KINGSTON
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# COMPRESSION RECOVERY OF RIGID POLYMER FOAMS FOLLOWING CONFINEMENT AT ELEVATED TEMPERATURE

## SHEHLA DARR

A Thesis Submitted in Partial Fulfilment of The Requirements of Kingston University For The Degree of Doctor of Philosophy

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# Abstract

Cellular materials are all around us. They can be found in nature as in bone, wood, leaves and even in our food. In the last fifty years, man has produced many synthetic cellular materials: firstly with polymeric foams and more recently with foamed metals, ceramics and glass. Polymer foams are used in a variety of applications ranging from coffee mugs to the feet of the Apollo Lunar Module, for which they were used as shock absorbers.

This project was aimed at understanding the recovery from long-term compression of rigid polymer foams.

Understanding the dynamics involved in the recovery process of foams is very important, especially in the automotive industry where it determines safety of the driver, passengers and pedestrians, for example, in car bumpers.

In this study, foam samples were compressed by strains which spanned their linear elastic and stress plateau regions, i.e. 2.5% - 35% for one month at various temperatures.

Recovery occurred in two stages, designated phase 1 and phase 2. Phase 1 is the initial recovery, which dominates the full recovery process and is complete within hours or days. Phase 2 is a lesser recovery occurring over a much longer period of approximately 100 days. The initial recovery is associated with the polymer itself, whilst phase 2 recovery is associated with the cellular structure. Recovery of all

samples was monitored for a minimum of 100 days at ambient temperature. Tests were also carried out to see how the environmental surroundings affect the polymer recovery.

The different polymer foams which were investigated were:

- Polyethylene
- Polyetherimide
- Polyurethane
- Polysulphone

The polymers tested all showed very different responses to the changes in temperature. All polymers investigated at different compressive strains demonstrated reproducible Arrhenius plot slopes under different conditions and hence a reasonably reproducible set of values of recovery process. Analyses were based on the final total recovery of the thickness as the most reliable parameter of recovery. It has been demonstrated that the mechanism of polymer deformation and recovery probably does not involve chain scission but backbone vibration; that the best parameter for characterising the recovery process is the final total dimensional recovery of the sample; and that subtle environmental changes have a large effect on the recovery from compression, although temperature and humidity are not responsible.

Contents page

# 1.0 Introduction

Cellular foams touch our lives every day: they are utilized in a wide variety of applications. Some applications are overlooked such as thermal insulators for housing and inside our refrigerators, while other foam applications are more noticeable, for example cushioning for our furniture and packaging. Polymer products are very important in our daily lives.

*Figure 1: polymer foams*

Flexible foams are chemically and physically complex materials. The major markets for flexible foams are for cushioning materials, transportation and packaging applications.

Flexible foams can range from the soft, cosy lounge chair in our living rooms to the durable, yet comfortable seat of our bicycles. The automotive industry uses flexible foams for arm rests, crash pads, side panels, and even dashboards, not to mention seat cushions. The padding in motorcycle helmets and seats is flexible foam. Flexible foam is used as padding for the trucking industry, to protect produce from being damaged in transit. The medical industry uses flexible foams for airless wheelchair tires as well as for various prosthetic devices. The sporting goods, recreation, and entertainment industries use flexible foam for playing balls, archery targets, and movie props to name a few applications.

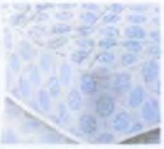
| Flexible Foams | | Rigid Foams | |
|---|---|---|---|
| Padding used in clothes |  | Used in the automotive industry |  |
| Used in mattress |  | Almost all refrigerators and freezers are now made using rigid polyurethane foam |  |

*Figure 2: Table to show different applications of flexible and rigid foam*

On the other hand, rigid foams continue to be of great importance to industrial products in construction, thermal appliance insulation and other applications. Rigid foams have a variety of uses including thermal or sound insulation for the aerospace, aircraft and construction industries as well as decoration or reinforcement of building structures for the construction industry. Rigid foams can be found as flotation devices for the marine or sporting goods industries. They can also be used in decorative applications such as moulded picture frames or furniture components. Rigid foams are used to create synthetic rocks and corals for aquariums and landscaping. Even the entertainment industry uses rigid foams for theme park structures and set decorations.

The major benefit of rigid foamed materials is their high strength- to weight ratio. Foams have replaced many of the traditional uses of elastomers, since they often have superior recovery responses. This quality often enables them to compete with metals in some applications.

Understanding the dynamics involved in the recovery process of foams following long-term compression is very important, for example in the automotive industry where it can determine the safety of the driver, passengers and pedestrians, and in the heat insulation and earthquake protection of large structures.

Cellular plastic is defined as a plastic material the apparent density of which is decreased substantially by the presence of numerous cells dispersed throughout its mass. [1] Cellular plastics or plastic foams can also be referred to as expanded or sponge plastic which usually consists of a minimum of two phases; a gaseous phase, which is derived from the blowing agent, and a solid phase which is the plastic.

The dominant factor in determining foam properties comes from the chemical nature of the solid plastic phase; the composition of the gaseous phase has an important effect on some selected properties such as thermal insulation.

An advantage of using polymeric foam is the small amount of polymer mass needed to obtain the same volume as an unfoamed polymer, due to the gas. [2] A disadvantage of using foam is the relatively expensive production process.

The gas in the foam is normally considered as a lightweight filler or extruder for the solid plastic phase. [3]

A blowing agent is defined as any substance that produces a cellular structure; therefore the gaseous phase in most polymeric foam material is derived from the blowing agent. The blowing agent plays a very important role in determining the manufacturing and performance of polymer foam; it is the dominant factor controlling the density of the foam; and it also affects the cellular microstructure and morphology of the foam, which in turn define the end use performance. [4]

There are two types of blowing agent used to produce foams: chemical blowing agents and physical blowing agents. [5] Gases are given off during the foaming process by the chemical blowing agents; this can either be due to the chemical polymerization reaction or thermal decomposition of a secondary agent. Physical blowing agents are basically inert gases such as nitrogen, carbon dioxide, freon, etc.

A cellular solid is made up of an interconnected network of solid struts or plates which form the edges and faces of cells. [6] Foams may be classified as closed-cell or open-cell. If the solid of which the foam is made is contained in the cells edges only and the cells connect through open faces, the foam is said to open-celled. If the faces are solid too, each cell is sealed off from neighbours. It is said to be closed-celled. The degree of connectivity has a significant effect on the properties of the foam. All gases expand when pressure is released; $p V = n R T$. Blowing agents include volatile liquids which evaporate on heating or when pressure is released.

*Figure 2*

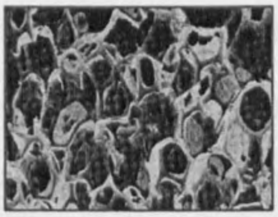


*Figure 3*

*(2) Photomicrograph* of cross-section of rigid polyurethane foam (closed cell), 10X.* [7]

*(3) SEM** micrograph of cross-section of flexible polyurethane foam (open cell), 20X.* [7]

Closed-cell foams are generally rigid while open-cell foams are generally flexible. [5] The density and the strength of the solid polymer are decreased due to the amount of cells present. In closed cell materials the gas is dispersed in the form of discrete bubbles and the polymer matrix forms a continuous phase. In open-cell foams the voids coalesce so that both the solid and the fluid phases are continuous. The fluid is able to flow thought the matrix under the action of some driving potential, whereas in closed-cell solids, the gas transport takes place only by diffusion through cell walls.

The ease of the movement of the fluid phase through the matrix is one of the factors governing the physical and mechanical properties of the cellular polymer.

Cellular plastics can also be classified to their stiffness, the two extremes being termed rigid and flexible. Skochdopole and Rubens defined a rigid foam as one in which the polymer matrix exists in the crystalline state. [8] Foams may be flexible or rigid depending upon whether their glass transition temperatures are below or above ambient temperature, which also depends upon their chemical composition, degree of crosslinking and degree of crystallinity.

# 2.0 Polyethylene foam

## 2.1 Chemistry:

Polyethylene has the simplest polymer structure. It consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon. [9] End groups are notable but have little effect on high molecular weight polymers. However, they have a major contribution to free volume(less so with high molecular weight polymers)

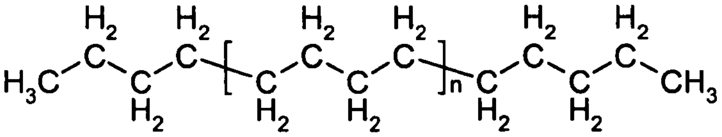


*Figure 2.1: Chemical structure of polyethylene*

Polyethylene foams can exist in either crosslinked or non-crosslinked form. The latter are manufactured using an extrusion process which is particularly applicable to low density foams (LDPE) whilst the crosslinking is achieved either by chemical or irradiation methods and is associated with high density polyethylene (HDPE).

Polyethylenes are classified according to their density, which in turn depends on the extent and type of branching present in the material. LDPE has many more branches then HDPE, therefore, the chains do not fit well together; it has less strong intermolecular forces as the instantaneous dipole-induced-dipole attraction is less, resulting in a low density and tensile strength. HDPE has practically no branching and therefore has much stronger forces and tensile strength. **[10]**

Foam density is a measurement of mass per unit volume where the greatest contributor to the mass is the polymer, while the greatest contributor to the volume is the cells. The densities of solid polymers vary very little from ~1000kg $m^{-3}$ ($1gcm^{-3}$). High density polyethylene foam is available in broad range of densities, ranging from as low as $30kgm^{-3}$ to high $115kgm^{-3}$. Foam density is a function of the density of unfilled foam. The limiting maximum value of the foam density is that of the polymer density itself.

Polyethylene foam is one of the most important plastic foams. Production of commercial polyethylene foams started in the 1940s. Until the 1980s studies concentrated on the processing mechanisms and since the 1990s researchers have started to study the effect of molecular structure. [11]

Polyethylene foam used in this research has been provided by Zotefoam plc in Croydon. The foam has been supplied as slab stock.

### 2.1.1 Blowing agents:

The blowing agent plays an important role in both the manufacture and performance of polymer foam. Blowing agents are normally gaseous materials used for the formation of plastic foams. In preparing thermoset foams there are two kinds of blowing agents which can be used:

- ➤ Chemical blowing agent
- ➤ Physical blowing agent

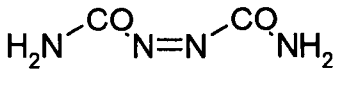
### 2.1.1.1 Chemical blowing agent:

These are compounds which release gases under the foam processing conditions, either due to thermal decomposition or due to chemical reaction. The use of chemical blowing agents results in the decomposition of the original molecule, one or more gases for polymer expansion, and one or more solid residues that remain in the foamed polymer. [4]

Chemical agents are becoming prominent and are now the standard ingredient for producing the crosslinked variety of polyethylene foam. Some examples of those that are in commercial use include sodium bicarbonate and sodium borohyride [12] Sodium bicarbonate is deemed undesirable as its decomposition commences at a temperature close to the melting point of polyethylene. In addition, the carbon dioxide and water that are produced from this decomposition diffuse much more rapidly through the polyethylene than air and, as such, result in unwanted foam shrinkage.

Azodicarbonamide (ADC) is most commonly used for the production of polyethylene foam. It has the highest gas yield of any commercial chemical blowing agent. ADC produces a mixture of nitrogen, carbon monoxide and carbon dioxide.

The reaction products produce little odour or discolouration.



$H_2N-CO-N=N-CO-NH_2$

*Figure 2.2 Azodicarbonamide (ADC)*

The decomposition of ADC is quite rapid at high temperatures. Various additives can be included into the polymer to lower the decomposition temperature.

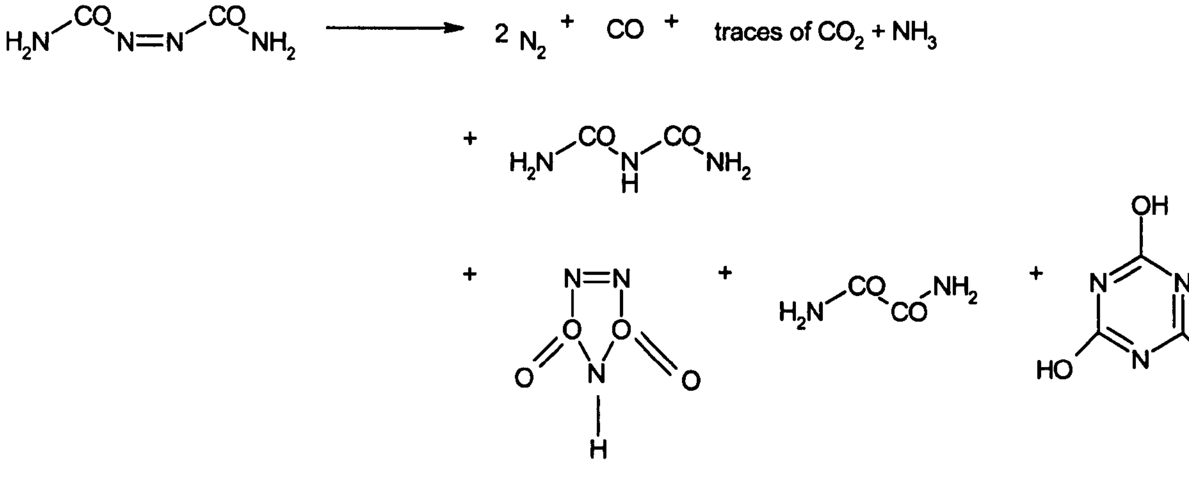


*Figure 2.3 Decomposition of Azodicarbonamide (ADC)*

#### 2.1.1.2 Physical blowing agents

Physical blowing agents provide gas for the expansion of polymers by undergoing change in the physical state. [4] Carbon dioxide, nitrogen and low boiling point organic liquids are the standard physical blowing agents. Chlorofluorocarbons are an ideal candidate for the organic liquid variety due to their non- flammability and inertness. [13]

CFCs have gradually been reduced in applications, because of the ozone depletion problems. The use of CFCs does affect the ozone layer; it destroys the ozone in the stratosphere.

Hydrochlorofluoroalkanes (HCFC) are an alternative solution given that their ozone depletion properties are less. But there is still a disadvantage as they are too expensive and there are expenditure problems associated with storage of the product prior to use and equipment costs. Therefore the use of chemical blowing agents is more suitable and they are the standard ingredient for producing crosslinked polyethylene.

#### 2.1.2.3 Azote process

This unique process involves the expansion of foams using nitrogen gas. This process creates low odour, highly pure foams with excellent chemical and water resistance properties. A more detailed description will be explained later on in the chapter.

## 2.2 Manufacturing techniques of expanded polyethylene foams

Polyethylene is a typical crystalline polymer; therefore it exhibits very high visco- elasticity at temperatures below its melting point. At temperatures above the melting point, it shows a drastic decline in visco-elasticity.

Polyethylene is generally crosslinked to modify its visco-elasticity, so the material can withstand the expansion pressure which normally results from the decomposing foaming type agents when foaming is carried out. [14, 15]

Extrusion process is the most common and economically feasible for producing large amounts of crosslinked polyethylene. The processes for manufacturing extruded crosslinked foams were developed in Japan in the 1960s. [4, 15-17] There are two techniques which are available for the manufacture of crosslinked polyethylene. They are:

a) Irradiation crosslinking process
b) Chemically crosslinked process

The use of these techniques produces highly expanded polyethylene foams. Both processes traditionally use a chemical blowing agent for expansion.

### 2.2.1 Irradiation crosslinking process:

Crosslinking via irradiation techniques is conducted via the Toray and Sekisui processes. This process is normally described as a continuous extrusion process. There are three stages involving the extrusion of a polymer sheet. Irradiation crosslinking is effected by bombarding electron rays from an accelerator.

*Figure 2.4 Schematic flow diagram of Irradiation crosslinking process [18]*

In irradiation crosslinking, the crosslinking and expansion stages are separate, therefore reducing the problems of balancing levels of crosslinking and expansion in the final stage. [18]

#### 2.2.1.1 Extrusion:

This method simply entails a mixture of polyethylene and the blowing agent which is then heated and kneaded at a temperature which is lower then the decomposition point of the blowing agent; this is then followed by the extrusion of the mixture, which is released as a thin film or sheet at the same temperature.[15]

#### 2.2.1.2 Crosslinking:

The unexpanded matrix is exposed to a radiation source; it can either be an electron beam source or a cobalt 60 gamma ray source. Crosslinking is possible at high or low temperature.[19, 20]

#### 2.2.1.3 Expansion:

The expanding of the sheet is carried out as a separate procedure; this involves a wide range of heating systems. The foam is expanded by passing the matrix through UV hot air vertical oven, where three dimensional expansion takes place.

There are certain advantages in using the irradiation technique; this technique produces a white, low density sheet with extremely fine cell structures. The separation stage minimises the variation in crosslink density and therefore the melt elasticity in the polymer matrix at the foaming stage.

A disadvantage of this technique is the additional costs of maintaining and shielding the radiation source; this includes restriction on the final expanded thickness of the sheet which can be produced.

Problems such as reversion on outer surfaces of the sheets can occur, if you try to compensate an increase in the thickness of the unexpanded sheet by increasing the radiation amount.

### 2.2.2 Chemically crosslinked process:

Development of this technique utilising the chemically crosslinked system was originally developed by Hitachi Chemical Co and Furakawa Electric Co, in Japan. Both processes are very similar.[21]

The basic principal of crosslinked foam techniques are shown below:

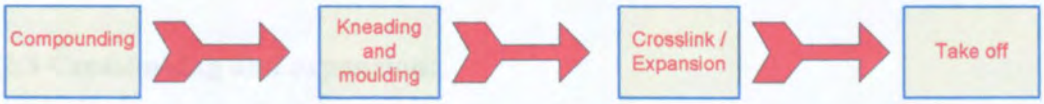


Figure 2.5 Schematic flow diagram of chemically crosslinked process

#### 2.2.2.1 Compounding:

The compounding technique is used for the incorporation of peroxide crosslinking agent. To avoid pre-decomposition the expandable concentrates require an extremely accurate control over the melt temperature and dwell time. Chemical compounding with polymers, other polymers or additives such as plasticizers, gases and pigments are added to the basic polymer resin before it in processed into the finished product. Internal mixers are being used by feeding directly on to a pelletising line and twin screw compounding units are being used for the production of concentrates based on peroxides (e.g. benzoyl peroxide or cumyl peroxide) or azodicarbonamide. [18, 22]

### 2.2.2.2 Kneading and moulding:

Polyethylene, the foaming agent and the crosslinking agent are mixed, the mixing and kneading occurs in an internal mixer or a twin screw extruder and the product is obtained in pellet form. The sample is heated at a temperature which will decompose the crosslinking agent and then the temperature is raised further more to decompose the foaming agent. The foaming agent is decomposed to produce the gas which helps expands the material.

### 2.2.2.3 Crosslinking and expansion:

The unexpanded, non-crosslinked sheet is passed through a high velocity oven to gain the necessary amount of expansion. The heat is transferred into the unexpanded sheet by directly impinging air flow from series slots in the plenum chambers which is positioned above the conveyor. It is important to maintain a crosslinking expansion balance or this can lead to poor release. Low levels of crosslinking results in low levels of melt strength causing cell collapse and in extreme cases can lead to tearing and breaking of sheets whilst in the hot air expansion oven. [18, 19, 23]

### 2.2.3 Foaming:

The foaming process involves heating an expandable mixture to decompose the foaming agent. The foam is made as the gas expands the bubbles [14] A few techniques have been listed which can be used.

#### 2.2.3.1 Air cushion system:

This technique is used for the chemically crosslinked foams. The material is crosslinked by passing the expandable material on an endless belt which is made up of polytetrafluoroethylene plate. The crosslinked sample has enough strength to support itself. The sample is placed in the hot air oven where foaming takes place.

#### 2.2.3.2 Gravity draw-down system:

This technique is suitable for the irradiation crosslinked foaming technique. A crosslinked sheet is transferred straight down by the gravity, it is self-supported by its own strength and heated to foam. The crosslinked sheet is passed through rollers in the oven, it is drawn down continuously. The sheet is preheated by the infra red heaters and hot air blowers. The foamed sheet is removed and left to cool.

#### 2.2.3.3 Liquid bath floating system:

The expandable material is floated on a liquid bath that is heated at a temperature above the decomposition point of the foaming agent, then heated by infra red heaters, which allows third dimensional expansion.

#### 2.2.3.4 Mesh wire conveyor system:

The expandable sheet is evenly heated on both sides; the sheet makes contact with a conveyor which is made up of a wire mesh, this results in the expanded sheet adhering to the mesh wire.

### 2.2.4 The autoclave process:

The autoclave process is a unique technique which was developed and is used by a company called Zotefoams plc. [16] The products are made by a unique high pressure nitrogen gas solution process.

The advantage of these products, compared with other polyethylene foams made by other technologies, stems directly from the use of this high pressure gas technology. This produces foams with regular cell walls without using any chemical blowing agents.

The process comprises three main stages:

- Extrusion and crosslinking
- Impregnation with nitrogen gas
- Expansion

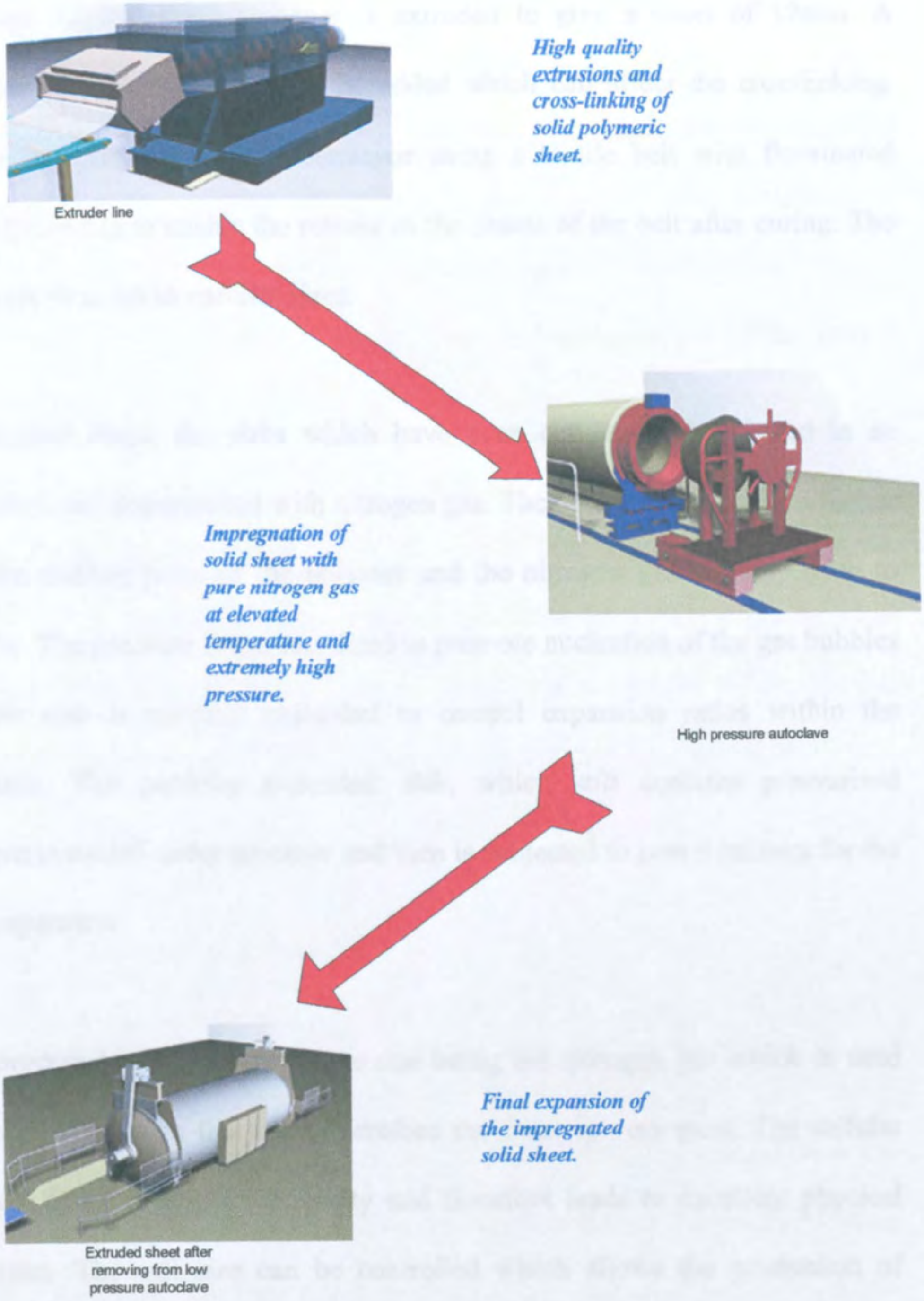


*Figure 2.5: Flow diagram of Zotefoams process [24]*

The first stage the raw polymer is extruded to give a sheet of 12mm. A peroxide crosslinking agent can be added which can affect the crosslinking. The sheets are passed on a conveyor using a textile belt with fluorinated polymer coating to enable the release of the sheets of the belt after curing. The sheets are then cut to specific sizes.

The second stage, the slabs which have been cut are heat softened in an autoclave, and impregnated with nitrogen gas. The temperature is raised higher then the melting point of the polymer and the nitrogen gas is pumped up to 70MPa. The pressure is the decreased to promote nucleation of the gas bubbles and the slab is partially expanded to control expansion ratios within the autoclave. The partially expanded slab, which still contains pressurized nitrogen is cooled under pressure and then is subjected to post treatment for the final expansion.

This process has many advantages one being the nitrogen gas which is used leaves no residue in the foam, therefore the foam is very pure. The cellular structure is of excellent uniformity and therefore leads to excellent physical properties. The cell size can be controlled which allows the production of foams with cell sizes in the range 0.2-0.8mm.

The only disadvantage is the high cost of equipment which is used in this technique. For example they rely on the large high pressure vessels which are expensive and also difficult to accommodate.

### 2.2.5 Single stage process:

This technique basically involves the polymer, crosslinker and the blowing agent, being mixed together and placed in mould cavity. The compound is heated under pressure and once the expansion cycle is complete the press is released, allowing for rapid expansion. The product jumps out of the mould upon expansion.

There are some mechanical problems which can affect this process for example, high mould pressures can be generated therefore requiring high clamping forces and heavy duty presses. Also only part of the platen area can be used, to avoid contact of the expanding foam with guide pillars. [25]

### 2.2.6 Two stage moulding process:

This technique was produced to overcome the problems which occur in the single stage process. Different forms can be produced. This process basically involves crosslinked foam, which is partially expanded by a conventional moulding technique and then fully expanded in a hot air oven, as a completely separate stage.

The advantage of using this technique over the single stage process is that the reduced volume expansion of the expandable blank after the mould opening allows maximum utilisation of the platen area, within the restraints of the clamping forces. [25]

### 2.2.7 Injection moulding technique:

This technique is very versatile for several reasons: it allows the production of complex shapes, it minimises secondary fabrication technique and also it accommodates a reduction in waste. Items such as bottles, dustbins, razors and gear wheels are only a few items which are produced by injection moulding.

*Figure 2.6 Plastic bottles*

Two items are needed for injection moulding: an injection moulding machine and a mould.

Plastic granules which have already been heated are injected under pressure into a pre-heated mould. The pressure is maintained to prevent the plastic creeping back into the screw chamber. The plastic is cooled and takes the shape of the mould cavity, the plastic component is solidified. The mould is opened and the contents are ejected.

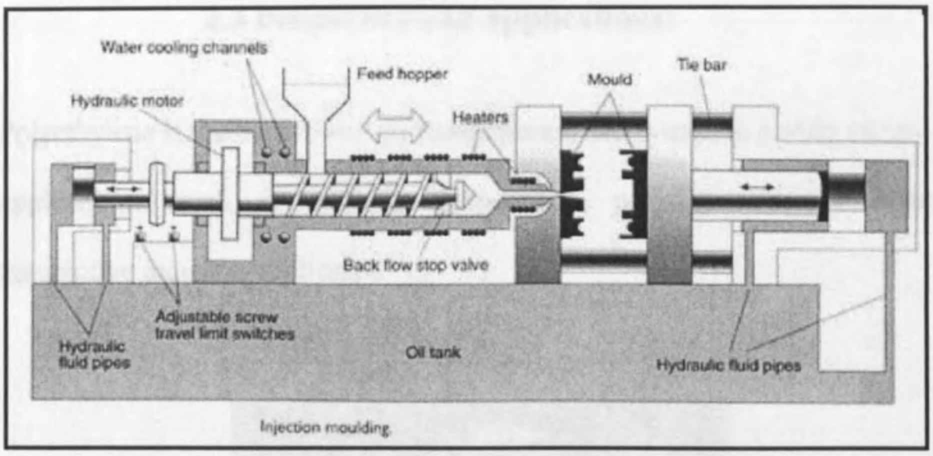


*Figure 2.7: Injection moulding [26]*

Heat transfer within the mould cavity can pose problems and constitutes together with the heat transfer over the total internal mould surface. The major problem is designing a suitable mould. The design of the mould is important to produce a high quality product. The mould should be suitable to withstand temperatures of 160-200° C.

## 2.3 Properties and applications:

Polyethylene is the most common thermoplastic and is used in a wide variety of applications, such as example construction, packaging, and buoyancy, automotive industry, medical.

*Figure 2.8: Polyethylene foam used in the manufacture of sports and leisure equipments as buoyancy aids. [27]*

Polyethylene is available for commercial use in two different forms: low density polyethylene and high density polyethylene. Both forms are used in many applications and both of which can be formed. High density polyethylene foams have demonstrated excellent performance, and are now being used extensively as improved substitutes for wood and solid polymers in many areas. Low density polyethylene plays a big role in safe packaging and cushioning of fragile and expensive pieces of equipment.

Crosslinked polyethylene adds two significant properties to the material, one being high heat resistance, and the second being that the material when crosslinked behaves as a thermoset and therefore can be heated above its crystalline melting point without distorting. [28]

Polyethylene can also be coloured which is good for the point of purchase, it also has a high sunlight resistance and maintains compression resistance and fatigue resistance over a wide range of temperatures and environmental conditions. [28]

Properties of polyethylene foam depend highly on the foam density. Polyethylene foams are normally closed-cell, therefore the gas which is trapped in the foam can contribute to the properties. The technique which is used to produce the foam can also affect the structure. Data provided by Zotefoams, indicate that the autoclave process produces foams with improved cellular structure compared with foams which are produced using chemical or blowing agents.

| Grade | LD24 | LD33 | LD45 |
|---|---|---|---|
| Nominal density(kg/m$^3$) | 24 | 33 | 45 |
| Compression strength(25%)(kPa) | 35 | 40 | 50 |
| Compression set (72 h, 50%RH) (%) | 32 | 27 | 22 |
| Tear strength (N/m) | 410 | 690 | 1130 |
| Tensile strength (kPa) | 340 | 455 | 600 |

*Table 2.1: Properties of low density polyethylene foams (autoclave process).*

The structure of the foam can make significant contribution to properties such as compression set, tensile strength and tear strength. [16]

### 2.3.1 Compression set:

A compression device consists of two metal steel plates which are equipped with spacers which are used to determine the degree of compression. See figure (2.9). Thickness of the sample is measured before and after placing in a compression jig. Compression set is defined in terms of stress in other words a sample with a fixed weight on it.

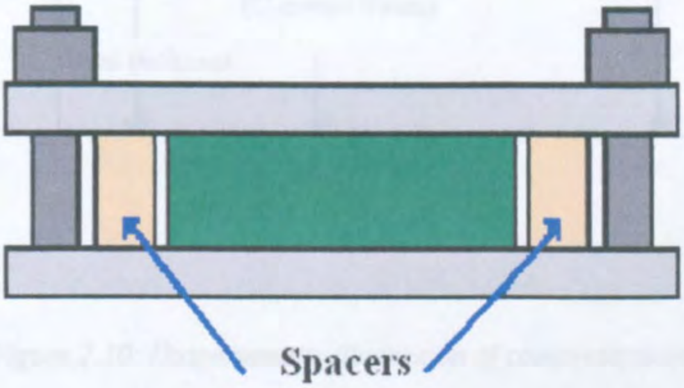


*Figure 2.9: Determination of compression set [29]*

Compression set is determined from the following equation:

$$CS = \frac{T_o - T_r}{T_o} \times 100$$

A schematic diagram of a set measurement in compression is given below. The amount of compression set is brief and partially permanent. The final measurement is made at an arbitrary and relatively short time after release of the test piece, before the sample has recovered. [30]

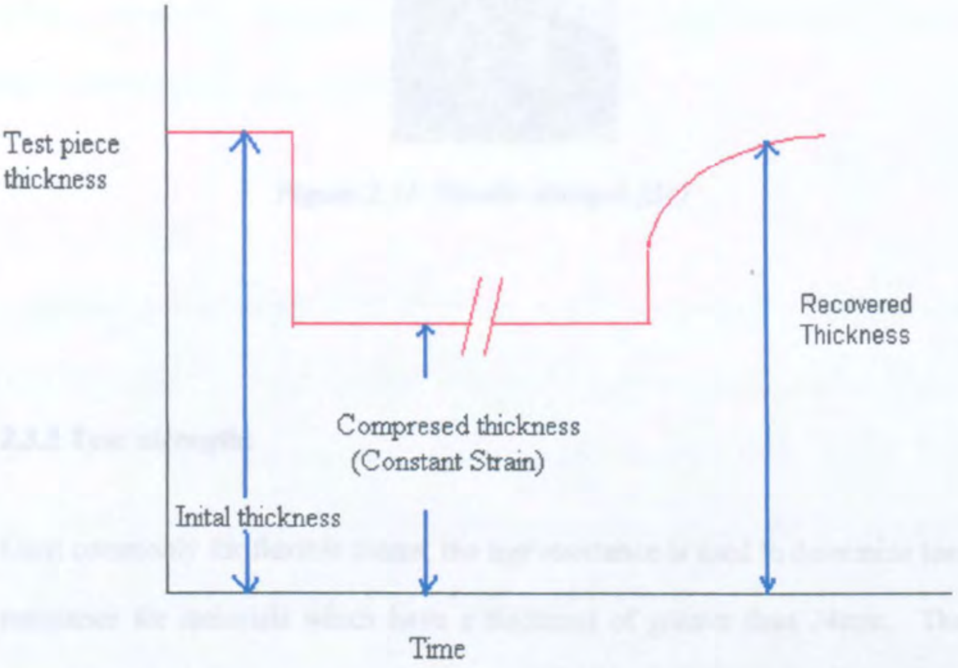


*Figure 2.10: Diagrammatic illustration of compression set [30]*

### 2.3.2 Tensile strength:

To determine the tensile strength of cellular material, the force required to elongate a sample as a function of applied elongation is recorded. The test piece is usually dumbbell-shaped, and is usually placed in the jaws of a machine. The force is noted at the point at which the foam snaps, also the separation between the gauge marks.

