
4.5	9	.9542425
3	9.25	.9661417

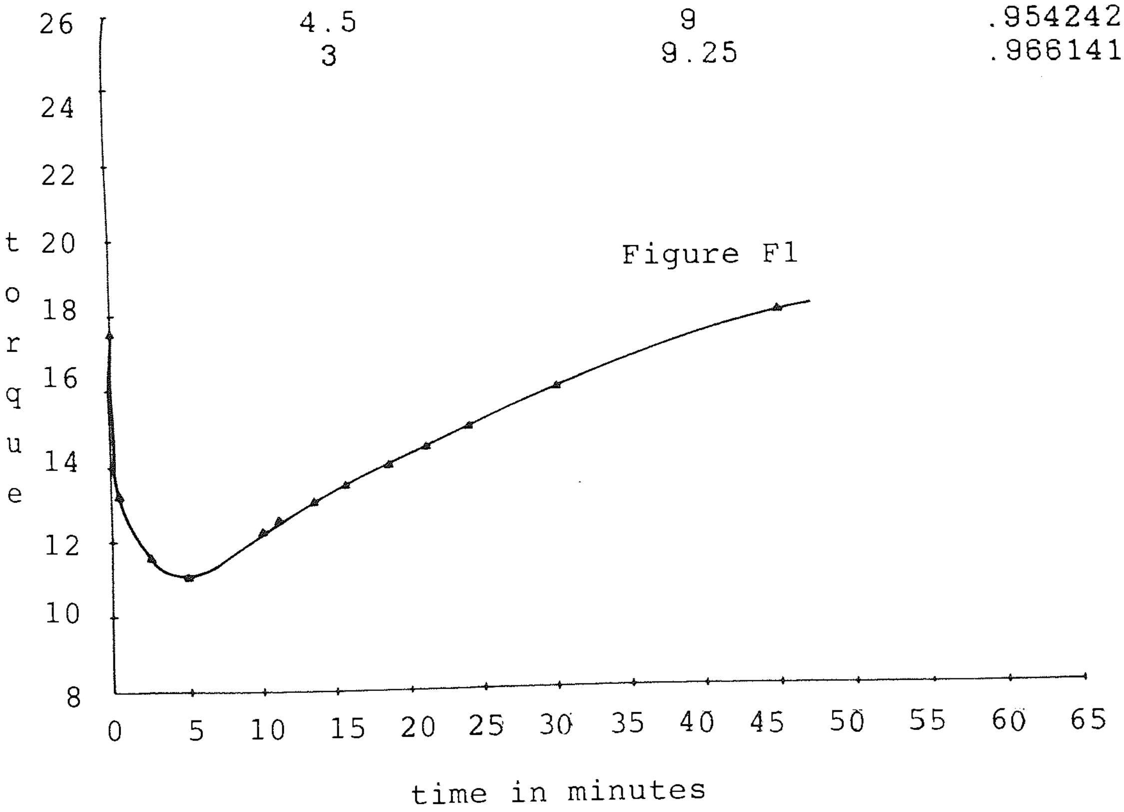


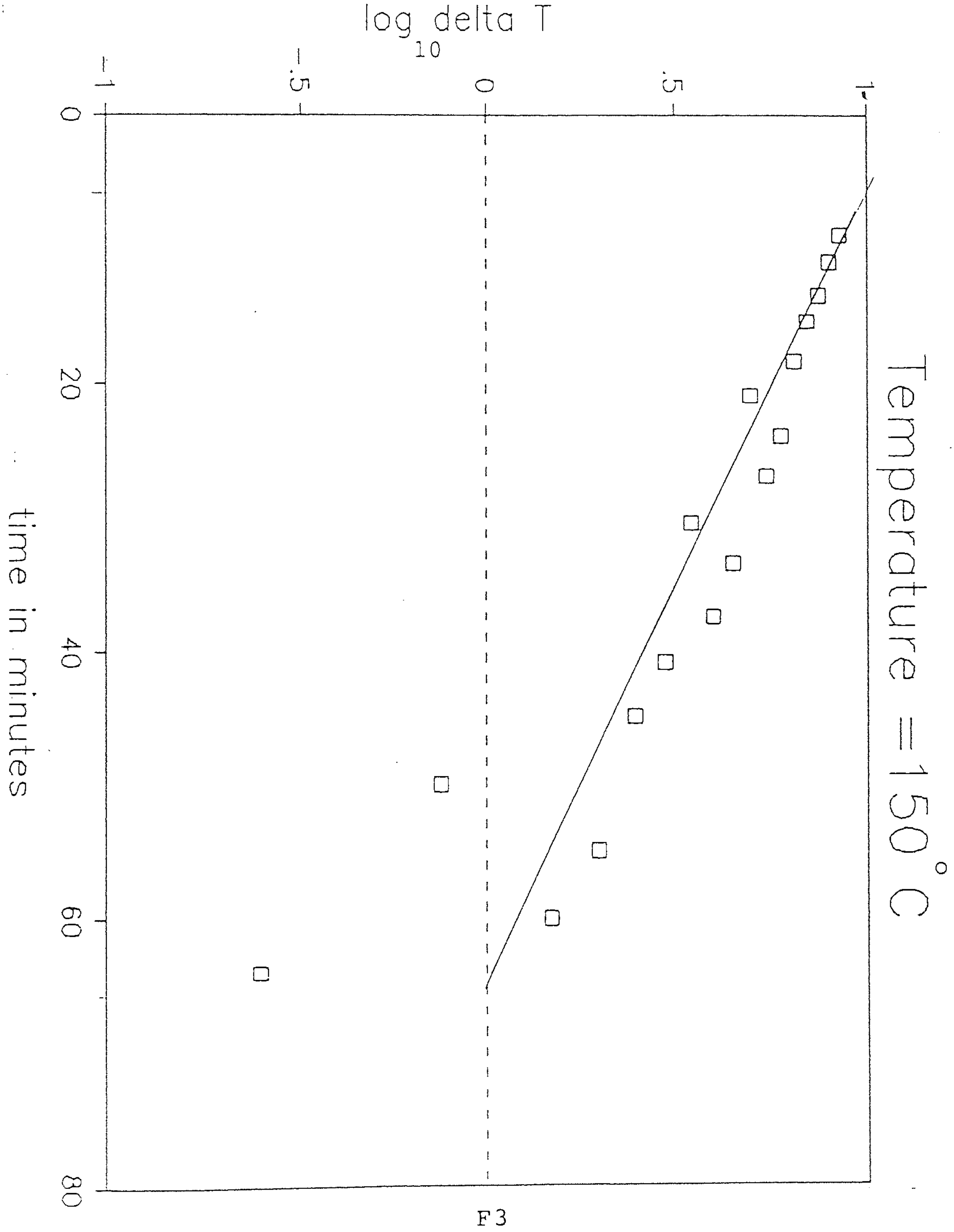
Figure F1

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 150°C.

Gradient of the line = -0.016

$\therefore$ The half life at this temperature is 18 minutes

Figure F2



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 155°C

Table F2

Temperature =155°C

time/minutes	delta T	log$_{10}$ delta T
50.5	.5	-.301030
46.5	1	0
42.5	1.5	.1760913
38	2	.3010300
35.5	2.5	.3979400
32.5	3	.4771213
29.5	3.5	.5440680
26.5	4	.6020600
23.75	4.5	.6532125
21	5	.6989700
18	5.5	.7403627
16.5	6	.7781513
14.5	6.5	.8129134
12.5	7	.8450980
11	7.5	.8750613
8.5	8	.9030900
8	8.5	.9294189
4.5	9	.9542425
3	9.25	.9661417

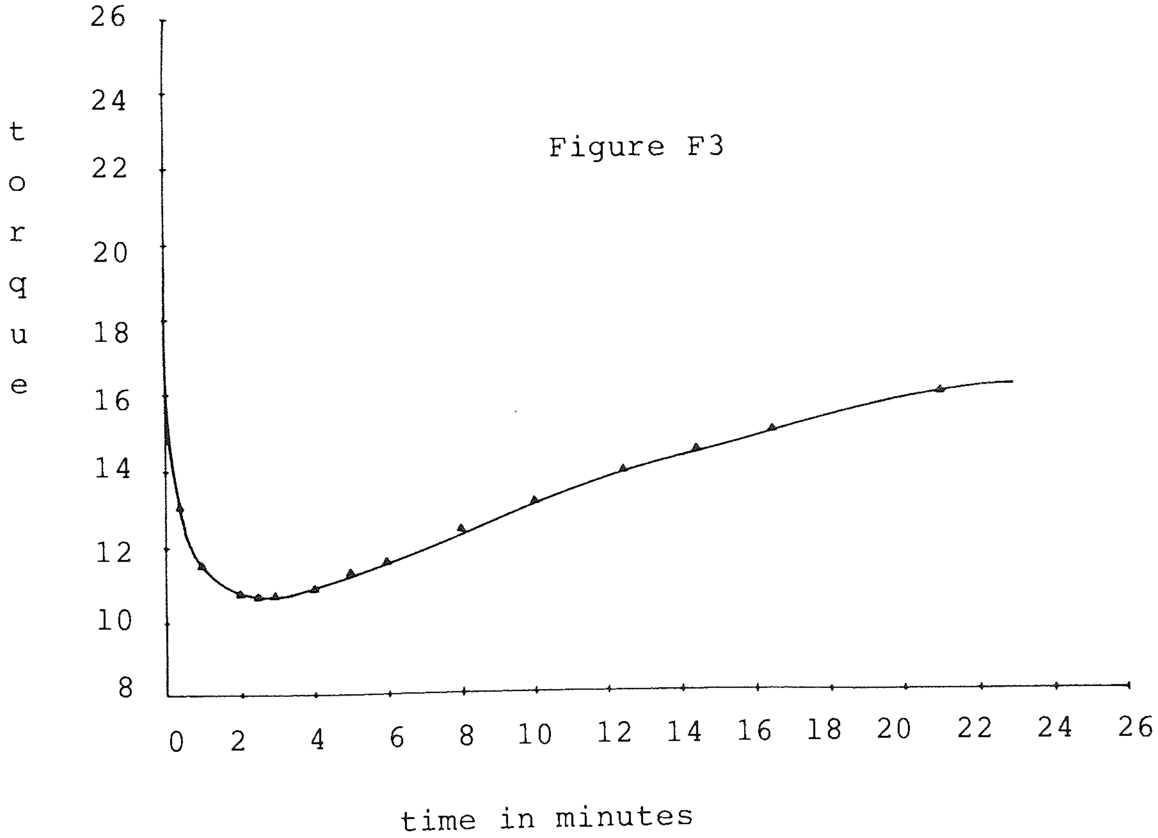


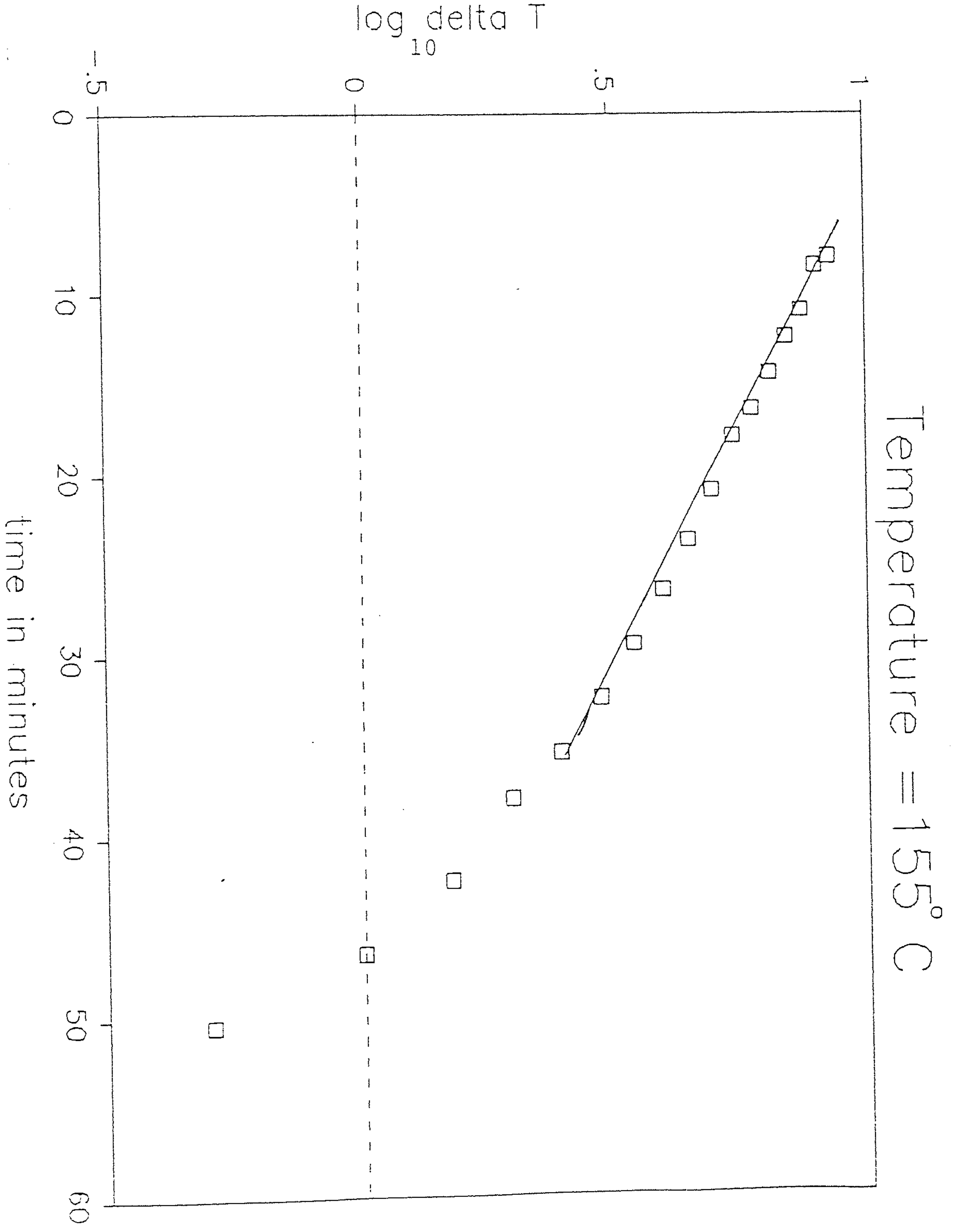
Figure F3

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 155°C.

Gradient of the line = -0.018

$\therefore$ The half life at this temperature is 17 minutes.

Figure F4



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 160°C.

