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DEVELOPMENT OF HDPE FUEL TANKS

BY

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SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS

FOR THE AWARD OF DOCTOR OF PHILOSOPHY

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ABSTRACT

Plastics fuel tanks have been used successfully abroad; metal counterparts are still predominant in this country; plastics tanks have to satisfy stringent performance regulations: low temperature impact tests; permeability; and fire resistance.

Blow moulded high density polyethylene (HDPE) fuel tanks have superior strength to mass ratio compared with metal equivalents (the density of steel is about 8000 kg/m$^3$ compared with HDPE, which has a density of under 1000 kg/m$^3$). HDPE will tend to drip in a fire situation, thus reducing explosion risk. HDPE is the chosen material because it possesses inherent properties suitable for the blow moulding process: it has a high viscosity at low stresses; and is highly inert.

Rotational moulded HDPE fuel tanks can also be considered. However, these are shown to have inferior properties when compared with blow moulded tanks; attraction of rotational moulding is the cheapness of equipment.

Petrol immersion was found to enhance impact properties of HDPE, although yield stresses were lowered slightly.

The thickness distributions of blow moulded fuel tanks were found to vary; this is because of the present difficulty of predicting parison behaviour with respect to time. Thickness is important because of impact strength and permeation considerations.
Impact properties of fuel tanks were assessed; peak force of impact was found to be heavily dependent on thickness (raised to the power 1.1) and temperature of mould in the blow moulding process (a low mould temperature led to inferior properties). Pinch-offs were found to be particularly detrimental to impact properties.

Cooling behaviour was investigated. With the aid of a cooling model for blow mouldings, it was found that a warm mould (40°C) could be used with internal air circulation to obtain a cooling time the same as that with a cold mould and no air circulation. Thus optimising mechanical strength and maintaining economic viability.

Welding of injection moulded fittings to the main blow moulded body of the fuel tank was found to be faulty, in all of the tanks examined; many weld failures have been reported in use. This work determines optimum welding conditions for HDPE grades, these are Rigidex H060-45P and Lupolen 4261-A.
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CHAPTER 1

1. Objectives

To understand the effects of materials, and processing variables on the properties and performance of fuel tanks for road vehicles and other equipment. Willamot Industries have collaborated in this programme and have supplied tanks:

International Harvester; right and left handed tanks (with some service failures);
Ford Sierra (development tanks by Willamot);
Ford Triton (production tanks from Belgium);
Peugeot Talbot (production tanks).

These tanks have been made by blow moulding and have been considered with respect to

(a) design;
(b) manufacturing process, including welding of sub-components;
(c) relevant properties, especially those covered by specifications; and
(d) performance of the tank.

The capacity for fuel tanks is about 50 litres and their median mass is around 6 kg.

It is sometimes suggested that rotational moulding offers a viable shaping process alternative to blow moulding for
large containers; an investigation of this proposition, in respect of fuel tanks, is made.

Since the use of plastics fuel tanks is not common with UK manufacturers, investigation of the failure in service of other containers in HDPE is made. Further, a number of programmes dedicated to examination of particular features of the overall problem, have been established making liberal use of model systems.
CHAPTER 2

2. Literature Review

2.1. Different Processes for Manufacturing Tanks

Apart from blow moulding, a number of other processes are feasible for making plastics fuel tanks: thermoforming; injection moulding of two halves, followed by joining; glass reinforced plastics processing; and rotational moulding.

A brief examination, at least, is necessary to ascertain the viability of each process for the considered application.

2.1.1. Thermoforming

In thermoforming, two concepts of the 'shaping' step should be emphasised. First, the processing temperature is an important operational variable. The lowest practical forming temperature is that at which a cube with fairly sharp corners can be drawn from the sheet without whitening or other visible damage. The highest practical forming temperatures is that which brings about no excessive sagging of the sheet in the clamp and does not degrade the polymer. Sagging is
the combined results of thermal expansion and gravitational (viscous) deformation. It is noteworthy that polymers commonly used in thermoforming (ABS, high impact polystyrene) exhibit high 'yield' values in thermoelastic stress-strain relationships, which help avoid sagging. The actual thermoforming temperature selected, within the operating range, involves a number of considerations. Low temperatures are advantageous in reducing both the heating and cooling segment of the cycle. Furthermore, a higher degree of the imposed biaxial orientation will increase the impact resistance of the thermoform. Higher temperatures are advantageous because high extensions and exact mould reproduction are achieved.

The sheets for thermoforming are generally extruded. Die forming imparts to the sheets considerable molecular orientation. Schmidt and Carley,¹ for example, have observed a 31% shrinkage of 1.52 mm thick, high impact PS sheets in the extrusion direction. The heating step brings about annealing of some of this strain history. High forming temperatures ease this annealing process.