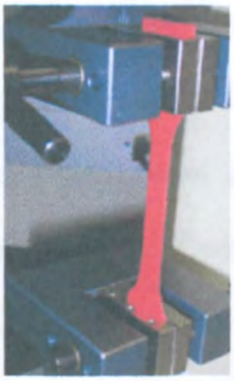


*Figure 2.11: Tensile strength [31]*

### 2.3.3 Tear strength:

Used commonly for flexible foams, the tear resistance is used to determine tear resistance for materials which have a thickness of greater than 24mm. The sample is placed in a machine where the rupture force is measured.

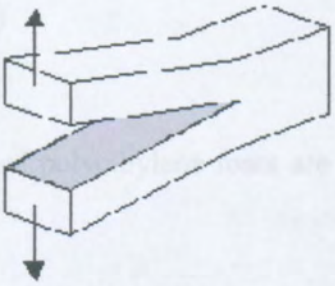


*Figure 2.12: Method used for tear strength [32]*

Properties of polyethylene foam are affected by the cellular structure and the mechanical properties of the matrix polymer. Mechanical properties of the polymer matrix can normally determine the type of the base polymer used; the processing conditions and the crosslinking can affect the crystallinity and molecular orientation of the polymer phase. Compressive strength increases rapidly as foam density increases.[21]

Low density polyethylene (LDPE) is an excellent electrical insulator, the outstanding dielectric properties led to its early use as a high frequency cable insulator. [33] The entire food production chain benefits from LDPE, from black mulching film and baling film and translucent materials for green houses through direct food packaging to supermarket carrier bags.

High density polyethylene foam (HDPE) is a material which offers a combination of high strength, rigidity, temperature resistance, and electrical insulation properties. [33]

Applications of crosslinked polyethylene foam are extremely varied. Some are listed below:

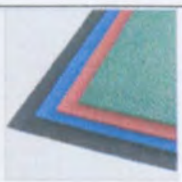
| Application: | Reason for use: | Example: |
|---|---|---|
| Protective Padding | High energy absorption and repeated compression resistance |  |
| Pipe insulation | Good insulation properties and heat resistance |  |
| Shoe Innersoles | Ability to mould the product after heating to fit the foot. |  |
| Gaskets | Used for moulded gaskets in electric wing mirrors, one of many applications in the automotive industry |  |
| Gymnastic mats | High energy absorption and fatigue resistance |  |

*Table 2.2: Examples of polyethylene foam [27, 34, 35]*

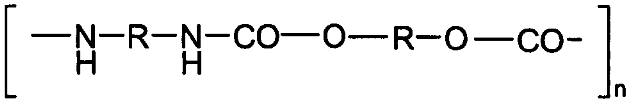
Foamed polyethylene used in this study has been kindly provided by Zotefoams plc. The major benefit of using polyethylene which is processed by Zotefoam is control of the cell diameter by using crosslinked polyethylene and nitrogen as the expanding gas. The block can be cut into sheets when cold and gives full control of the thickness of the sheet.

# 3.0 Polyurethane foams

## 3.1: Introduction:

Polyurethanes are the largest and most distinctive group of polymers, available as thermoplastics, thermosets and solutions. They are outstanding because of their ability to motivate important properties such as strength, durability and toughness.

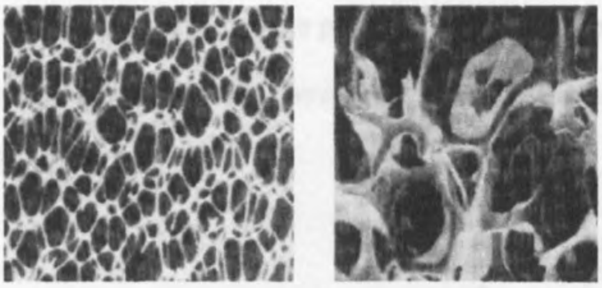
The polyurethanes include polymers which contain urethane groups. Usually these polymers are obtained by a combination of a polyisocyanate and polyols. Polyurethanes are copolymers containing blocks of low molecular – weight polyesters or polyethers covalently bonded by a urethane group. [36]



$$\left[ -\underset{H}{N}-R-\underset{H}{N}-CO-O-R-O-CO- \right]_n$$

*Figure3.1: Polyurethane*

Polyurethane foams can be classified into two major types; i.e. flexible (include semi-rigid) and rigid foams. Rigid foams are produced by a reaction between polyfunctional isocyanates with low molecular weight polyols which have three or more reactive hydroxyl groups. Flexible polyurethane foams are produced from a reaction between long chain triols, water and isocyanates. The polymer structure of rigid polyurethane foams are normally closed-cell and flexible polyurethane foams have open- cell morphology.



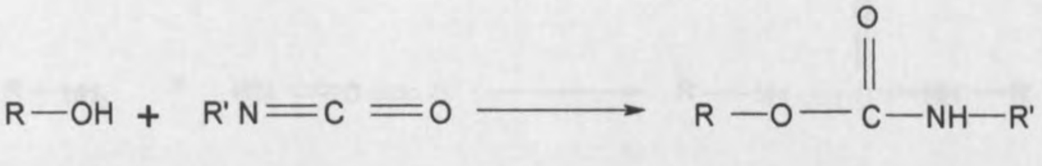
*Open cell* *Closed cell*

*Figure3.2: Rigid and flexible structures of polyurethane foam (open and closed cell) [7]*

**3.2 Chemistry of polyurethane foams:**

The chemistry behind polyurethane is based on the reactions of isocyanates with active hydro-containing compounds. The chemical reaction that occurs in polyurethane is relative simple and there are three main steps involved.

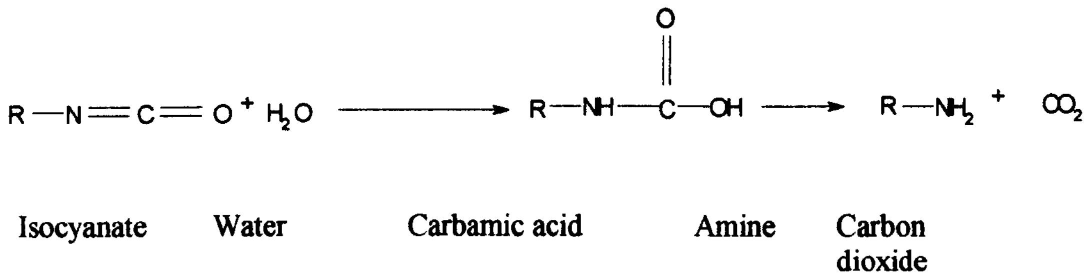
**Step one:** the reaction of isocyanates with hydroxyl to form urethane, where R and R' are alkyl or aryl groups. Linear polyurethane is formed by a hydrogen atom which is active attaching to the nitrogen atom of an isocyanate.



$$\underset{\text{Alcohol}}{R{-}OH} + \underset{\text{Isocyanate}}{R'N{=}C{=}O} \longrightarrow \underset{\text{Urethane}}{R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R'}$$

Alcohol Isocyanate Urethane

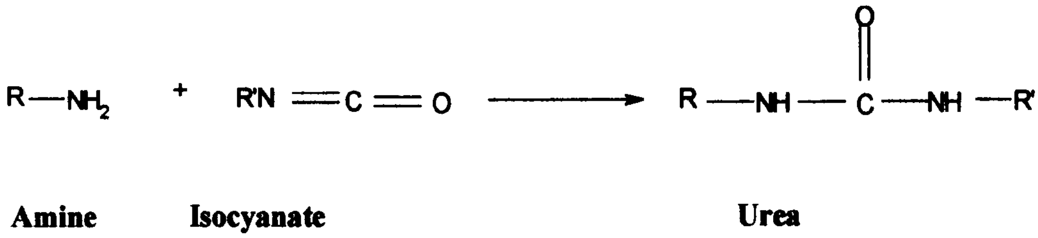
**Step two:** reaction of isocyanate with water leads to an intermediate product of a temporary carbamic acid which decomposes to produce carbon dioxide and an amine. To make foam, polyurethane polymer has to be expanded or blown by the introduction of gas bubbles. The carbon dioxide which is produced is a useful source for this.



$$R{-}N{=}C{=}O + H_2O \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \longrightarrow R{-}NH_2 + CO_2$$

The intermediate product of this reaction is a thermally unstable carbamic acid, which decomposes to an amine and carbon dioxide. The carbon dioxide disperses into bubbles which lead to expansion and production of a foam.

**Step three:** Reaction of amine with isocyanate to form a urea linkage. The urea is substituted with additional reactive groups which provide another pathway for polymer growth. Heat is released which is useful in kinetically driving the reaction and additional expansion of gas filled bubbles.



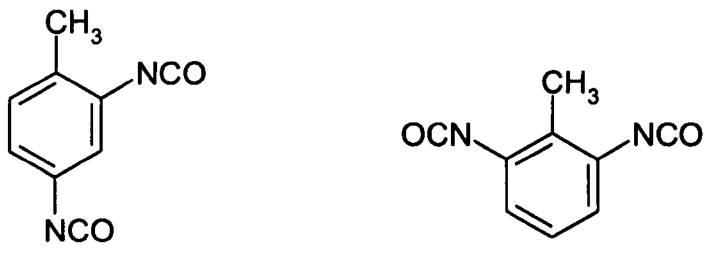
$$R{-}NH_2 + R'N{=}C{=}O \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R'$$

The complexity arises because of the close control, or balance that is needed of the order in which the specific reactions occur during a comparatively fast series of reactions [37]

### 3.2.1 Isocyanates:

Polyurethane foams are most commonly produced from an aromatic isocyanate component. There are two main isocyanates which are: toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

TDI is a colourless liquid and is commercially available in blend of 80% 2, 4- and 20% 2, 6-isomers. [16] TDI is commonly used for flexible foams. Pure 2, 4 isomer is generally more reactive than the pure 2, 6-isomer because of steric hindrance effects at the isomer positions. [38]



**2, 4-TDI** **2, 6-TDI**

*Figure3.3: Isomers of Toluene Diisocyanate*

Rigid foams can be made from TDI prepolymer but are most often based on diphenylmethane diisocyanate MDI. This also exists in two isomeric forms 2,4 -MDI and 4,4′-MDI. The most commonly used isomer is 4,4′-MDI.

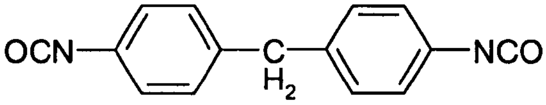


*Figure3.4: structure of 4,4 - MDI*

### 3.2.2 Polyols

Polyol component is usually in the form of a linear or branched weight hydroxyl terminated polyesters or polyethers. [39] Polyester-based foams have good mechanical properties but only moderate hydrolytic stability while polyether-based foams are more hydrolytically stable but are prone to oxidation.

Polyether polyols are produced by an anionic polymerisation of alkylene oxides (propylene oxide), an initiator (glycerol) and a catalyst. This material is used for both rigid and flexible polyurethane foams. Initiators normally are low molecular weight hydroxylated compounds whose functionality determines the result of the polyol. [4]

Polyester polyols are no longer used in large amounts in the production of polyurethanes foams; they have been discontinued due to their high cost. They are only used in specialised foam applications such as shoulder pads for clothing which need resistance to dry cleaning.

The catalyst used most commonly is potassium hydroxide, but there are side products which form. This causes difficulties in the production of polyol with molecular weight greater than 5,000gmol$^{-1}$ therefore giving greater flexibility and softness.

## 3.3 Polyurethane foam preparation techniques:

Polyurethane foam formation involves many reactions and there is much complexity in their synthesis and production.[40] There are three processes in which urethane foams can be formed; one shot, prepolymer and quasi-prepolymer process.

### 3.3.1 One shot process:

This process is commonly used for both flexible and rigid foams; it involves mixing all the essential ingredients simultaneously which are isocyanates, polyol, water, or other blowing agent, catalyst and additives. The reaction components are added one by one to the mixing head to achieve a higher viscosity control and mixing accuracy. [38, 41]

Polymerisation begins immediately; the molecular weight starts to increase which allows the process of expansion and the foam begins to rise. This is a very short process, all the reaction takes place after mixing and is normally carried out at room temperature.[38, 41]

### 3.3.2 Prepolymer process

The prepolymer process for producing polyurethane is a two step procedure. The isocyanate reacts with a polyol in a prereaction to form a low molecular weight prepolymer. Most prepolymers are solids at ambient temperatures. This is then mixed with water, catalyst, surfactant and auxiliary blowing agents which produces the foam. The prepolymer has a high viscosity, with poor flow characteristic and the isocyanate available for the reaction with water is limited. As the prepolymer is viscous this causes problems with the accuracy in metering and mixing. This process is employed extensively in the manufacture of rigid foams, rarely used for flexible foams.[38, 41]

### 3.3.4 Quasi-prepolymer process

This process consists of characteristics from both one shot process and the prepolymer process. A fraction of the polyol is preheated with isocyanate to produce a prepolymer which contain a large amount of unreacted isocyanate; the quasi- prepolymer is then reacted with additional amounts of polyol. The advantage of this technique is the ease of processing, stabilised foam increase and low exotherm. This technique is preferred for these reasons despite the additional costs. It is commonly used for the manufacture of rigid foams. [38, 41]

### 3.4 Properties and Applications

Polyurethanes are finding increasing applications and use in many industries due to the diversity of properties available. Polyurethanes are one of the most widely used and of the fastest growing polymer markets in the world; they have been applied in numerous applications which range from rigid polymers used for construction materials to flexible material which are used for cushions and mattresses.

*Fig3.5: Polyurethane foam [42]*

As explained earlier, polyurethanes, are engineered materials which are created by a production process that mixes polyisocyanate and polyol chemicals. This process allows polyurethanes to be formulated with greatly varying properties from stiff and hard to soft and flexible depending on the desired applications.

Polyurethane foams are remarkable because of their ability to promote important engineering properties exhibiting durability, strength and toughness. Durability is up to 10 times that of rubber or other plastics; the impact performance is superior to structural plastic and is significantly better than rubber.

Polyurethanes display greater compression strength than other elastomers; they have an ability to sustain loads, combined with wear resistance, which has made polyurethane an ideal material for off road heavy duty tyres and rollers. They also have a high temperature capability and can maintain flexibility at low temperatures. They are available in variety of colours; they can be manufactured continuously for further cutting and shaping. [43]

There are two main sectors for rigid polymer foams which are construction and appliances. In the construction industry, foams can be used for internal or cavity insulation (fig: 3.6), floor slabs, boards used for pitched roofs or they can also be combined with wood to form sandwich panels which can be used for wall cladding. The demand in the construction industry has been rising and the growth is expected to get greater and greater. For appliances, refrigerator insulations are the main application for rigid polyurethane foam. It has been estimated that approximately 75-80 per cent is used in refrigerator-freezers and the remaining 20-25 per cent is used in other appliances such as display cabinets, water heaters, portable coolers, commercial appliances and vending machines.

*Fig3.6: This is an example of foam being used as the exterior insulation. Three inches of foam is shown in this example [44]*

Polyurethane foam can be sprayed on under pressure and cures immediately into a hard surface which you can walk on without damaging it.

*Fig 3.7: Polyurethane being sprayed on roofs [45]*

The major applications for flexible polyurethane foam are furniture cushioning, mattresses, seating, and carpet backing. A vast amount of flexible foam is also used in packaging, particularly for holding instruments; the foam can be cut to precise size to hold and protect the instrument. Moulded flexible polyurethane foams are primarily being used in the automotive industry for interiors for e.g. seating, head rests.

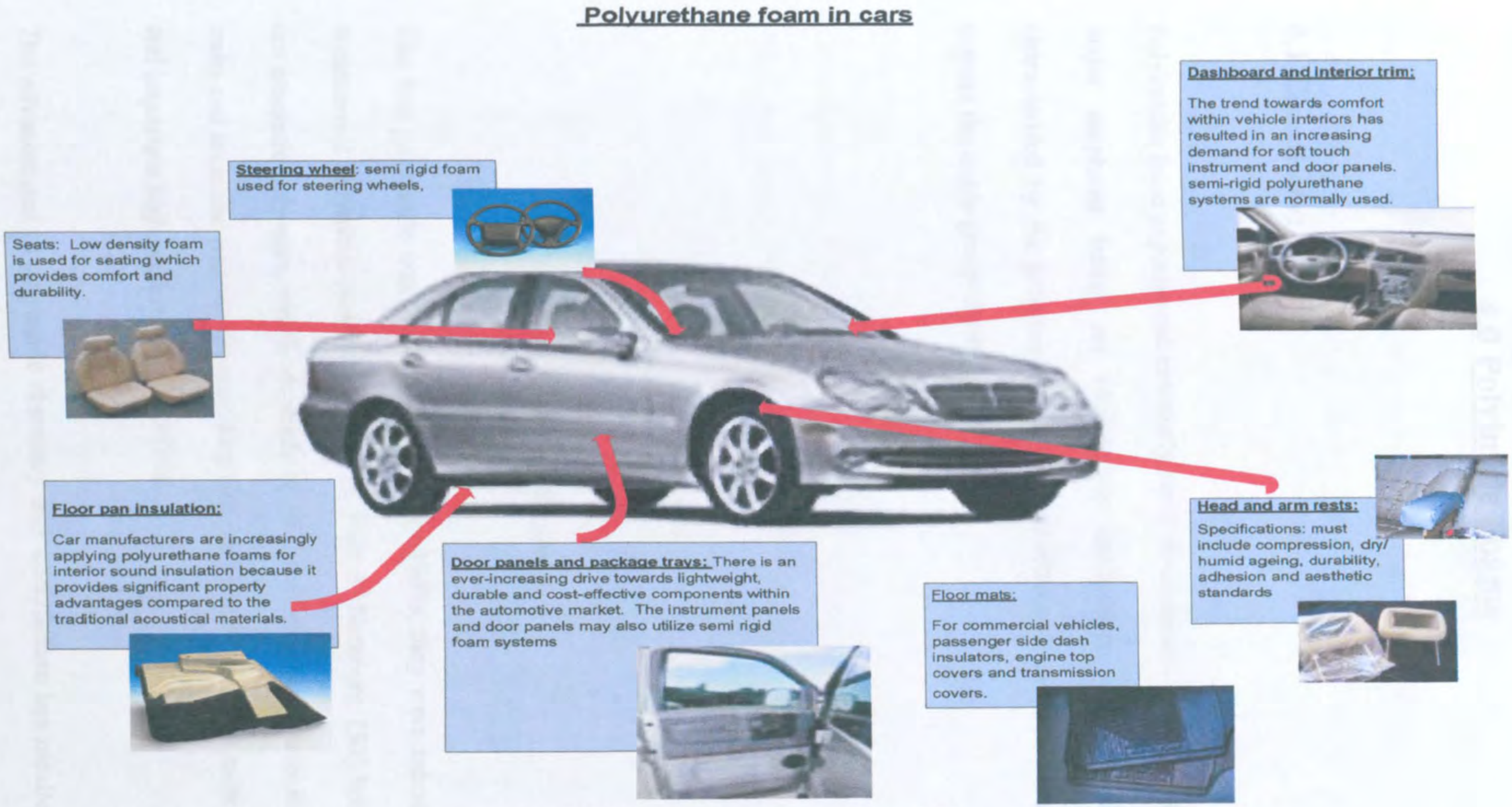
*Figure 3.8: Uses of flexible polyurethane foam*

### 3.4.1 Automotive industry

Polyurethane foams are used extensively in the automotive industry due to their excellent properties, which include flexibility, high mechanical strength, chemical resistance and high abrasion resistance. [46] Polyurethane foams are light weight, thus helping to cut down fuel requirements and emissions to the atmosphere. The major uses of polyurethane foam are for the interior trimming, seats, headrests, dashboards and soundproofing. A detailed diagram had been provided to illustrate the uses of polyurethane foam in a car. (Fig 3.9)

One of the main reasons why plastics are used instead of steel is due to the light weight of the material; cars are designed to protect passengers by sacrificing themselves during a crash. Cellular foams are also used because they absorb the energy impacting on the passenger during a collision. [47] Another reason why plastics are used instead of steel is because they do not rust.

In the interior of a car, plastic materials have gained an application saturation of approximately 80%. [48] Industries are trying to increase the use of plastic in certain components such as airbags, seat shells and pedals. Only 10 % [48]of plastics are being used under the car bonnet. There is still research being carried out to find new plastic components, which can be used under the car bonnet, the main aspect of using plastic components are weight saving. 5% of plastic components are used for car bodies. These are basically the front and rear bumpers of a car which are 100% plastic.



**Polyurethane foam in cars**

**Steering wheel**: semi rigid foam used for steering wheels,

Seats: Low density foam is used for seating which provides comfort and durability.

**Dashboard and interior trim:**

The trend towards comfort within vehicle interiors has resulted in an increasing demand for soft touch instrument and door panels. semi-rigid polyurethane systems are normally used.

**Floor pan insulation:**

Car manufacturers are increasingly applying polyurethane foams for interior sound insulation because it provides significant property advantages compared to the traditional acoustical materials.

**Door panels and package trays:** There is an ever-increasing drive towards lightweight, durable and cost-effective components within the automotive market. The instrument panels and door panels may also utilize semi rigid foam systems

**Floor mats:**

For commercial vehicles, passenger side dash insulators, engine top covers and transmission covers.

**Head and arm rests:**

Specifications: must include compression, dry/humid ageing, durability, adhesion and aesthetic standards

*Figure3.9: Schematic diagram of a car [49]*

# 4.0 Polyimide Foams

## 4.1 Chemistry:

Polyimides have experienced extremely rapid development in recent years, the major emphasis being on engineering applications. Polyimides are characterised by the presence in the polymer chains of cyclic structures that contain the imide group shown below.

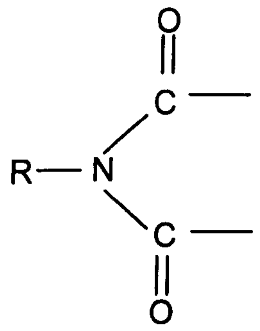


*Figure 4.1 Imide group*

The first polyimide was produced in the early 1960s, they were introduced as commercial polymeric materials by E.I. du Pont de Nemours. [50] Polyimides are aromatic polymers, which are made up of a five-membered aromatic imide units and aromatic rings in the repeating unit, and are some of the most popular and important high performance materials. [50]

The advancement in polyimide chemistry and manufacture has resulted in the production of several types. Unmodified polyimides contain the imide group which is the main functional group. Others, such as polyamides and polyetherimides, are referred to as modified polyimides. These have been produced in order to provide materials with the same outstanding physical and mechanical properties as their unmodified counterparts but are easier to manufacture.

Polyetherimide engineering thermoplastics find a wide range of extrusion and injection molding applications. These polymers find applications in many industries which include microelectronics, power electronics, lighting, transportation and medical equipment. [51-53]

The polyimide foam used in this study is an uncrosslinked polyetherimide (PEI). Its chemical configuration is given in figure 4.2

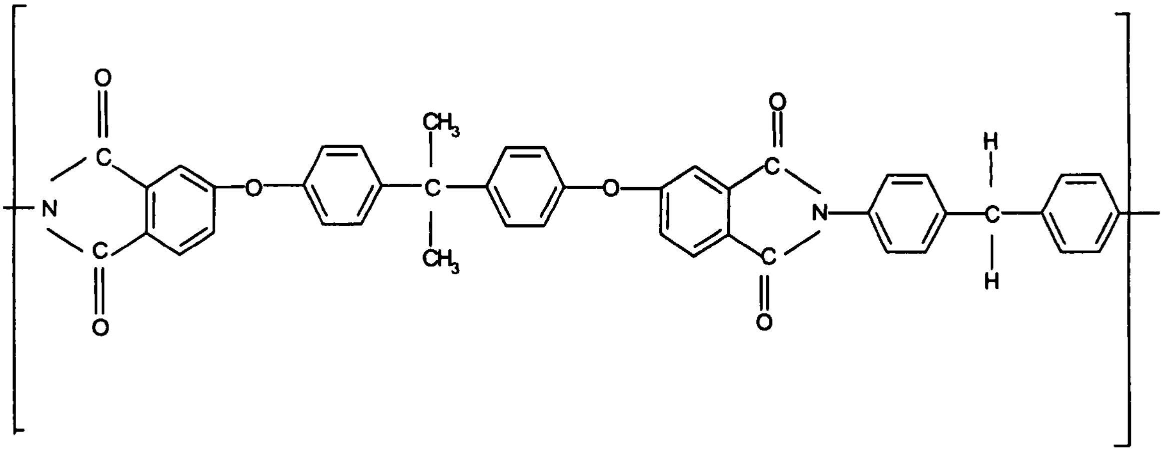


*Figure 4.2 Chemical formulation of polyetherimide*

### 4.1.1 Polymer syntheses:

There are two routes by which polyimides can be synthesized.

- Polycondensation
- Polyaddition

The first method is the most popular technique used for the preparation of thermoplastic polyimide. It involves the polycondensation of dianhydride and diamines at ambient conditions in a dipolar aprotic solvent *(figure 4.3)* such as N,N-dimethylacetamide or N,N-methylpyrrolidinone which leads to the formation of poly (amic acid) which is then cyclized into polyimide.

Polyimidization takes place in a hot solvent, the COOH groups in the poly (amic acid) acting between the two polymer chains as a catalyst. The conversion of poly (amic acid) is a slow a process at ambient temperature.[50] Cosolvents like *o* –dichlorobenzene facilitate the azeotropic removal of the by-product; water is produced by cyclodehydration of the intermediate polymeric acids.

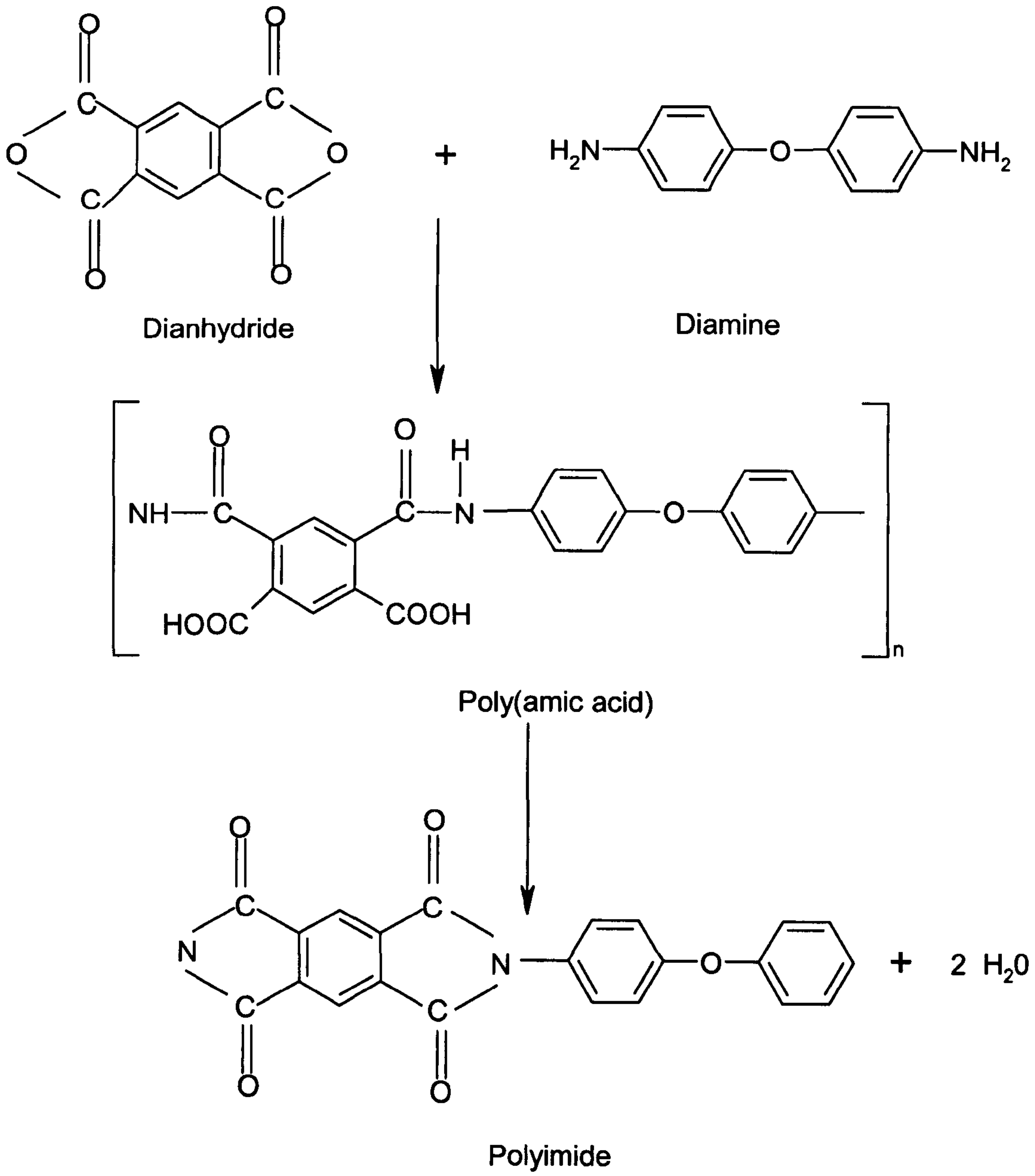


*Figure 4.3: Preparation polyimide using carboxylic dianhydrides and aromatic diamine [54, 55]*

The other synthetic route is the reaction of an aromatic diisocyanate with carboxylic dianhydride (*Figure 4.4*). The carbon dioxide which is evolved acts as a blowing agent. In the absence of a catalyst, the reaction of an aromatic dianhydride with an aromatic diisocyanate form a seven-membered cyclic ring intermediate, which then goes on to release carbon dioxide which forms the desired polyimide.

Production of polyimide can take longer at 180 ° C if an aromatic isocyanate is used instead of an aliphatic isocyanate. Catalysts such as tertiary amine, alkali, water or alcohols can be used to accelerate the reaction. In the presence of a catalytic amount of water, the amine resulting from hydrolysis of the isocyanates reacts with the anhydride to produce polyimides and regenerates the water molecule. This approach is good in preparing polyimide foams, as the evolution of carbon dioxide is utilized as a blowing agent.

The procedure for making isocyanate- based polyimide foams is outlined in figure 4.4; this includes a one shot process by mixing carboxylic dianhydrides with an organic polyisocyanate at room temperature in the presence of an organic solvent. This stage involves the mechanical blending of the dianhydride with a polymeric isocyanate. Crosslinking can be achieved by adding a highly functional polyol which reacts with part of the isocyanate therefore the foam contains urethane structures. Silicone surfactants can be added to the mixture which helps to control the cell size. The mixture is left to expand at room temperature after it has been poured into a mould. Once the mixture is solidified, the moulded part is removed and placed in an oven which removes excess solvents. [54, 55]

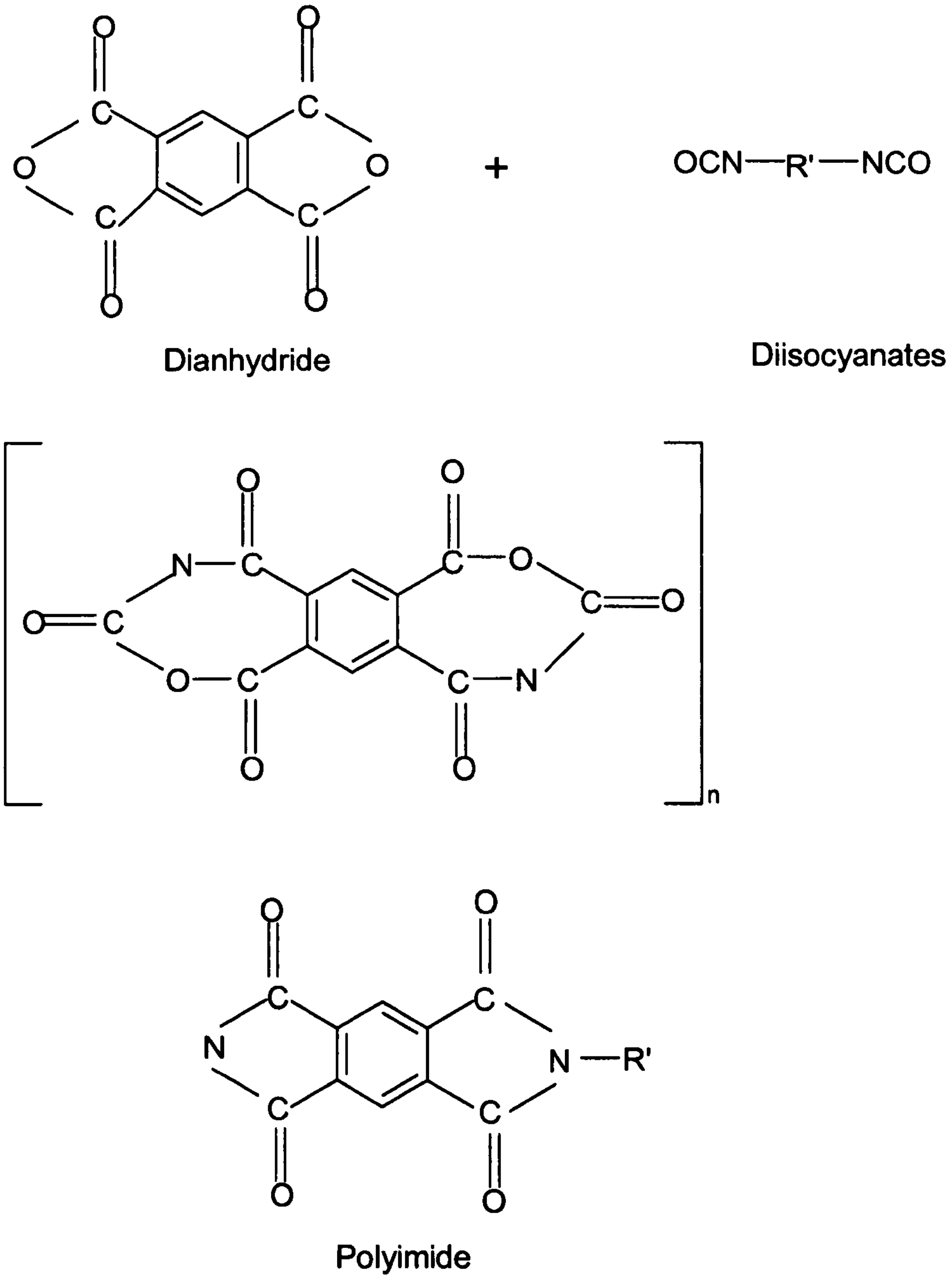


*Figure 4.4: Preparation polyimide using aromatic diisocyanates with carboxylic dianhydrides [54]*

### 4.2 Properties and applications:

Polyetherimides, a class of high performance engineering thermoplastics, are finding increasing utility in applications such as the aerospace and electronic industries.