Table F3

Temperature=160 °C

time/minutes	delta T	log$_{10}$ delta T
42.5	0	
39	.5	-.301030
35	1	0
32.5	1.5	.1760913
29.5	2	.3010300
27	2.5	.3979400
24.5	3	.4771213
22.1	3.5	.5440680
20	4	.6020600
18	4.5	.6532125
16.25	5	.6988700
14.5	5.5	.7403627
13	6	.7781513
11.5	6.5	.8129134
10	7	.8450980
8.5	7.5	.8750613
7.25	8	.9030900
6	8.5	.9294189
5	9	.9542425
4	9.5	.9777236
2.5	10	1

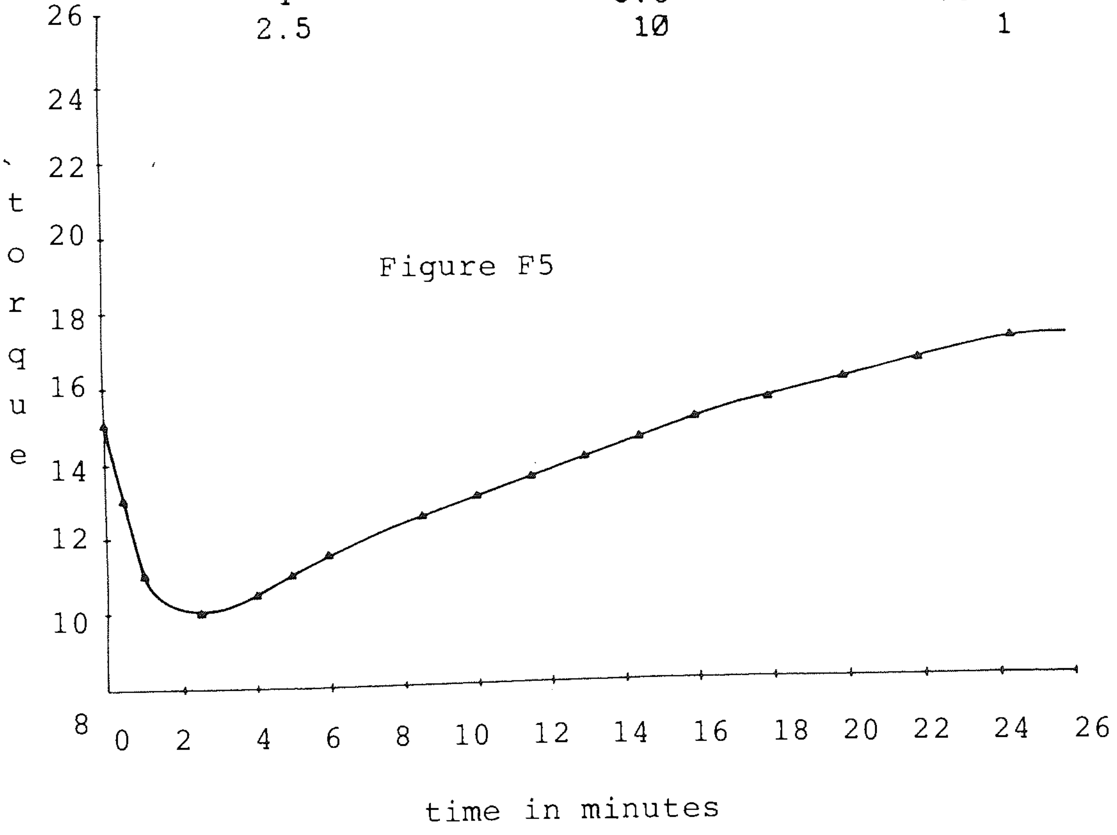


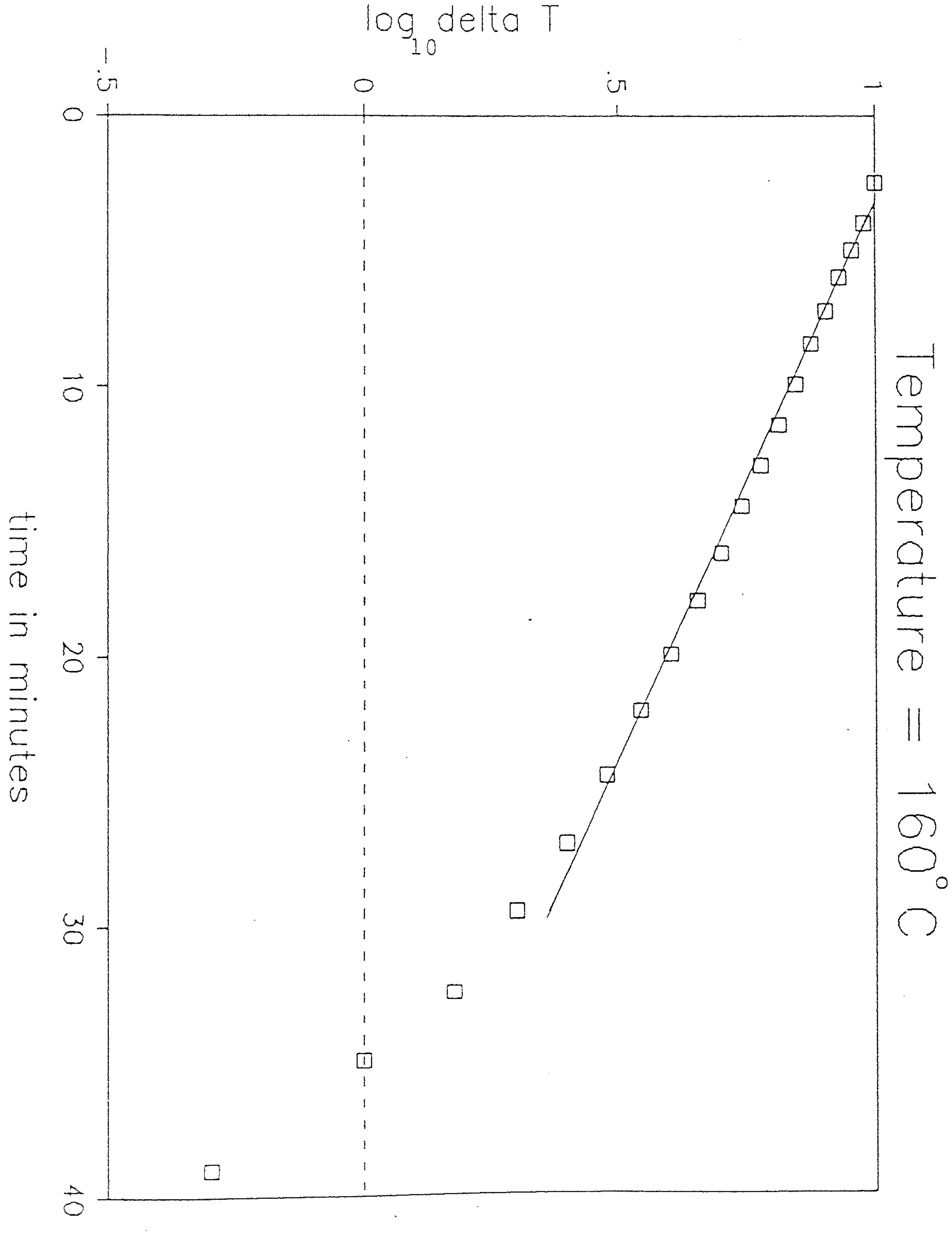
Figure F5

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 160°C

Gradient of the line =-0.025

∴ The half life at this temperature is 12 minutes.

Figure F6



The Monsanto trace used to determine the half life of cumene hydroperoxide at 165°C

Table F4

Temperature=165°C

time/minutes	delta T	$\log_{10}$ delta T
42	.5	-.301030
38	1	0
34	1.5	.1760913
31	2	.3010300
28	2.5	.3979400
25	3	.4771213
22.75	3.5	.5440680
20.5	4	.6020600
18.5	4.5	.6532125
16.5	5	.6989700
15	5.5	.7403627
13.25	6	.7781513
11.75	6.5	.8129134
10.25	7	.8450980
9	7.5	.8750613
7.75	8	.9030900
6.5	8.5	.9294189
5.5	9	.9542425
4.75	9.5	.9777236
3.6	10	1

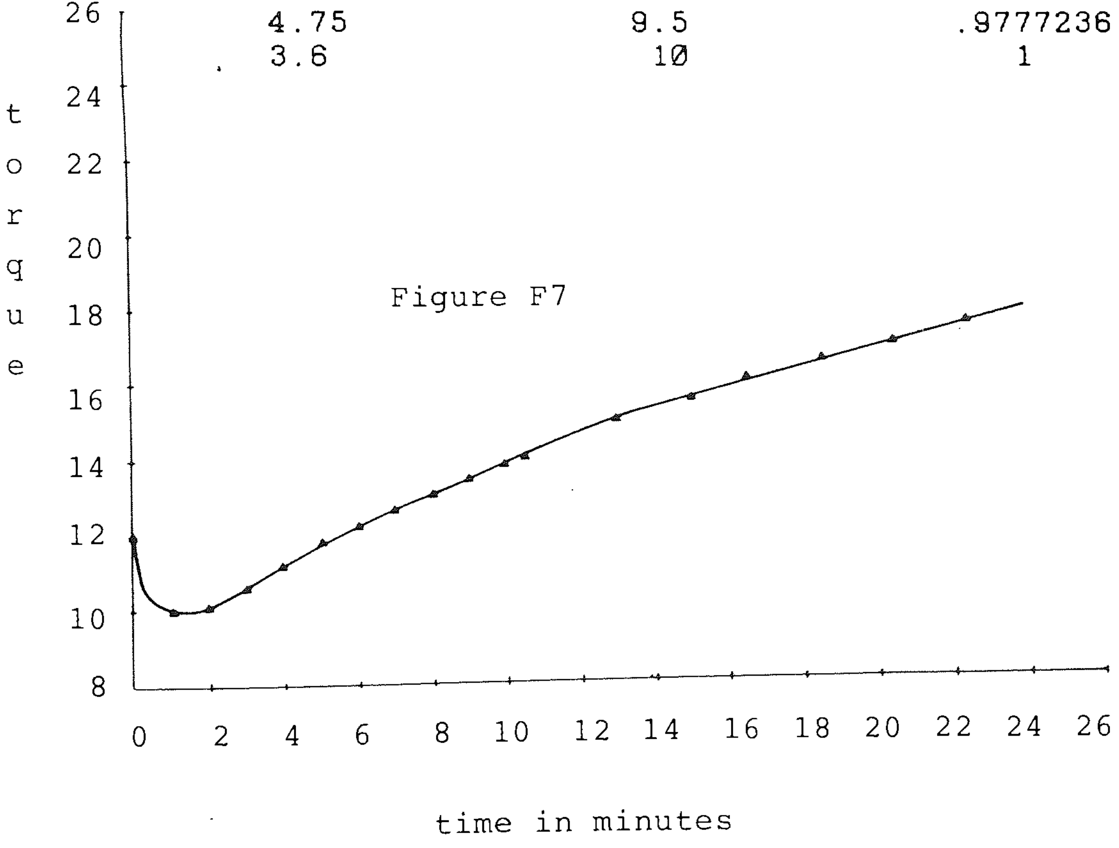


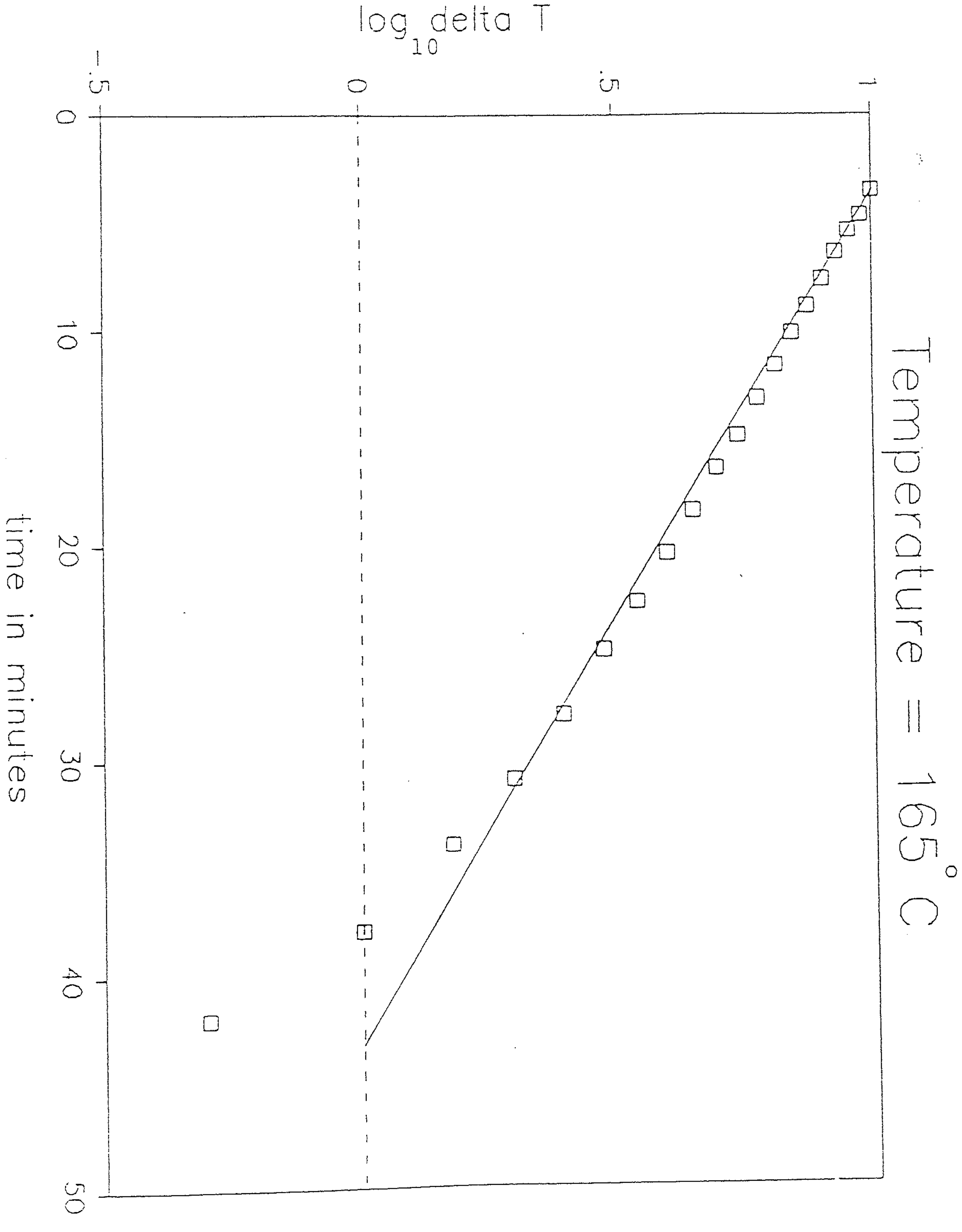
Figure F7

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 165°C

Gradient of the line = -0.025

∴ The half life at this temperature is 12 mins.

Figure F8



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 170°C

Table F5

Temperature=170°C

time/minutes	delta T	$\log_{10}$ delta T
29	0	
24.2	.5	-.301030
21.5	1	0
19	1.5	.1760913
16.75	2	.3010300
14.75	2.5	.3979400
13	3	.4771213
11.5	3.5	.5440680
10.25	4	.6020600
9	4.5	.6532125
8	5	.6989700
7.2	5.5	.7403627
6.3	6	.7781513
5.8	6.5	.8129134
5	7	.8450980
4.95	7.5	.8750613

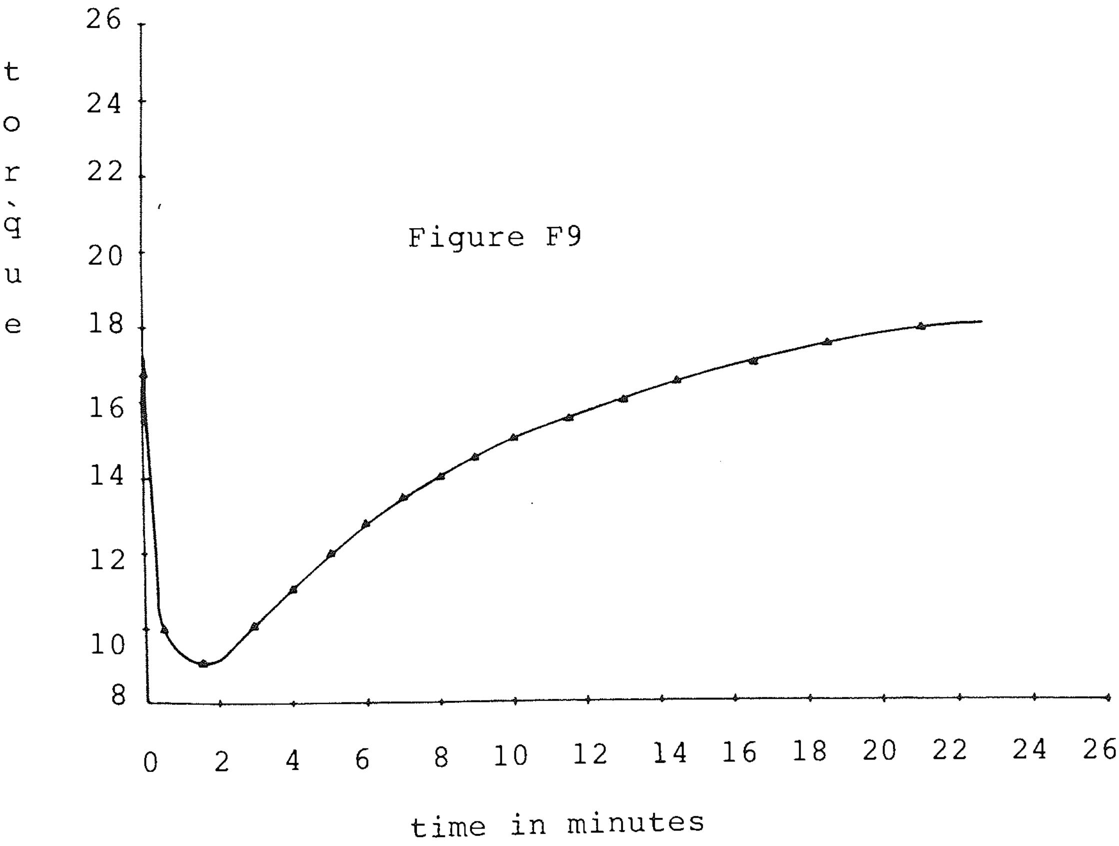


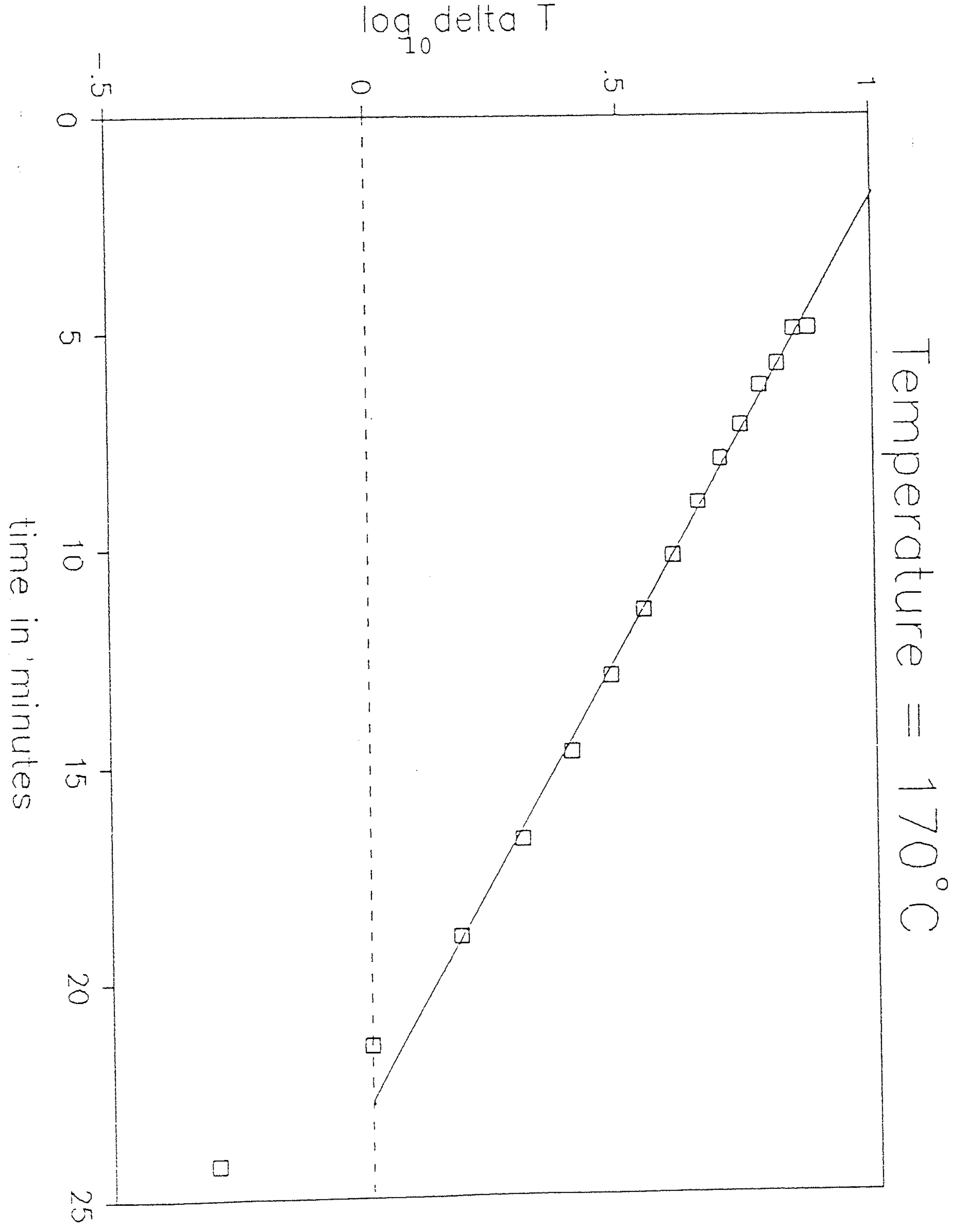
Figure F9

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 170°C.

Gradient of the line = -0.048

∴ The half life at this temperature is 6 minutes.

Figure F10



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 180°C.

Table F6

Temperature=180° C

time/minutes	delta T	$\log_{10}$ delta T
12.5	.5	-.301030
10.5	1	0
8.75	1.5	.1760913
7.5	2	.3010300
6.5	2.5	.3979400
5.75	3	.4771213
5	3.5	.5440680
4.5	4	.6020600
4	4.5	.6532125
3.5	5	.6989700
3.2	5.5	.7403627
2.8	6	.7781513

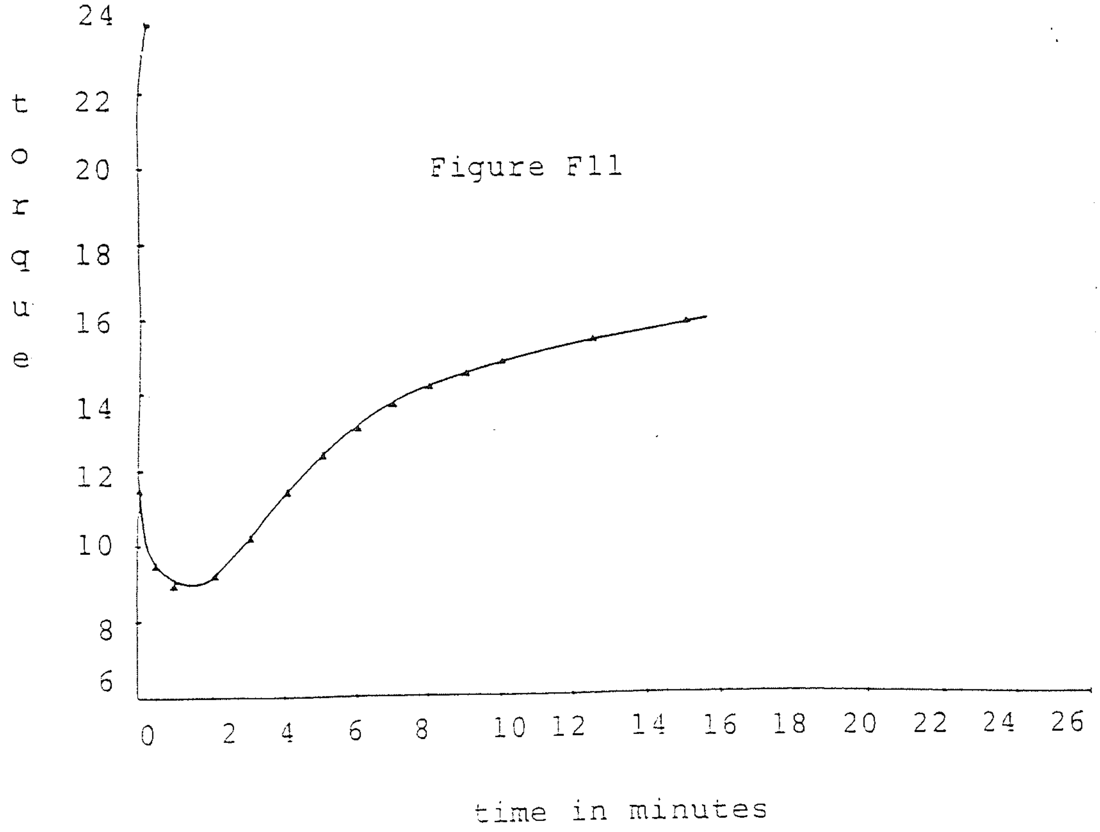


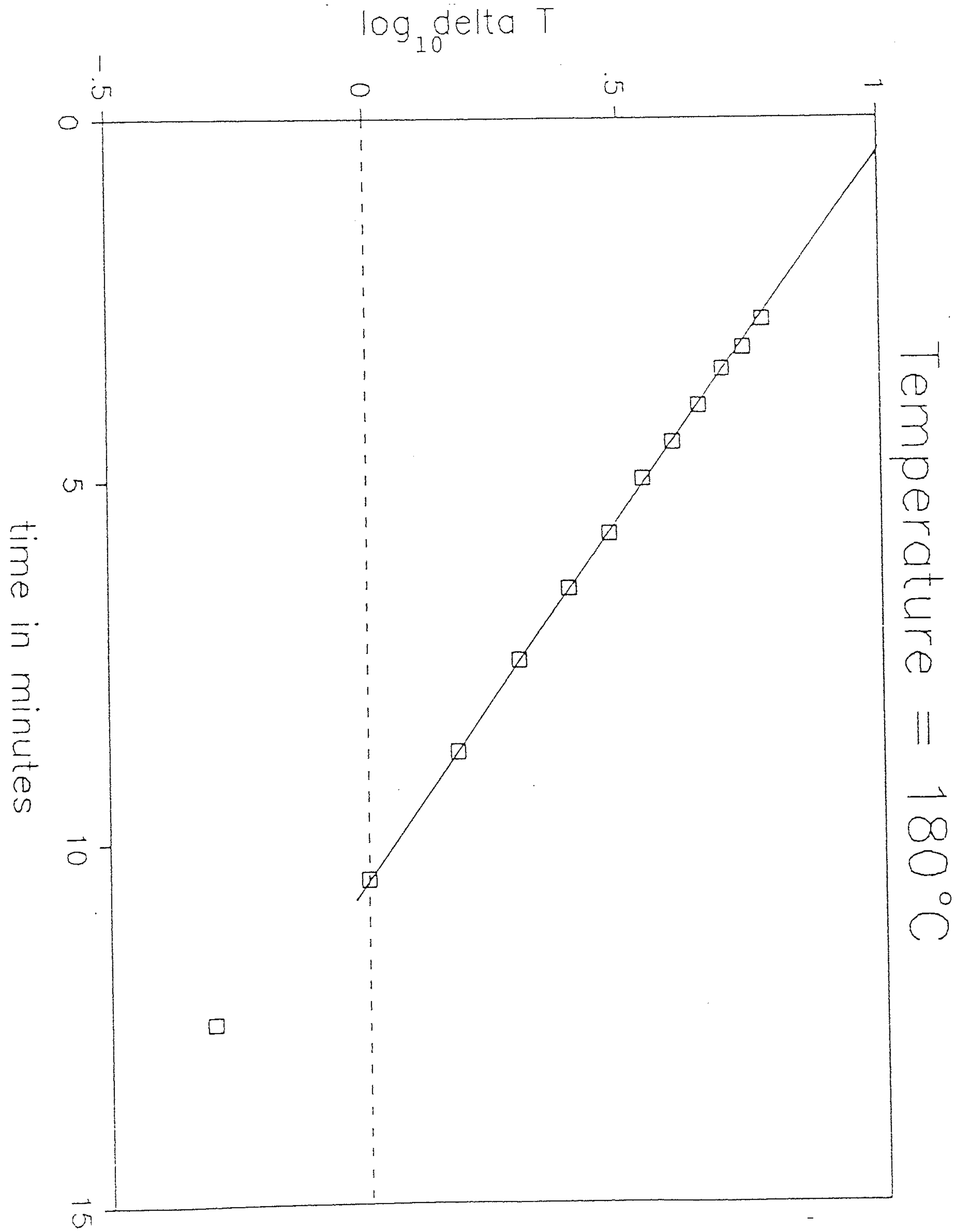
Figure F11

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 180°C.