This material is characterised by high strength at elevated temperatures, long–term heat resistance, good electrical properties, broad chemical resistances and has excellent fatigue resistance. They are structurally stable under a wide thermal range which varies from -196 ° C to 371 ° C. These materials do not ignite in air and often produce little or no smoke when burned in a propane- air flame. [56-58]

Polyimide foams can be manufactured at densities ranging from 0.008gcm$^{-3}$ to 0.128gcm$^{-3}$ and higher. Polyimides were developed at the NASA Langley research centre for high performance applications like the reusable launch vehicles program. [59]

In this study, there were two sets of polyimide foams provided by Airex.

**Airex R.63.** This is a closed-cell thermoplastic foam with an extremely high damage tolerance. It is a suitable core material for dynamically loaded and shock absorbing sandwich structures. This foam has been used for front ends of trains, and used on ships as hulls.

*Figure 4.5 Swiss locomotive 2000 [60]*

Airex R63 [34] foam was produced for the Swiss locomotive 2000. The sandwich components were manufactured for the roofing, skirt panels and the front cabs. The use of R63 core produces a structure with high impact resistance. The high stiffness to weight ratio of the core achieved allows for energy to be saved. [60]

Using a sandwich construction, a high stiffness to weight ratio then with a single skin is achieved and energy is saved. The cabs are produced in a one piece process which involves a short production cycle and cost is saved due to the easy assembling.

**Airex R82 [34]** is a thermoplastic foam that has excellent fire resistance properties, with low smoke and toxicity, and also excellent dielectric properties. It is an exceptional core material for use in applications that demand structural fire resistance, which are required to be transparent to radar, or to operate in extreme hot or cold environments.

They are used in aircrafts and aerospace for interiors, cockpit doors, and cryogenic tanks, insulating panels, helicopter rotor blades, also used in the industry as fire resistant foams *(figure 4.6)*

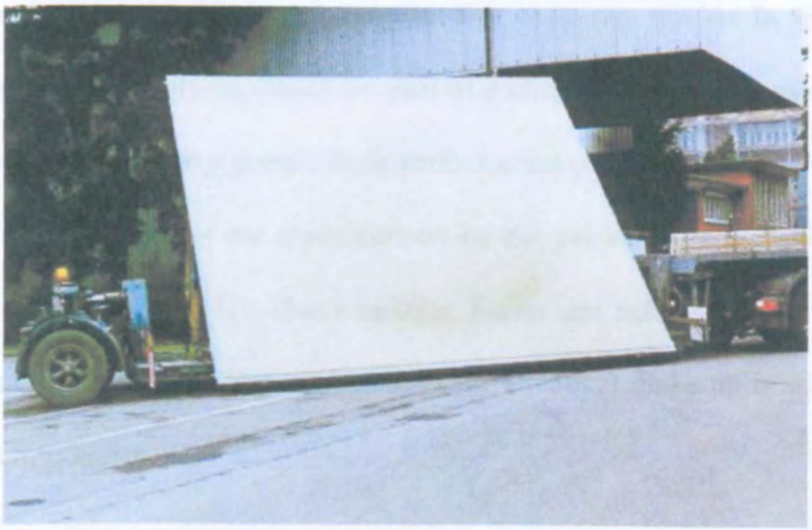


*Figure 4.6: Fire resistant foam [61]*

Polyimide foams have been developed for applications where flammability and fire safety are important. The advantage of polyimide forms when compared to other foams are: resistance to fire, no detectable smoke formation below 204°C, no incapacitating toxic by products below 204°C and resiliency and flexibility. [62]

# 5.0 Polysulphones

## 5.1 Chemistry

Polysulphones (PSU) were introduced into the American market in 1965 by Union Carbide. [63] Polysulphones are part of a family of aromatic amorphous thermoplastics which have unique high performance properties as engineering materials. Polysulphones are characterised by the presence of the following structural group. *(Fig: 5.1)* These cellular foams are relatively new to the polymer industry, the literature concerning their chemical make-up is still brief and difficult to locate.

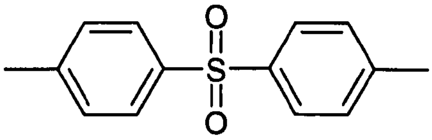


*Figure 5.1 : Polysulphone[64]*

Polysulphones can be synthesised by either of two routes:

- Nucleophilic displacement route
- Electrophilic Friedel- Crafts synthesis

### 5.1.1 Nucleophilic displacement route:

This route is used extensively in the commercial production of polysulphones. Synthesis of polysulphones is achieved by a two step process; the first step involves the conversion of bisphenol A to its diisodium salt using sodium hydroxide. The reaction is normally carried out in dimethyl sulphoxide.

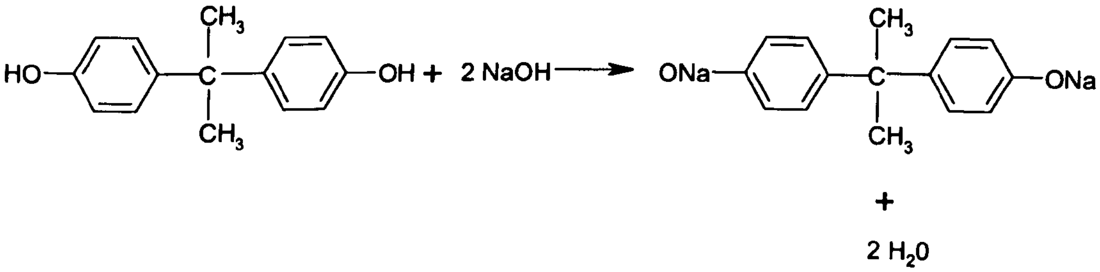


*Figure 5b: Step one, Conversion of bisphenol A [64]*

The water which is produced from this reaction needs to be removed thoroughly to prevent any hydrolysis of the 4, 4′dichlorodiphenylsulphone monomer which is added in the second reaction.

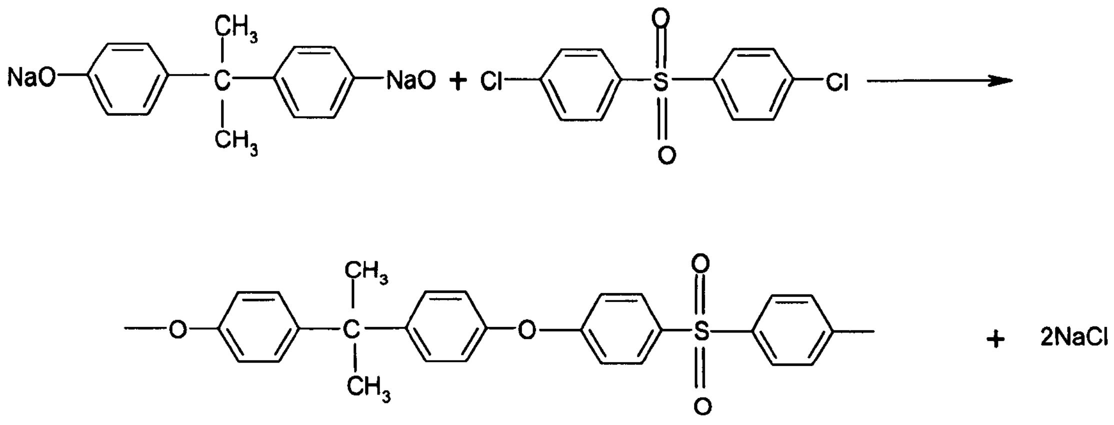


*Figure 5c: Step two [50, 64, 65]*

Water can be removed by the presence of small amounts of cosolvents such as chlorobenzene or toluene which distils out in the form of azeotropic mixture with water.

## 5.1.2 Other synthetic routes:

There are other synthetic routes which can be used to produce polysulphones, but there are various reasons why they are not produced commercially this way. The Friedel–Crafts synthesis is based on the reaction of *bis*-(4 chlorosulphonylphenyl) ether with diphenylether.

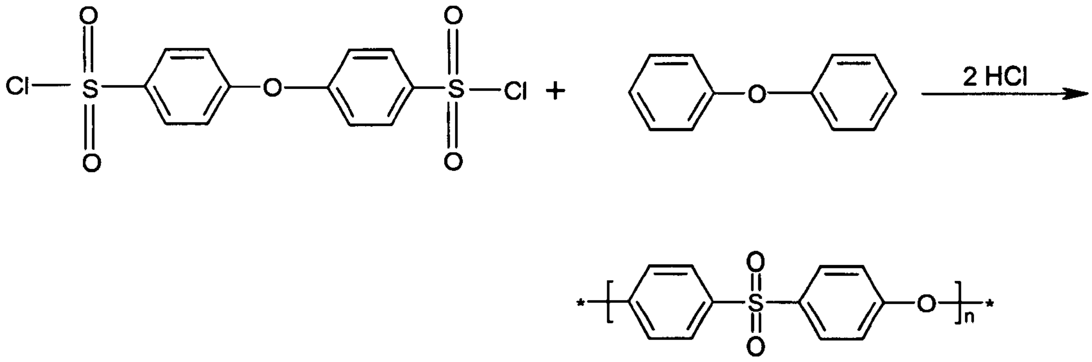
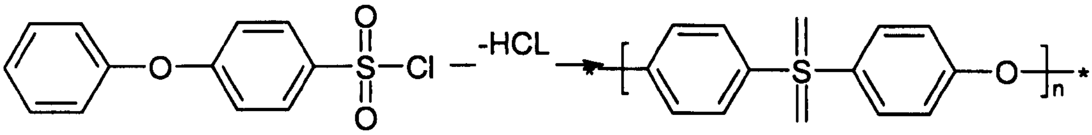


*Figure 5d: Friedel- Craft synthesis[50, 64]*

There is another reaction which can be used to make polysulphone, by using 4-chlorosulphonyldiphenylether as a monomer:



Production of polysulphones is achievable via these syntheses, but the backbone is not always linear. The single monomer route is the preferred route as it produces structures which are free from branching; also they are *para*-linked which produces the toughness in polysulphones.

## 5.2 Processing of polysulphones

Thermoplastic processing methods such as injection moulding, blow moulding and solution casting can be used to produce polysulphones. The most common process used for processing polysulphones is injection moulding, due to the ease of processing for many engineers. Polysulphones can be extruded into sheets, tubing, films and other profiles. The processing temperature is slightly higher than other thermoplastics, but the temperature is within the capability of most modern screw injection moulding and other machines. The polymer has a high softening point and hence the processing temperature can range from 320-400 ° C. [66, 67]

### 5.2.1 Rheology and drying:

Even though the processing temperature is high for polysulphones, it still appears as a viscous melt which requires robust equipment.

The polymer absorbs some moisture and at the high temperatures employed, this can be troublesome, resulting in surface defects like bubbles, streaks and splash marks. Therefore before polysulphones can be subjected to melt fabrication operations, the resin needs to be dried to remove any moisture. The drying can be achieved by placing samples in either a conventional forced air oven or a desiccated hopper dryer unit at temperatures ranging from 135-165°C for 3-4 hr.

### 5.2.2 Injection moulding

Injection moulding is the preferred technique used for polysulphones; it consists of a reciprocating screw injection moulding machine equipped with a barrel, the mould temperatures can vary from 100-160°C, the higher temperatures giving the more stress-free moulding. As the melt viscosity is high, runners and gates are used for obtaining defect free parts. They are normally placed in position where the resin can flow from thick to thin.

The amount of frozen-in stress is not only reduced by high mould temperature but also increasing the mould cycle by annealing air. A qualitative idea of the degree of frozen-in stress can be obtained by immersing the moulds into ethyl acetate; if the mould does not show any cracks within three seconds the mould is considered satisfactory.

Techniques such as extrusion and blow moulding the polysulphones are used for higher molecular weight. Melt temperature for blow moulding may be reduced.

### 5.3. Properties and applications

Polysulphones are a family of engineering thermoplastics [68, 69] and can be used continuously under load bearing conditions to temperatures in excess of 205° C. The main features of the commercial polysulphones are their exceptional resistance to creep and good high temperature resistance. They are transparent in their natural form, they display high rigidity, have excellent dimensional stability and have very good electrical insulation properties .

Polysulphones are linear polymers; although it has a linear structure it has been reported that it is amorphous, due to the number of benzene rings present which leads to a high Tg value of about 190 ° C. [70, 71] The diarylsulphone grouping enhances the stabilisation of the S-C bonds through conjugation with the aromatic groups.

Polysulphones have excellent chemical resistance and thermal stability. Polysulphones are ideal for high temperature applications, including those in composite sandwich complexes with either high operating temperatures or high processing temperatures. PSU can be used in a variety of applications.

| Applications | Examples | |
|---|---|---|
| Food service | @ Microwave cookware<br>@ Milking equipment components<br>@ Non-stick cookware coatings | <br>[72] |
| Household plumbing | @ Corrosion resistant pipes<br>@ Fittings<br>@ Pump components | <br>[73] |
| Electrical | @ Light sockets<br>@ Circuit breakers<br>@ Electronic connectors | <br>[74] |
| Medical | @ Dental instruments<br>@ Surgical instrumental trays | <br>[75] |

*Figure 5f: Applications of polysulphones*

# 6.0 Mechanical properties of cellular foams

Cellular materials are composed of cells of gas which are dispersed in the walls of the solid. The main properties associated with the foams in the low density range are low thermal conductivity and high ratio of strength to weight. [76-78] Gas components of the foam possess of low strength, low density and low conductivity; this represents the major portion of volume. However the solid component represents the major portion by weight, with high density, high thermal conductivity and high strength.

One of the great advantages of cellular foams compared to solid thermoplastics is their high stiffness to weight ratio. This feature often enables them to compete with metals in some applications, where limited weight is critical and with wood when total fabrication costs are taken into account. [79]

## 6.1 Mechanical properties:

The growth rate of polymer foams is increasing continuously by new products being improved or being replaced into the industry. The demand for new material has led in part to today's drive for more and better polymer composites. When producing a new material, one must be able to predict properties of the foam. There are certain structural variables which can affect mechanical properties, such as density, cell structure, plastic state, and temperature and gas composition. [76, 80]

### 6.1.0 Density:

This is an important structural variable in determining mechanical properties of foam. When a foam sample is cut in cross section an increase in density of foam will result in an increase in the cross sectional area of polymer material and an increase in the number of cell walls within the cross section or may be a combination of both. This results in a higher value of all strengths and moduli of the composite foam.

### 6.1.1 Cell structure:

This complex nature of this variable makes it ideal to separate it into more specific categories of cell size; cell geometry and open cell fraction. There is very little data relating to the cell size or cell geometry of rigid plastic foams,

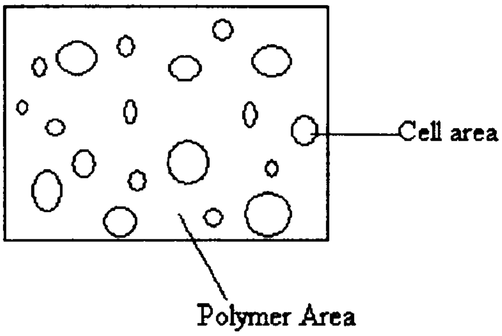


*Fig 6.1:*

because of the difficulty in preparing foam samples with large cell structures while maintaining all other structural variables constant.

### 6.1.2 Gas phase composition:

There are a large number of cases where the expanding gas diffuses from the foam cells and air diffuses into the cells, but there are some cases where the expanding or blowing agent is retained in the foam cells because of its slow diffusion rate through the plastic. The gas pressure inside foam cells can be determined by gas composition and temperature; gas composition can be governed by diffusion of gases through the foam. This contributes to the mechanical properties of closed cell foam.

### 6.1.3 Temperature:

It has been shown that the strengths and moduli of plastics generally increase as the temperature is decreased. [81] This increase in properties of the solid plastic results in the increase of strength and modulus of the corresponding plastic foams at lower temperature.

### 6.1.4 Plastic phase composition:

The plastic composition influences the mechanical properties of foams. This reflects the properties of the actual plastic; the plastic phase composition includes additives such as heat and light stabilizers and pigments.

## 6.2 Stress-strain curves

In many applications of cellular materials, the mechanical properties are of great importance. The compressive stress-strain curves of foams are characterised by three distinct stages which are illustrated in figure 6.2. The three regions are the linear elastic region, plateau region and densification.

### 6.0.1 Linear elasticity:

This is observed at low stresses within a corresponding strain of less than approximately 5%. [82] It is controlled by cell walls bending or cell walls stretching. Young's modulus is associated with the initial slope of the stress-strain curve.

### 6.0.2 Plateau region:

Beyond the elastic limit lies the plateau region which is associated with the collapse of the cells. It is attributed to the buckling of the cells; buckling is the failure mode of a structure which is characterised by a failure to react to the bending moment generated by a compressive load. It is the stress at which irrecoverable plastic deformation starts, as the cell walls become irreversibly damaged.

### 6.0.3 Densification:

This is the third and final stage; this is where the opposing cell walls are crushed together and the cell –wall material is compressed. The slope of the curve within this region increases quickly and approaches the elastic modulus of the unfoamed polymer.

The results of stress-strain testing of polymer foams can be directly related to the recovery mechanism observed in rigid polymer foams released after prolonged compression, depending on where the confining strain places the foam within its stress-strain curve.

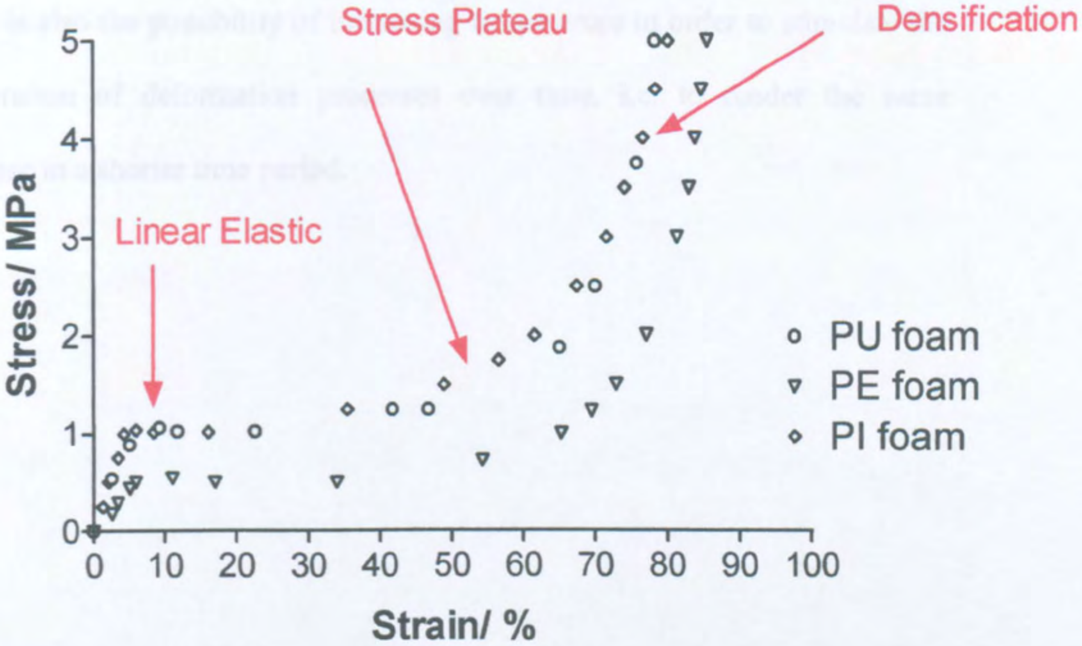


*Figure 6.1: typical compressive stress- strain at ambient temperature*

Most cellular foams are used near ambient temperatures, temperatures ranging from 20 - 40 ° C. However there are certain applications as in thermal insulation, catalytic converters or heat exchangers, when the range of temperature is much wider. [83]

There is also the possibility of increasing temperature in order to stimulate the acceleration of deformation processes over time, i.e. to render the same response in a shorter time period.

# 7.0 Experimental techniques:

## 7.0.1 Compression set:

The techniques described in this section are aimed to provide a clearer understanding of the microstructural properties of these foamed materials. The materials which have been analysed can be seen in table (1.0)

| **Polymer** | **Supplier** | **Density/ kg m$^{-3}$** | **Crosslinked** |
|---|---|---|---|
| Polyethylene<br>HD80 | Zotefoams plc | 80 | Lightly crosslinked |
| Polyethylene<br>HD115 | Zotefoams plc | 115 | Lightly crosslinked |
| Polyurethane | A.W.E | 100 | Highly crosslinked |
| Polyetherimide<br>R63.80 | Alcan Airex AG | 80 | Uncrosslinked |
| Polyetherimide<br>R82.80 | Alcan Airex AG | 80 | Uncrosslinked |
| Polysulphone | Zotefoams plc | 175 | Unknown |

*Table 7.0: Polymers used*

Compression set testing measures the ability of the polymer foam to return to its original thickness after prolonged compressive stress at a given temperature. Compression set is defined as a failure to recover after a period of constant stress. As our tests are carried out as constant strain, however, we have to make it clear we are unable to assess this, even though the effect is much the same. Compression set testing was conducted on all six foams. The foams were cut 20 x 20 x 10mm and were obtained by a process of band sawing and then accurate milling.

*Figure 7.0: foam cubes [84]*

Each sample was then labelled with appropriate compressive strains. Each side of the cube was marked so that the thickness was always measured at the same point.

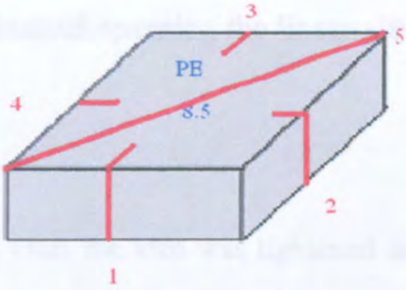


*Figure 7.1: foam measurements*

The thickness of the samples were obtained by averaging out five thicknesses obtained by measuring each side and measuring vertically (fig7.1). All of the thickness measurements were made by using Mitutoyo electronic callipers, which were regularly calibrated to engineering standards.

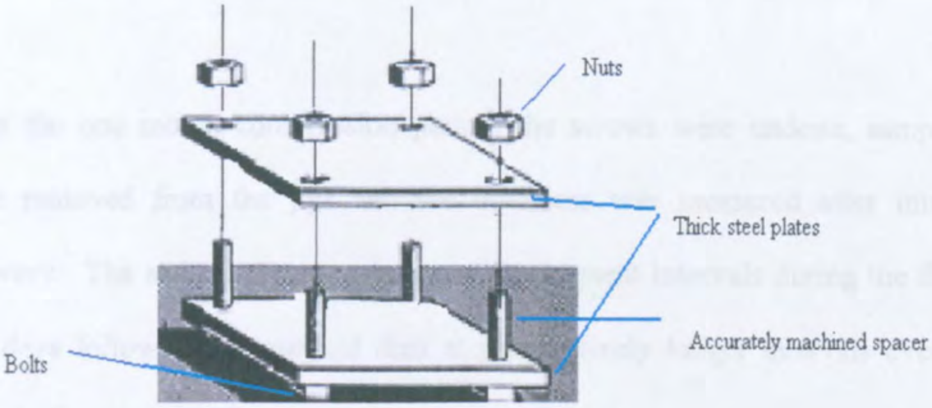


*Figure 7.2: Illustration of a Jig*

Each jig consisted of two steel plates with four corner bolts. The bolts were equipped with accurately machined spacing washers; the length of the washers varied from 6.5mm to 9.75mm, therefore the compression was investigated at nominal strains of 2.5, 5,10,15,20 and 35%. The values were selected to ensure that the data would be obtained spanning the linear elastic and stress plateau regions.

The jigs were placed in a vice; the vice was tightened until contact was made between washers and platen. The nuts were tightened to fix the platen securely in position and the jig was removed from the vice.

The jigs were left at various temperatures; for example, polyethylene foam placed in oven (Gallenkamp model no.OMT228.XX2.C) at 50°C for one month. All foam samples were either compressed at sub –ambient, ambient or elevated temperatures, up to 75 °C.

After the one month compression period, the screws were undone, samples were removed from the jigs and the thickness was measured after initial recovery. The samples were re-measured at frequent intervals during the first few days following release and then at progressively longer intervals over a period of several months.

Measurements of the thickness of each specimen were made daily on a basis for the first weeks following release of the sample and then at regular intervals to monitor the recovery of the foams. It should be noted that this technique did not involve conditioning of the samples prior to the compression testing and that sustained compression was done at elevated temperatures and the recovery process was always conducted under ambient conditions. Table 7.1 illustrates some of the dates and temperatures of compression set of foams. A detailed list can be found in the appendices.

| **Job Number** | **Polymer** | **Temperature °C** | **Samples in jigs** | **Samples released** |
|---|---|---|---|---|
| | | | | |
| 1 | PE- HD 80 | RT | 14/05/2002 | 10/05/2002 |
| 2 | PI -63/80 | RT | 14/05/2002 | 10/06/2002 |
| 3 | PI-82/80 | RT | 14/05/2002 | 10/0602002 |
| 4 | PE- HD80 | 40 | 28/08/2002 | 24/09/2002 |
| 5 | PE- HD115 | 40 | 28/08/2002 | 24/09/2002 |
| 6 | PU | 40 | 28/08/2002 | 24/09/2002 |
| 7 | PE- HD80 | 60 | 05/11/2002 | 02/12/2002 |
| 8 | PE- HD115 | 60 | 05/11/2002 | 02/11/2002 |
| 9 | PU | 60 | 05/11/2002 | 02/11/2002 |
| 10 | PE | RT | Comparison of results | |
| 11 | PE- HD115 | 50 | 27/02/2003 | 26/03/2003 |

*Table 7.1: Material log*

### 7.0.2: Scanning electron microscopy (SEM)

Scanning electron microscopy was used to study and compare the cellular structure of the different materials and to give an indication of the variation of cellular structures between the foamed materials used in this study. The technique was also used to view the foam while they were compressed at different constraints.

| **Polymer** | **Original thickness** | **2.5 %** | **5%** | **10%** | **15%** | **20%** | **35%** |
|---|---|---|---|---|---|---|---|
| Polyurethane | √ | √ | √ | √ | √ | √ | √ |
| Polyethylene (HD80) | √ | √ | √ | √ | √ | √ | √ |
| Polyethylene (HD15) | √ | √ | √ | √ | √ | √ | √ |
| Polyetherimide (R63.80) | √ | √ | √ | √ | √ | √ | √ |
| Polyetherimide (R82.80) | √ | √ | √ | √ | √ | √ | √ |
| Polysulphone | √ | - | - | - | - | - | - |

*Table 7.2: samples used for SEM*

This technique imposed restrictions on the size of the sample to be viewed. Large specimens were found to be difficult to balance on the holder and could not be accommodated in the SEM chamber. Therefore the samples were cut small enough to fit on the stub. The foams were mounted on the stubs using conducting silver paint.

Samples were placed into a plastic box and were covered to protect them from dirt or dust and were left for approximately one hour to allow sufficient time for the silver paint to dry.

*Figure 7.3: Scanning electron microscopy [85]*

The mounted samples were then placed in the chamber of the gold coater and sputter coated in an argon atmosphere. The coater allowed **six** samples to be coated and roughly took **20mins.** The coating was necessary to allow clearer images to be seen of the non- conducting samples.

## 8.0 Results & Discussion

Scanning Electron Microscopy:

The Scanning Electron Microscope was employed to help in the examination and comparison of the microstructure of the four different foams at different constraints.

Examples micrographs are shown below:

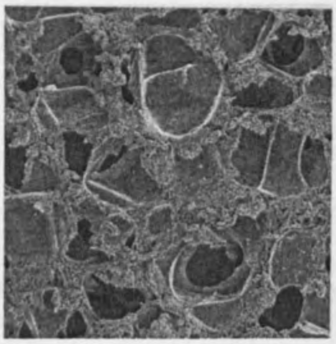


Fig 8.1 Polyetherimide

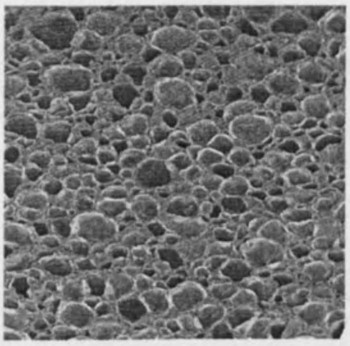


Fig 8.2 Polysulphone

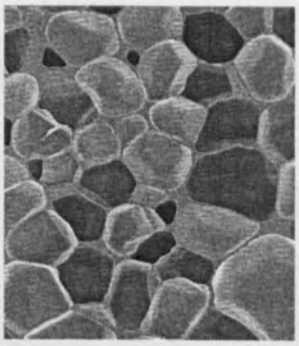


Fig 8.3 Polyethylene HD80

In closed–cell foams each cell is completely enclosed by a thin wall or membrane of polymer. The image of Polyetherimide (Fig 8.1) which was compressed at 20% shows clear cellular damage of the structure; full recovery is not possible after this compression.

It was clearly evident from the SEM micrographs for; all four foams that as strain levels were increased on the foams, this had caused serve damage to the cellular structure of the foams.

**Compression at ambient temperature:**

The dimensional recovery of all of the foams in the direction of compression has been defined in terms of a *normalised recovery*, $R_n$. The latter is a measure of the residual strain or loss of original sample thickness as the sample recovers after release.

$$R_n = \frac{\text{Original thickness} - \text{measured thickness}}{\text{Original thickness}}$$

According to the definition, a specimen has a normalised recovery equal to its compressive strain immediately prior to release and a value of zero upon full recovery of its original dimensions.

The fixed strain values employed were 2.5%, 5%, 10%, 15%, 20% and 35% to encompass strains both within and beyond the linear elastic region of the foams.

Recovery curves for all of the foams highlight the presence of two distinct regions. The recovery curve of HD115 polyethylene foam has been used to illustrate this phenomenon. (Fig: 8.4). The total amount of compression of each specimen is indicated in the legend beside the graph which is equivalent to the spacer size by 2.5 %( 9.75mm spacer) to 35% compression (6.5mm spacer)

All data has been analysed and graphically presented using a programme called Prism.[86-89]

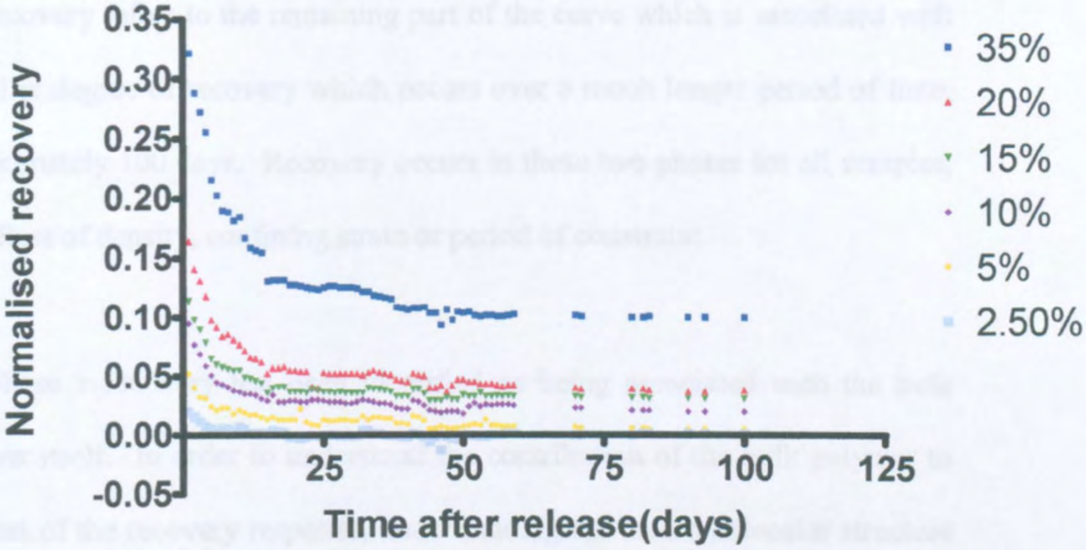


*Figure 8.4: Polyethylene (HD115) foam compressed for one month at ambient conditions.*

Recovery of all foam samples following release was initially very rapid. All samples tested showed 70-80% of their total recovery within the first day following release. This is referred to as phase one recovery of the curve. Phase two recovery refers to the remaining part of the curve which is associated with a smaller degree of recovery which occurs over a much longer period of time, approximately 100 days. Recovery occurs in these two phases for all samples, regardless of density, confining strain or period of constraint.

The phase 1 recovery has been identified as being associated with the bulk polymer itself. In order to understand the contribution of the bulk polymer to this part of the recovery response, understanding the macromolecular structure of the polymers is important; for instance, the chemical configuration for polyurethane foam consists of bulky side groups and has a high degree of crosslinking which results in an amorphous configuration. [21, 90-92]

It is important to understand the interrelations between the different regions of mechanical properties and how molecules would respond to stress. The atoms or molecules in a condensed phase at equilibrium occupy states of minimum free energy by vibrating about certain mean positions in the potential energy fields which are created by interactions with neighbouring molecules. If the polymer foam is unstressed this means positions are also minima in the potential energy fields. The potential energy is distributed quite evenly through out the foam.

Therefore when a compressive stress is applied to a polymer sample, the main position of the molecular vibrations are moved instantly to new equilibrium positions which are somewhat displaced from the potential energy minima.

No substances have structures so perfect that all the free energy minima are occupied. There are always some vacant minima and some atoms situated in between minima in what are called dislocations.

The vacant sites are most important when considering the deformability of an amorphous substance. There is always a chance with vibrating molecules that if situated next to a vacant site they will gain enough energy and move into the vacant space. This leads to the disruption of the chain configurations which results to a new arrangement, which is different from their usual distribution. Therefore the chains are pushed together or pushed into any available free volume.

In an unstressed material, although molecules are constantly jumping from one equilibrium position to another, no direction of motion is preferred. When stress is applied each molecule is subjected to a tiny force in the direction of stress. A jump is made in the direction of the stress.

When the compressive stress is removed the polymer chains try to revert to their original configuration. The molecules try to jump backwards, but they require a high thermal activation energy. When a molecule tries to jump in the reverse direction more work is required to be done against the prevailing force. When stress is applied, the chance of a molecule jumping forward into a hole under stress is thus greater then the chance of a molecule jumping back and therefore a net movement take place in the stress direction.

The latter manifests in the form of phase 1 recovery. This particular phase is related to the polymer constituents, and one can expect that recovery of the polymer foams in this phase would most likely be affected by the polymer itself, the microstructural details and additives.

An amorphous polymer is described as a matrix with randomly uneven polymer chains. [80] The space that is unoccupied around the packing of the disordered chains is referred to as *free volume (v)*. On that basis the volume of the polymer, V, will be composed of the volume actually occupied by the polymer molecules, $V_o$, and the free volume in the system, $V_f$. [80, 93]

$$V = V_o + V_f$$

Phase 2 recovery contributes up to 30% of the total to the recovery process and is associated with recovery of the cellular structure of the polymer foam. When foam is compressed beyond its elastic limit, the cellular structure undergoes deformation and the possibility of extensive damage with increasing compressive strain. The cellular structure may be permanently and irreversibly damaged. Subsequently, when the cellular structure is compressed beyond its elastic limit and is maintained under such conditions for a period of time, the cellular structure becomes deformed and shows less recovery. Up to the elastic limit there is no major effect on the cellular structure. In plateau region, deformation and possible cell damage occur. The compression region shows permanent cell damage.

Phase 2 recovery is influenced by certain structural variables such as cell size and anisotropy and also environmental conditions, such as ambient temperature and humidity, as well as the time, temperature and degree of compression.

Figure 8.5 shows polyethylene foam compressed for one month at ambient temperature. The graph shows a closer look in distinguishing phase 1 and phases 2 recovery. As mentioned earlier environmental conditions can affect results, and is visible by sudden fluctuations seen occurring simultaneously in figure 8.5-6.

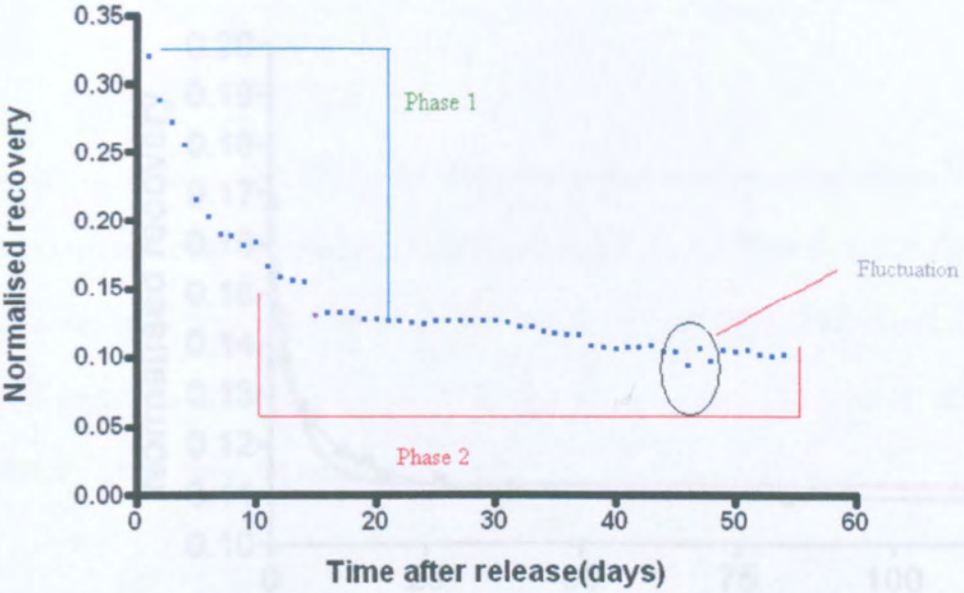


*Figure 8.5: Polyethylene foam compressed for one month at ambient temperature. Curve showing phase one and phase two recoveries*

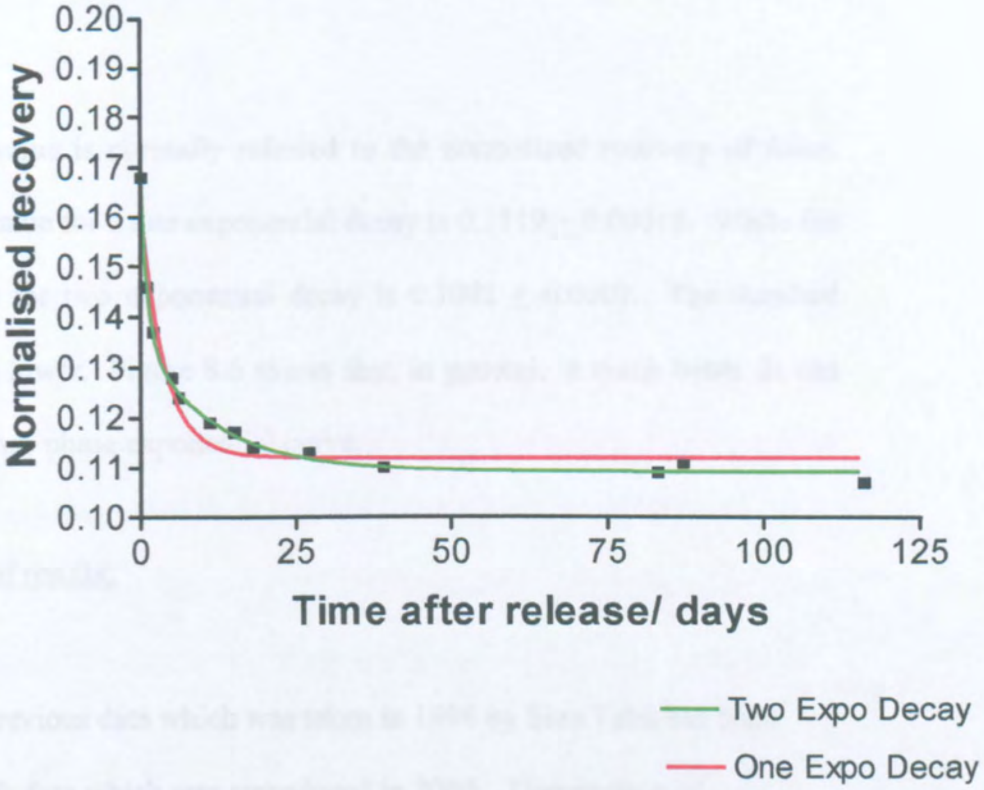


*Fig 8.6: PU foam compressed by 20% for 1 month at room temperature*

|  | One Expo Decay | Two Expo Decay |
|---|---|---|
| Plateau | 0.1119 | 0.1091 |
| Standard Error | 0.0015 | 0.00709 |

The plateau value is normally referred to the normalized recovery of foam. The plateau value for a one exponential decay is 0.1119 ± 0.00015. While the plateau value for two exponential decay is 0.1091 ± 0.0007. The standard error is much lower. Figure 8.6 shows that, in general, a much better fit can be seen by a two phase exponential curve.

Comparison of results:

Analysis of previous data which was taken in 1998 by Sina Talal has been compared with data which was reproduced in 2005. Comparison of Polyethylene HD 80 was analyzed at 40° C.

|  | **Rate constant (K)** | **Span Phase** | **Plateau** | **Base Line** |
|---|---|---|---|---|
|  |  |  |  |  |
| A 35 % | 0.4163 | 0.1037 | 0.2326 | 0.226 |
| B 35 % | 0.04603 | 0.1086 | 0.2179 | 0.22 |
|  |  |  |  |  |
| A 20% | 0.07873 | 0.02422 | 0.1147 | 0.115 |
| B 20% | 0.03431 | 0.07937 | 0.1091 | 0.115 |
|  |  |  |  |  |
| A 15 % | 0.08108 | 0.0201 | 0.08592 | 0.086 |
| B 15% | 0.01162 | 0.1134 | 0.02509 | 0.08 |
|  |  |  |  |  |
| A 10 % | 0.3361 | 0.02486 | 0.05367 | 0.052 |
| B 10% | 0.05006 | 0.0467 | 0.03855 | 0.04 |

Key:

A – Results taken by Sina Talal in 1998
B – Results taken by Shehla Darr in 2005

When analyzing the results it was discovered Polyethylene was not the best material to do a comparison with, especially at elevated temperature. As mentioned earlier Polyethylene shows an almost single- phase exponential recovery, i.e one of the recovery phases either does not take place, or happens so fast that it is not observed. Under these circumstances, coupled with the inherent measurement error, a two-exponential recovery model gives almost random values to $k_1$ and $k_2$, and $s_1$ and $s_2$, so distorting the analysis. This is also why convergence fails in two of the analyses.

Under these circumstances, it is more appropriate to simplify the model to a single exponential fit. There are still some problems – the 5% and 2.5% samples are so close to full recovery that the error associated with the plateau values is large, but the plateau is nearly zero in both cases. In these cases, there is no clear agreement and has been stated earlier in the thesis.

The 15% compression results still do not agree well, and it is clear from the graph that they never will. (Fig: 8.8) However, if you tabulate the single-exponential parameters of rate constant (k), span (S) and plateau (P) for the 35%, 20%, 15% and 10% compressions, it becomes clear that the best agreement is between the plateau values overall.

Fig 8.7: Polyethylene Foam HD80 foam compressed for 1 month at 40 $^{o}$ C

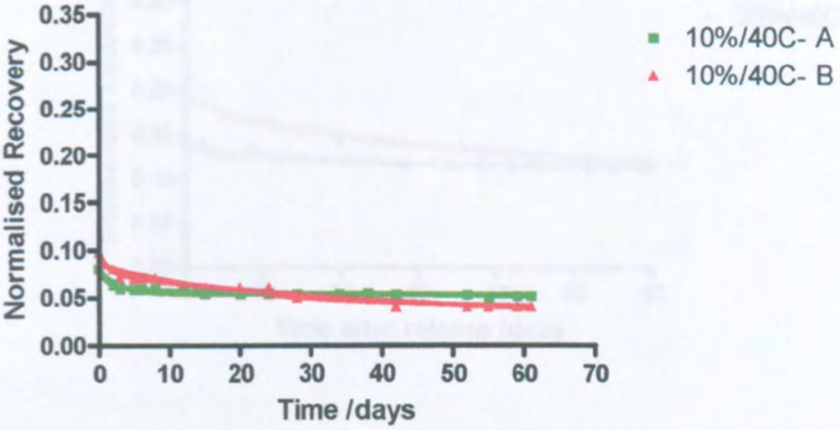


Fig 8.8: Polyethylene Foam HD80 foam compressed for 1 month at 40 $^{o}$ C

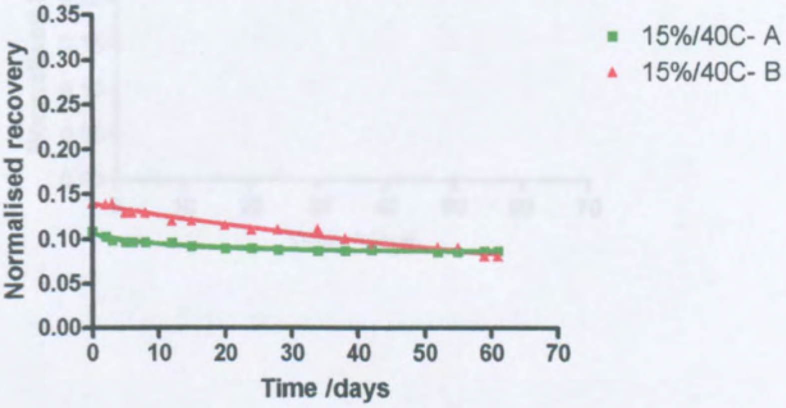


Fig 8.9 : Polyethylene Foam HD80 foam compressed for 1 month at 40 ° C

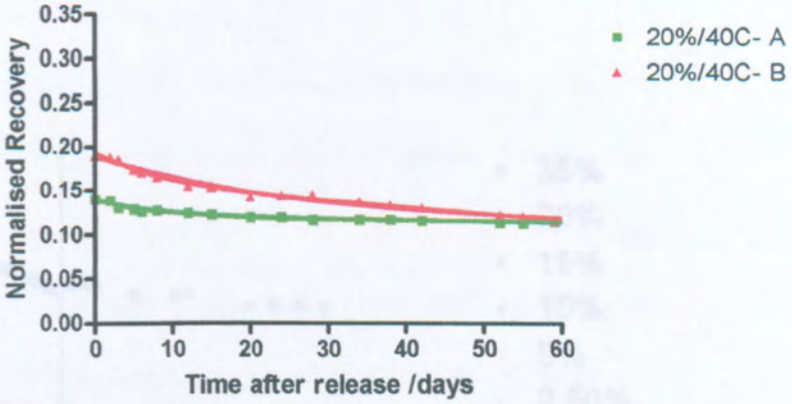
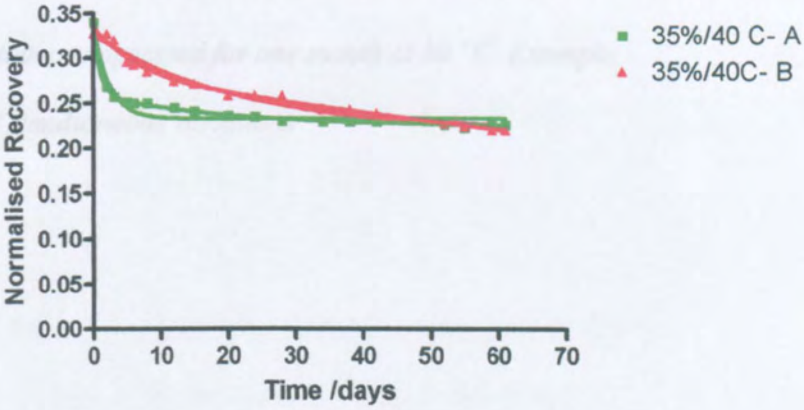


Fig 8.10: Polyethylene Foam HD80 foam compressed for 1 month at 40 °



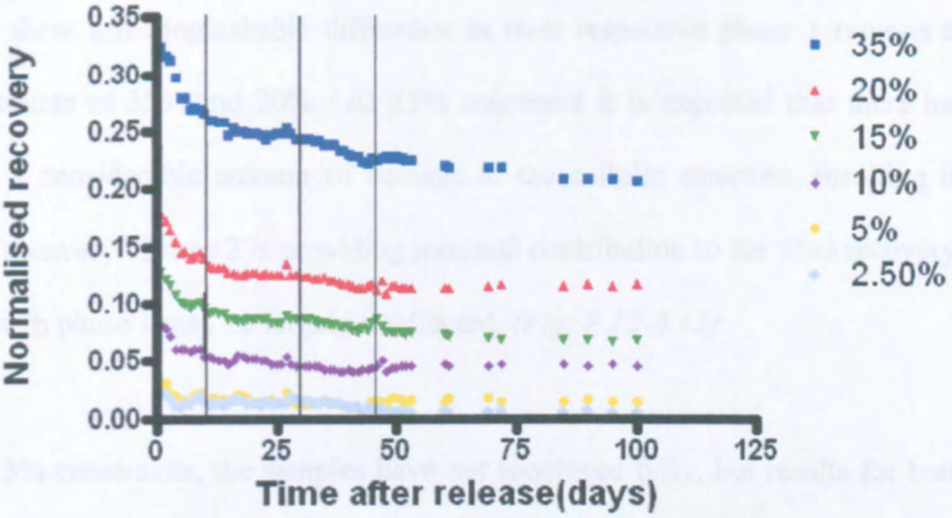


*Figure 8.11: Polyurethane foam compressed for one month at 30 ° C. Example of simultaneous variations*

When you compare the two phases together, phase one recovery contributes most of the final recovery of the foam and although some recovery does occur in phase 2, often only 10% is associated with this phase.

A comparison of the recovery for polyethylene foams of different densities does show a distinguishable difference in their respective phase 1 regions at constraints of 35% and 20%. At 35% constraint it is expected that there has been a considerable amount of damage to the cellular structure, resulting in poor recovery. Phase 2 is providing minimal contribution to the final recovery, although phase 1 may be largely unaffected. *(Fig: 8.12-8.13)*

At 15% constraints, the samples have not recovered fully, but results for both densities are consistent. Samples lie in the plateau region of the stress strain curve. At 10% constraint samples have recovered fully and are still in the linear elastic region. At 5% constraint both samples have recovered fully as can be seen in *(Fig: 8.14-8.15)*

At lower strains of 2.5% and 5%, recovery curves cannot be easily distinguished from each other. However, full recovery is observed within the boundaries of experimental error in most cases when the foams are compressed within the elastic limit, i.e. confining strains of 2.5% and 5% as expected. *(Fig: 8.16-8.17)*

Please note that recovery does commence from the confining strain of 0.15, 0.10, and 0.05. The phase 1 region for both densities are identical within boundaries of experimental error. As stated earlier, the polymer-induced phase 1 dominates the full recovery process while phase 2 only provides a minimal contribution. Therefore it can be predicted that the full recovery is not significantly influenced by the variation in foam densities, given that the bulk polymer remains unchanged in all cases and so does the amount of free volume in the solid phase. The slight variation in recovery between both densities may be associated with experimental differences.

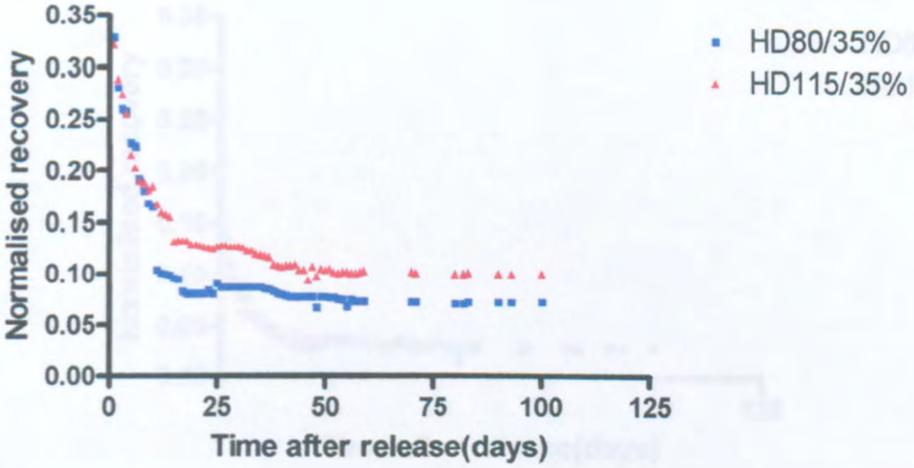


*Figure 8.12: Polyethylene HD80 & HD115 foam compressed by 35 % for one month at ambient temperature.*

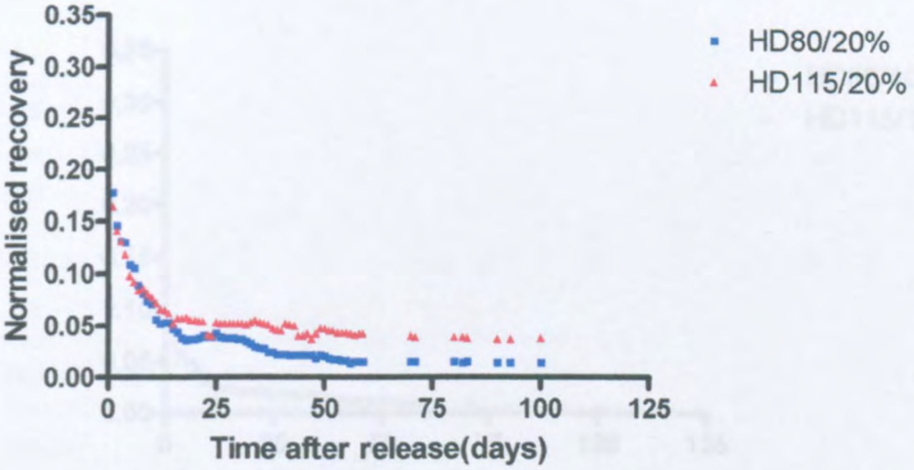


*Figure 8.13: Polyethylene HD80 & HD115 foam compressed by 20 % for one month at ambient temperature.*

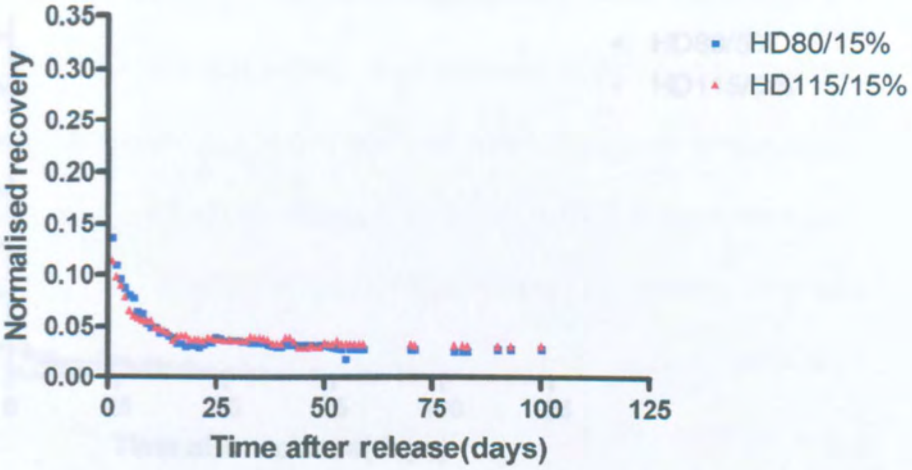


*Figure 8.14: Polyethylene HD80 & HD115 foam compressed by 15 % for one month at ambient temperature.*

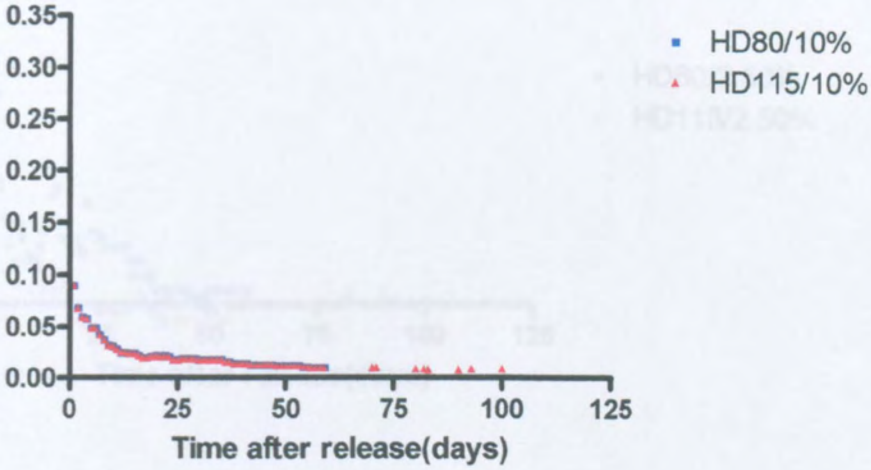


*Figure 8.15: Polyethylene HD80 & HD115 foam compressed by 10 % for one month at ambient temperature.*

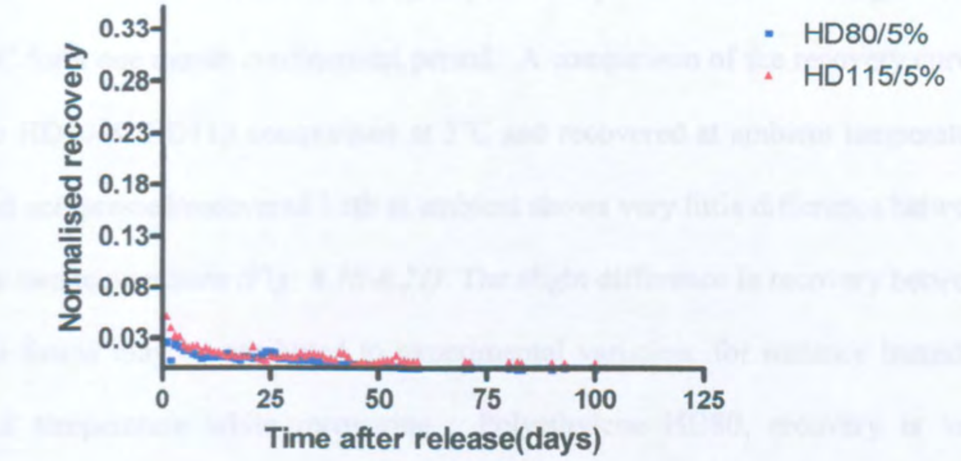


*Figure 8.16: Polyethylene HD80 & HD115 foam compressed by 5 % for one month at ambient temperature.*

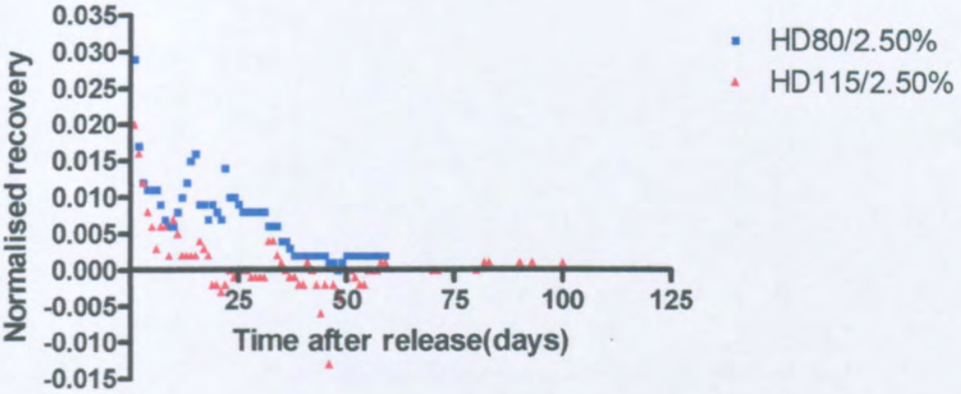


*Figure 8.17: Polyethylene HD80 & HD115 foam compressed by 2.50 % for one month at ambient temperature.*

Tests were also carried out on polyethylene samples which were refrigerated at 3°C for a one month confinement period. A comparison of the recovery curves for HD80 & HD115 compressed at 3°C and recovered at ambient temperature and compressed/recovered both at ambient shows very little difference between the two temperature *(Fig: 8.18-8.21).* The slight difference in recovery between the foams may be attributed to experimental variation, for instance humidity and temperature while recovering. Polyethylene HD80, recovery is very similar for phase 1, whilst Polyethylene HD115 displays a slightly different phase 1 recovery.

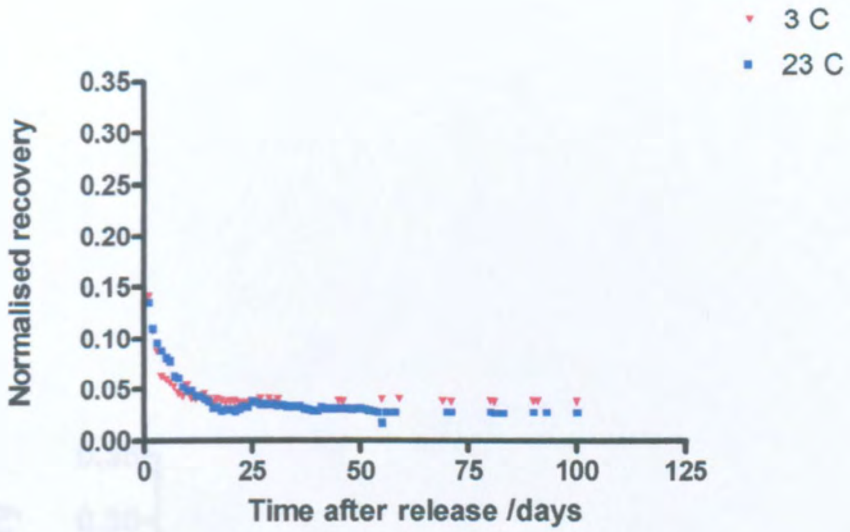


*Figure 8.18: Comparison of Polyethylene HD80 foam compressed by 15 % for one month at 3 °C and ambient temperature.*

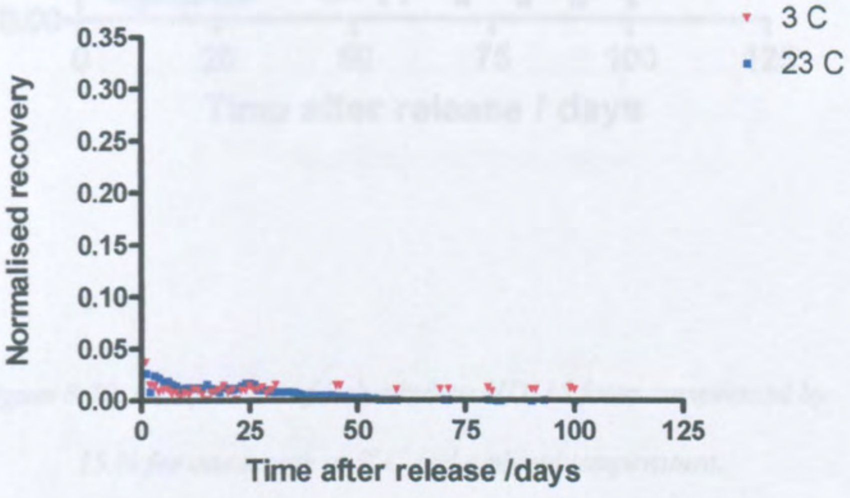


*Figure 8.19: Comparison of Polyethylene HD80 foam compressed by 5 % for one month at 3° C and ambient temperature.*

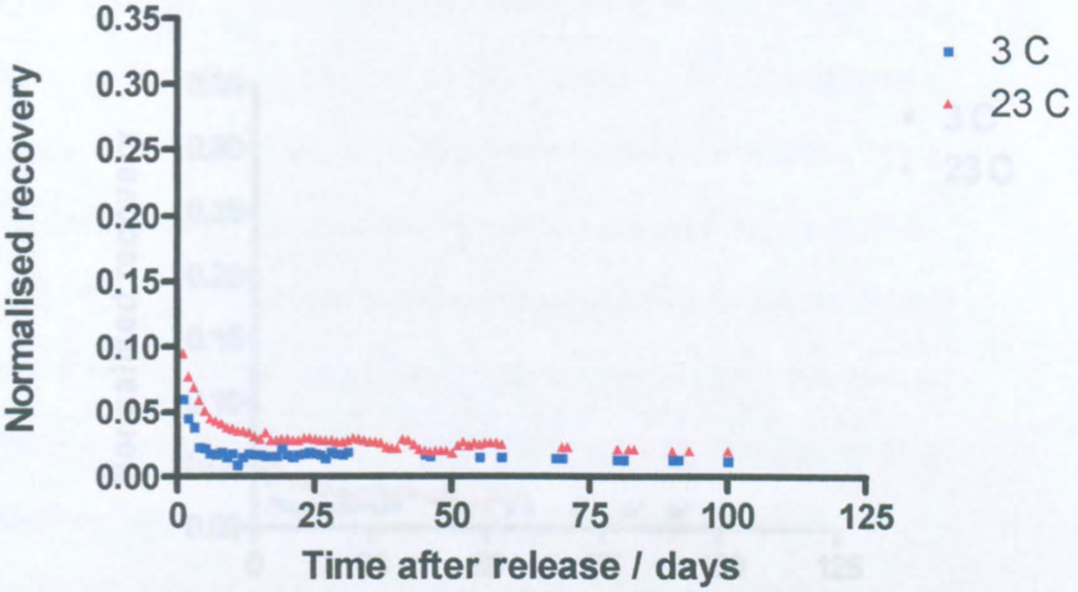


*Figure 8.20: Comparison of Polyethylene HD115 foam compressed by 15 % for one month at 3° C and ambient temperature.*

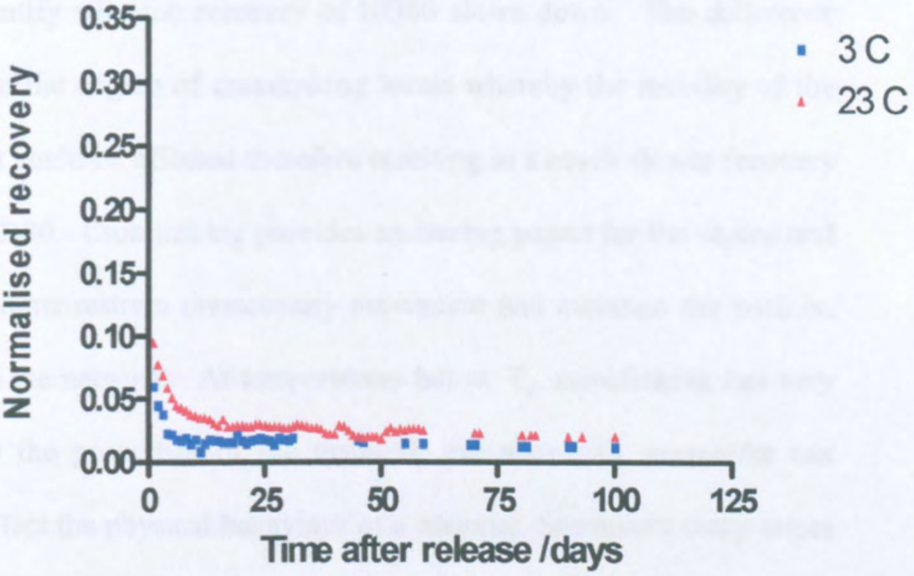


*Figure 8.21: Comparison of Polyethylene HD115 foam compressed by 10 % for one month at 3 °C and ambient temperature.*

Whilst density effects were found to be absent from the ambient temperature results, the foam density appears to have more effect on the full recovery of the samples that had been compressed at 75 ° C. Change in recovery starts to take place above 30°C when recovery is compared to that at ambient temperature.