Gradient of the line = -0.1

$\therefore$ The half life at this temperature is 3 minutes.

Figure F12



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 190°C.

Table F7

Temperature=190 C °

time/minutes	delta T	$\log_{10}$ delta T
7	.5	-.301030
5.5	1	0
4.5	1.5	.1760913
3.75	2	.3010300
3.25	2.5	.3979400
2.8	3	.4771213
2.5	3.5	.5440680
2.3	4	.6020600
1.8	4.5	.6532125
1.6	5	.6989700
1.3	5.5	.7403627

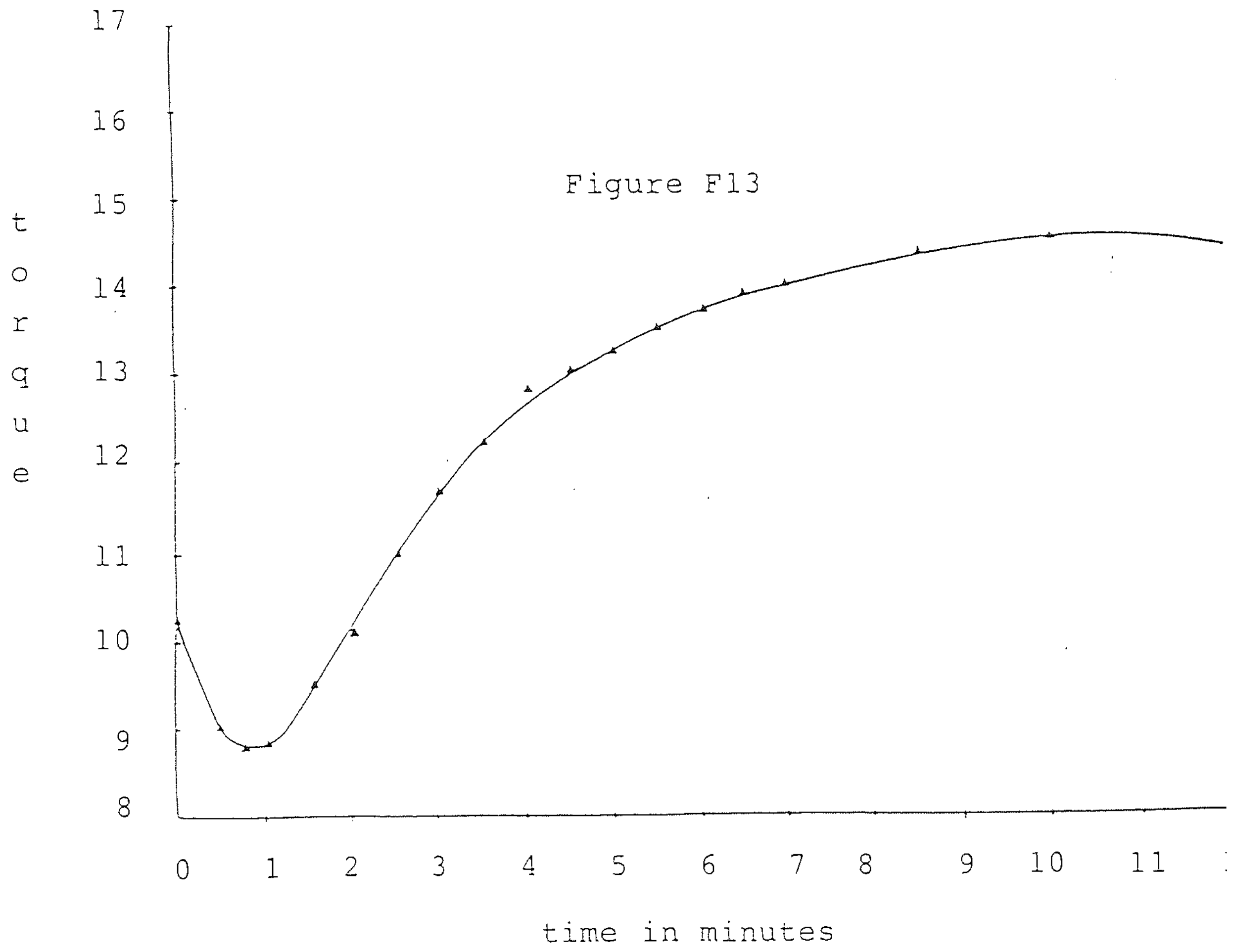


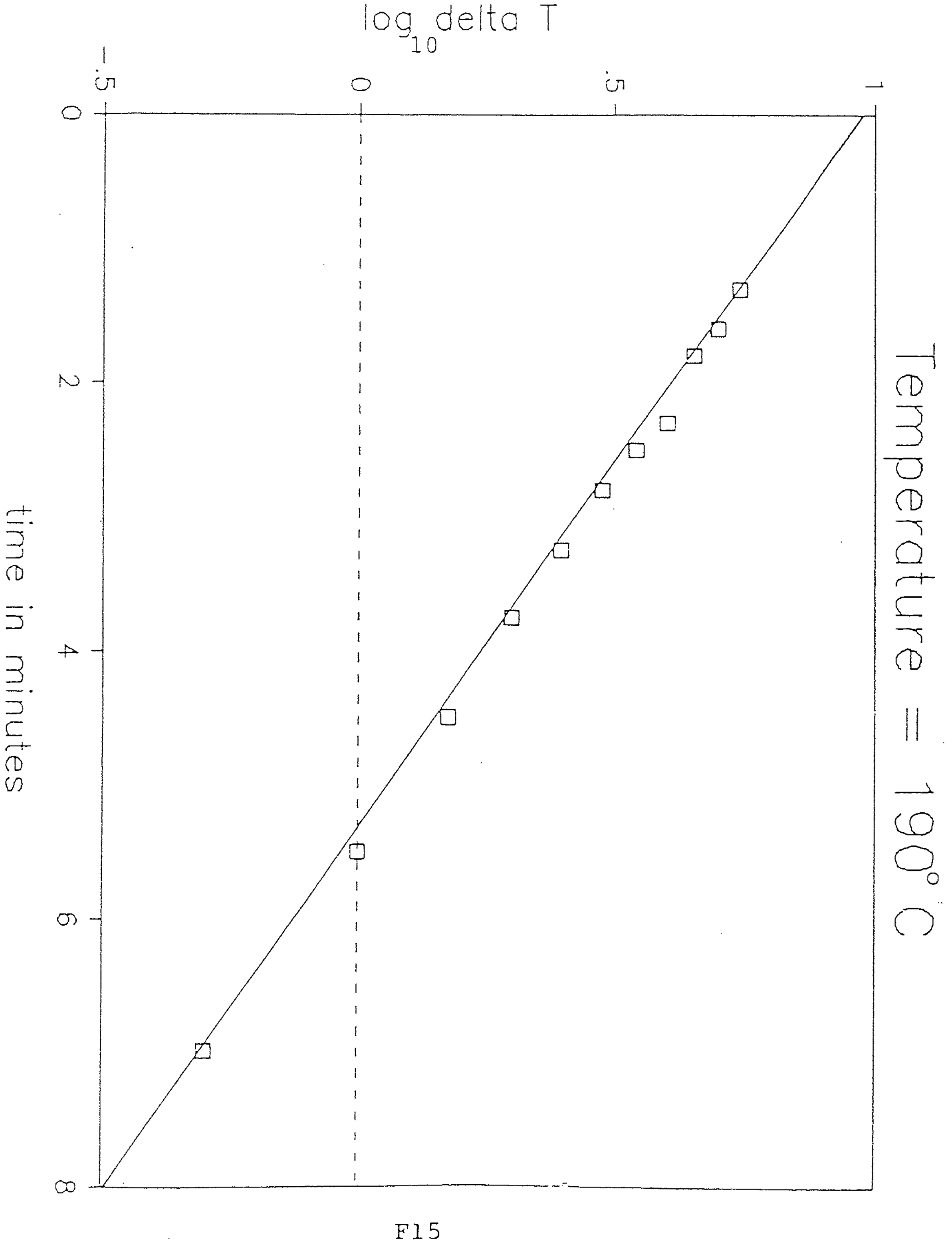
Figure F13

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 190°C.

The gradient of the line = -0.19

∴ The half life at this temperature is 1.5 minutes.

Figure 14



The Monsanto trace and the calculated values are to determine the half life of cumene hydroperoxide at 195°C

Table F8

Temperature=195 °C

time/minutes	delta T	$\log_{10}$ delta T
4.1	1	0
3.5	1.25	.0969100
3.1	1.5	.1760913
2.78	1.75	.2430380
2.55	2	.3010300
2.35	2.25	.3521825
2.2	2.5	.3979400
2.05	2.75	.4393327
1.85	3	.4771213
1.75	3.25	.5118834
1.65	3.5	.5440680
1.5	3.75	.5740313
1.4	4	.6020600
1.25	4.25	.6283889
1.15	4.5	.6532125
1	4.75	.6989700
.75	5	-.602060
7	.25	-.301030
6.1	.5	-.124939
5	.75	

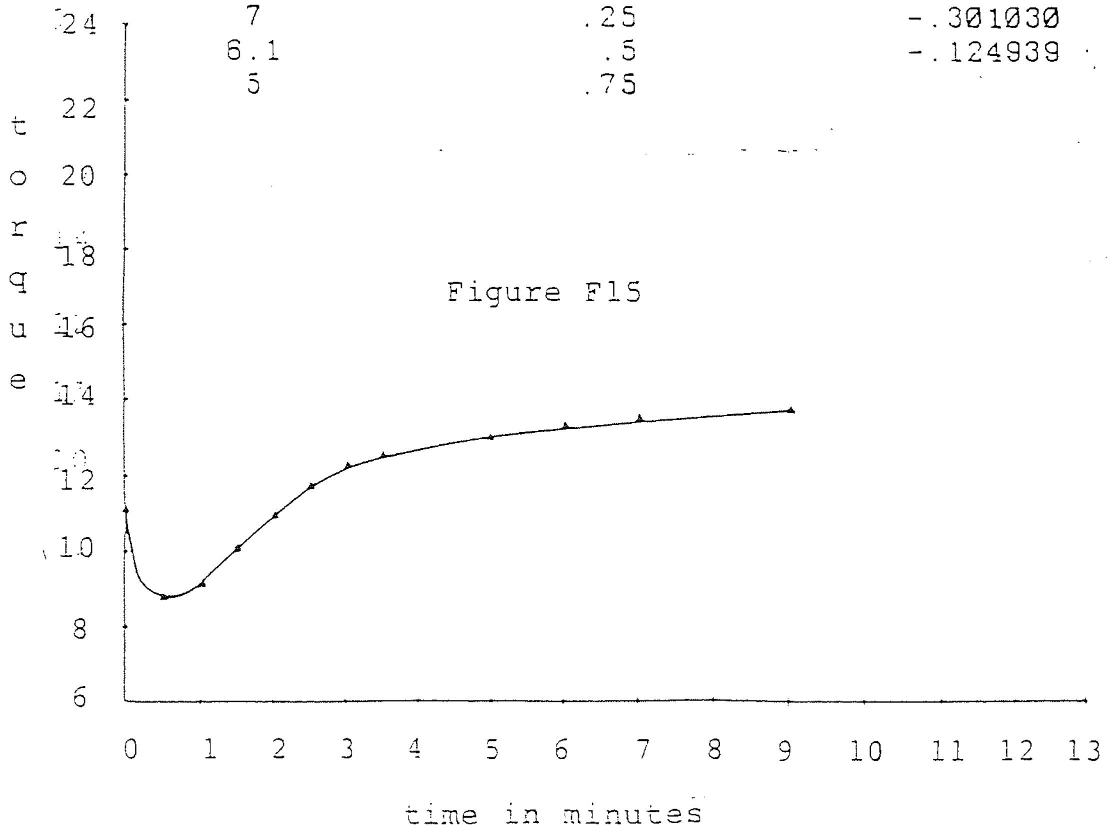


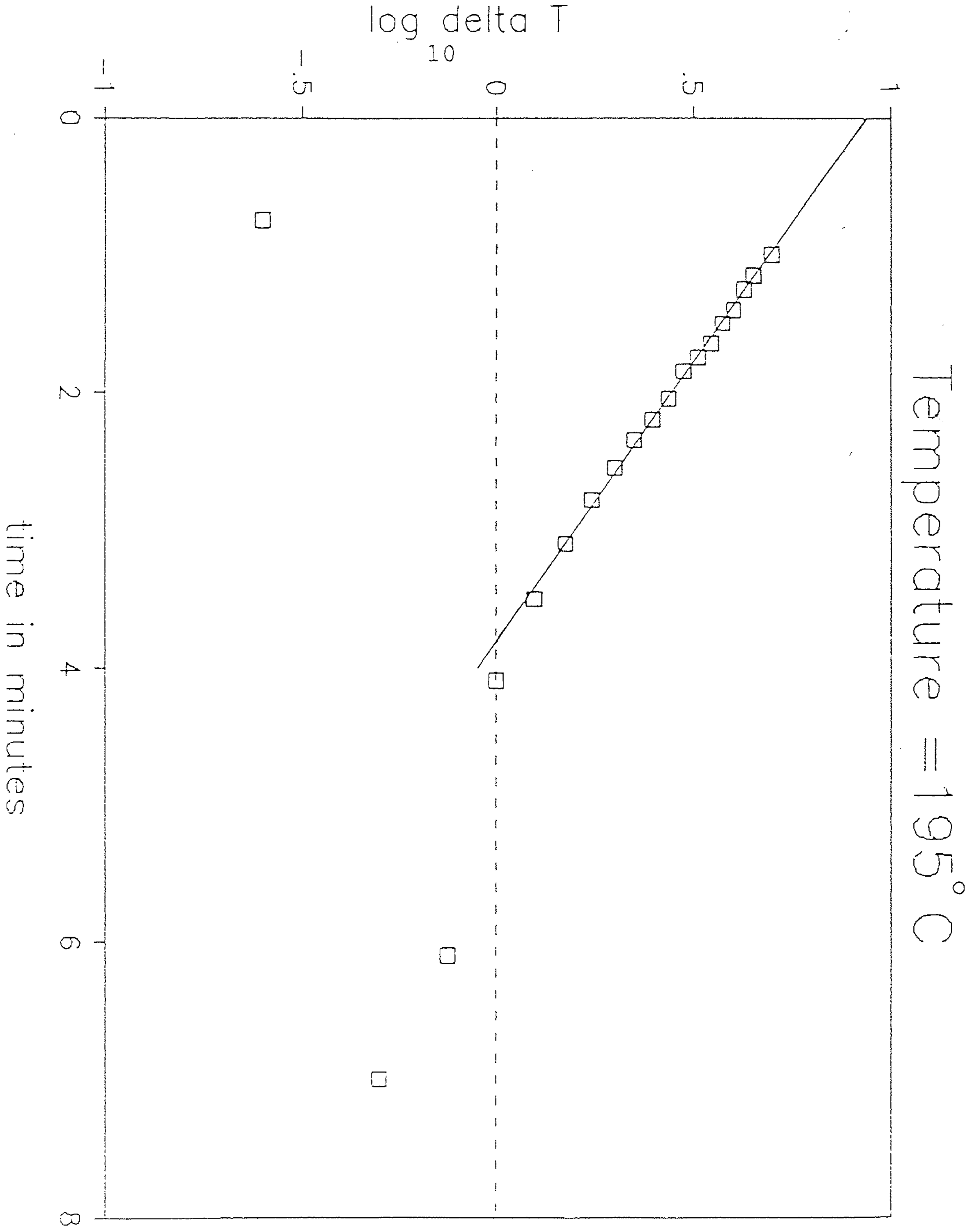
Figure F15

The $\log_{10}$ delta T plotted against time. The gradient (m) of this line is used in equation F1 to calculate the half life of cumene hydroperoxide at 195°C.