An increase in temperature during confinement results in a much slower recovery response for polyethylene HD80 compared to HD115. It has been difficult to identify why the recovery of HD80 slows down. The difference could be due to the degree of crosslinking levels whereby the mobility of the polymer chains could be affected therefore resulting in a much slower recovery response for HD80. Crosslinking provides anchoring points for the chains and these anchor points restrain unnecessary movement and maintain the position of the chain in the network. At temperatures below $T_g$, crosslinking has very little effect on the properties of the material, but above $T_g$, crosslinks can significantly affect the physical behaviour of a material. Secondary creep arises from irreversible viscous flow which is reduced.

Recovery curves of polyethylene at elevated temperatures *(fig: 8.22-8.24)* shows curves that are parallel and are consistent. But when we take a close look at the curves phase 1 is identical at all temperatures whilst phase 2 is different. Referring back to the recovery model, phase1 is attributed to the polymer itself whilst phase 2 which displays a much slower degree of recovery is associated with the cellular structure. Relating the curves to this model it fits very well. As phase 1 is related to the polymer which is polyethylene for both HD80 and HD115, whilst phase 2 is related to cellular structure implying that the density is different. Therefore an increase in temperature is resulting in the cellular structure undergoing deformation and extensive damage with increasing compressive strain. The change to the cellular structure is permanent and irreversible. When specimens are compressed beyond their elastic limit and maintained under such conditions of high temperature and strain, the cellular structure adapts to a new configuration.

A polymer is a conglomeration of chains packed together and the extra empty space around the molecules is referred to as free volume, which essentially consists of all the holes in the matrix. [80] An increase in temperature results in sufficient thermal energy, where the molecules start to vibrate and cause the fragment to jump into free volume by cooperative bond rotation, and because of this the polymer chains change into new positions. Heating the polymer sample causes expansion thereby creating more room for movement and application of a compressive load on a sample encourages flow by segmental motion in the direction of the stress. The segmental transposition involving six carbon atoms is called "crankshaft" motion and requires an activation energy of about 25kJ mol$^{-1}$; this is the motion associated with the phase change at $T_g$.

As the chains rotate and move into the free unoccupied space, the mobility of a polymer chain is reduced which results in entanglement which can be thought of as knots at crossings in a system. Entanglements are the roots of many remarkable polymeric properties e.g. high melt viscosities, transient rubber-like behaviour and toughness. As the polymer chains become entangled the polymer becomes tougher and adopts a new configuration resulting in less ability to untangle on recovery.

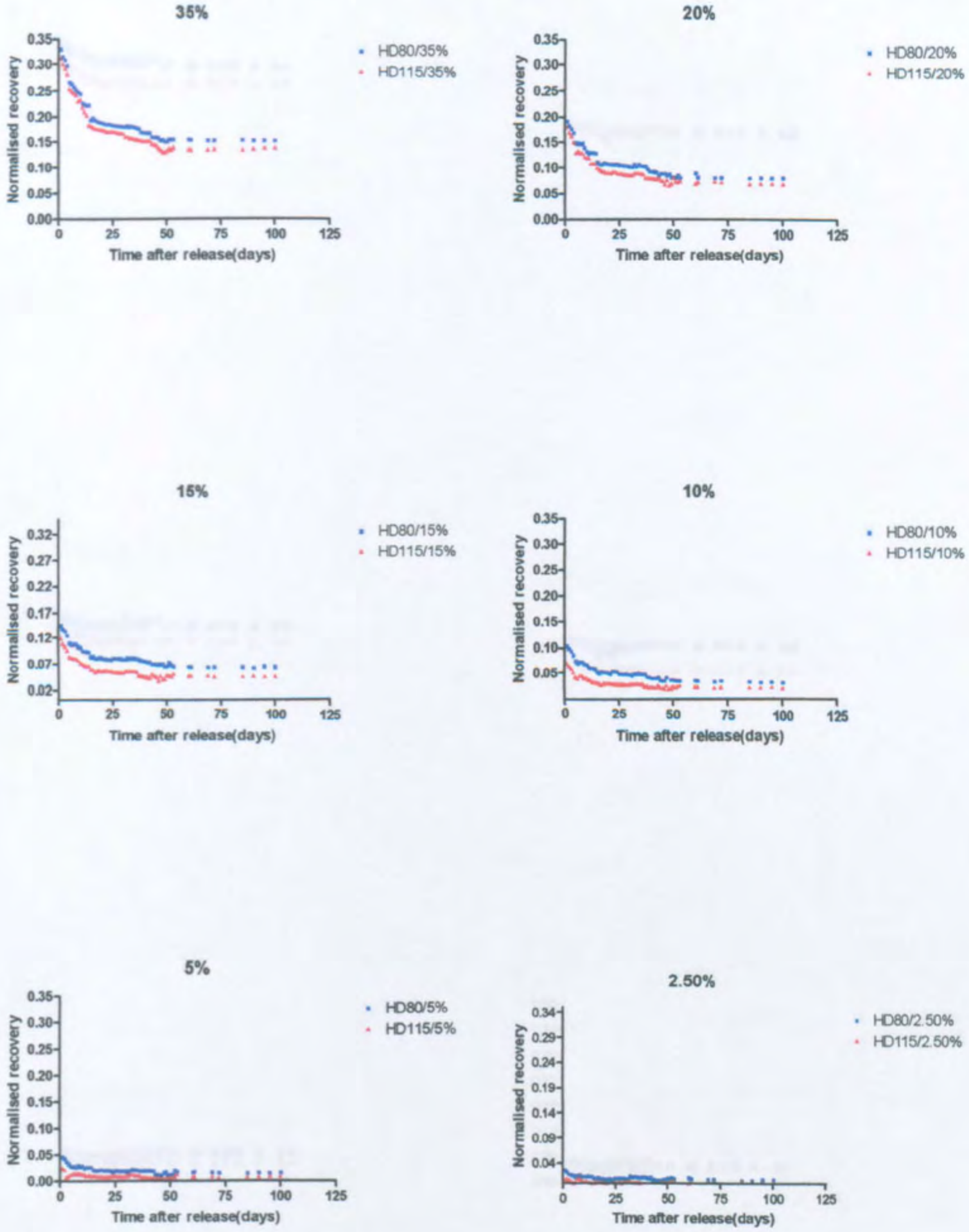


*Figure 8.22: polyethylene foam compressed for one month at 30 ° C*

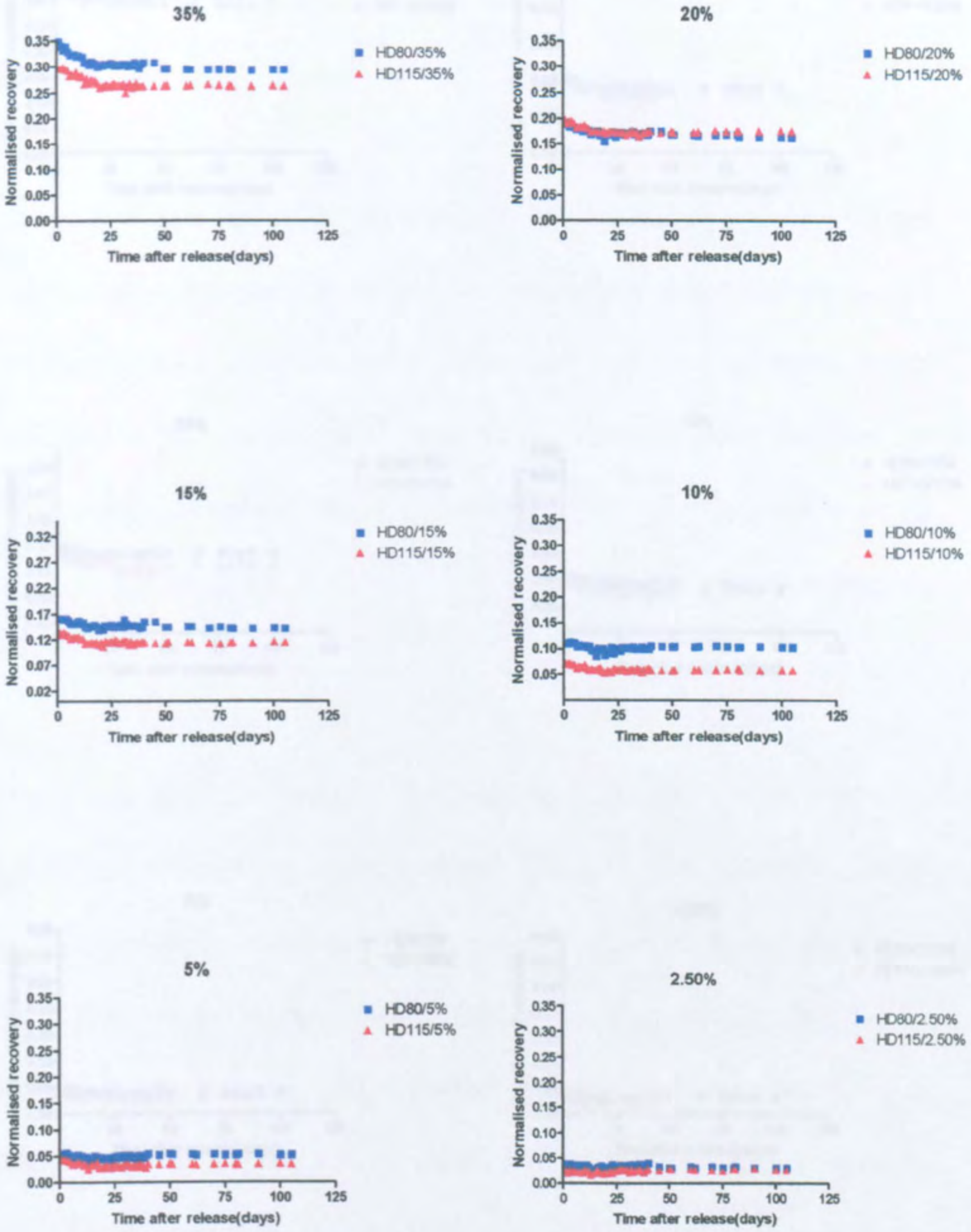


*Figure 8.23: polyethylene foam compressed for one month at 60 °C*

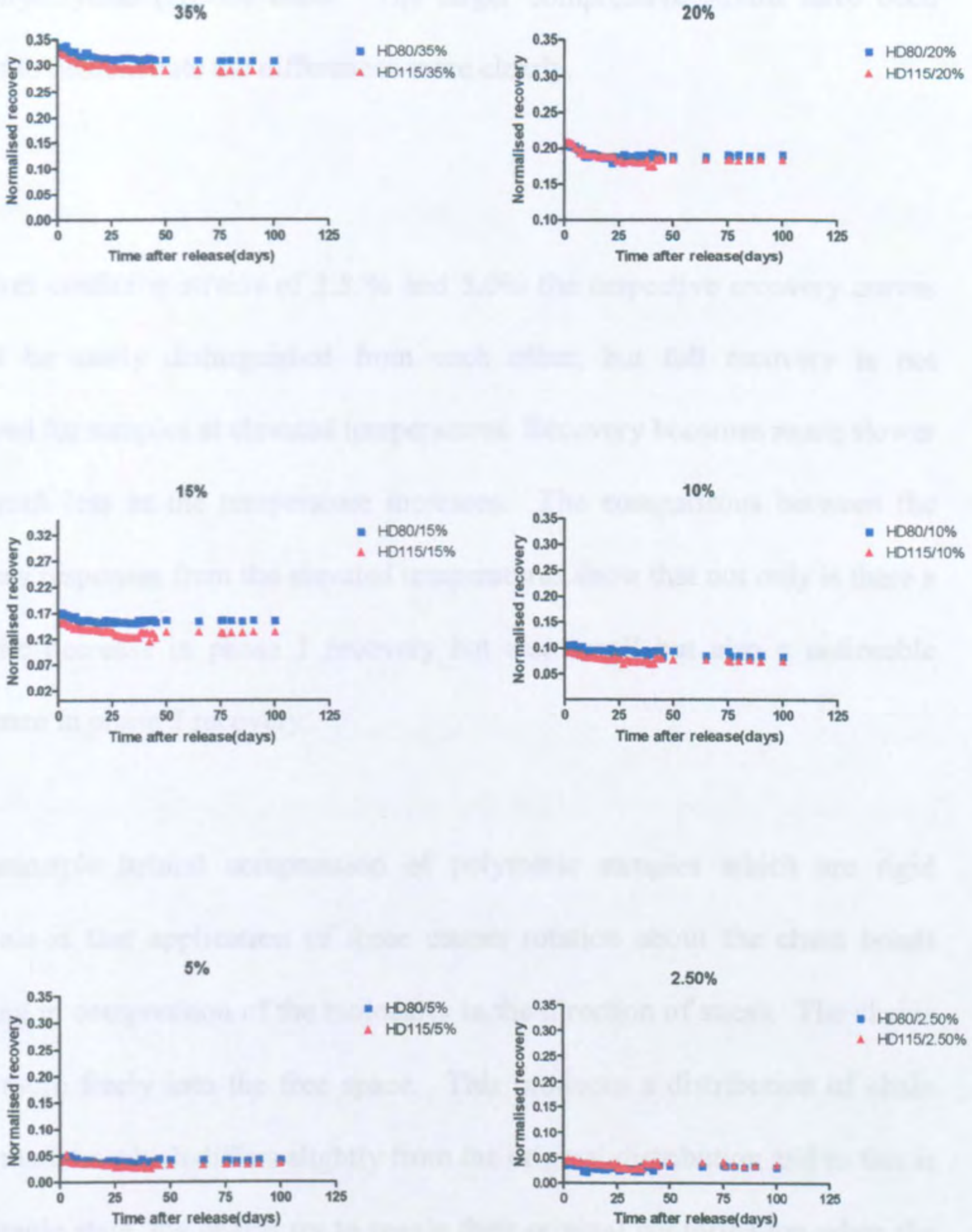


*Figure 8.24: polyethylene foam compressed for one month at 75° C*

Figures 8.27-8.36 sow how final recovery is affected at elevated temperatures for Polyethylene (HD80) foam. The larger compressive strains have been chosen to demonstrate the differences more clearly.

At lower confining strains of 2.5 % and 5.0% the respective recovery curves cannot be easily distinguished from each other, but full recovery is not observed for samples at elevated temperatures. Recovery becomes much slower and much less as the temperature increases. The comparisons between the recovery responses from the elevated temperatures show that not only is there a dramatic decrease in phase 1 recovery but also small but also a noticeable difference in phase 2 recovery.

The principle behind compression of polymeric samples which are rigid materials is that application of force causes rotation about the chain bonds resulting in compression of the molecules in the direction of stress. The chains move more freely into the free space. This produces a distribution of chain conformations which differs slightly from the original distribution and as this is an unstable state, the chains try to regain their original conformation when the stress is released. Similarly, if the temperature is increased further above the glass transition, the molecular motion increases to a sufficiently high level, where the chains behave like weak springs. This means movement of the chains increases therefore allowing a greater ease of chain entanglement. The loss of elastic recovery at each stress is observed; until a point is reached that there is no recovery and the polymer foam remains deformed as the temperature is further raised.

The presence of highly polar groups along polymer chains can increase the intermolecular forces which pulls the chains together, which leads to the reduction of the free volume which sounds the chains. Highly polar groups can increase glass transition temperature. [80, 94]

The glass transition temperature plays an important role in polymer performance, stating the physical properties, such as hardness and elasticity which can be observed. The glass transition temperature ($T_g$) is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. [80, 94]

Flexibility of the chain is certainly the most important factor which influences $T_g$. It is the measure of the ability of a chain to rotate about the constituent chain bonds; hence a flexible chain has a lower $T_g$ whereas a rigid chain has a high $T_g$. Flexibility of polymers is obtained when the chains are made up of a bond sequence which is able to rotate easily. Polymers that contain – ($CH_2$-$CH_2$) - , - ($CH_2$-O-$CH_2$) - or - (Si-O-Si)- have low values for $T_g$. [80]

$T_g$ can vary over a wide range of temperature depending on the polymer; it depends highly on the amount of thermal energy required to keep the chains moving. Therefore if a polymer has a physically stiff group attached e.g. a benzene ring, this interferes with the process of chains sliding past one another and consequently increases the value for $T_g$.

The effect is highlighted by increasing the size of the side group and there is some evidence of correlation between $T_g$ and the molar volume $V_x$ of the pendant group. [80, 94]

Steric effects can also restrict rotation; this can arise by polymers having bulky pendant groups which hinder rotation around the backbone and can cause $T_g$ to increase. It can be seen in table 8.1, increasing the size of the side groups that there is some evidence of correlation between Tg and the molar volume Vx of the pendant group. An increase in the force in the bulk state will hinder molecular motion and increase $T_g$. If you apply this theory to the polymers that have been used in this research, the curves comply well with the rules.

Polyethylene has the simplest structure whilst polyimide is rather more complex. Polyethylene foams tend to recover much more when compared with polyimide foam. This is due to the complex structure of polyimide. The chains slide past each other and lock into a new position and upon removal of compression load the chains become accustomed to their new configuration. Polyethylene is an ideal system, the inter molecular attraction is low ( absence of non-carbon hydrogen bonding) and can be controlled by crosslinking by new polymer system s can be developed by grafting several different polymers structures together.[20]

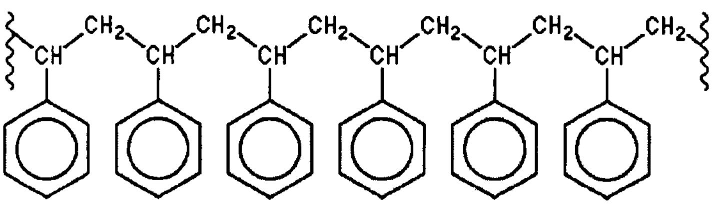
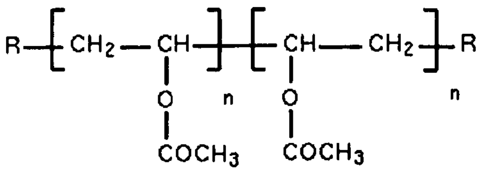


*Fig 8.25: Polystyrene*

Polystyrene is a hydrocarbon polymer which is used extensively in the packaging industry; it has weak van der Waals forces between the chains. However, the bulky nature of the side groups this makes it difficult to rotate the chains (fig 8.18) therefore giving a glass transition temperature of 373K (Table 8.1).



$$R\!-\!\left[CH_2-\underset{\underset{COCH_3}{|}}{\underset{O}{|}}{CH}\right]_n\!\left[\underset{\underset{COCH_3}{|}}{\underset{O}{|}}{CH}-CH_2\right]_n\!-\!R$$

*Fig 8.26: Polyvinyl acetate( head to tail tacticity)*

If you look at poly (vinyl acetate) this has similar arrangement and about the same molecular volume as the phenyls in polystyrene. However the internal flexibility of the chain and their extra polarity obstruct rotation of the chain segments less then the phenyl groups found in polystyrene, therefore the transition temperature is 301K.

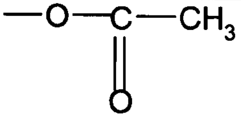
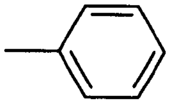
| Polymer | Tg/K | Vx/cm$^3$ mol$^{-1}$ | Group X |
|---|---|---|---|
| Polyethylene | 188 | 3.7 | —H |
| Poly(vinyl acetate) | 301 | 60.1 |  $-O-C(=O)-CH_3$ |
| Poly (vinyl alcohol) | 358 | 11.1 | —OH |
| Polystyrene | 373 | 92.3 |  |

*Table 8.1: Glass transition temperatures for atactic polymers. [80, 94]*

Fig 8.27: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 35% for one month

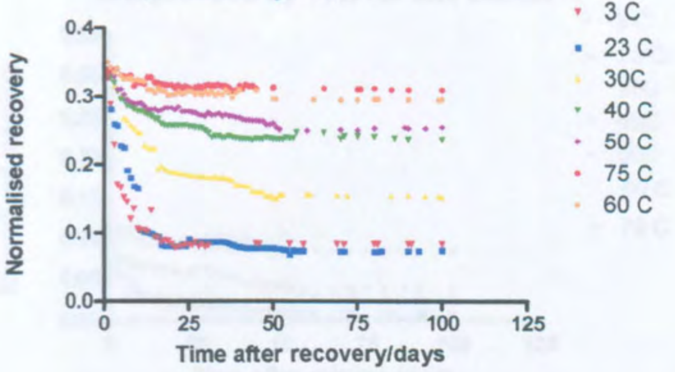


Fig 8.28: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 20% for one month

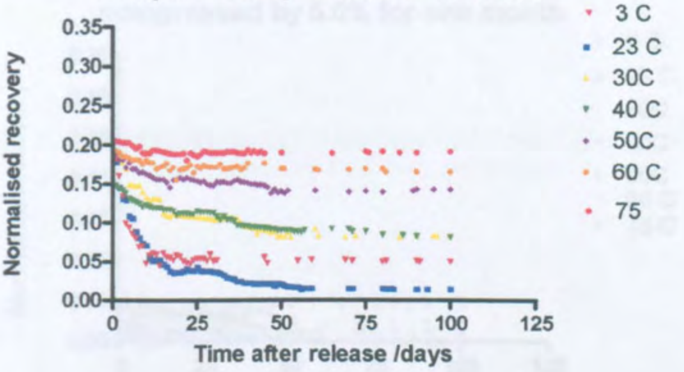


Fig 8.29: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 15% for one month

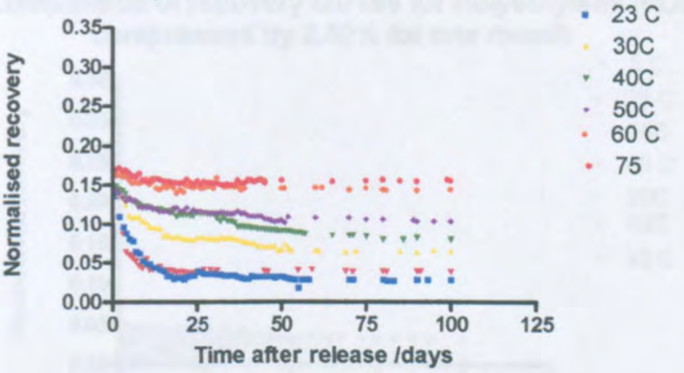


Fig 8.30: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 10% for one month

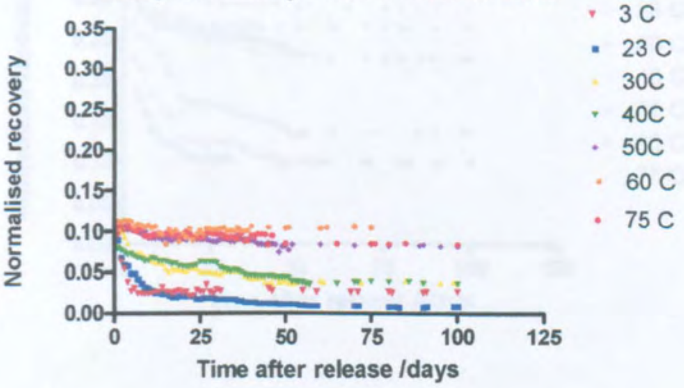


Fig 8.31: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 5.0% for one month

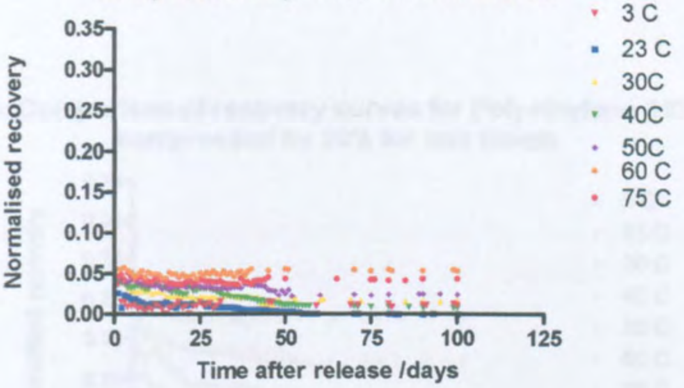


Fig 8.32: Comparison of recovery curves for Polyethylene (HD80) foam compressed by 2.50% for one month

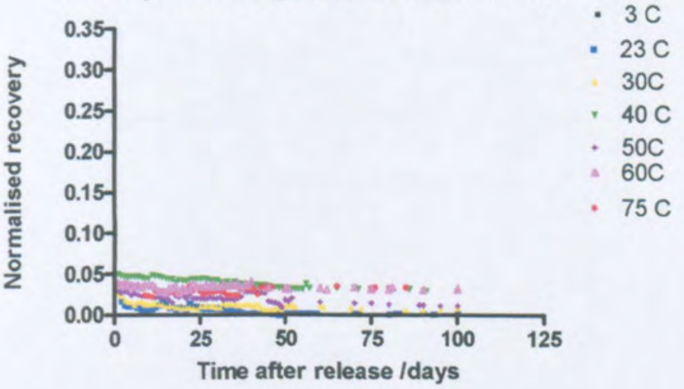


Fig 8.33: Comparison of recovery curves for Polyethylene (HD115) foam compressed by 35% for one month

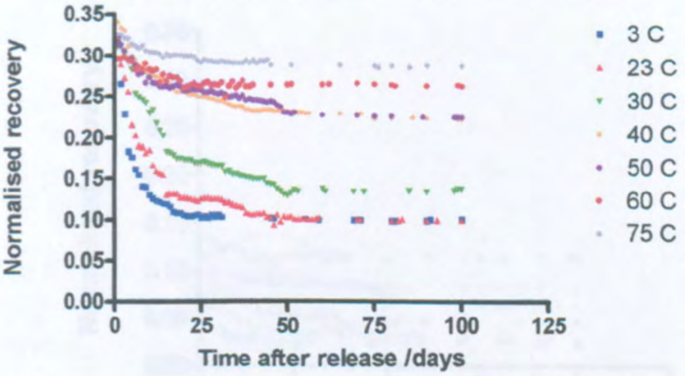


Figure 8.34: Comparison of recovery curves for Polyethylene (HD115) foam compressed by 20% for one month

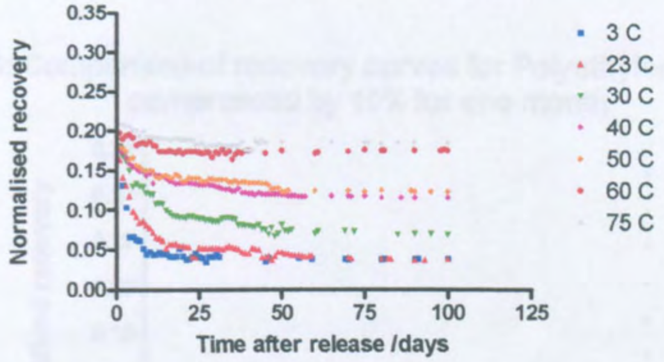


Fig 8.35: Comparison of recovery curves for polyethylene (HD115) foam compressed by 15% for one month.

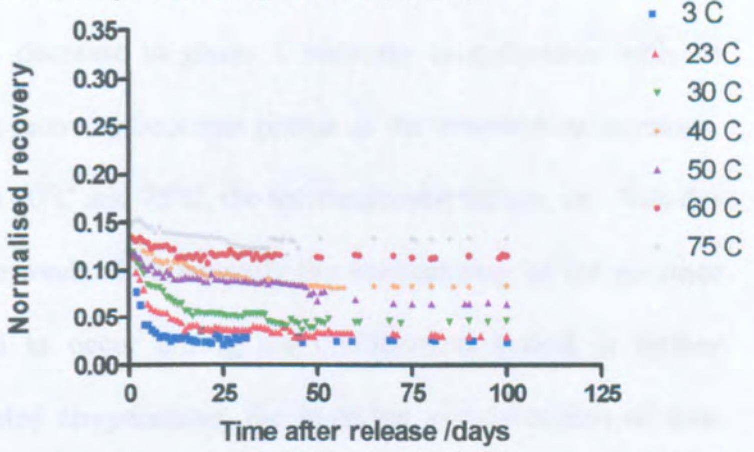
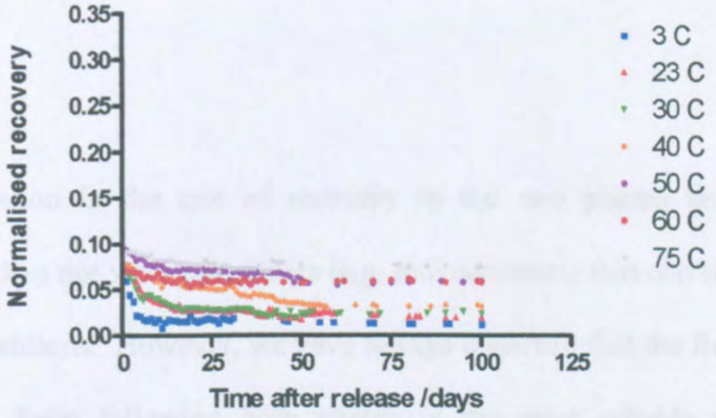


Figure 8.36: Comparison of recovery curves for Polyethylene (HD115) foam compressed by 10% for one month



Variation in temperature has a more pronounced effect on recovery. Figure 8.27-8.36 shows how elevated temperature during confinement affects a polymer specimen. A decrease in phase 1 recovery is noticeable with an increase in temperature; recovery becomes poorer as the temperature increases. At temperatures such as 60°C and 75°C, the intermolecular forces, i.e. Van der Waals forces tend to be weak. Subsequently the restructuring of the polymer chains that is believed to occur during the confinement period is further increased at such elevated temperatures, the breaking and formation of new secondary bonds occurring with ease.

Phase 2 recovery at ambient test conditions was found to present only a minimal contribution to the overall recovery of a polymer foam. However, recovery following elevated temperature testing appears to have flattened the phase 2 recovery of the curve with the suggestion that this part of the recovery has also deteriorated.

The noticeable variation in the rate of recovery in the two phases under different conditions does not yield parameters (e.g. rate constants) that correlate reliably with test conditions. However, we have always observed that the final, total recovery of a foam following both phases is the most reliable and reproducible indicator of the recovery process.

## 8.1 Effect of humidity on recovery:

As mentioned earlier, phase 2 recovery is influenced by certain environmental conditions, such as ambient temperature and humidity, as indicated by sudden fluctuations seen occurring simultaneously in several samples. Therefore tests were carried out to see whether humidity affects the rate of recovery. Polyethylene HD80 was compressed at the normal constraints, placed in the oven at 50°C. Samples were removed after one month and placed in two separate desiccators. One desiccator contained water and the other desiccator contained dry magnesium sulphate. Results are shown in figure 8.37- 8.43. Results do not show any obvious difference in recovery, which appears to suggest that ambient humidity does not affect recovery. This leaves two other likely candidates: (i) ambient temperature variation which we have tried and failed to correlate with recovery anomalies or (ii) barometric pressure change, which would appear to be too small to change the sample dimensions by the amount observed.

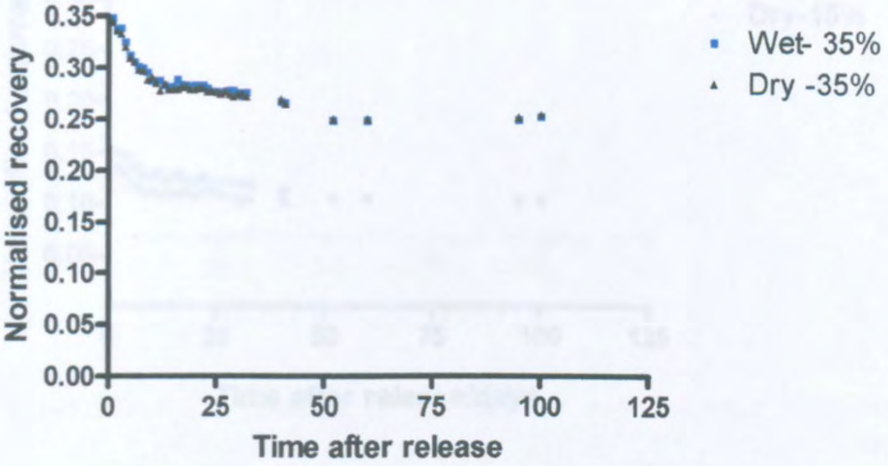


*Figure 8.37: Comparison of Polyethylene foam under wet and dry recovery conditions*

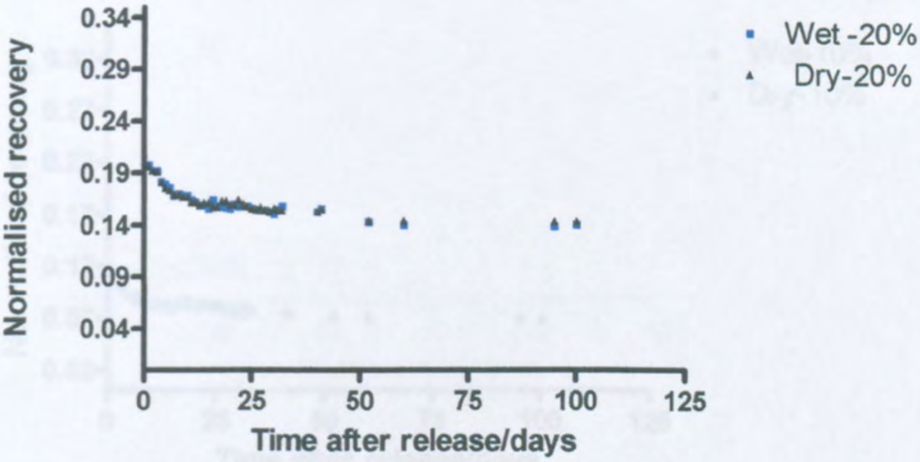


*Figure 8.38: Comparison of Polyethylene foam under wet and dry recovery conditions*

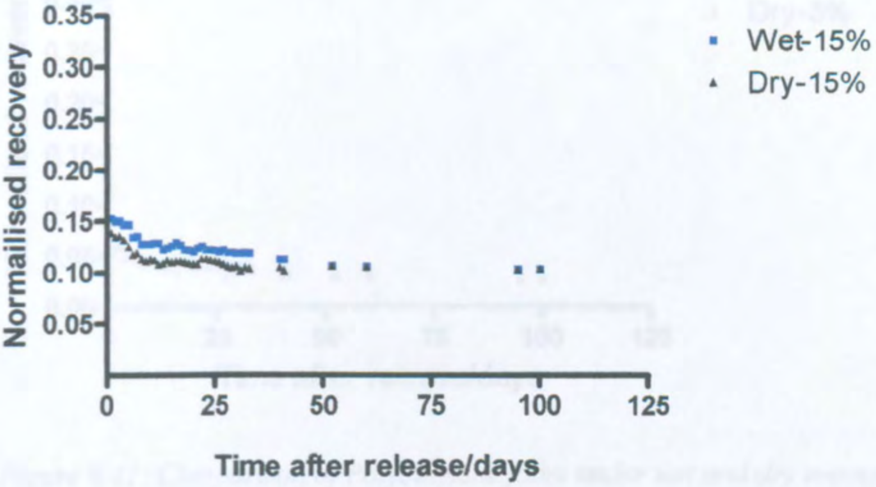


*Figure 8.39: Comparison of Polyethylene foam under wet and dry recovery conditions*

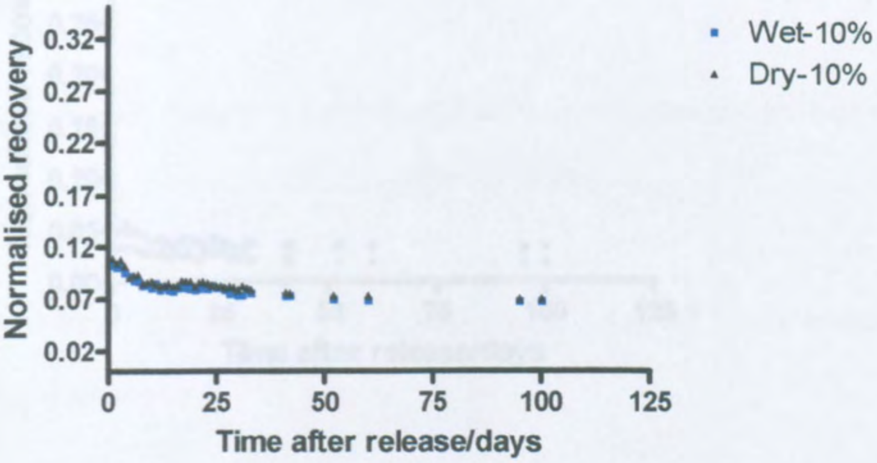


*Figure 8.40: Comparison of Polyethylene foam under wet and dry recovery conditions*

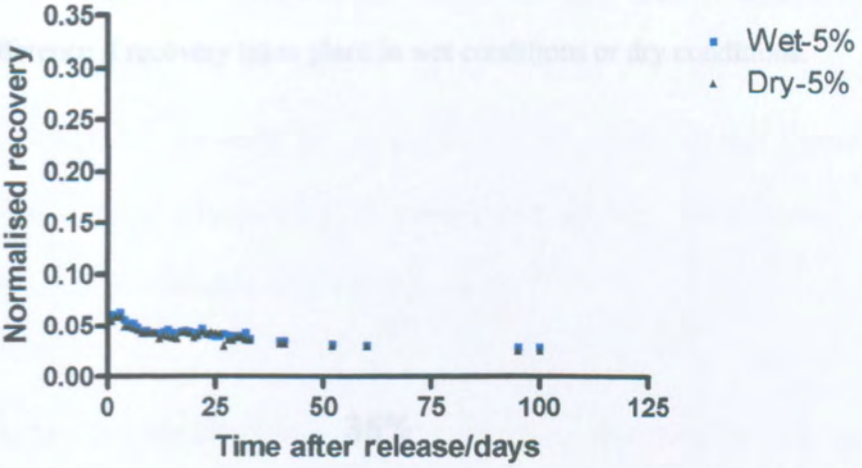


*Figure 8.41: Comparison of Polyethylene foam under wet and dry recovery conditions*

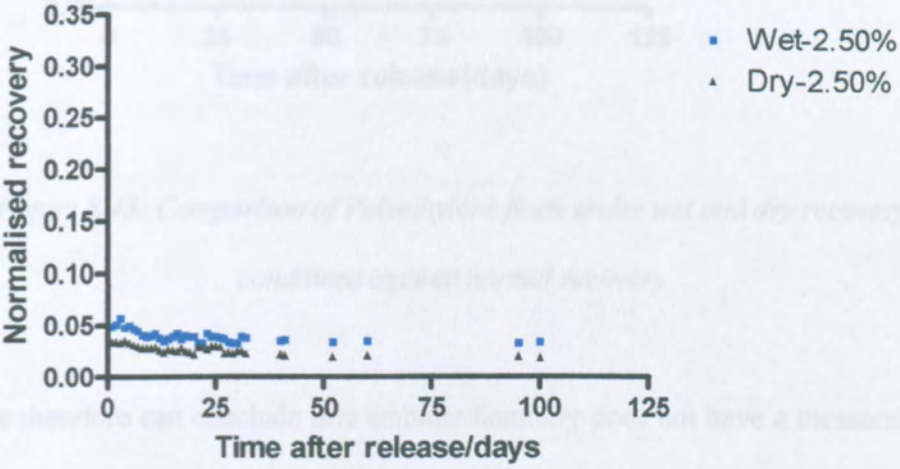


*Figure 8.42: Comparison of Polyethylene foam under wet and dry recovery conditions*

When recovery is compared to normal ambient recovery, the graph shows no difference if recovery takes place in wet conditions or dry conditions.

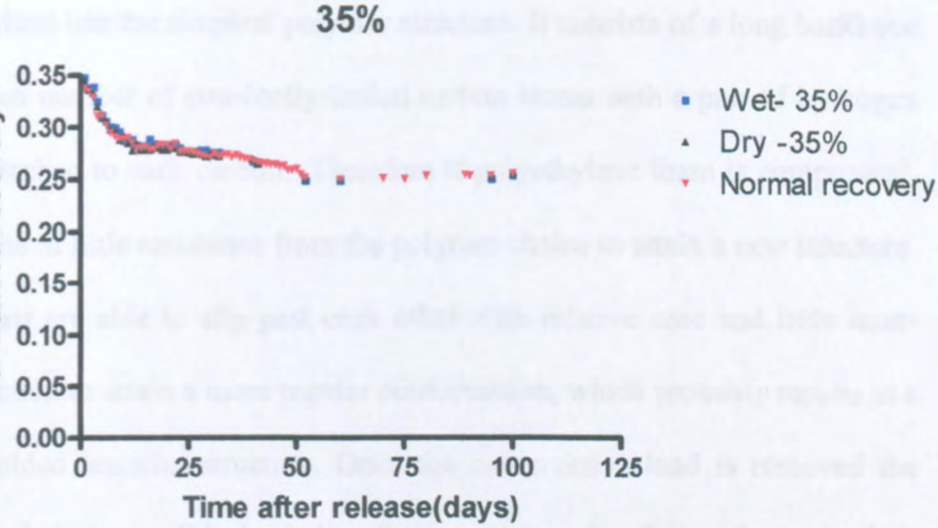


*Figure 8.43: Comparison of Polyethylene foam under wet and dry recovery conditions against normal recovery*

We therefore can conclude that ambient humidity does not have a measurable effect on recovery.

Figures (8.45:8.48) compare the recovery of the four different polymer foams following compression for one month at ambient temperature. There are visible differences between phase 1 and full recoveries of the foams. The polyethylene foam which is lightly crosslinked displays the best recovery by comparison with a substantially large phase 1.

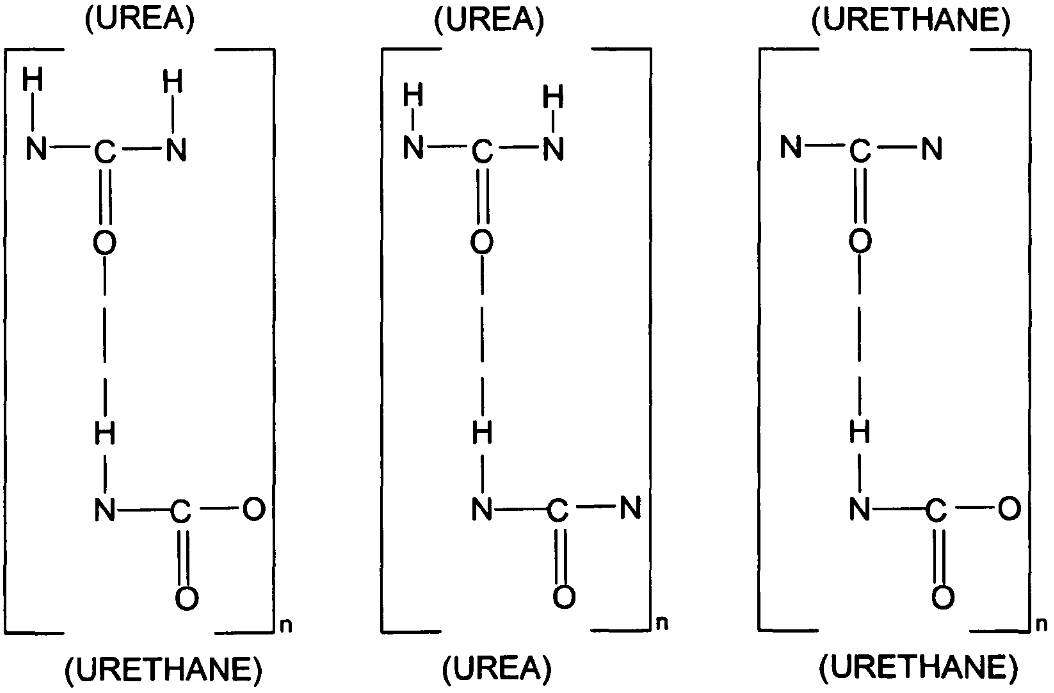
Polyethylene has the simplest polymer structure. It consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon. Therefore if polyethylene foam is compressed, this results in little resistance from the polymer chains to attain a new structure. The chains are able to slip past each other with relative ease and little inter-chain friction to attain a more regular conformation, which probably results in a partial folded lamellar structure. Once the compressive load is removed the polymer chains can slide back by slipping past each other and regain their original conformation much more successfully. This manifests itself in a large phase 1 recovery.

It has already been stated that some of the factors that can be expected to affect phase 1 recovery include the type of polymer and the microstructural details such as crosslinking and pendant groups. Crosslinking can have a profound effect on $T_g$ of a polymer; the density of the polymer tends to be higher therefore restricting the molecular motion in the sample which results in $T_g$ values increasing. Bear in mind, analysis has been conducted using a non-crosslinked polyimide and a lightly crosslinked polyethylene. The polyurethane used is highly crosslinked leading to the molecular motion being restricted and therefore resulting in intermediate recovery when compared to polyimide and polysulphone.

Whilst taking into consideration the mechanism of fatigue in polyurethane foam cushions, it was illustrated by Wolfe [21, 95] that new hydrogen bonds are formed when the foam is compressed. He determined that in urethane foam, a hydrogen bond existed between the hydrogen of either urea or urethane bond and the oxygen of a carbonyl group of these two groups in another chain.

When a compressive load is applied to polyurethane foam (fig 8.44), the chains are thought to shift forming new hydrogen bonds upon removal of the compressive load. The hydrogen bonding slowly tends to revert to the original position, but does not completely achieve this.

*Fig 8.44: Hydrogen bonding in urethane foam[21]*



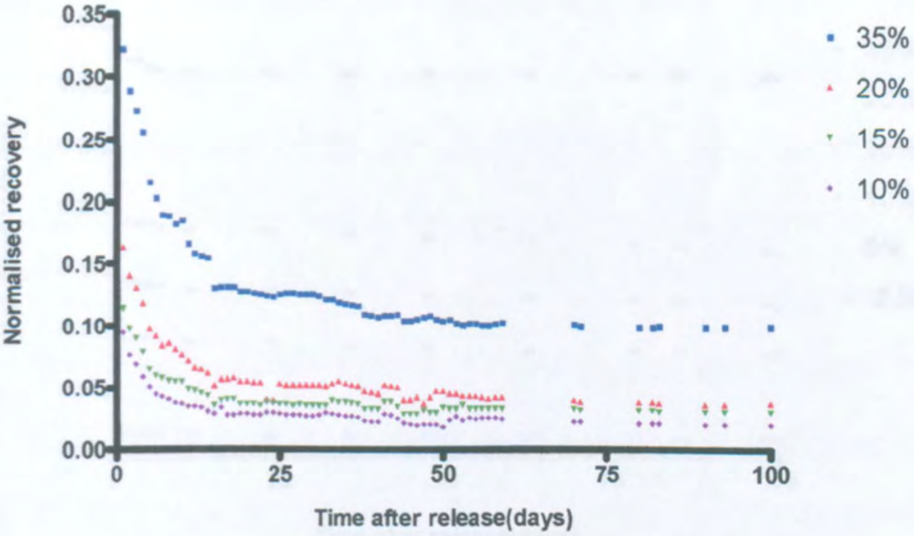


*Figure 8.45: Polyethylene (HD115) compressed for one month at ambient temperature.*

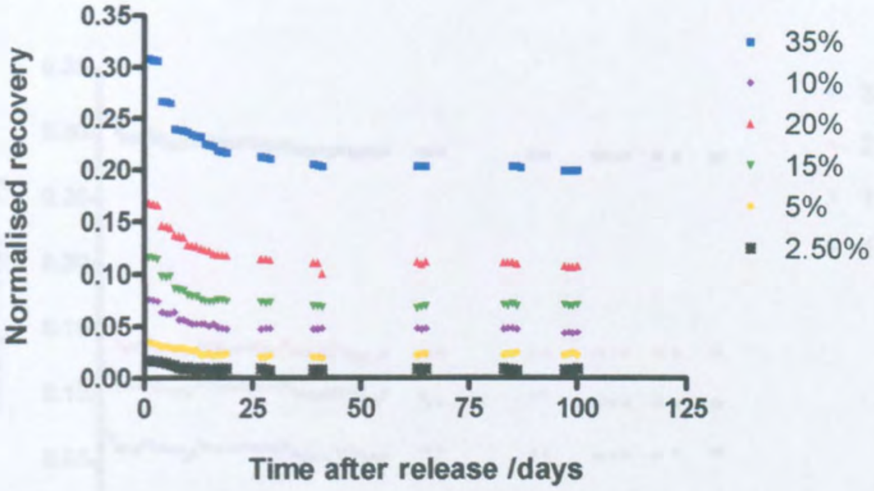


*Figure 8.46: Polyurethane foam compressed for one month at ambient temperature.*

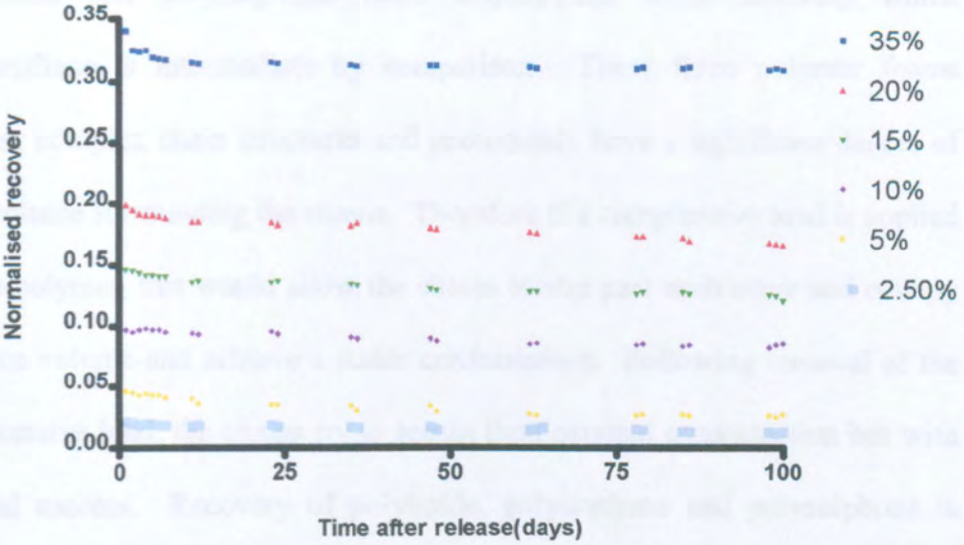


*Figure 8.47: Polyetherimide foam compressed for one month at ambient temperature*

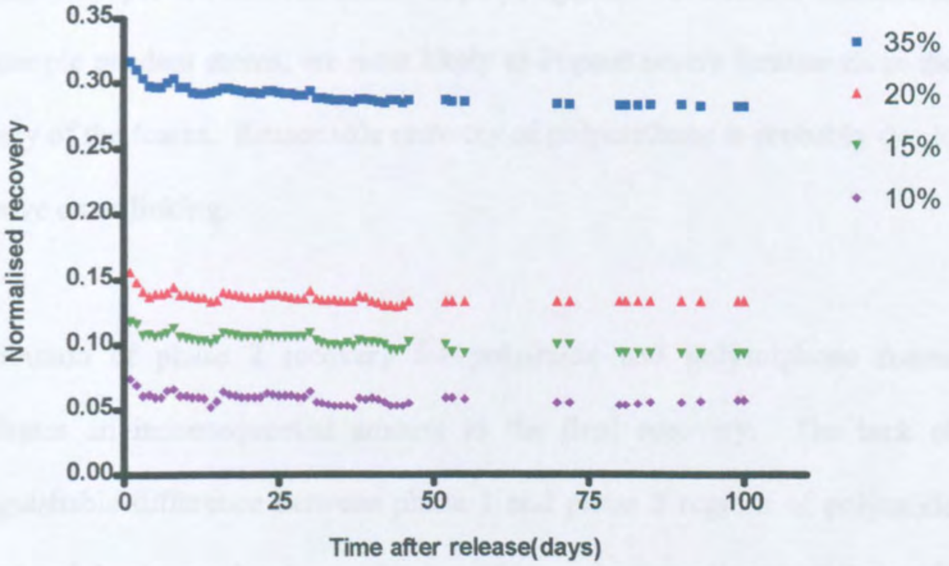


*Figure 8.48: Polysulphone foam compressed for one month at ambient temperature*

Polyimide and polysulphone foam display the worst recovery whilst polyurethane is intermediate by comparison. These three polymer foams possess complex chain structures and presumably have a significant degree of free volume surrounding the chains. Therefore if a compressive load is applied to the polymer, this would allow the chains to slip past each other and occupy the free volume and achieve a stable conformation. Following removal of the compressive load, the chains try to regain their original conformation but with limited success. Recovery of polyimide, polyurethane and polysulphone is restricted and is obvious in the minimal phase 1 recovery. Once the compressive load is removed the polymer chains try to revert to their original position, but the chains are restricted; this could be due to the increased inter-chain friction that occurs with complicated structures as opposed to the reasonably simple and smooth chains of polyethylene. Mechanical limitations, for example pendant atoms, are most likely to impose severe limitations in the recovery of the foams. Reasonable recovery of polyurethane is probably due to extensive cross linking.

Contribution of phase 2 recovery for polyimide and polysulphone foams contributes an inconsequential amount to the final recovery. The lack of distinguishable difference between phase 1 and phase 2 regions of polyimide and polysulphone may be due to the resemblance in the cell size of their cell structures. However it should be noted that the transition from phase 1 and phase 2 appears very sudden for polyurethane, polyimide and polysulphone whereas the polyethylene foams display a much more gradual transition between the two phases. In fact, Polyethylene recovery may often be modelled reasonably well with a single exponential function.

Fig 8.49: Comparison of the recovery curves of all polymer foams compressed by 35% for one month at ambient temperature

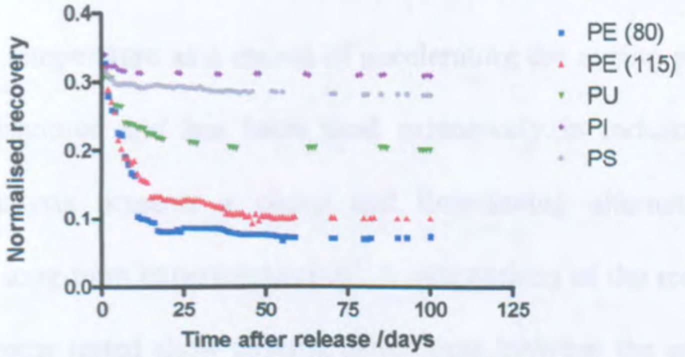


Fig 8.50:Comparison of the recovery curves of all polymer foams compressed by 15% for one month at ambient temperature

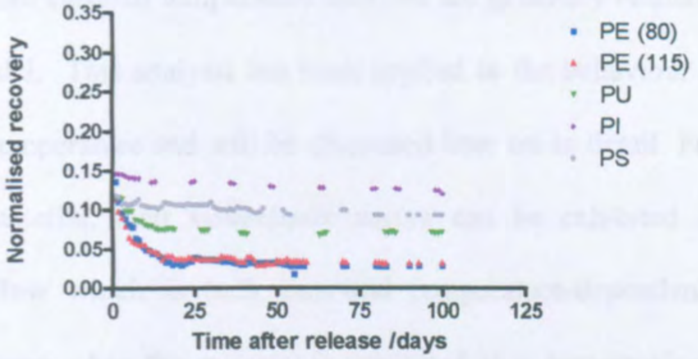
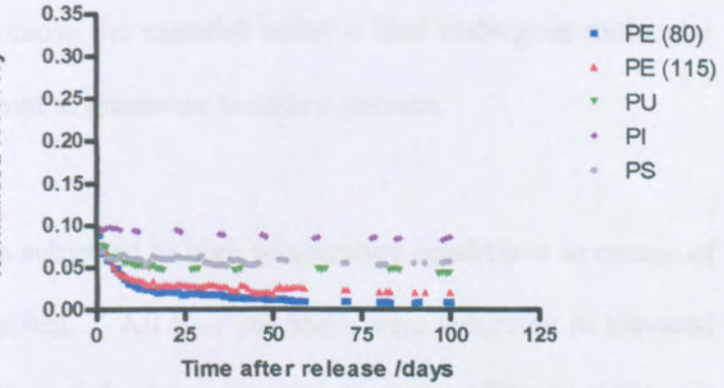


Fig 8.51: Comparison of the recovery curves of all polymer foams compressed by 10% for one month at ambient temperature



## 8.2: Elevated temperature

The use of elevated temperature as a means of accelerating the ageing process is a well-known technique and has been used extensively in industry.[80] Such means of analysis presents a cheap and time-saving alternative to otherwise laborious long-term experimentation. A comparison of the recovery curves of all five foams tested show striking differences between the ambient and elevated-temperatures responses.

Results acquired from elevated temperature analysis are generally related to an Arrhenius-type model. This analysis has been applied to the behaviour of the foams at elevated temperature and will be discussed later on in detail. For any given polymeric material, their viscoelastic nature can be exhibited during deformation and flow which is both time-and temperature-dependent. For instance this can occur when the material is subjected to a compressive load; the deformation or strain exhibited by the material will increase over a period of time. This occurs because the material under a load undergoes molecular rearrangement in an attempt to minimize localized stresses.

The polymer foams were subjected to high temperature conditions as means of accelerating the ageing effect. All four polymers were subjected to elevated temperature testing. This involved confinement between 3°C and 75°C and recovery at ambient conditions. However it should be noted that polysulphone and polyetherimide were not subjected to all temperatures because of limited supply.

It can be seen that as the temperature increases the recovery response for all polymers decreases. (Fig 8.52-8.61) The intermolecular forces become weak and the polymer chains restructure at elevated thermal conditions. By the time of removal of compressive load at ambient temperature the chains have become so tangled up and the polymeric conformation resists recovery to such an extent that it is found to cause a profound reduction of phase 1 recovery.

Under ambient test conditions it was found that phase 2 recovery contributed minimally to the overall full recovery of foam. However with compression at elevated temperature phase 2 recovery becomes quite flattened implying that this phase has also been affected.

Fig 8.52: Polyethylene (HD80) compressed for one month at 30C

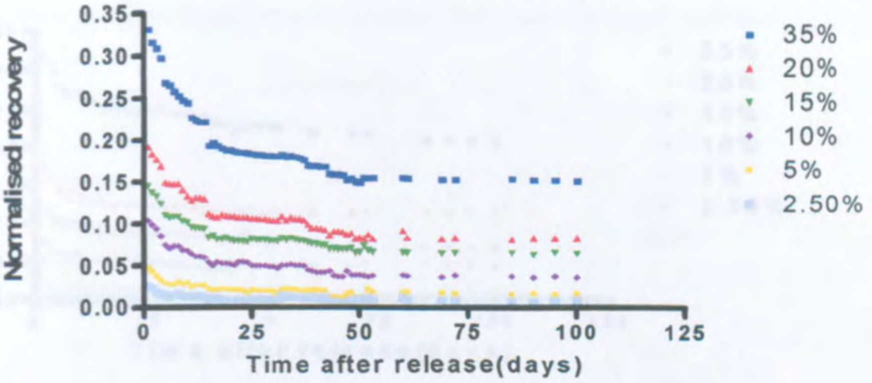


Fig 8.53:Polyethylene (HD80) compressed for onemonth at 50C

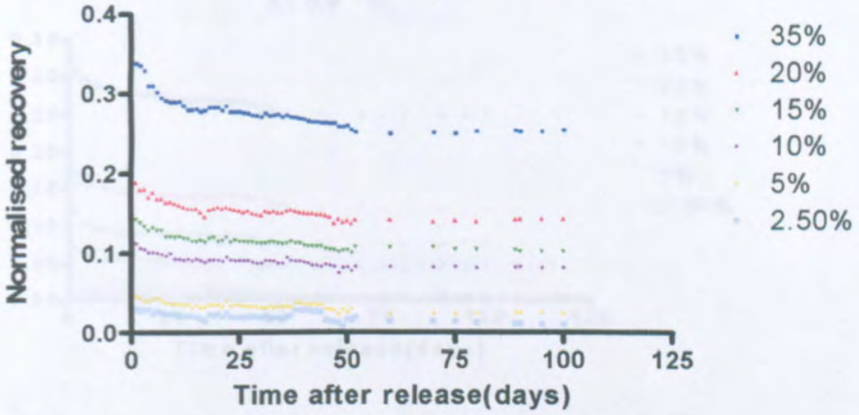


Fig 8.54: Polyethylene (HD80) compressed for one month at 75C

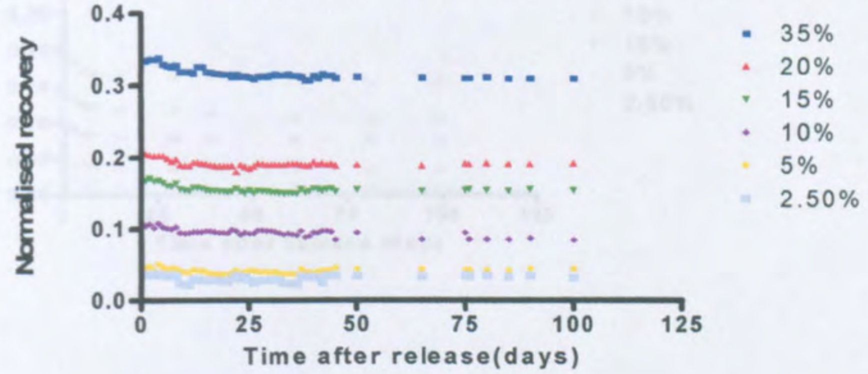


**Fig 8.55: Polyurethane compressed for one month at 30 °C**

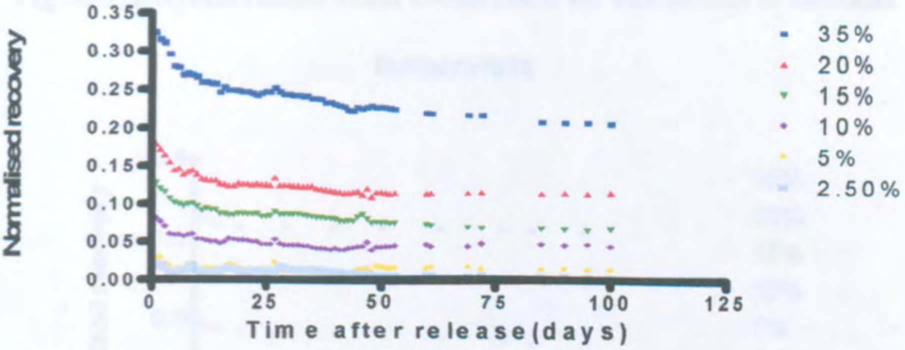


**Fig 8.56: Polyurethane compressed for one month at 50 °C**

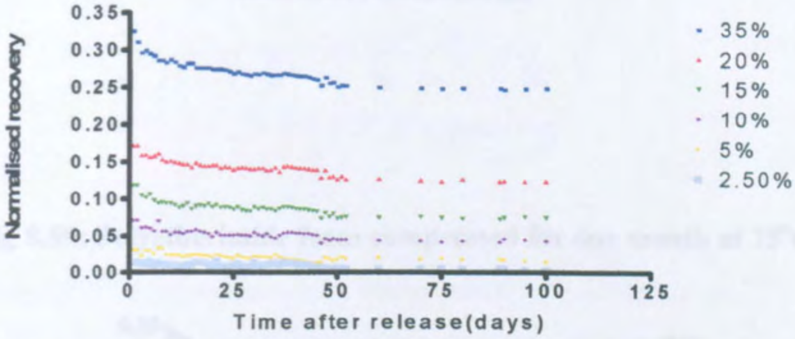


**Fig 8.57: Polyurethane compressed for one month at 75°C**

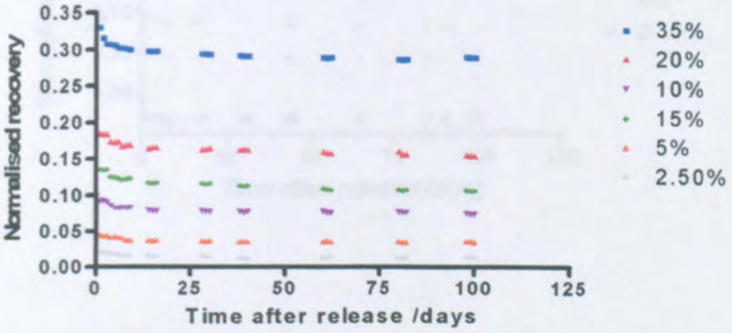


Fig 8.58: Polyetherimide foam compressed for one month at ambient temperature

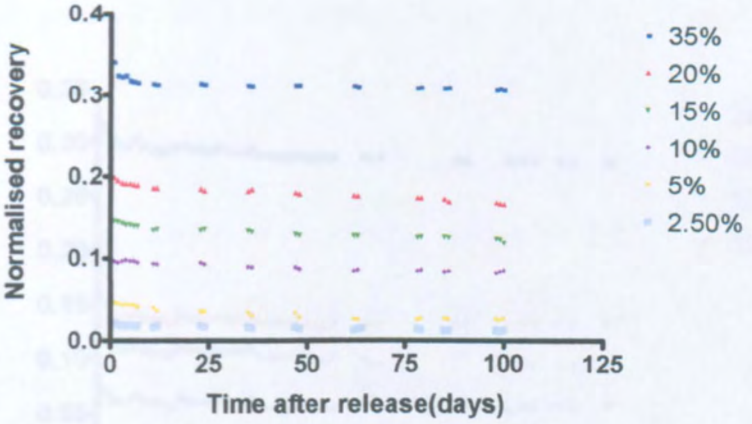


Fig 8.59: Polyetherimide foam compressed for one month at 75°C

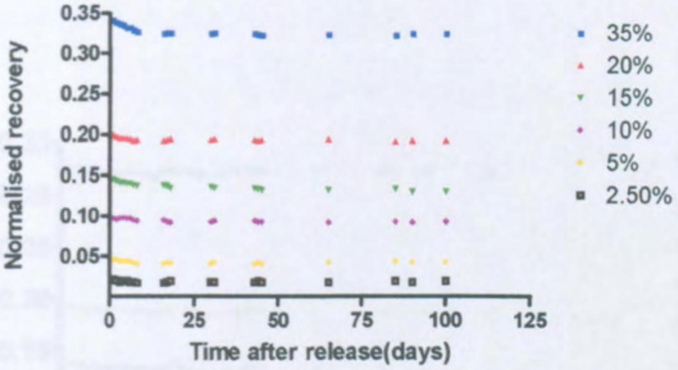


Fig 8.60: Polysulphone foam compressed for one month at ambient temperature

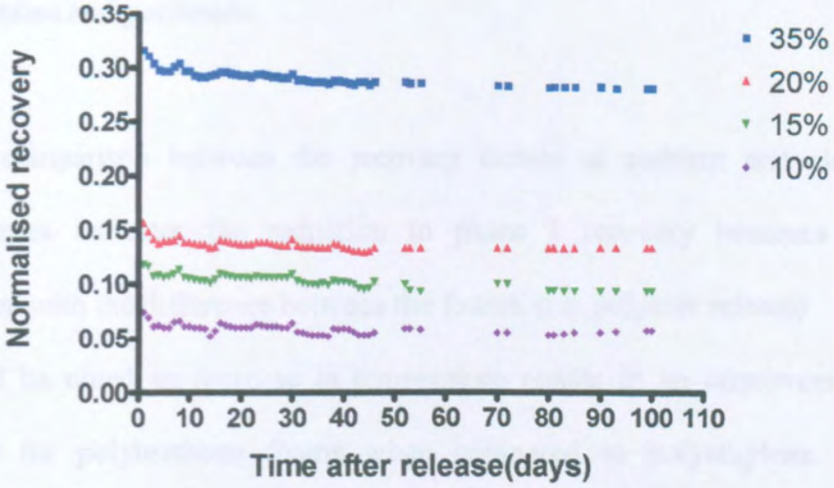


Fig 8.61: Polysulphone foam compressed for one month at 75°C

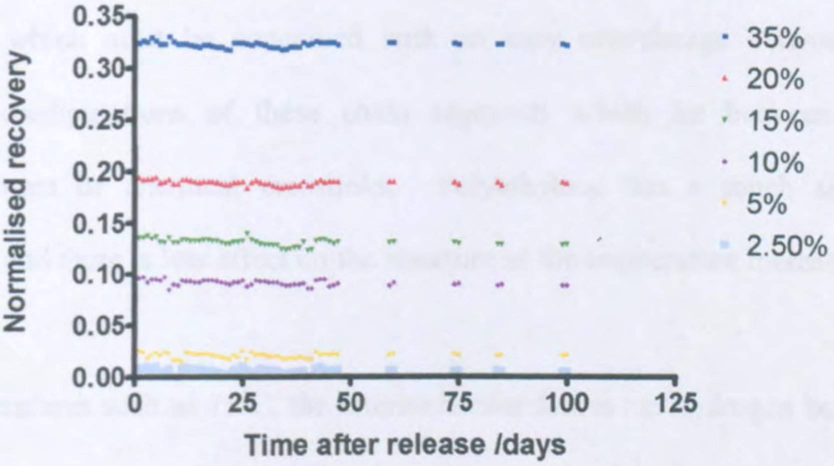


Figure 8.62-8.76 compares the final recovery of all five polymer foams compressed by 35% for one month at ambient temperature. The plots highlight the superior recovery of polyethylene foam, followed by polyurethane, polysulphone and polyimide.