Gradient of the line = -0.25

$\therefore$ The half life at this temperature is 1 minute.

Figure F16



The Monsanto trace and the calculated values used to determine the half life of cumene hydroperoxide at 200°C.

Table F9

Temperature=200°C

time/minutes	delta T 10	log delta T
5.25	.25	-.602060
4	.5	-.301030
3	.75	-.124939
2.5	1	0
2.25	1.25	.0969100
2.1	1.5	.1760913
1.85	1.75	.2430380
1.75	2	.3010300
1.65	2.25	.3521825
1.5	2.5	.3979400
1.35	2.75	.4393327
1.25	3	.4771213
1.1	3.25	.5118834
.8	3.5	.5440680

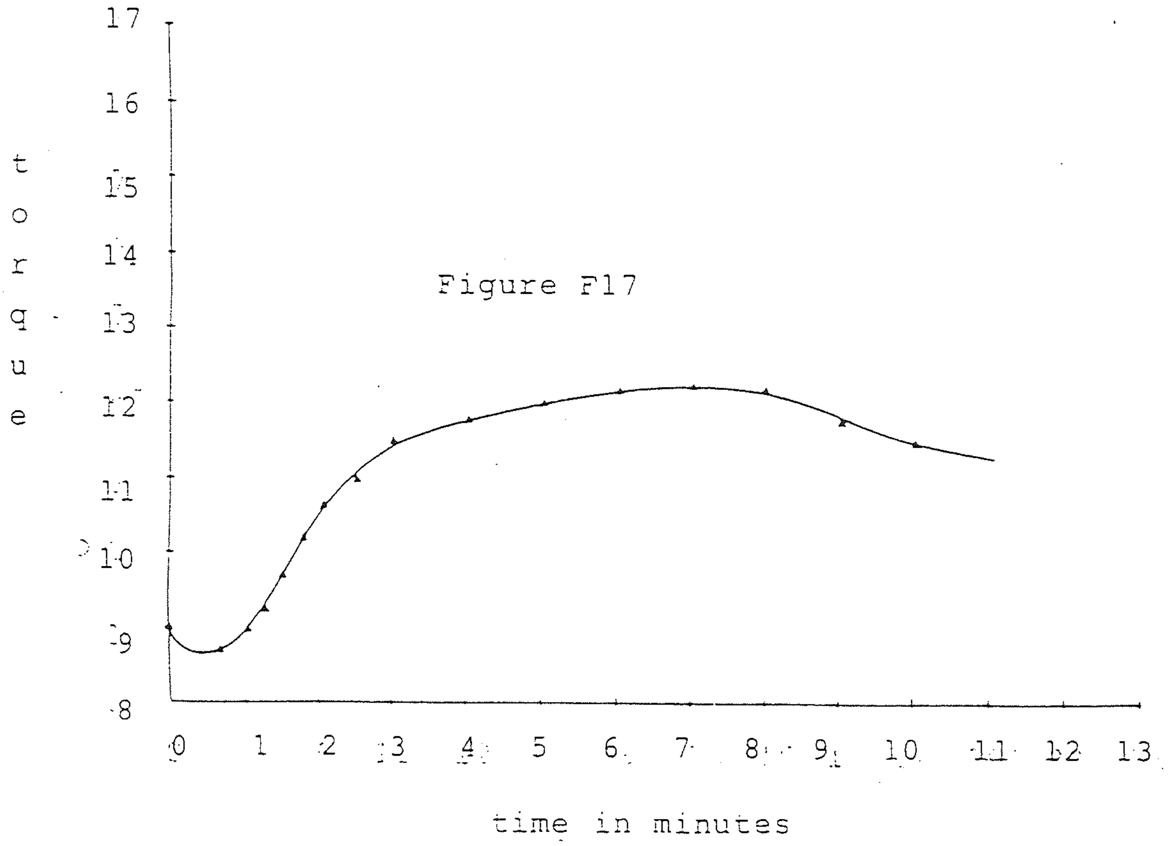


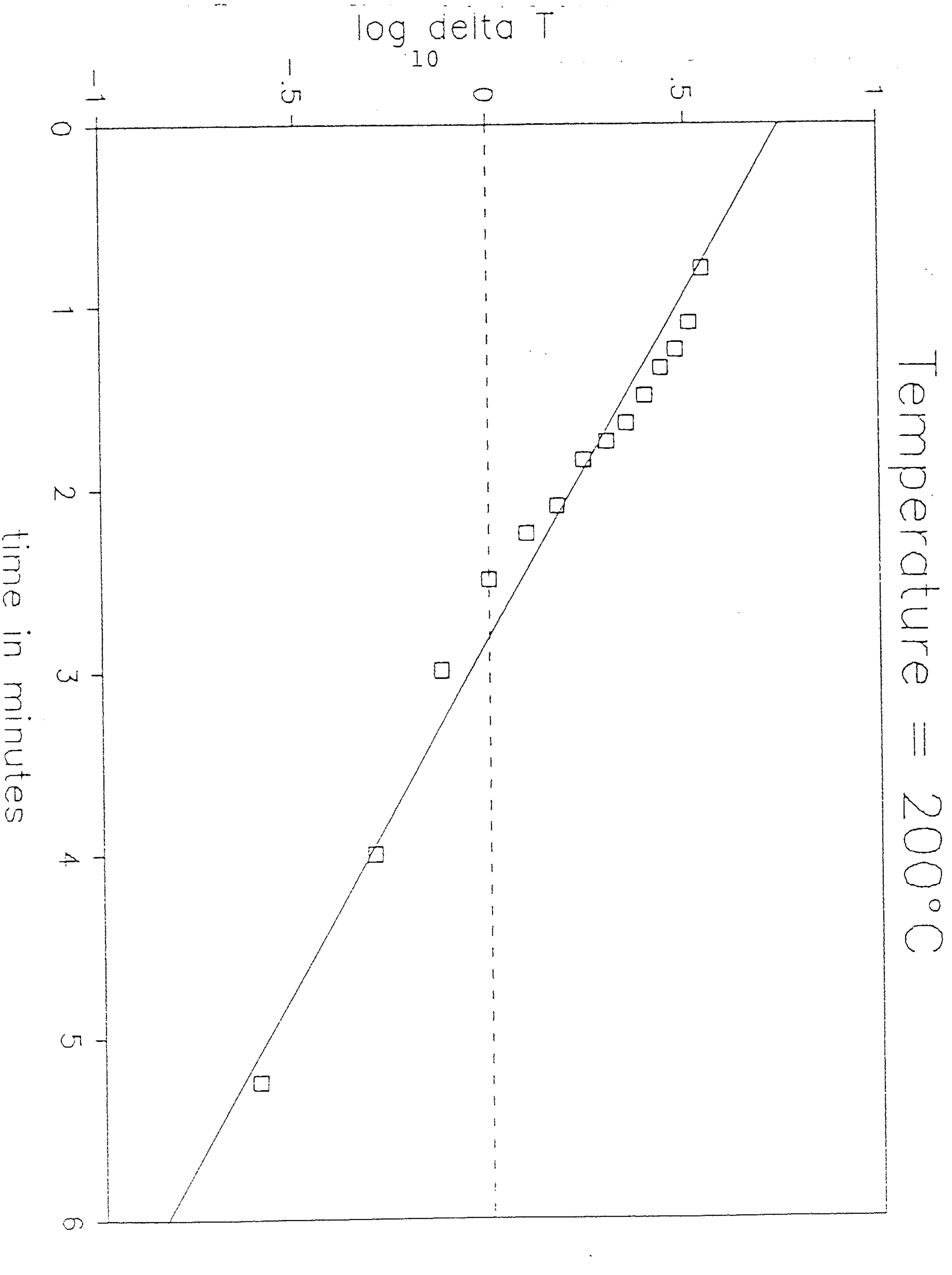
Figure F17

he $\log_{10}$ delta T plotted against time. The gradient (m) of this ine is used in equation F1 to calculate the half life of cumene ydroperoxide at 200°C.

radient of the line = -0.25

. The half life at this temperature is 1 minutes.

Figure F18



PPENDIX G: THE RESIDENCE TIME DISTRIBUTION

```
SERIES G; Fe=20rpm; Xe=70rpm; CTM=55C
                                                     E
 Sample     ti      Ci      dti          Cidti    Ci/SCidti       tiEdti        titiEdti
   1        10      0       10           0        0               0             0
   2        20      0       10           0        0               0             0
   3        30      0       10           0        0               0             0
   4        40      0       5            0        0               0             0
   5        45      0       5            0        0               0             0
   6        50      0       5            0        0               0             0
   7        55      0       5            0        0               0             0
   8        60      0       5            0        0               0             0
   9        65      0       5            0        0               0             0
  10        70      0       5            0        0               0             0
  11        75      0       5            0        0               0             0
  12        80      .79     5            3.95     .0117647        4.705882      376.4706
  13        85      1.185   5            5.925    .0176471        7.5           637.5
  14        90      1.185   5            5.925    .0176471        7.941176      714.7059
  15        95      1.185   5            5.925    .0176471        8.382353      796.3235
  16        100     1.58    5            7.9      .0235294        11.76471      1176.471
  17        105     1.185   5            5.925    .0176471        9.264706      972.7941
  18        110     .79     5            3.95     .0117647        6.470588      711.7647
  19        115     .79     5            3.95     .0117647        6.764706      777.9412
  20        120     .79     5            3.95     .0117647        7.058824      847.0588
  21        125     .79     5            3.95     .0117647        7.352941      919.1176
  22        130     .79     5            3.95     .0117647        7.647059      994.1176
  23        135     .79     5            3.95     .0117647        7.941176      1072.059
  24        140     .395    5            1.975    .0058824        4.117647      576.4706
  25        145     .395    5            1.975    .0058824        4.264706      618.3824
  26        150     .395    5            1.975    .0058824        4.411765      661.7647
  27        155     .395    5            1.975    .0058824        4.558824      706.6176
  28        160     0       180          0        0               0             0
  29        340     0       0            0        0               0             0

                              SCidti  67.15           StiEdti   110.15   StitiEdti 12559.56

                                                                                MEAN     110.15

                                                                                VAR.     427.18

                                                                                S.D.     20.67
```

```
SERIES H; Fe=38rpm; Xe=70rpm; CTM=55C
                                                    E
 Sample     ti      Ci      dti          Cidti   Ci/SCidti        tiEdti          titiEdti
   1        10      0       10             0        0               0               0
   2        20      0       10             0        0               0               0
   3        30      0       5              0        0               0               0
   4        35     .79      5            3.95    .0024396        .4269281        14.94248
   5        40     3.95     5           19.75    .0121979        2.439589        97.58357
   6        45     3.95     5           19.75    .0121979        2.744538        123.5042
   7        50     5.9      5           29.5     .0182197        4.554929        227.7465
   8        55     7.9      5           39.5     .0243959        6.708871        368.9879
   9        60     7.9      5           39.5     .0243959        7.318768        439.1261
   10       65     4.94     5           24.7     .0152552        4.957925        322.2651
   11       70     4.94     5           24.7     .0152552        5.339304        373.7513
   12       75     4.94     5           24.7     .0152552        5.720682        429.0512
   13       80     4.94     5           24.7     .0152552        6.102061        488.1649
   14       85     3.95     5           19.75    .0121979        5.184127        440.6508
   15       90     3.16     5           15.8     .0097584        4.391261        395.2135
   16       95     2.37     5           11.85    .0073188        3.476415        330.2594
   17       100    1.975    5           9.875    .0060990        3.049487        304.9487
   18       105     1.58    5            7.9     .0048792        2.561569        268.9647
   19       110     .79     5            3.95    .0024396        1.341774        147.5952
   20       115     .79     5            3.95    .0024396        1.402764        161.3178
   21       120     0       5             0         0               0               0
   22       125     0       5             0         0               0               0
   23       130     0       75            0         0               0               0
   24       205     0       0             0         0               0               0

                               SCidti   323.83          StiEdti    67.72     StitiEdti 4934.07

                                                                                      MEAN      67.72

                                                                                      VAR.      347.94

                                                                                      S.D.      18.65
```

SERIES K; Fe=38rpm; Xe=40rpm; CTM=55C

					E		
Sample	ti	Ci	dti	Cidti	Ci/SCidti	tiEdti	titiEdti
1	10	1.975	5	9.875	.0051151	.2557545	2.557545
2	15	3.16	5	15.8	.0081841	.6138107	9.207161
3	20	3.55	5	17.75	.0091942	.9194212	18.38842
4	25	3.55	5	17.75	.0091942	1.149276	28.73191
5	30	3.95	5	19.75	.0102302	1.534527	46.03581
6	35	3.95	5	19.75	.0102302	1.790281	62.65985
7	40	3.95	5	19.75	.0102302	2.046036	81.84143
8	45	3.95	5	19.75	.0102302	2.301790	103.5806
9	50	4.94	5	24.7	.0127942	3.198550	159.9275
10	55	4.94	5	24.7	.0127942	3.518405	193.5123
11	60	4.94	5	24.7	.0127942	3.838260	230.2956
12	65	4.94	5	24.7	.0127942	4.158115	270.2774
13	70	4.94	5	24.7	.0127942	4.477970	313.4579
14	75	4.94	5	24.7	.0127942	4.797824	359.8368
15	80	3.95	5	19.75	.0102302	4.092072	327.3657
16	85	3.16	5	15.8	.0081841	3.478261	295.6522
17	90	3.16	5	15.8	.0081841	3.682864	331.4578
18	95	2.76	5	13.8	.0071482	3.395383	322.5614
19	100	1.58	5	7.9	.0040921	2.046036	204.6036
20	105	1.185	5	5.925	.0030691	1.611253	169.1816
21	110	1.185	5	5.925	.0030691	1.687980	185.6777
22	115	.79	5	3.95	.0020460	1.176471	135.2941
23	120	.79	5	3.95	.0020460	1.227621	147.3146
24	125	.5925	5	2.9625	.0015345	.9590793	119.8849
25	130	.395	5	1.975	.0010230	.6649616	86.44501
26	135	0	60	0	0	0	0
27	195	0	0	0	0	0	0