Careful comparison between the recovery curves at ambient and elevated temperatures indicates the reduction in phase 1 recovery becomes more significant with the difference between the foams. (i.e. polymer related)
It should be noted an increase in temperature results in an improvement in recovery for polyurethane foams when compared to polyethylene. The temperature increase results in a faster recovery at temperatures greater than 30° C. This could be due to the complex structure of the polyurethane, the polymer bonds become weaker as the temperature increases. Polyurethane is highly crosslinked, therefore an increase in temperature could be resulting in motions which must be concerned with an easy interchange between the various configurations of these chain segments which lie between tight entanglement or chemical crosslinks. Polyethylene has a much simpler structure and there is less effect on the structure as the temperature increases.

At temperatures such as 75°C, the intermolecular forces i.e. hydrogen bonding and van der Waals forces, tend to be weak. Subsequently the permanent reorganization of the polymer chains that is thought to occur during confinement period is further enhanced at elevated temperatures. The increase in temperature results in an increase in breaking of bonds such as Van der

Waals or hydrogen bonds and formation of new ones. Release of the compressive load results in the polymeric specimen resisting recovery to such an extent that is found to have serious consequences on phase 1 recovery.

Fig 8.62: Comparison of the recovery curves of all polymer foams compressed by 35% for one month at 30 °C

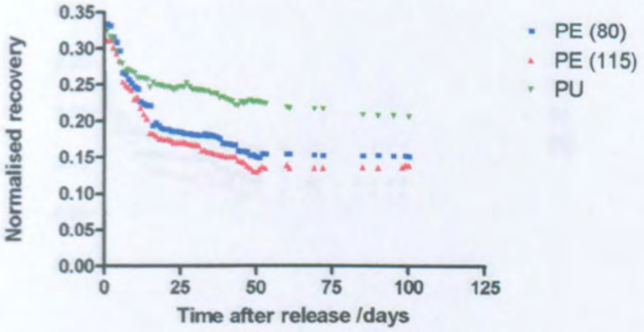


Fig 8.63: Comparison of the recovery curves of all polymer foams compressed by 35% for one month at 40° C

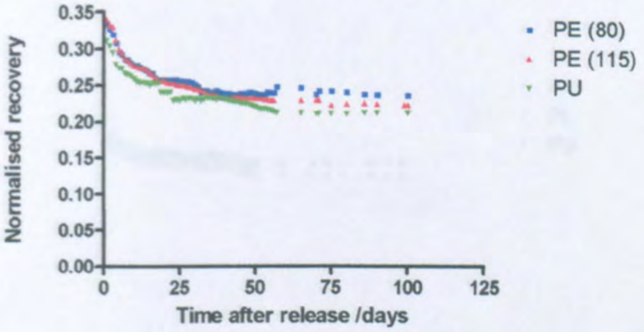


Fig 8.64:Comparison of the recovery curves of all polymer foams compressed by 35% for one month at 75 °C

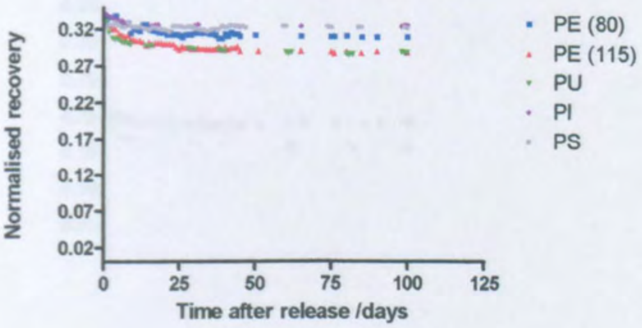


Fig 8.65: Comparison of the recovery curves of PU and PE foams compressed by 20% for one month at 30° C

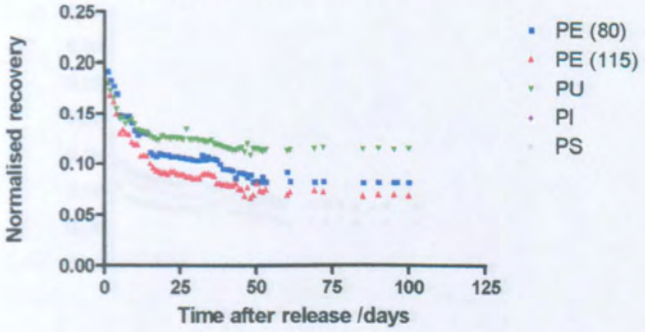


Fig 8.66: Comparison of the recovery curves of PU and PE foams compressed by 20% for one month at 50° C

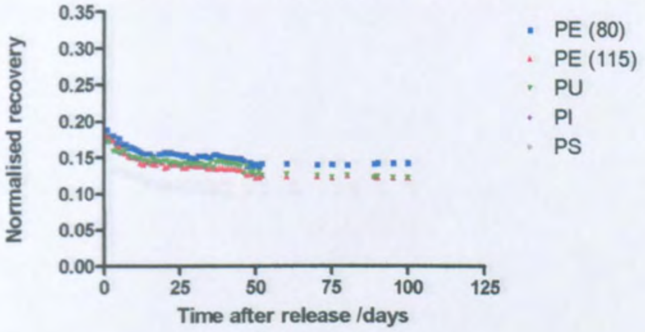


Fig 8.67: Comparison of the recovery curves of all polymer foams compressed by 20% for one month at 75° C

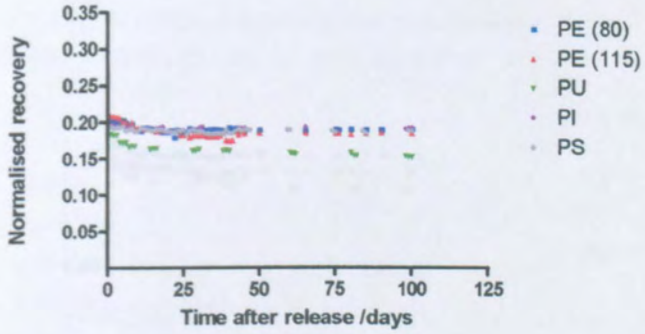


Fig 8.68: Comparison of the recovery curves of all polymer foams compressed by 15% for one month at 40° C

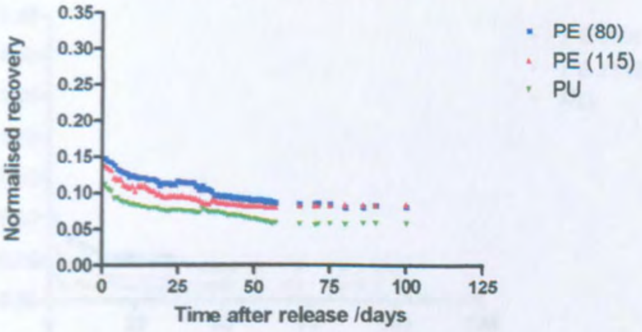


Fig 8.69: Comparison of the recovery curves of all polymer foams compressed by 15% for one month at 60 °C

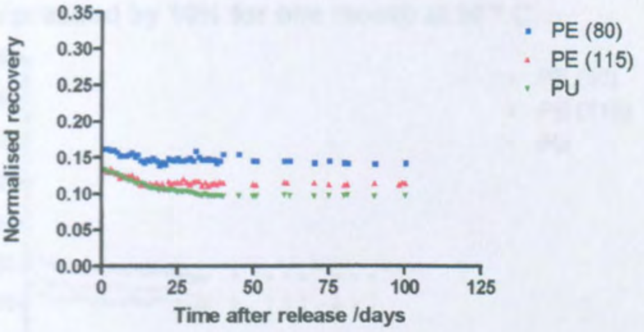


Fig 8.70: Comparison of the recovery curves of all polymer foams compressed by 15% for one month at 75° C

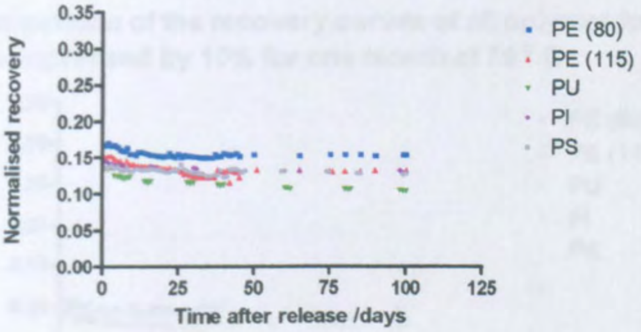


Fig 8.71: Comparison of the recovery curves of PU and PE foams compressed by 10% for one month at 30 ° C

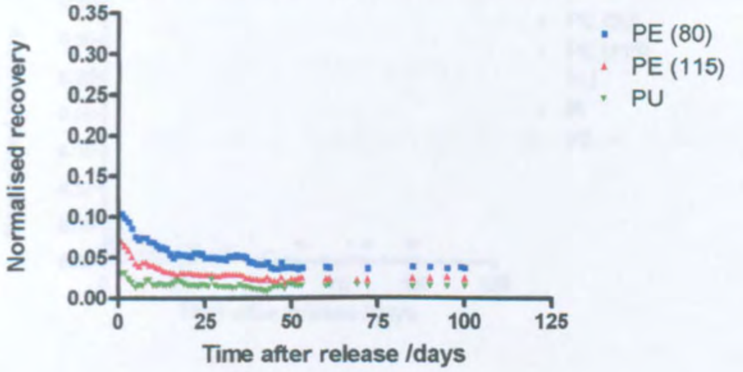


Fig 8.72: Comparison of the recovery curves of all PU and PE compressed by 10% for one month at 50 ° C

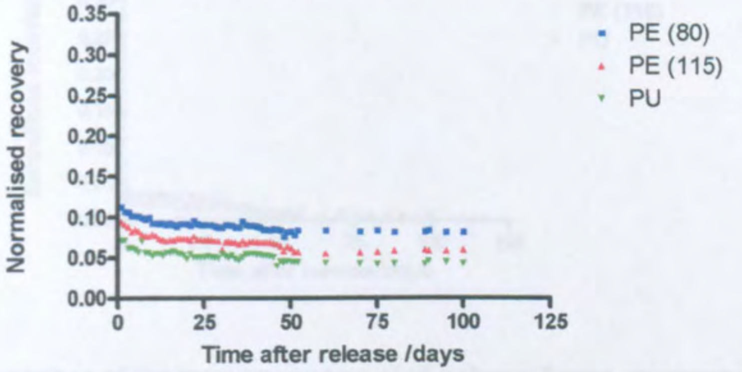


Fig 8.73: Comparison of the recovery curves of all polymer foams compressed by 10% for one month at 75 ° C

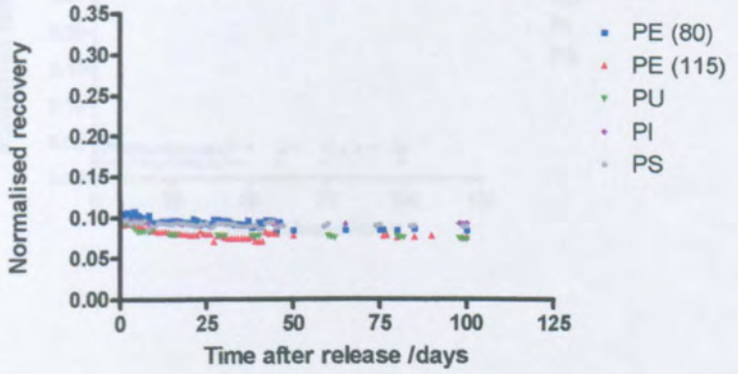


Fig 8.74: Comparison of the recovery curves of all polymer foams compressed by 5% for one month at ambient temperature

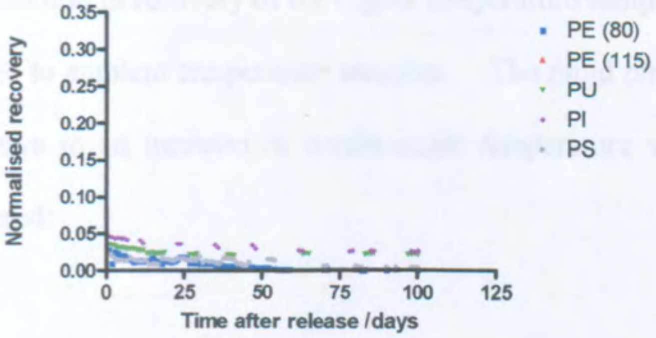


Fig 8.75: Comparison of the recovery curves of all polymer foams compressed by 5% for one month at 40 °C

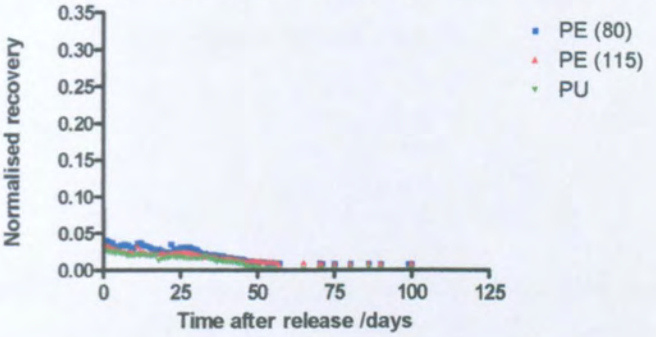
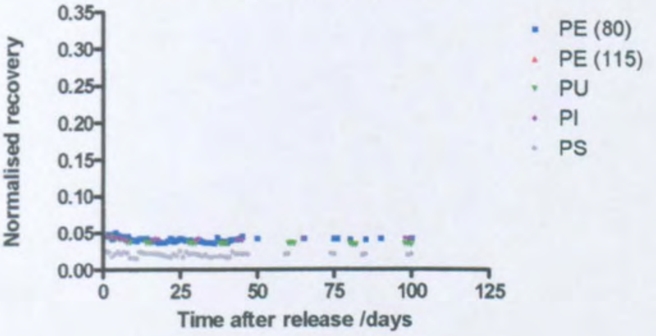


Fig 8.76: Comparison of the recovery curves of all polymer foams compressed by 5% for one month at 75° C



Recovery of polyurethane foam at various temperatures is illustrated in figure 8.77-78. A reduction in recovery of the higher temperature samples is observed when compared to ambient temperature samples. The rapid phase 1 recovery is more sensitive to an increase in confinement temperature whilst phase 2 remains unaltered.

Figure 8.77: Polyurethane foam compressed by 35% at various temperatures for one month

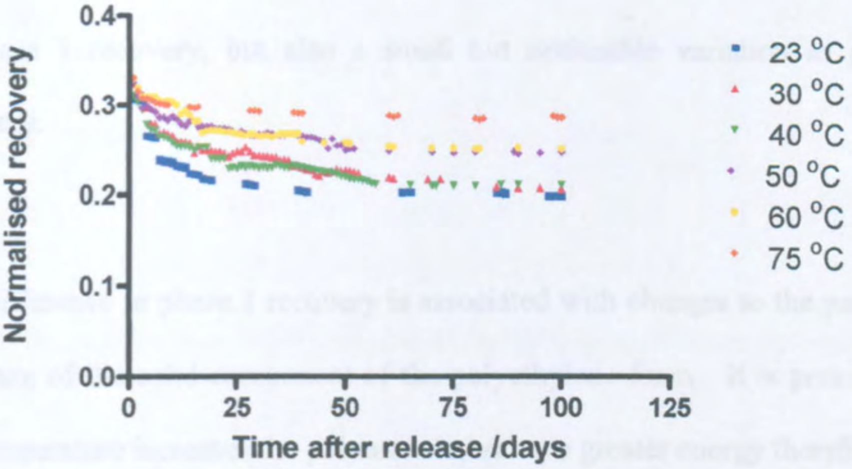
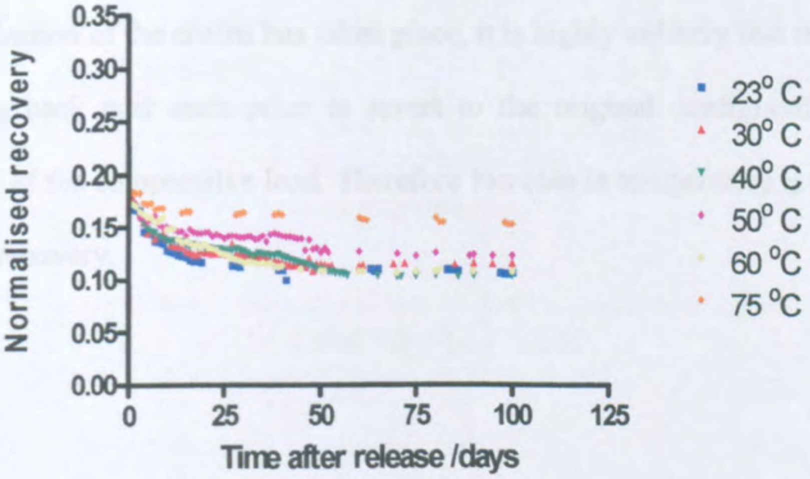


Figure 8.78: Polyurethane foam compressed by 20% at various temperatures for one Month



Polyethylene foam exhibits by the far the best recovery from compression at ambient temperature. However, this recovery dramatically decreases as the temperature is increased. The comparison between the recovery responses from the elevated temperatures shows not only is there a remarkable decrease in phase 1 recovery, but also a small but noticeable variation in phase 2 recovery.

The difference in phase 1 recovery is associated with changes to the polymeric structure of the solid component of the polyethylene foam. It is presumed as the temperature increases the polymer chains have greater energy therefore they are able to relocate and adopt a new permanent position more easily. Increase in temperature results in the polymer chains realigning into a more ordered lamellar structure with relative ease into the surrounding free volume with an inevitable increase in polymer foam density. The chains can slide past each other and therefore facilitate the packing process. Once the permanent reorganisation of the chains has taken place, it is highly unlikely that the chains will slip back past each other to revert to the original configuration upon removal of the compressive load. Therefore increase in temperature is reflected in poor recovery.

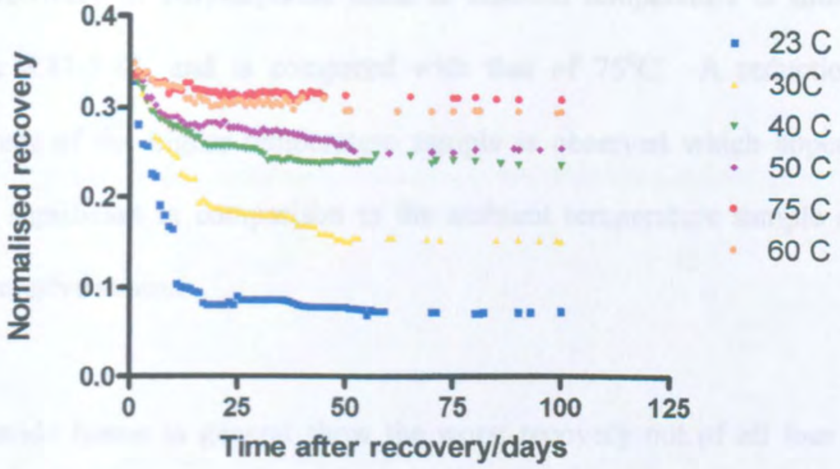


Figure 8.79: Polyethylene foam compressed by 35% at various temperatures for one month

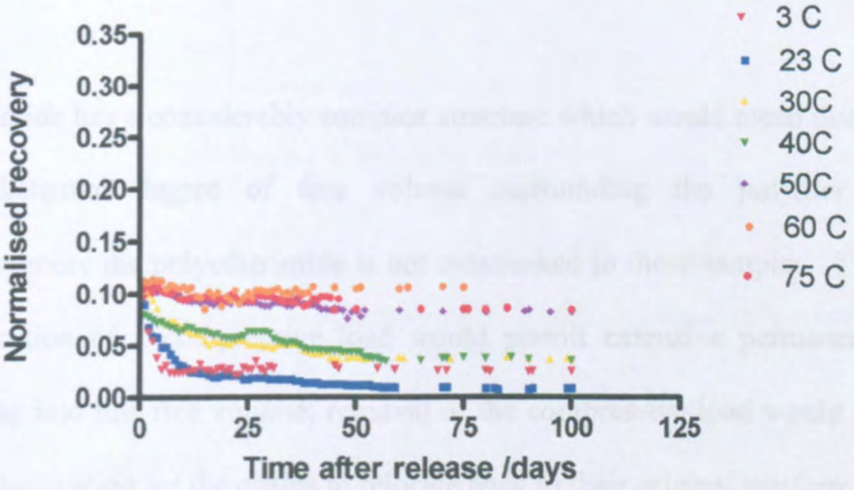


Figure 8.80: Polyethylene foam compressed by 10% at various temperatures for one month

The recovery of polysulphone foam at ambient temperature is illustrated in figure 8.81-8.83, and is compared with that of 75°C. A reduction in the recovery of the higher temperature sample is observed which appears to be more significant in comparison to the ambient temperature sample at higher compressive strains.

Polyimide foams in general show the worst recovery out of all four polymer foams which is somewhat poor at the test temperatures. (Fig: 8.84-8.86) When compared with other polymers, phase one has been affected at elevated temperature, whilst polyimide foam displays little recovery even at ambient test temperature. Phase 2 appears to be unaffected by an increase in temperature from ambient to 75°C.

Polyimide has a considerably complex structure which would mean that there is a substantial degree of free volume surrounding the polymer chains. Furthermore the polyetherimide is not crosslinked in these samples. Therefore application of a compressive load would permit extensive permanent chain folding into this free volume; removal of the compressive load would result in little inclination for the chains to relocate back to their original conformations.

This is consistent with one of the major applications for polyetherimide foams which is to absorb mechanical energy on collisions, i.e. to crush easily.

Fig 8.81: Polysulphone foam compressed by 35% at ambient temperature and at 75 °C for one month

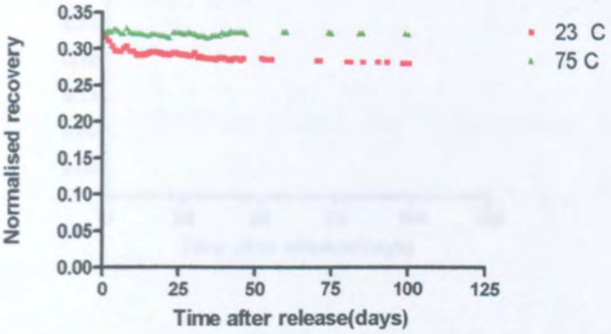


Fig 8.82: Polysulphone foam compressed by 10% at ambient temperature and at 75 °C for one month

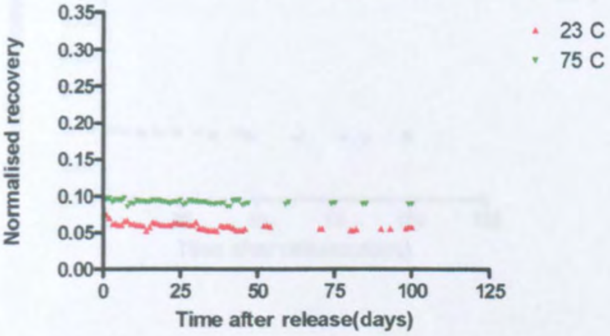


Fig 8.83: Polysulphone foam compressed by 5% at ambient temperature and at 75 °C for one month

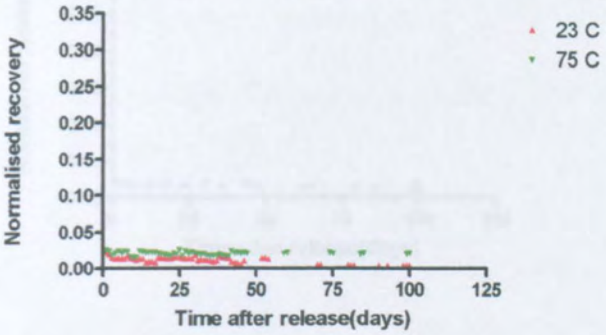


Fig 8.84: Polyetherimide foam compressed by 35% at ambient temperature and at 75°C for one month

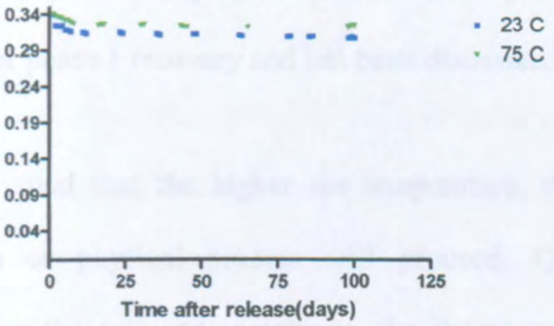


Fig 8.85: Polyetherimide foam compressed by 10% at ambient temperature and at 75°C for one month

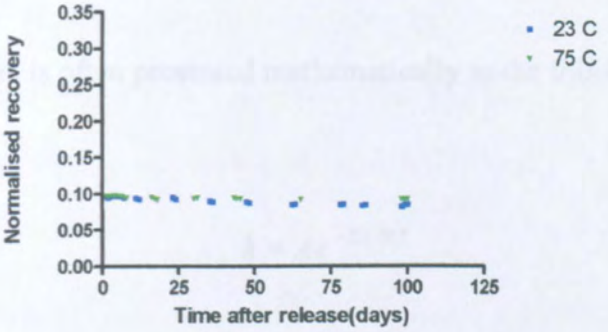
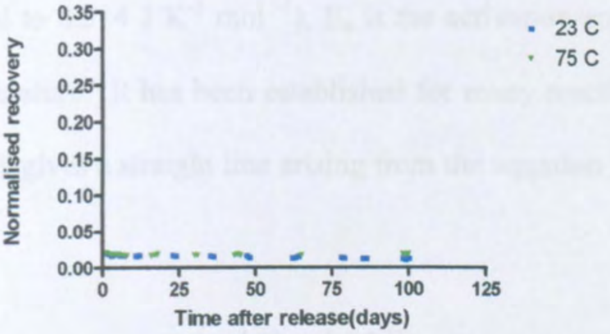


Fig 8.86: Polyetherimide foam compressed by 2.50% at ambient temperature and at 75°C for one month



Phase 1 recovery is linked to the polymer structure, and a decline in recovery of each particular foam is affected by an increase in test temperature which results in poor response for phase 1 recovery and has been discussed previously.

It has often been cited that the higher the temperature, the faster a given chemical reaction or physical process will proceed. Quantitatively this relationship between the rate and sometimes, the extent to which a reaction proceeds and its temperature is often determined by the Arrhenius Equation.

The relationship is often presented mathematically in the following manner:

$$k = Ae^{-Ea/RT}$$

Where k is the rate constant, A is the pre-exponential factor, R is the gas constant (equal to 8.314 J $K^{-1}$ mol $^{-1}$), $E_a$ is the activation energy and T is the absolute temperature. It has been established for many reactions that a plot of ln k against 1/T gives a straight line arising from the equation in the form:

$$ln\, k = ln\, A\, \frac{E_a}{RT}$$

Parameter A can be determined from the intercept of the line at 1/T=0 whilst the slope is equivalent to – $E_a/R$. Using an Arrhenius graph, the relationship between temperature and lifetimes can be identified by plotting the median lives. Since the resulting relationship has a large (negative) slope, small changes in temperature can be expected to produce large changes in median lives. Although the Arrhenius equation strictly applies to chemical kinetics, the progress of many other processes often follows an Arrhenius law.

The influence of temperature on a specific reaction rate is that for many processes, at ordinary temperatures, the rate increases by 10 to 15% for each one kelvin rise in temperature. The increasing reaction velocity comes from the increasing frequency of collisions of the reacting species.

At higher temperatures, the probability that two molecules will collide is higher. This higher collision rate results from a higher kinetic energy, which offers more opportunity to reach the activation energy of a particular reaction. The activation energy is the amount of energy required to ensure that a reaction process can happen.

With results from just two temperatures, the activation energy can be determined by direct substitution. For more temperatures, the activation energy is better determined by graphical plotting. As with lognormal plotting, activation energy plotting can be more precisely done mathematically.

This analysis has been applied to all data obtained from one month compression period test for all four polymer foam types at a series of elevated temperatures with the assumption that the total recovery can be correlated with "rate constant".[80] Calculated values are shown in tables 8.1-8.5 and are presented graphically in figures 8.87-8.91. Arrhenius data has been used to determine activation energy (Ea), at each compressive stress, for all the polymers tested.

It can be seen in tables 8.2-8.6 the values of the activation energy for polyethylene are high when compared with polyurethane, polyimide and polysulphone. It is interesting to note that polyethylene has the simplest structure out of all four polymers but still displays a relatively larger activation energy. Activation energy depends on the free volume in a sample. More free volume is related to a lower activation barrier.