SCidti 386.11

StiEdti 58.62

StitiEdti 4205.75

MEAN 58.62

VAR. 769.21

S.D. 27.73

SERIES S; Fe=20rpm; Xe=60rpm; CTM=55C

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	10	0	0	0	0
2	20	0	10	0	0	0	0
3	30	0	10	0	0	0	0
4	40	0	5	0	0	0	0
5	45	0	5	0	0	0	0
6	50	0	5	0	0	0	0
7	55	0	5	0	0	0	0
8	60	0	5	0	0	0	0
9	65	0	5	0	0	0	0
10	70	0	5	0	0	0	0
11	75	.5925	5	2.9625	.0014410	.5403885	40.52914
12	80	1.975	5	9.875	.0048035	1.921381	153.7105
13	85	2.76	5	13.8	.0067127	2.852887	242.4954
14	90	3.55	5	17.75	.0086341	3.885325	349.6793
15	95	5.9	5	29.5	.0143496	6.816040	647.5238
16	100	5.9	5	29.5	.0143496	7.174779	717.4779
17	105	5.9	5	29.5	.0143496	7.533518	791.0194
18	110	5.9	5	29.5	.0143496	7.892257	868.1482
19	115	3.95	5	19.75	.0096069	5.523972	635.2567
20	120	3.95	5	19.75	.0096069	5.764144	691.6973
21	125	3.95	5	19.75	.0096069	6.004317	750.5396
22	130	3.95	5	19.75	.0096069	6.244490	811.7837
23	135	3.95	5	19.75	.0096069	6.484662	875.4294
24	140	3.55	5	17.75	.0086341	6.043839	846.1375
25	145	3.55	5	17.75	.0086341	6.259691	907.6551
26	150	3.16	5	15.8	.0076855	5.764144	864.6217
27	155	3.16	5	15.8	.0076855	5.956282	923.2238
28	160	2.76	5	13.8	.0067127	5.370140	859.2223
29	165	1.58	5	7.9	.0038428	3.170279	523.0961
30	170	1.58	5	7.9	.0038428	3.266348	555.2792
31	175	1.58	5	7.9	.0038428	3.362418	588.4231
32	180	1.58	10	15.8	.0038428	6.916973	1245.055
33	190	1.185	10	11.85	.0028821	5.475937	1040.428
34	200	.5925	10	5.925	.0014410	2.882072	576.4144
35	210	.395	10	3.95	.0009607	2.017451	423.6646
36	220	.395	10	3.95	.0009607	2.113520	464.9743
37	230	.395	10	3.95	.0009607	2.209589	508.2054
38	240	0	80	0	0	0	0
39	320	0	0	0	0	0	0

SCidti 411.16 StiEdti 129.45 StitiEdti 17901.69

MEAN 129.45

VAR. 1145.21

S.D. 33.84

```
SERIES T; Fe=20rpm; Xe=40rpm; CTM=55C
                                                           E
Sample    ti      Ci      dti         Cidti         Ci/SCidti        tiEdti          titiEdti
  1       10      0       5             0               0               0               0
  2       15      0       5             0               0               0               0
  3       20     .5925    5           2.9625        .0012966        .1296605        2.593211
  4       25      .79     5            3.95         .0017288        .2161009        5.402522
  5       30      .79     5            3.95         .0017288        .2593211        7.779632
  6       35      .79     5            3.95         .0017288        .3025412        10.58894
  7       40      .79     5            3.95         .0017288        .3457614        13.83046
  8       45     1.58     5            7.9          .0034576        .7779632        35.00834
  9       50     2.37     5           11.85         .0051864        1.296605        64.83027
  10      55     1.185    5           5.925         .0025932        .7131329        39.22231
  11      60     1.58     5            7.9          .0034576        1.037284        62.23705
  12      65     1.975    5           9.875         .0043220        1.404656        91.30262
  13      70     1.975    5           9.875         .0043220        1.512706        105.8894
  14      75     1.975    5           9.875         .0043220        1.620757        121.5567
  15      80     2.37     5           11.85         .0051864        2.074568        165.9655
  16      85     1.975    5           9.875         .0043220        1.836858        156.1329
  17      90     2.37     5           11.85         .0051864        2.333890        210.0501
  18      95     3.55     5           17.75         .0077687        3.690128        350.5621
  19      100    3.16     5            15.8         .0069152        3.457614        345.7614
  20      105    3.55     5           17.75         .0077687        4.078562        428.2490
  21      110    3.95     5           19.75         .0086440        4.754219        522.9641
  22      115    3.95     5           19.75         .0086440        4.970320        571.5868
  23      120    3.16     5            15.8         .0069152        4.149137        497.8964
  24      125    3.55     5           17.75         .0077687        4.855431        606.9289
  25      130    3.55     5           17.75         .0077687        5.049648        656.4543
  26      135    3.95     5           19.75         .0086440        5.834724        787.6877
  27      140    3.55     5           17.75         .0077687        5.438083        761.3316
  28      145    3.16     5            15.8         .0069152        5.013540        726.9634
  29      150    3.55     5           17.75         .0077687        5.826517        873.9776
  30      155    3.16     5            15.8         .0069152        5.359302        830.6918
  31      160    2.76     10           27.6         .0060399        9.663813        1546.210
  32      170    2.76     10           27.6         .0060399        10.26780        1745.526
  33      180    1.975    10          19.75         .0043220        7.779632        1400.334
  34      190    1.58     10           15.8         .0034576        6.569467        1248.199
  35      200    1.185    10          11.85         .0025932        5.186421        1037.284
  36      210     .79     10           7.9          .0017288        3.630495        762.4039
  37      220    .1975    10          1.975         .0004322        .9508439        209.1857
  38      230     0       70            0               0               0               0
  39      300     0       0             0               0               0               0

                                SCidti   456.96                StiEdti    122.39   StitiEdti  17002.59

                                                                                           MEAN     122.39

                                                                                           VAR.    2023.89

                                                                                           S.D.      44.99
```

SERIES V; Fe=20rpm; Xe=70rpm; CTM=55C

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	60	0	0	0	0
2	70	0	5	0	0	0	0
3	75	.1975	5	.9875	.0006604	.2476489	18.57367
4	80	.395	5	1.975	.0013208	.5283177	42.26541
5	85	.79	5	3.95	.0026416	1.122675	95.42738
6	90	1.185	5	5.925	.0039624	1.783072	160.4765
7	95	1.185	5	5.925	.0039624	1.882132	178.8025
8	100	1.185	5	5.925	.0039624	1.981191	198.1191
9	105	1.975	5	9.875	.0066040	3.467085	364.0439
10	110	2.37	5	11.85	.0079248	4.358621	479.4483
11	115	2.76	5	13.8	.0092288	5.306583	610.2571
12	120	3.55	5	17.75	.0118704	7.122257	854.6708
13	125	3.55	5	17.75	.0118704	7.419018	927.3772
14	130	3.95	5	19.75	.0132079	8.585162	1116.071
15	135	3.55	5	17.75	.0118704	8.012539	1081.693
16	140	3.16	5	15.8	.0105664	7.396447	1035.503
17	145	3.16	5	15.8	.0105664	7.660606	1110.788
18	150	3.16	5	15.8	.0105664	7.924765	1188.715
19	155	2.76	5	13.8	.0092288	7.152351	1108.614
20	160	2.76	5	13.8	.0092288	7.383072	1181.292
21	165	2.37	5	11.85	.0079248	6.537931	1078.759
22	170	1.975	5	9.875	.0066040	5.613375	954.2738
23	175	1.975	5	9.875	.0066040	5.778474	1011.233
24	180	1.975	10	19.75	.0066040	11.88715	2139.687
25	190	1.975	10	19.75	.0066040	12.54754	2384.033
26	200	.5925	10	5.925	.0019812	3.962382	792.4765
27	210	.5925	10	5.925	.0019812	4.160502	873.7053
28	220	.5925	10	5.925	.0019812	4.358621	958.8966
29	230	.1975	10	1.975	.0006604	1.518913	349.3501
30	240	0	80	0	0	0	0
31	320	0	0	0	0	0	0

SCidti 299.06

StiEdti 145.70

StitiEdti 22294.55

MEAN	145.70
VAR.	1066.52
S.D.	32.66

```
SERIES W; Fe=38rpm; Xe=40rpm; CTM=55C
                                                                E
  Sample      ti        Ci          dti            Cidti    Ci/SCidti        tiEdti              titiEdti
    1         5       1.975          5             9.875     .0099010        .2475248            1.237624
    2         10       3.16          5              15.8     .0158416        .7920792            7.920792
    3         15       3.16          5              15.8     .0158416        1.188119            17.82178
    4         20       3.16          5              15.8     .0158416        1.584158            31.68317
    5         25       2.37          5             11.85     .0118812        1.485149            37.12871
    6         30       2.37          5             11.85     .0118812        1.782178            53.46535
    7         35       2.37          5             11.85     .0118812        2.079208            72.77228
    8         40      1.975          5             9.875     .0099010        1.980198            79.20792
    9         45      1.975          5             9.875     .0099010        2.227723            100.2475
    10        50       1.58          5               7.9     .0079208        1.980198            99.00990
    11        55       1.58          5               7.9     .0079208        2.178218            119.8020
    12        60      1.975          5             9.875     .0099010        2.970297            178.2178
    13        65      1.975          5             9.875     .0099010        3.217822            209.1584
    14        70       1.58          5               7.9     .0079208        2.772277            194.0594
    15        75       1.58          5               7.9     .0079208        2.970297            222.7723
    16        80       1.58          5               7.9     .0079208        3.168317            253.4653
    17        85       1.58          5               7.9     .0079208        3.366337            286.1386
    18        90      1.185          5             5.925     .0059406        2.673267            240.5941
    19        95        .79          5              3.95     .0039604        1.881188            178.7129
    20        100       .79          5              3.95     .0039604        1.980198            198.0198
    21        105      .395          5             1.975     .0019802        1.039604            109.1584
    22        110      .395          5             1.975     .0019802        1.089109            119.8020
    23        115      .395          5             1.975     .0019802        1.138614            130.9406
    24        120        0          185              0           0               0                   0
    25        305        0           0               0           0               0                   0

                                       SCidti   199.48              StiEdti    45.79    StitiEdti  2941.34

                                                                                                  MEAN     45.79

                                                                                                  VAR.     844.42

                                                                                                  S.D.     29.06
```

```
SERIES Y; Fe=38rpm; Xe=70rpm; CTM=55C
                                                              E
Sample     ti       Ci       dti           Cidti         Ci/SCidti         tiEdti           titiEdti
  1         5        0        5              0               0                0                 0
  2        10      .1975      5            .9875         .0014601          .0730062          .7300619
  3        15     1.185       5           5.925          .0087607          .6570557         9.855836
  4        20      1.58       5            7.9           .0116810         1.168099         23.36198
  5        25      1.58       5            7.9           .0116810         1.460124         36.50310
  6        30      1.58       5            7.9           .0116810         1.752149         52.56446
  7        35      1.58       5            7.9           .0116810         2.044173         71.54607
  8        40      1.58       5            7.9           .0116810         2.336198         93.44793
  9        45      1.58       5            7.9           .0116810         2.628223         118.2700
 10        50      2.76       5            13.8          .0204048         5.101192         255.0596
 11        55      2.37       5           11.85          .0175215         4.818409         265.0125
 12        60      2.37       5           11.85          .0175215         5.256446         315.3867
 13        65     1.975       5           9.875          .0146012         4.745402         308.4512
 14        70      1.58       5            7.9           .0116810         4.088347         286.1843
 15        75     1.185       5           5.925          .0087607         3.285279         246.3959
 16        80     1.185       5           5.925          .0087607         3.504297         280.3438
 17        85     .5925       5           2.9625         .0043804         1.861658         158.2409
 18        90     .5925       5           2.9625         .0043804         1.971167         177.4050
 19        95      .395       5           1.975          .0029202         1.387118         131.7762
 20       100      .395       5           1.975          .0029202         1.460124         146.0124
 21       105      .395       5           1.975          .0029202         1.533130         160.9787
 22       110     .1975       5           .9875          .0014601          .8030681         88.33749
 23       115     .1975       5           .9875          .0014601          .8395712         96.55069
 24       120       0         0              0               0                0                 0

                               SCidti   135.26                   StiEdti   52.77   StitiEdti 3322.41

                                                                                                    MEAN    52.77

                                                                                                    VAR.    537.29

                                                                                                    S.D.    23.18
```

SERIES Z; Fe=20rpm; Xe=60rpm; CTM=55C

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	10	0	0	0	0
2	20	0	10	0	0	0	0
3	30	0	10	0	0	0	0
4	40	0	5	0	0	0	0
5	45	0	5	0	0	0	0
6	50	0	5	0	0	0	0
7	55	0	5	0	0	0	0
8	60	0	5	0	0	0	0
9	65	0	5	0	0	0	0
10	70	.395	5	1.975	.0013386	.4685051	32.79536
11	75	.395	5	1.975	.0013386	.5019698	37.64773
12	80	.5925	5	2.9625	.0020079	.8031516	64.25213
13	85	1.185	5	5.925	.0040158	1.706697	145.0693
14	90	1.975	5	9.875	.0066929	3.011819	271.0637
15	95	1.975	5	9.875	.0066929	3.179142	302.0185
16	100	1.975	5	9.875	.0066929	3.346465	334.6465
17	105	2.76	5	13.8	.0093532	4.910408	515.5928
18	110	2.76	5	13.8	.0093532	5.144237	565.8661
19	115	3.16	5	15.8	.0107087	6.157496	708.1120
20	120	3.16	5	15.8	.0107087	6.425213	771.0255
21	125	3.16	5	15.8	.0107087	6.692930	836.6163
22	130	3.16	5	15.8	.0107087	6.960647	904.8841
23	135	3.16	5	15.8	.0107087	7.228364	975.8292
24	140	2.76	5	13.8	.0093532	6.547211	916.6095
25	145	2.76	5	13.8	.0093532	6.781040	983.2507
26	150	2.76	5	13.8	.0093532	7.014868	1052.230
27	155	2.76	5	13.8	.0093532	7.248697	1123.548
28	160	2.76	5	13.8	.0093532	7.482526	1197.204
29	165	1.975	5	9.875	.0066929	5.521667	911.0751
30	170	1.975	5	9.875	.0066929	5.688991	967.1284
31	175	1.58	5	7.9	.0053543	4.685051	819.8839
32	180	1.58	10	15.8	.0053543	9.637819	1734.807
33	190	1.185	10	11.85	.0040158	7.629940	1449.689
34	200	.79	10	7.9	.0026772	5.354344	1070.869
35	210	.5925	10	5.925	.0020079	4.216546	885.4746
36	220	.395	10	3.95	.0013386	2.944889	647.8756
37	230	.395	10	3.95	.0013386	3.078748	708.1120
38	240	0	80	0	0	0	0
39	320	0	0	0	0	0	0

SCidti 295.09 StiEdti 140.37 StitiEdti 20933.18

MEAN 140.37

VAR. 1229.61

S.D. 35.07

```
SERIES Ph1; Fe=30rpm; Xe=46rpm; CTM=55C; THROUGHPUT=.79Kg/h
                                                      E
 Sample     ti        Ci       dti          Cidti    Ci/SCidti         tiEdti             titiEdti
   1        10        0        10             0          0              0                  0
   2        20        0        10             0          0              0                  0
   3        30        0        10             0          0              0                  0
   4        40       2.76      10           27.6     .0019397        .7758666          31.03466
   5        50       4.94      10           49.4     .0034717        1.735861          86.79305
   6        60       4.94      10           49.4     .0034717        2.083033          124.9820
   7        70       9.9       10           99       .0069575        4.870250          340.9175
   8        80       15.8      10           158      .0111039        8.883110          710.6488
   9        90       21.7      10           217      .0152503        13.72525          1235.272
  10       100       19.75     10           197.5    .0138799        13.87986          1387.986
  11       110       15.8      10           158      .0111039        12.21428          1343.570
  12       120       13.8      10           138      .0096983        11.63800          1396.560
  13       130       11.8      10           118      .0082928        10.78061          1401.479
  14       140       7.9       10           79       .0055519        7.772722          1088.181
  15       150       5.9       10           59       .0041464        6.219583          932.9374
  16       160       3.95      10           39.5     .0027760        4.441555          710.6488
  17       170       2.76      10           27.6     .0019397        3.297433          560.5636
  18       180       .5925     10           5.925    .0004164        .7495124          134.9122
  19       190       0         10           0          0              0                  0
  20       200       0         10           0          0              0                  0
  21       210       0         10           0          0              0                  0
  22       220       0         10           0          0              0                  0
  23       230       0         10           0          0              0                  0
  24       240       0         10           0          0              0                  0
  25       250       0         10           0          0              0                  0
  26       260       0         30           0          0              0                  0
  27       290       0         30           0          0              0                  0
  28       320       0         30           0          0              0                  0
  29       350       0         0            0          0              0                  0

                                     SCidti  1422.93            StiEdti    103.07   StitiEdti  11486.49

                                                                                                    MEAN     103.07

                                                                                                    VAR.     863.70

                                                                                                    S.D.     29.39
```

```
SERIES Ph2; Fe=30rpm; Xe=57rpm; CTM=55C; THROUGHPUT=.72Kg/h
                                                           E
Sample     ti       Ci        dti         Cidti       Ci/SCidti          tiEdti           titiEdti
  1        10       0         10            0             0                0                 0
  2        20       0         10            0             0                0                 0
  3        30       0         10            0             0                0                 0
  4        40       0         10            0             0                0                 0
  5        50      1.58       10           15.8       .0009327          .4663587          23.31794
  6        60      2.76       10           27.6       .0016293          .9775823          58.65494
  7        70      9.9        10           99         .0058442         4.090969          286.3679
  8        80     21.7        10          217         .0128101        10.24809           819.8468
  9        90     31.6        10          316         .0186543        16.78891          1511.002
 10       100     23.7        10          237         .0139908        13.99076          1399.076
 11       110     17.8        10          178         .0105078        11.55861          1271.447
 12       120     13.8        10          138         .0081465         9.775823         1173.099
 13       130     11.8        10          118         .0069659         9.055624         1177.231
 14       140      9.9        10           99         .0058442         8.181939         1145.471
 15       150      7.9        10           79         .0046636         6.995381         1049.307
 16       160      5.9        10           59         .0034829         5.572691          891.6306
 17       170      4.94       10           49.4       .0029162         4.957570          842.7869
 18       180      3.55       10           35.5       .0020957         3.772193          678.9947
 19       190      1.975      10           19.75      .0011659         2.215204          420.8887
 20       200      .5925      10            5.925     .0003498          .6995381         139.9076
 21       210       0         10            0             0                0                 0
 22       220       0         10            0             0                0                 0
 23       230       0         10            0             0                0                 0
 24       240       0         10            0             0                0                 0
 25       250       0         10            0             0                0                 0
 26       260       0         10            0             0                0                 0
 27       270       0         10            0             0                0                 0
 28       280       0         10            0             0                0                 0
 29       290       0         30            0             0                0                 0
 30       320       0         30            0             0                0                 0
 31       350       0         30            0             0                0                 0
 32       380       0         0             0             0                0                 0

                                  SCidti  1693.98          StiEdti    109.35   StitiEdti  12889.03

                                                                                          MEAN     109.35

                                                                                          VAR.     932.21

                                                                                          S.D.     30.53
```

```
SERIES Ph3; Fe=30rpm; Xe=68rpm; CTM=55C; THROUGHPUT=.81Kg/h
                                                        E
Sample     ti       Ci      dti         Cidti        Ci/SCidti          tiEdti            titiEdti
   1       10       0       10            0              0                0                  0
   2       20       0       10            0              0                0                  0
   3       30       0       10            0              0                0                  0
   4       40      3.95     10           39.5         .0033088         1.323532           52.94130
   5       50      5.9      10           59           .0049423         2.471152           123.5576
   6       60     15.8      10          158           .0132353         7.941195           476.4717
   7       70     19.75     10          197.5         .0165442         11.58091           810.6637
   8       80     19.75     10          197.5         .0165442         13.23532           1058.826
   9       90     15.8      10          158           .0132353         11.91179           1072.061
  10      100     11.8      10          118           .0098846         9.884610           988.4610
  11      110      7.9      10           79           .0066177         7.279429           800.7372
  12      120      5.9      10           59           .0049423         5.930766           711.6919
  13      130      3.95     10           39.5         .0033088         4.301481           559.1925
  14      140      3.55     10           35.5         .0029738         4.163264           582.8569
  15      150      2.76     10           27.6         .0023120         3.467990           520.1985
  16      160      1.185    10           11.85        .0009926         1.588239           254.1182
  17      170       .79     10            7.9         .0006618         1.125003           191.2504
  18      180      .5925    10            5.925       .0004963         .8933844           160.8092
  19      190       0       10            0              0                0                  0
  20      200       0       10            0              0                0                  0
  21      210       0       10            0              0                0                  0
  22      220       0       10            0              0                0                  0
  23      230       0       10            0              0                0                  0
  24      240       0       10            0              0                0                  0
  25      250       0       30            0              0                0                  0
  26      280       0       30            0              0                0                  0
  27      310       0       30            0              0                0                  0
  28      340       0       0             0              0                0                  0

                                  SCidti  1193.78              StiEdti    87.10    StitiEdti 8363.84

                                                                                                  MEAN      87.10

                                                                                                  VAR.      777.76

                                                                                                  S.D.      27.89
```

```
SERIES Ph4; Fe=30rpm; Xe=75rpm; CTM=55C; THROUGHPUT=.83Kg/h
                                                        E
Sample    ti      Ci      dti          Cidti      Ci/SCidti         tiEdti          titiEdti
  1       10      0       10            0            0                0                0
  2       20      0       10            0            0                0                0
  3       30      0       10            0            0                0                0
  4       40     2.76     10           27.6       .0011176         .4470314         17.88126
  5       50     5.9      10           59         .0023890         1.194513         59.72567
  6       60     17.8     10          178         .0072076         4.324543         259.4726
  7       70     31.6     10          316         .0127955         8.956825         626.9778
  8       80     39.5     10          395         .0159943         12.79546         1023.637
  9       90     39.5     10          395         .0159943         14.39490         1295.541
 10      100     31.6     10          316         .0127955         12.79546         1279.546
 11      110    19.75     10          197.5       .0079972         8.796882         967.6570
 12      120     15.8     10          158         .0063977         7.677279         921.2735
 13      130     13.8     10          138         .0055879         7.264261         944.3539
 14      140     11.8     10          118         .0047781         6.689275         936.4985
 15      150     5.9      10           59         .0023890         3.583540         537.5310
 16      160     3.95     10           39.5       .0015994         2.559093         409.4549
 17      170     2.76     10           27.6       .0011176         1.899884         322.9802
 18      180    1.975     10           19.75      .0007997         1.439490         259.1082
 19      190     .79      10            7.9       .0003199         .6077846         115.4791
 20      200    .5925     10            5.925     .0002399         .4798299         95.96599
 21      210     .395     10            3.95      .0001599         .3358810         70.53500
 22      220     .395     10            3.95      .0001599         .3518753         77.41256
 23      230    .1975     10            1.975     .0000800         .1839348         42.30501
 24      240    .1975     10            1.975     .0000800         .1919320         46.06367
 25      250      0       10            0            0                0                0
 26      260      0       30            0            0                0                0
 27      290      0       30            0            0                0                0
 28      320      0       30            0            0                0                0
 29      350      0       0             0            0                0                0
                                 SCidti 2469.63              StiEdti    96.97    StitiEdti 10309.40

                                                                                               MEAN     96.97

                                                                                               VAR.     906.28

                                                                                               S.D.     30.10
```

```
SERIES Ph5; Fe=30rpm; Xe=85rpm; CTM=55C; THROUGHPUT=.75Kg/h
                                                        E
Sample    ti      Ci      dti       Cidti        Ci/SCidti         tiEdti           titiEdti
  1       10      0       10          0              0               0                 0
  2       20      0       10          0              0               0                 0
  3       30      0       10          0              0               0                 0
  4       40      0       10          0              0               0                 0
  5       50     2.76     10         27.6        .0013399         .6699680          33.49840
  6       60     17.8     10         178         .0086416         5.184969          311.0982
  7       70    27.65     10        276.5        .0134236         9.396543          657.7580
  8       80     39.5     10         395         .0191766         15.34130          1227.304
  9       90     39.5     10         395         .0191766         17.25896          1553.306
 10      100     23.7     10         237         .0115060         11.50597          1150.597
 11      110     15.8     10         158         .0076706         8.437712          928.1484
 12      120     13.8     10         138         .0066997         8.039615          964.7539
 13      130     7.9      10          79         .0038353         4.985921          648.1697
 14      140     4.94     10         49.4        .0023983         3.357608          470.0651
 15      150     3.95     10         39.5        .0019177         2.876493          431.4739
 16      160     3.55     10         35.5        .0017235         2.757549          441.2079
 17      170     2.76     10         27.6        .0013399         2.277891          387.2415
 18      180     1.58     10         15.8        .0007671         1.380717          248.5290
 19      190     .79      10          7.9        .0003835         .7287115          138.4552
 20      200      0       10          0              0               0                 0
 21      210      0       10          0              0               0                 0
 22      220      0       10          0              0               0                 0
 23      230      0       10          0              0               0                 0
 24      240      0       10          0              0               0                 0
 25      250      0       10          0              0               0                 0
 26      260      0       10          0              0               0                 0
 27      270      0       10          0              0               0                 0
 28      280      0       10          0              0               0                 0
 29      290      0       30          0              0               0                 0
 30      320      0       30          0              0               0                 0
 31      350      0       30          0              0               0                 0
 32      380      0       0           0              0               0                 0

                               SCidti 2059.80          StiEdti    94.20    StitiEdti 9591.61

                                                                                         MEAN     94.20

                                                                                         VAR.     717.98

                                                                                         S.D.     26.80
```

SERIES Ph6; Fe=30rpm; Xe=94rpm; CTM=55C; THROUGHPUT=.77Kg/h

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	10	0	0	0	0
2	20	0	10	0	0	0	0
3	30	0	10	0	0	0	0
4	40	0	10	0	0	0	0
5	50	2.37	10	23.7	.0016604	.8302098	41.51049
6	60	7.9	10	79	.0055347	3.320839	199.2504
7	70	15.8	10	158	.0110695	7.748625	542.4038
8	80	35.55	10	355.5	.0249063	19.92504	1594.003
9	90	27.65	10	276.5	.0193716	17.43441	1569.097
10	100	19.75	10	197.5	.0138368	13.83683	1383.683
11	110	11.8	10	118	.0082671	9.093775	1000.315
12	120	7.9	10	79	.0055347	6.641679	797.0014
13	130	4.94	10	49.4	.0034610	4.499247	584.9021
14	140	3.55	10	35.5	.0024871	3.481977	487.4768
15	150	2.76	10	27.6	.0019337	2.900480	435.0720
16	160	1.975	10	19.75	.0013837	2.213893	354.2229
17	170	.79	10	7.9	.0005535	.9409045	159.9538
18	180	0	10	0	0	0	0
19	190	0	10	0	0	0	0
20	200	0	10	0	0	0	0
21	210	0	10	0	0	0	0
22	220	0	10	0	0	0	0
23	230	0	10	0	0	0	0
24	240	0	10	0	0	0	0
25	250	0	10	0	0	0	0
26	260	0	30	0	0	0	0
27	290	0	30	0	0	0	0
28	320	0	30	0	0	0	0
29	350	0	0	0	0	0	0