*Table8.2: Arrhenius data for Polyethylene foam (HD80)*

| Temperature /C | 1/T (K) | Ln 35% | Ln 20% | Ln 15% | Ln 10% |
|---|---|---|---|---|---|
| 3 | 0.0036 | -2.475 | -2.96 | -3.243 | -3.637 |
| 23 | 0.0034 | -2.015 | -2.586 | -2.926 | -3.503 |
| 30 | 0.0033 | -1.853 | -2.451 | -2.654 | -3.221 |
| 40 | 0.0032 | -1.546 | -2.28 | -2.54 | -3.1 |
| 50 | 0.0031 | -1.361 | -1.942 | -2.257 | -2.49 |
| 60 | 0.0030 | -1.207 | -1.777 | -1.923 | -2.29 |
| 75 | 0.0029 | -1.033 | -1.663 | -1.875 | -2.489 |
| Slope/K | | -2007 | -1856 | -1992 | -2231 |
| **$E_a$ ( J mol $^{-1}$)** | | **16686** | **15431** | **16561** | **18549** |
| $\tilde{\nu}$ ( cm $^{-1}$) | | 1394 | 1289 | 1384 | 1550 |

*Table8.3: Arrhenius data for Polyethylene foam (HD115)*

| Temperature /C | 1/T (K) | Ln 35% | Ln 20% | Ln 15% | Ln 10% |
|---|---|---|---|---|---|
| 3 | 0.0036 | -2.262 | -3.189 | -3.607 | -4.144 |
| 23 | 0.0034 | -1.952 | -2.773 | -3.38 | -3.76 |
| 30 | 0.0033 | -1.814 | -2.596 | -3.095 | -3.231 |
| 40 | 0.0032 | -1.6045 | -2.2 | -2.776 | -2.882 |
| 50 | 0.0031 | -1.484 | -2.066 | -2.444 | |
| 60 | 0.0030 | -1.336 | -1.757 | -2.1733 | -2.586 |
| 75 | 0.0029 | -1.238 | -1.679 | -2.056 | -2.419 |
| Slope | | -1441 | -2169 | -2336 | -2453 |
| **$E_a$ ( J mol $^{-1}$)** | | **11980** | **18036** | **19425** | **20394** |
| $\tilde{\nu}$ (cm$^{-1}$) | | 1001 | 1507 | 1623 | 1704 |

*Table8.4: Arrhenius data for Polyurethane foam*

| Temperature /C | 1/T (K) | Ln 35% | Ln 20% | Ln 15% | Ln 10% |
|---|---|---|---|---|---|
| 23 | 0.0034 | -1.589 | -2.2 | -2.667 | -3.071 |
| 30 | 0.0033 | -1.529 | -2.151 | -2.619 | -3.108 |
| 40 | 0.0032 | -1.499 | -2.152 | -2.599 | -3.097 |
| 50 | 0.0031 | -1.396 | -2.115 | -2.585 | -3.026 |
| 60 | 0.0030 | -1.372 | -2 | -2.337 | -2.936 |
| 75 | 0.0029 | -1.238 | -1.847 | -2.237 | -2.581 |
| Slope/K | | -666.66 | -678.23 | -864.45 | -896.62 |
| **$E_a$ ( J mol $^{-1}$)** | | **5543** | **5639** | **7187** | **7454** |
| $\tilde{\nu}$ (cm$^{-1}$) | | 463 | 471 | 600 | 623 |

*Table8.5 Arrhenius data for Polysulphone foam*

| Temperature /C | 1/T (K) | Ln 35% | Ln 20% | Ln 15% | Ln 10% |
|---|---|---|---|---|---|
| 23 | 0.0034 | -1.261 | -2.017 | -2.457 | -4.596 |
| 75 | 0.0029 | -1.13 | -1.674 | -2.059 | -2.4015 |
| Slope/K | | -250 | -679.46 | -709.17 | -4351.6 |
| **$E_a$ ( J mol $^{-1}$)** | | **2079** | **5649** | **5896** | **36179** |
| $\tilde{\nu}$ (cm$^{-1}$) | | 174 | 472 | 493 | 3022 |

*Table8.6 Arrhenius data for Polyetherimide foam*

| Temperature /C | 1/T (Kelvin) | Ln 35% | Ln 20% | Ln 15% | Ln 10% |
|---|---|---|---|---|---|
| 23 | 0.0034 | -1.125 | -1.88 | -2.1103 | -2.501 |
| 75 | 0.0029 | -1.067 | -1.646 | -2.031 | -2.377 |
| Slope/K | | -115.71 | -463.91 | -157.2 | -252.44 |
| **$E_a$ ( J mol $^{-1}$)** | | **962** | **3857** | **1307** | **2099** |
| $\tilde{\nu}$ (cm$^{-1}$) | | 80 | 322 | 109 | 175 |

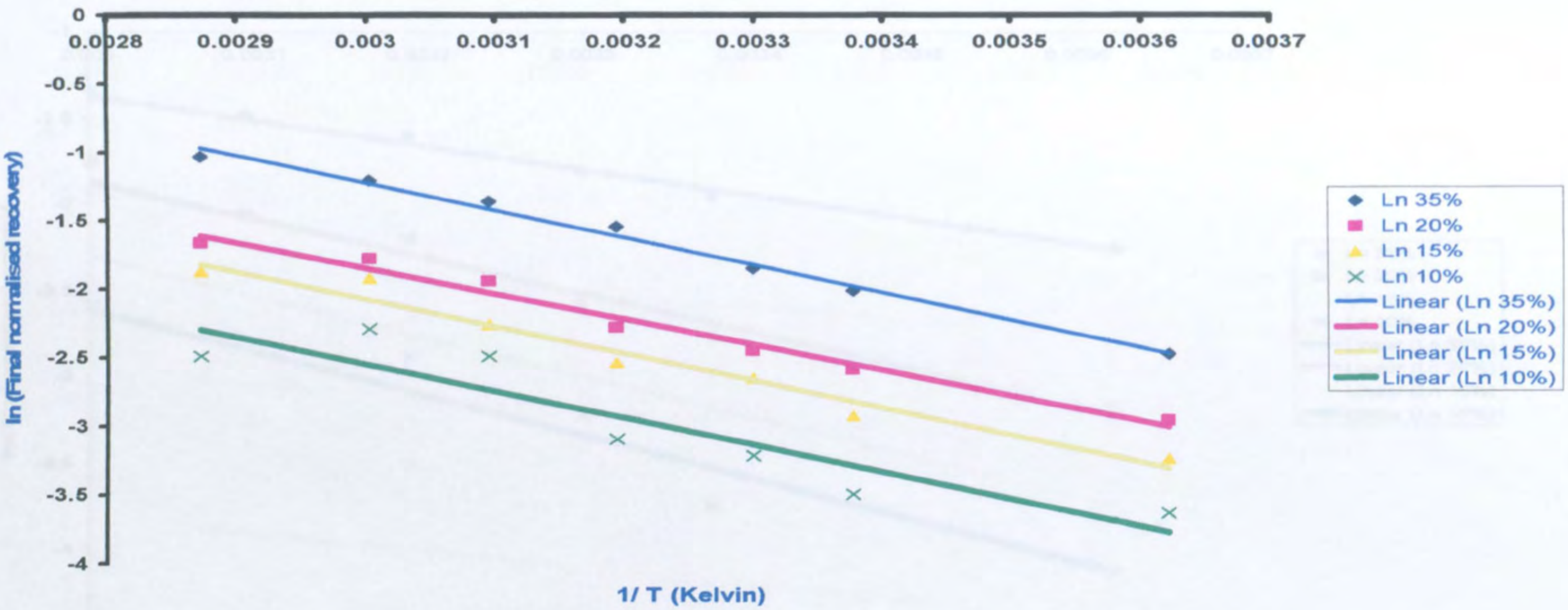


*Figure 8.87: Arrhenius plot of the data for Polyethylene foam HD 80*

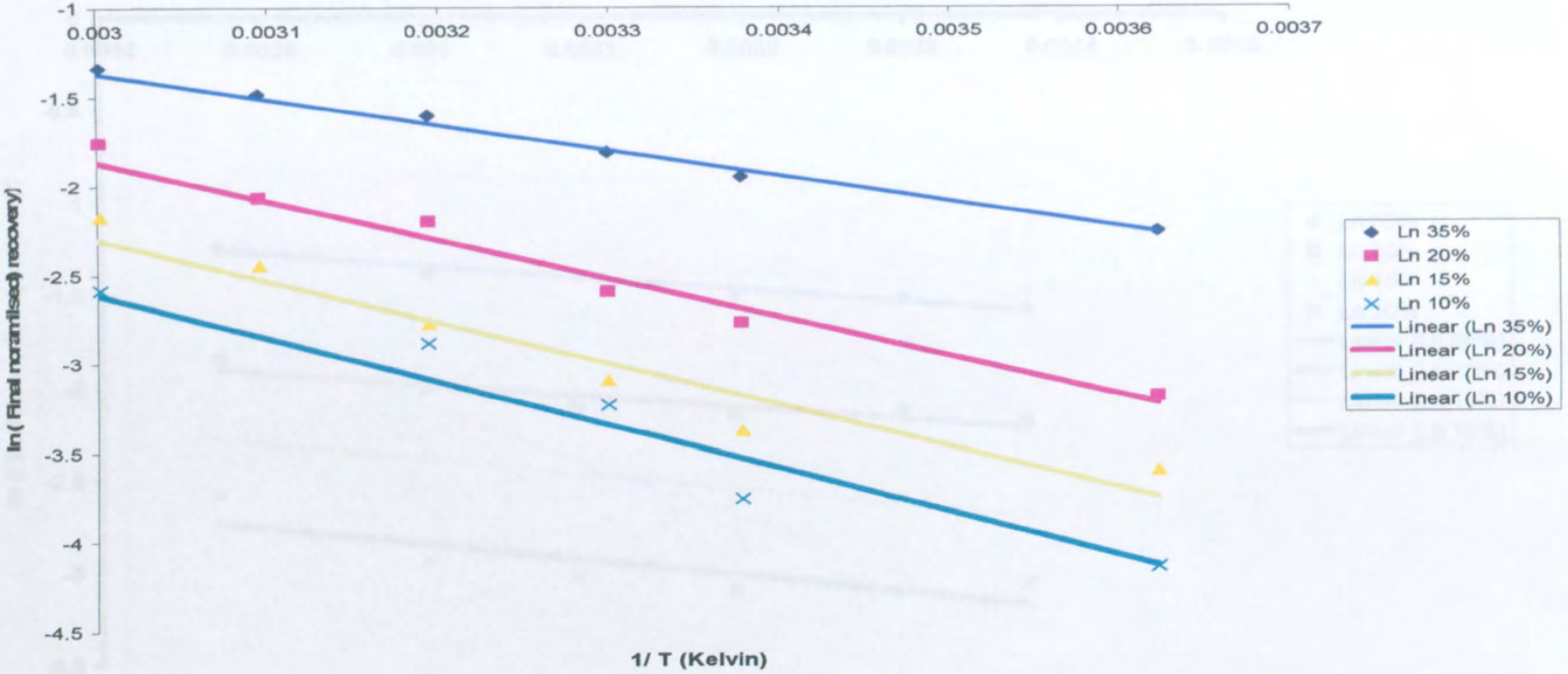


*Figure 8.88: Arrhenius plot of the data for Polyethylene foam HD 115*

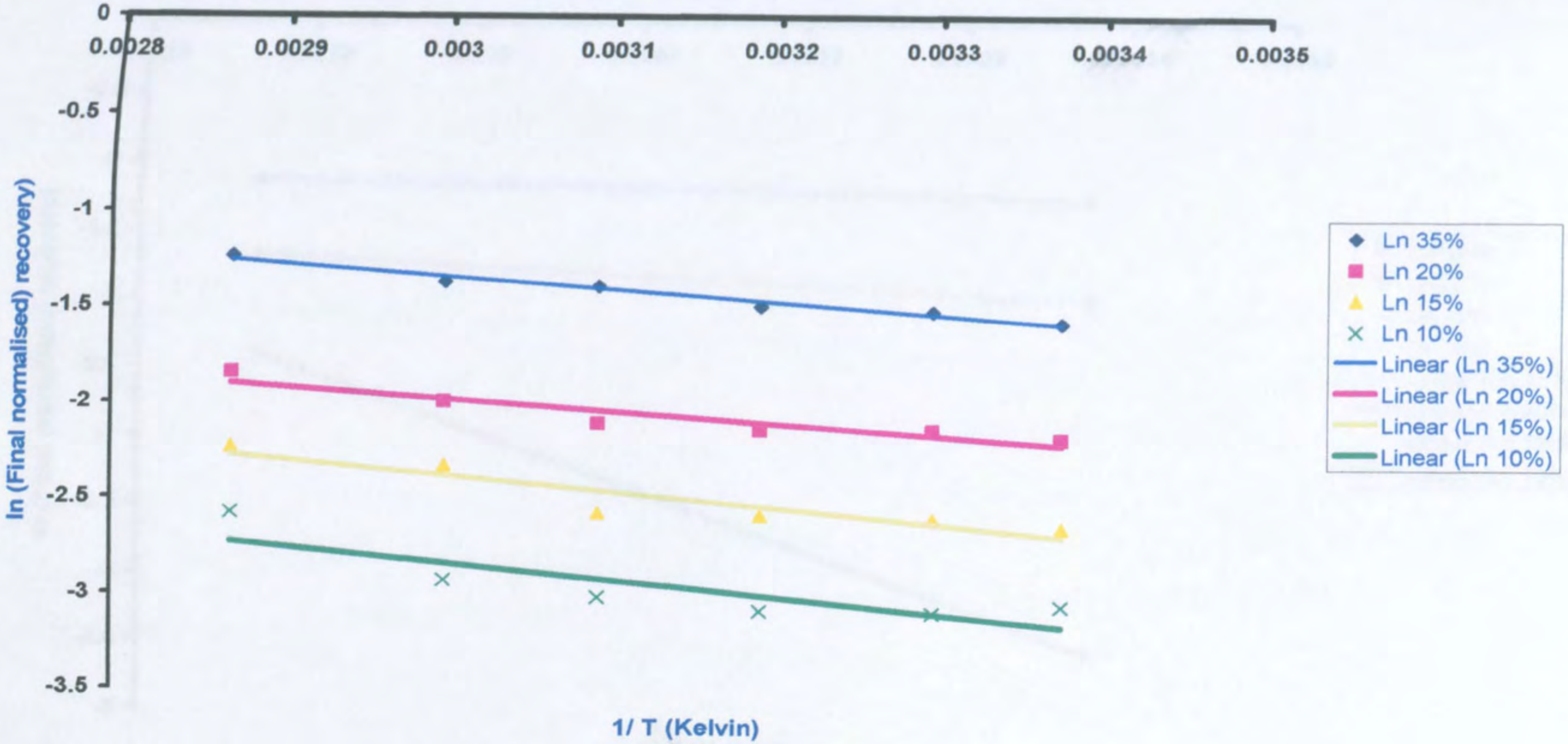


*Figure 8.89: Arrhenius plot of the data for Polyurethane foam*

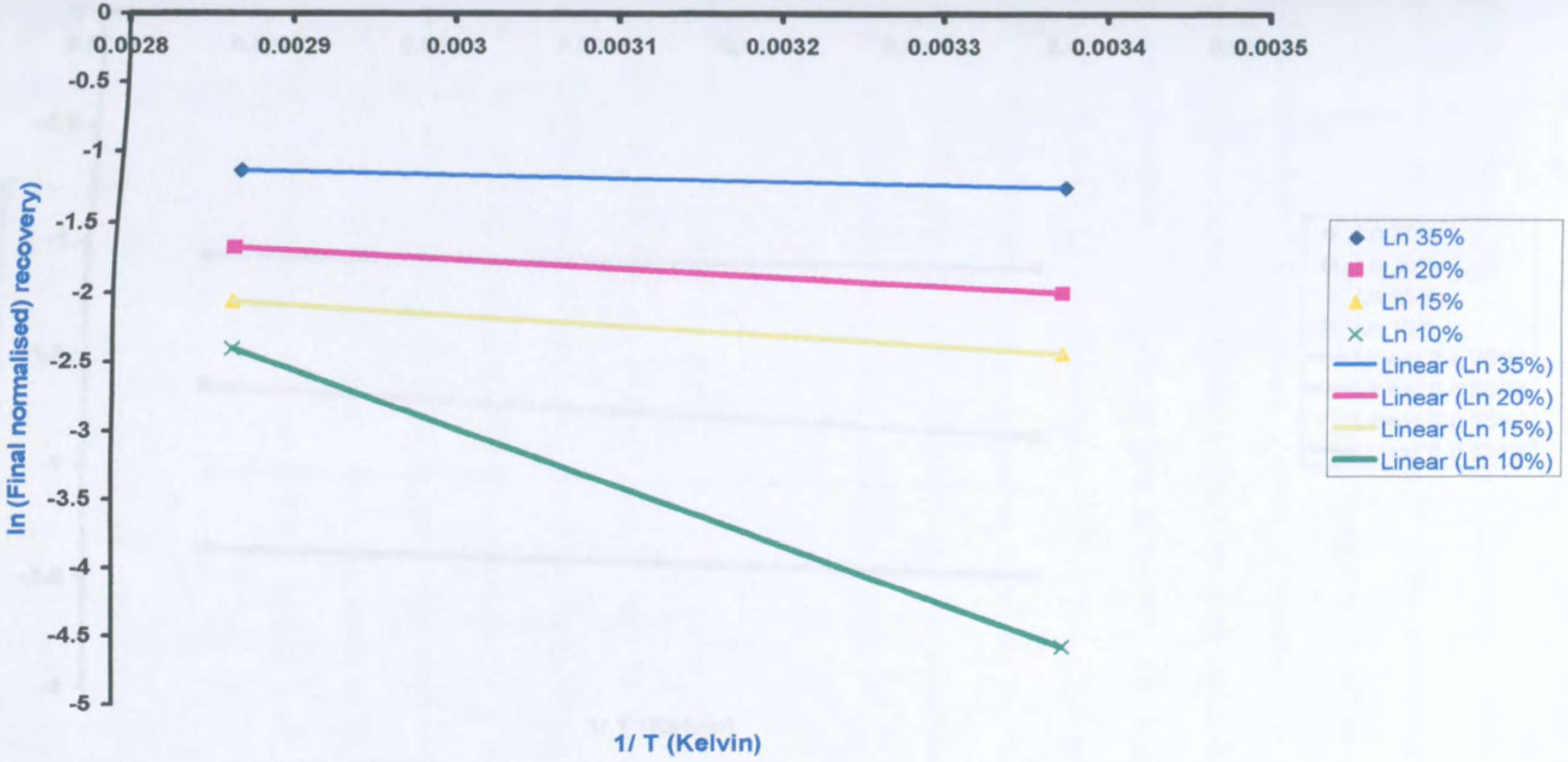


*Figure 8.90: Arrhenius plot of the data for Polysulphone foam*

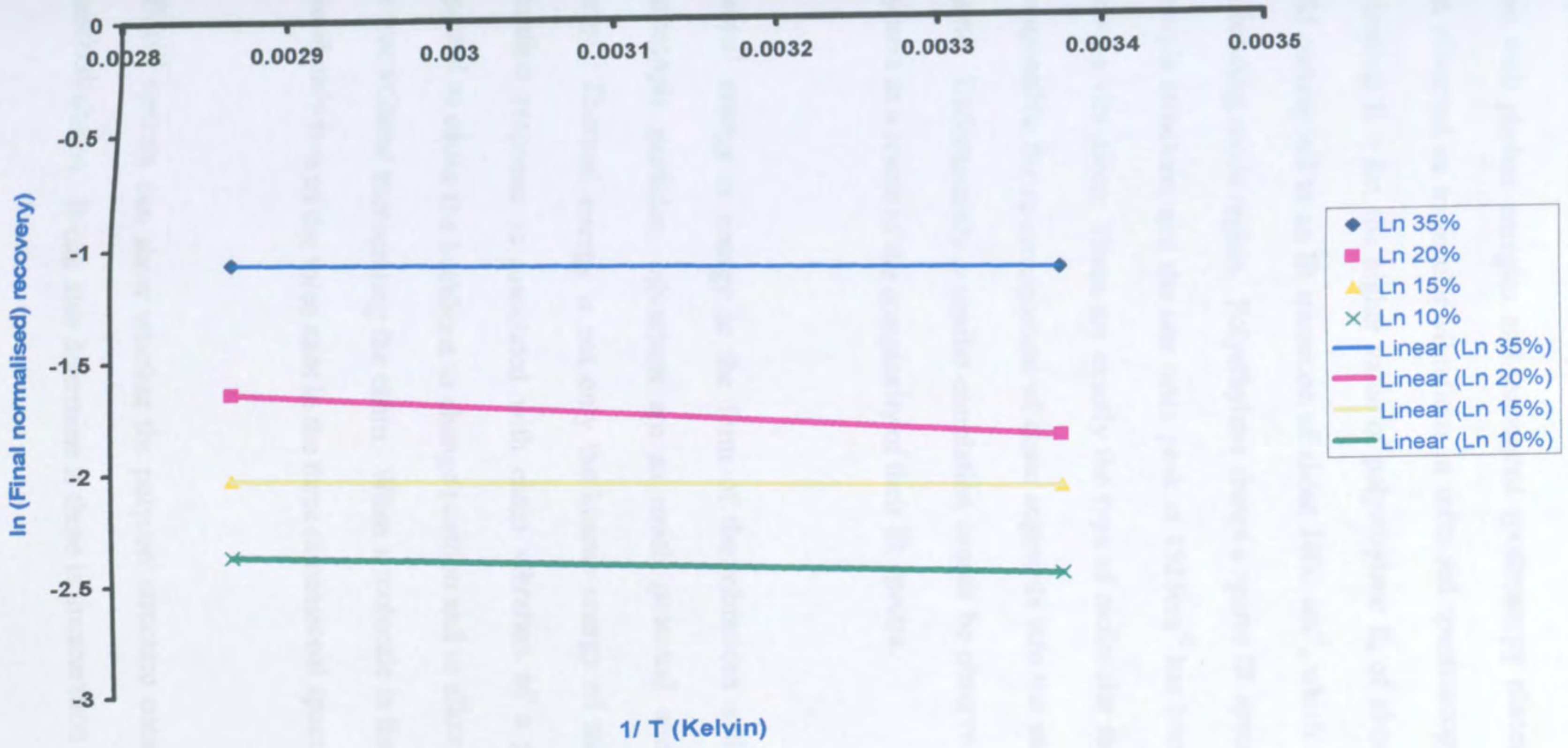


*Figure 8.91: Arrhenius plot of the data for Polyetherimide foam*

The activation energy values calculated are not high enough to be associated with the breaking of covalent bonds in the polymer, which has been suggested as a possible mechanism for compression set. Instead, comparison of these $E_a$ values with photon energies and associated spectroscopy places them in the range observed as molecular vibrations in infra red spectroscopy. Using the relationship E = hv, the higher value of polyethylene $E_a$ of about 17 kJ $mol^{-1}$ would correspond to an IR transition of about 1400 $cm^{-1}$, which is close to the C-H bending mode region. Polyethylene shows a sparse IR spectrum owing to its simple structure, and the one main peak at 1525$cm^{-1}$ has been attributed to backbone vibrations. These are exactly the type of molecular motion likely to be responsible for re-arrangement of chain segments into the surrounding free volume. Unfortunately a similar correlation cannot be observed for the other polymers as a result of the complexity of their IR spectra.

Thermal energy is energy in the form of the vibrations and movement of microscopic particles; vibrations are as much potential energy as kinetic energy. Thermal energy is not only the kinetic energy of moving particles. Vibration response is associated with chain vibration of a polymer. It is expected to cause the backbone to change position and to allow it to move into the free volume surrounding the chain. When a molecule is linear it can rotate around only two of the three axes in the three dimensional space.

Infrared spectra can show whether the polymer structure consists of linear or branched chains. It can also determine if there is unsaturation or aromatic ring in the structure. Finally it is possible to work out whether specific functional groups are present.

If we look at the polyethylene spectra: (Table 8.7)

The corresponding peaks are:

| Bond | Mode | Range | Observed |
|---|---|---|---|
| C-H | Stretching | 3000-2800cm$^{-1}$ | 2900cm$^{-1}$ |
| C-H | Bending | 1500-1300cm$^{-1}$ | 1525cm-1 |
| C-C |  | 1200-800cm$^{-1}$ | 700cm$^{-1}$ |

*Table 8.7: Infrared data*

As your can see from the spectra, the linkages present in polyethylene are C-H which are viewed as a functional groups, giving rise to the common group frequencies and the C-C linkages as the backbone producing the skeletal vibrations.

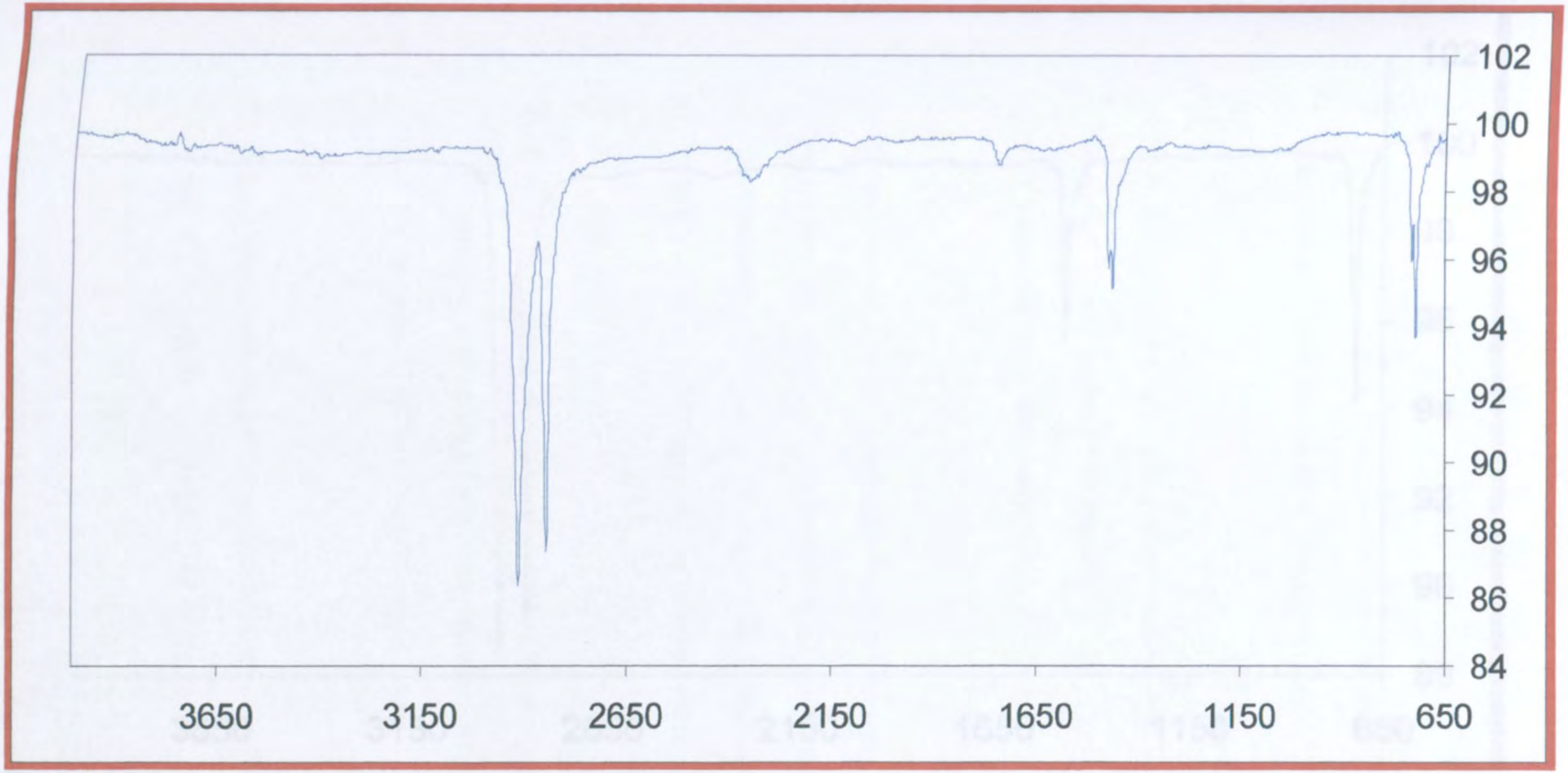


*Figure 8.92: FTIR spectrum of polyethylene (HD80) sample*

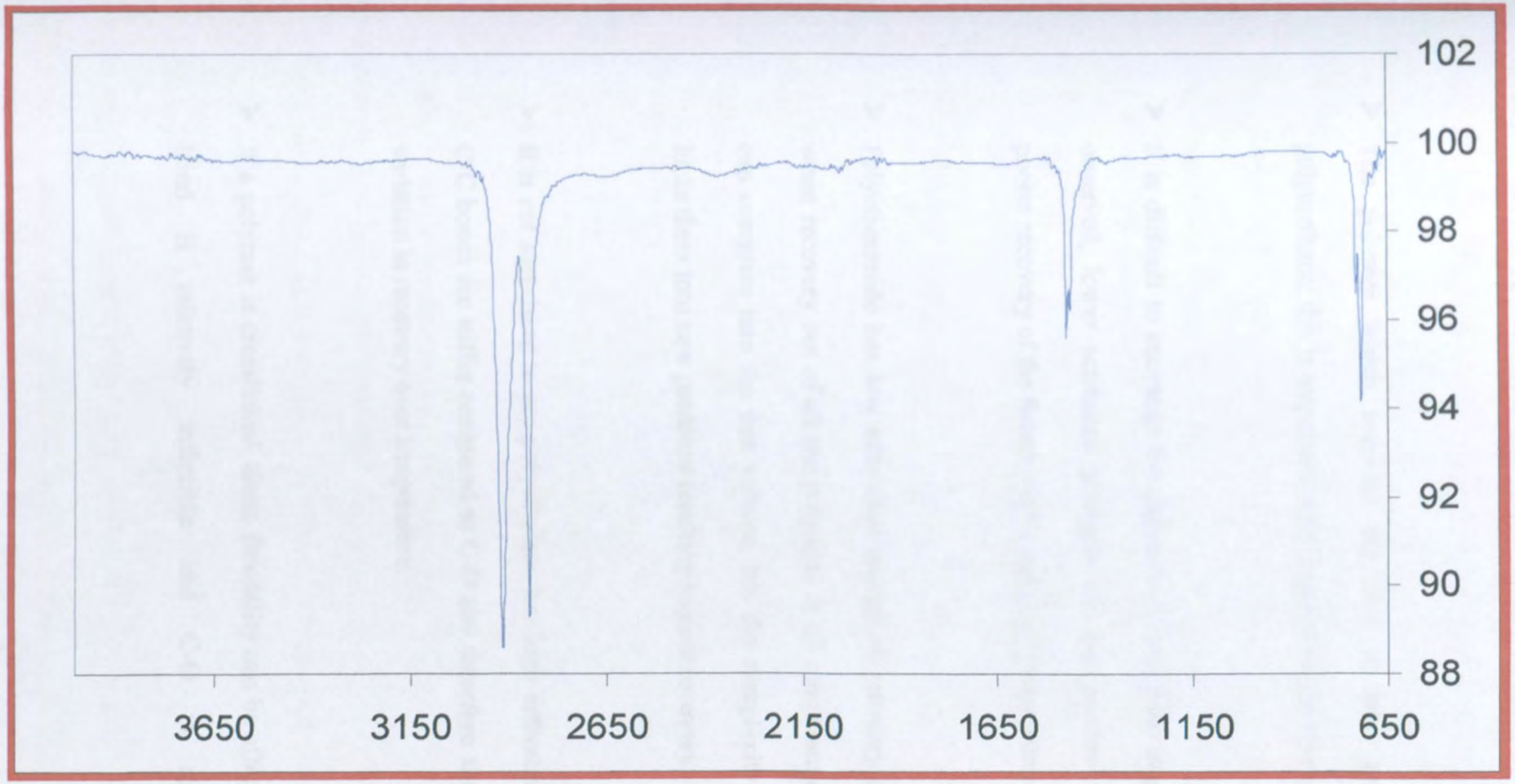


Figure 8.93: FTIR spectrum of polyethylene (HD115%) sample

To review the main points:

- The polymer which recovers the best at high temperatures is polyurethane; this is associated with high activation energy.

- It is difficult to rearrange the polymer chains. Also in general, as we observed, lower activation energies for this process correlate with poorer recovery of the foams over a range of temperatures.

- Polyetherimide has low activation energy of recovery and shows the worst recovery out of all the polymers at all temperatures. Polyimide can compress into the free volume, but the complexity of the chains locks them into new positions resulting in poor recovery.

- It is not surprising to see polyethylene has high activation energy. The C-C bonds are stiffer compared to C-O and therefore show the biggest variation in recovery over temperature.

- If a polymer is crosslinked, chain flexibility can be affected. The C-C bond is relatively inflexible and C-O is more flexible.

# 9.0 Conclusion

This thesis continues the investigation started and reported by Sina Talal, [21] whilst extending it to encompass polyetherimide and polysulphone rigid foams. Polyethylene, polyurethane, polyetherimide and polysulphone rigid foams have been compressed in constant strain jigs for varying periods and at a range of temperatures and compressive strains. In choosing the range of compression conditions, we drew on the general conclusions of the preceding thesis. Following the period of compression the samples were released and their thickness recovery in the direction of compression was monitored over periods of several weeks to months.

The assertion in the previous work that recovery occurs in two phases was demonstrated to apply generally to all the foams investigated. This recovery follows a model type

$$R_n \text{ (recovery} = Ae^{-k_1 t} + Be^{-k_2 t} + C$$

Where $k_1$ and $k_2$ are the rate constants associated with two phases and C is the final residual deformation remaining after recovery. $k_1$ and $k_2$ commonly differ by a factor of one to two orders of magnitude. Their exact values are difficult to obtain accurately and reproducibly and could not be correlated with other experimental parameters. The value of C is remarkably reproducible and correlates well with a variety of compression parameters. It is the most valuable result parameter from each individual study.

Further evidence has been obtained to link phase 1 of the recovery from compression with the nature of the solid polymer of which the foam is composed, and phase 2 with the recovery of the cellular structure within the foam, although the latter is difficult to manipulate experimentally, relying as it does on the structure of the available commercial materials.

There has been extensive study of the effect of confinement temperature during compression on the recovery at ambient temperature. The different polymers show very different responses to the change of temperature. All polymers investigated at different at different compressive strains demonstrated reproducible Arrhenius plot slopes under the different conditions, and hence a reasonably reproducible set of values of recovery process. These analyses were based on the final total recovery of the thickness as the most reliable experimental parameter of recovery.

In the case of polyethylene, we have identified a vibrational motion consistent with both the activation energy value and a plausible mechanism of the molecular arrangement. In the case of the other polymers investigated, we can account for the different values of $E_a$ and correlate them to observed mechanical behaviour.

The results of this study are not consistent with a hypothetical deformation mechanism requiring covalent bond scission.

We have tried to account for consistent deviations of thickness which appear to occur in all samples due to changes in ambient conditions during recovery. These deviations do not appear to correlate with ambient temperature and experiments designed to investigate the recovery process in different ambient humidities showed no difference at all in the recovery of identical samples. Hence we conclude by default that small changes in atmospheric pressure, however unlikely, may cause the easily measurable deviations in sample thickness during recovery.

This is a limiting factor in the accuracy of recovery measurement, particularly during the second recovery phase. By comparison, the limiting factor during phase 1 recovery is the rapid change in dimensions that may be occurring during the measurement process.

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# 11.0 Appendix

## Mechanical Data