SCidti 1427.35   StiEdti 92.87   StitiEdti 9148.89

MEAN	92.87
VAR.	524.44
S.D.	22.90

```
SERIES Ph7; Fe=30rpm; Xe=102rpm; CTM=55C; THROUGHPUT=.79Kg/h
                                                          E
Sample     ti       Ci      dti          Cidti      Ci/SCidti          tiEdti          titiEdti
  1        10       0       10             0            0                0                0
  2        20       0       10             0            0                0                0
  3        30       0       10             0            0                0                0
  4        40       0       10             0            0                0                0
  5        50      3.95     10           39.5       .0029099         1.454934         72.74669
  6        60      13.8     10           138        .0101661         6.099672         365.9803
  7        70      19.75    10           197.5      .0145493         10.18454         712.9176
  8        80      27.65    10           276.5      .0203691         16.29526         1303.621
  9        90      19.75    10           197.5      .0145493         13.09440         1178.496
 10       100      13.8     10           138        .0101661         10.16612         1016.612
 11       110      11.8     10           118        .0086928         9.562046         1051.825
 12       120      7.9      10            79        .0058197         6.983683         838.0419
 13       130      5.9      10            59        .0043464         5.650300         734.5390
 14       140      3.55     10           35.5       .0026152         3.661277         512.5787
 15       150      2.76     10           27.6       .0020332         3.049836         457.4754
 16       160      2.37     10           23.7       .0017459         2.793473         446.9557
 17       170     1.185     10           11.85      .0008730         1.484033         252.2855
 18       180      .79      10            7.9       .0005820         1.047552         188.5594
 19       190     .5925     10           5.925      .0004365         .8293123         157.5693
 20       200     .1975     10           1.975      .0001455         .2909868         58.19736
 21       210       0       10             0            0                0                0
 22       220       0       10             0            0                0                0
 23       230       0       10             0            0                0                0
 24       240       0       10             0            0                0                0
 25       250       0       10             0            0                0                0
 26       260       0       10             0            0                0                0
 27       270       0       30             0            0                0                0
 28       300       0       30             0            0                0                0
 29       330       0       30             0            0                0                0
 30       360       0        0             0            0                0                0

                                  SCidti 1357.45             StiEdti    92.65    StitiEdti 9348.40

                                                                                        MEAN     92.65

                                                                                        VAR.     764.86

                                                                                        S.D.     27.66
```

SERIES Ph8; Fe=30rpm; Xe=107rpm; CTM=55C; THROUGHPUT=.84Kg/h

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	10	0	0	0	0
2	20	0	10	0	0	0	0
3	30	0	10	0	0	0	0
4	40	0	10	0	0	0	0
5	50	3.95	10	39.5	.0046477	2.323871	116.1936
6	60	13.8	10	138	.0162377	9.742609	584.5566
7	70	19.75	10	197.5	.0232387	16.26710	1138.697
8	80	13.8	10	138	.0162377	12.99015	1039.212
9	90	11.8	10	118	.0138844	12.49596	1124.636
10	100	7.9	10	79	.0092955	9.295485	929.5485
11	110	5.9	10	59	.0069422	7.636417	840.0059
12	120	3.55	10	35.5	.0041771	5.012502	601.5002
13	130	2.76	10	27.6	.0032475	4.221797	548.8337
14	140	1.185	10	11.85	.0013943	1.952052	273.2872
15	150	.5925	10	5.925	.0006972	1.045742	156.8613
16	160	0	10	0	0	0	0
17	170	0	10	0	0	0	0
18	180	0	10	0	0	0	0
19	190	0	10	0	0	0	0
20	200	0	10	0	0	0	0
21	210	0	30	0	0	0	0
22	240	0	30	0	0	0	0
23	270	0	30	0	0	0	0
24	300	0	0	0	0	0	0

SCidti 849.88 StiEdti 82.98 StitiEdti 7353.33

MEAN	82.98
VAR.	467.04
S.D.	21.61

```
SERIES 2; Fe=20rpm; Xe=60rpm; CTM=110C
                                                            E
 Sample     ti        Ci        dti           Cidti      Ci/SCidti        tiEdti          titiEdti
   1        30        0         30             0            0              0                0
   2        60        0         30             0            0              0                0
   3        90        0         10             0            0              0                0
   4       100        0         10             0            0              0                0
   5       110      .1975       10           1.975      .0008337       .9170536         100.8759
   6       120      .1975       10           1.975      .0008337       1.000422         120.0507
   7       130      .1975       10           1.975      .0008337       1.083791         140.8928
   8       140      .1975       10           1.975      .0008337       1.167159         163.4023
   9       150       .79        10            7.9       .0033347       5.002111         750.3166
  10       160      1.185       10           11.85      .0050021       8.003377         1280.540
  11       170      2.76        10           27.6       .0116505       19.80583         3366.990
  12       180      2.76        10           27.6       .0116505       20.97087         3774.757
  13       190      1.975       10           19.75      .0083369       15.84002         3009.603
  14       200      2.37        10           23.7       .0100042       20.00844         4001.688
  15       210      1.975       10           19.75      .0083369       17.50739         3676.551
  16       220      1.58        10           15.8       .0066695       14.67286         3228.029
  17       230      1.58        10           15.8       .0066695       15.33981         3528.155
  18       240       .79        10            7.9       .0033347       8.003377         1920.810
  19       250      .5925       10           5.925      .0025011       6.252638         1563.160
  20       260      .5925       10           5.925      .0025011       6.502744         1690.713
  21       270      .395        10           3.95       .0016674       4.501900         1215.513
  22       280      .1975      180           35.55      .0008337       42.01773         11764.96
  23       460        0          0             0            0              0                0

                                    SCidti  236.90             StiEdti    208.60   StitiEdti 45297.01

                                                                                            MEAN     208.60

                                                                                            VAR.    1784.09

                                                                                            S.D.     42.24
```

SERIES 4; Fe=20rpm; Xe=40rpm; CTM=110C

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	30	0	10	0	0	0	0
2	40	0	10	0	0	0	0
3	50	0	10	0	0	0	0
4	60	0	10	0	0	0	0
5	70	0	10	0	0	0	0
6	80	0	10	0	0	0	0
7	90	0	10	0	0	0	0
8	100	0	10	0	0	0	0
9	110	0	10	0	0	0	0
10	120	0	10	0	0	0	0
11	130	0	10	0	0	0	0
12	140	0	10	0	0	0	0
13	150	.79	10	7.9	.0036036	5.405405	810.8108
14	160	1.58	10	15.8	.0072072	11.53153	1845.045
15	170	2.37	10	23.7	.0108108	18.37838	3124.324
16	180	2.37	10	23.7	.0108108	19.45946	3502.703
17	190	2.37	10	23.7	.0108108	20.54054	3902.703
18	200	2.37	10	23.7	.0108108	21.62162	4324.324
19	210	1.975	10	19.75	.0090090	18.91892	3972.973
20	220	1.58	10	15.8	.0072072	15.85586	3488.288
21	230	1.58	10	15.8	.0072072	16.57658	3812.613
22	240	1.185	10	11.85	.0054054	12.97297	3113.514
23	250	1.185	10	11.85	.0054054	13.51351	3378.378
24	260	1.185	10	11.85	.0054054	14.05405	3654.054
25	270	.79	10	7.9	.0036036	9.729730	2627.027
26	280	.5925	10	5.925	.0027027	7.567568	2118.919
27	290	0	130	0	0	0	0
28	420	0	0	0	0	0	0

SCidti 219.23 StiEdti 206.13 StitiEdti 43675.68

MEAN 206.13

VAR. 1187.70

S.D. 34.46

SERIES 7; Fe=20rpm; Xe=40rpm; CTM=55L

					E		
Sample	ti	Ci	dti	Cidti	Ci/SCidti	tiEdti	titiEdti
1	30	0	30	0	0	0	0
2	60	0	30	0	0	0	0
3	90	0	10	0	0	0	0
4	100	.5925	10	5.925	.0014851	1.485149	148.5149
5	110	.5925	10	5.925	.0014851	1.633663	179.7030
6	120	.79	10	7.9	.0019802	2.376238	285.1485
7	130	.79	10	7.9	.0019802	2.574257	334.6535
8	140	1.185	10	11.85	.0029703	4.158416	582.1782
9	150	1.975	10	19.75	.0049505	7.425743	1113.861
10	160	1.975	10	19.75	.0049505	7.920792	1267.327
11	170	1.975	10	19.75	.0049505	8.415842	1430.693
12	180	2.37	10	23.7	.0059406	10.69307	1924.752
13	190	3.16	10	31.6	.0079208	15.04950	2859.406
14	200	2.37	10	23.7	.0059406	11.88119	2376.238
15	210	3.16	10	31.6	.0079208	16.63366	3493.069
16	220	2.37	10	23.7	.0059406	13.06931	2875.248
17	230	2.37	10	23.7	.0059406	13.66337	3142.574
18	240	2.37	10	23.7	.0059406	14.25743	3421.782
19	250	1.975	10	19.75	.0049505	12.37624	3094.059
20	260	1.58	10	15.8	.0039604	10.29703	2677.228
21	270	1.58	10	15.8	.0039604	10.69307	2887.129
22	280	.5925	10	5.925	.0014851	4.158416	1164.356
23	290	.79	10	7.9	.0019802	5.742574	1665.347
24	300	.79	10	7.9	.0019802	5.940594	1782.178
25	310	1.185	10	11.85	.0029703	9.207921	2854.455
26	320	1.185	10	11.85	.0029703	9.504950	3041.584
27	330	.79	10	7.9	.0019802	6.534653	2156.436
28	340	.79	10	7.9	.0019802	6.732673	2289.109
29	350	.5925	10	5.925	.0014851	5.198020	1819.307
30	360	0	120	0	0	0	0
31	480	0	0	0	0	0	0
			SCidti	398.95	StiEdti	217.62	StitiEdti 50866.34

MEAN	217.62
VAR.	3506.23
S.D.	59.21

SERIES 8

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	30	0	30	0	0	0	0
2	60	0	30	0	0	0	0
3	90	0	10	0	0	0	0
4	100	.79	10	7.9	.0031746	3.174603	317.4603
5	110	1.58	10	15.8	.0063492	6.984127	768.2540
6	120	1.58	10	15.8	.0063492	7.619048	914.2857
7	130	1.975	10	19.75	.0079365	10.31746	1341.270
8	140	1.975	10	19.75	.0079365	11.11111	1555.556
9	150	1.975	10	19.75	.0079365	11.90476	1785.714
10	160	1.975	10	19.75	.0079365	12.69841	2031.746
11	170	1.975	10	19.75	.0079365	13.49206	2293.651
12	180	1.58	10	15.8	.0063492	11.42857	2057.143
13	190	1.58	10	15.8	.0063492	12.06349	2292.063
14	200	1.58	10	15.8	.0063492	12.69841	2539.683
15	210	1.185	10	11.85	.0047619	10	2100
16	220	1.185	10	11.85	.0047619	10.47619	2304.762
17	230	1.185	10	11.85	.0047619	10.95238	2519.048
18	240	.79	10	7.9	.0031746	7.619048	1828.571
19	250	.79	10	7.9	.0031746	7.936508	1984.127
20	260	.5925	10	5.925	.0023810	6.190476	1609.524
21	270	.5925	10	5.925	.0023810	6.428571	1735.714
22	280	0	150	0	0	0	0
23	430	0	0	0	0	0	0

SCidti 248.85 StiEdti 173.10 StitiEdti 31978.57

MEAN 173.10

VAR. 2016.61

S.D. 44.91

SERIES 14

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	80	0	0	0	0
2	90	0	5	0	0	0	0
3	95	.1975	5	.9875	.0044444	2.111111	200.5556
4	100	.395	5	1.975	.0088889	4.444444	444.4444
5	105	.395	5	1.975	.0088889	4.666667	490
6	110	.5925	5	2.9625	.0133333	7.333333	806.6667
7	115	.5925	5	2.9625	.0133333	7.666667	881.6667
8	120	.79	5	3.95	.0177778	10.66667	1280
9	125	.79	5	3.95	.0177778	11.11111	1388.889
10	130	.79	5	3.95	.0177778	11.55556	1502.222
11	135	.79	5	3.95	.0177778	12	1620
12	140	.79	5	3.95	.0177778	12.44444	1742.222
13	145	.395	5	1.975	.0088889	6.444444	934.4444
14	150	.5925	5	2.9625	.0133333	10	1500
15	155	.5925	5	2.9625	.0133333	10.33333	1601.667
16	160	.395	5	1.975	.0088889	7.111111	1137.778
17	165	.395	5	1.975	.0088889	7.333333	1210
18	170	.395	5	1.975	.0088889	7.555556	1284.444
19	175	0	5	0	0	0	0
20	180	0	5	0	0	0	0
21	185	0	135	0	0	0	0
22	320	0	0	0	0	0	0
			SCidti	44.44	StiEdti	132.78	StitiEdti 18025.00

MEAN 132.78

VAR. 395.06

S.D. 19.88

SERIES 17; Fe=20rpm; Xe=40rpm; CTM=55C

Sample	ti	Ci	dti	Cidti	E Ci/SCidti	tiEdti	titiEdti
1	10	0	70	0	0	0	0
2	80	0	5	0	0	0	0
3	85	.1975	5	.9875	.0007519	.3195489	27.16165
4	90	.79	5	3.95	.0030075	1.353383	121.8045
5	95	.79	5	3.95	.0030075	1.428571	135.7143
6	100	3.16	5	15.8	.0120301	6.015038	601.5038
7	105	3.55	5	17.75	.0135148	7.095270	745.0033
8	110	3.95	5	19.75	.0150376	8.270677	909.7744
9	115	3.95	5	19.75	.0150376	8.646617	994.3609
10	120	4.94	5	24.7	.0188065	11.28391	1354.069
11	125	3.95	5	19.75	.0150376	9.398496	1174.812
12	130	4.94	5	24.7	.0188065	12.22423	1589.150
13	135	3.95	5	19.75	.0150376	10.15038	1370.301
14	140	3.95	5	19.75	.0150376	10.52632	1473.684
15	145	3.16	5	15.8	.0120301	8.721805	1264.662
16	150	2.37	5	11.85	.0090226	6.766917	1015.038
17	155	1.975	5	9.875	.0075188	5.827068	903.1955
18	160	1.975	5	9.875	.0075188	6.015038	962.4060
19	165	1.185	5	5.925	.0045113	3.721805	614.0977
20	170	.79	5	3.95	.0030075	2.556391	434.5865
21	175	.79	5	3.95	.0030075	2.631579	460.5263
22	180	.5925	5	2.9625	.0022556	2.030075	365.4135
23	185	.395	5	1.975	.0015038	1.390977	257.3308
24	190	.395	5	1.975	.0015038	1.428571	271.4286
25	195	.395	5	1.975	.0015038	1.466165	285.9023
26	200	.395	5	1.975	.0015038	1.503759	300.7519
27	205	0	135	0	0	0	0
28	335	0	0	0	0	0	0

SCidti 262.68

StiEdti 130.77

StitiEdti 17632.68

MEAN	130.77
VAR.	531.21
S.D.	23.05

APPENDIX H: THE LITERATURE USED TO MARKET THE REACTIVE PROCESSING PROJECT

CONTINUOUS PRODUCTION OF REACTIVE POLYMERS

Development of a Reactive Processing System

11.9.87

RAPRA TECHNOLOGY LIMITED

REACTIVE PROCESSING

PROJECT PLAN