The other aspect of the melting step is the sheet temperature distribution. One common requirement is stringent temperature uniformity throughout the sheet. Local
temperature variations may cause undesirable local thickness variations. But even if the sheet is thermally balanced, the common vacuum forming method induces thickness variations. The deforming sheet comes into contact with the cold mould at different times. Hence the parts of the mould that are formed last (e.g. sharp corners) are the thinnest. This non-uniformity, inherent in the straight vacuum forming, is superimposed on the non-uniformity caused by the deformation process itself. There are a number of ways of reducing thickness non-uniformity. One means involves 'pattern heating' or 'programmable zone heating' techniques. By this method, a preset temperature distribution, \( T(x,y) \) (where \( x-y \) is the sheet plane) is imparted to the sheet, such that the temperatures in the regions of high deformation (thin sections) are lower.

Fuel tanks must have thicknesses of about 5 mm to combat permeation and strength problems. Thermoforming is not used in the manufacture of fuel tanks because it is difficult to control these sort of thicknesses in this process.

2.1.2. Injection Moulding of Polymers

Injection moulding of half fuel tanks is possible; these are further joined, for
example, by welding. This was, in fact, carried out in polypropylene coolant reservoir tanks in the automobile industry. Knowledge of the injection moulding process is also important because fittings to the tanks are usually manufactured by this method; frequently, failures are reported because of bad moulding conditions, e.g. low mould temperatures and fast cycle times may lead to an unwanted skin on the component.

Injection moulding involves five distinct phases: melt generation and mixing; pressurisation (flow processes that are carried out in the injection unit of the moulding machine); product shaping; and cooling (processes that take place in the mould cavity). Most injection moulding machines are the in-line, reciprocating screw type. The theoretical analysis of the injection unit involves all the facets of the steady continuous plasticating screw extrusion, with the added complication of transient operation owing to the periodic screw rotation, on which axial motion is superimposed. In the injection unit, the melting step is the dominant one regarding the design and operation. Experimental work on melting in injection units has revealed a melting mechanism similar to that in plasticating screw extrusion, which was then used to formulate a mathematical model for
the melting process. The product of the injection unit is the polymer melt accumulating in the front of the screw. Melt homogeneity affects the filling process and final product quality.

To secure the injection of the polymer melt into the mould, the melt must be pressurised. This is achieved by the forward thrust of the screw, which acts as a ram. Hence we have static mechanical pressurisation, and the resulting flow is a positive displacement type.

A typical injection mould is made of at least two parts, one of which is movable so that it can open and close during different parts of the moulding cycle. The entire mould is kept constantly at below the glass transition or the crystallisation temperatures, for amorphous or crystallising polymers respectively. The melt exits the nozzle of the injection unit and flows through the mould sprue, runner system and gate and into the mould cavity. All of these structural elements of the mould perform well defined functions and affect the moulding operation. Thus, the sprue forms the overall entrance into the mould. It should not generate large resistance to flow, yet at the same time, the melt in it should quickly solidify upon completion of injection and should be
extracted from it without difficulty. 
Finally, the sprue should form a streamlined transition between the nozzle and runner system. All these functions are attainable by a short, diverging conical shape.

The function of the runner system is to transfer the hot melt to the cavities. This should be done with the minimum of material waste and pressure drop. Therefore, the runner conduit length must be kept to a minimum level, and the cross section should be optimally set for a low pressure drop, low material waste, and relatively slow cooling, avoiding premature solidification and short shots. Generally, the runner is about 1.5 times the characteristic thickness of the moulded part, and it is of circular cross section to minimise heat loss as well as to facilitate easy machining. Polymer saving and faster cycles can occasionally be achieved by hot runner systems where the polymer in the runners is prevented from solidification through heating units built around them in the mould. Alternatively, in particular with large parts, it is sufficient to insulate the runner system from the mould. In both cases, the sprue can, in effect, be eliminated from the design.

The gate controls the flow of polymer melt into the die. Size, shape and position of
gate are affected by a number of considerations. First, a narrow gate is desirable from the standpoint of ease of separation of the moulded part from the runner system, as well as solidification after completion of the melt injection, to isolate the cavity from the rest of the system. Of course, early solidification must be prevented. Moreover, narrow gates may be detrimental to the finished product because they also bring about large shear rates and stresses (above the melt fracture region), and consequently temperature rises. When the stress level has to be reduced, divergent fan gates are used, spreading the flow. Generally speaking, the gate length is half the characteristic thickness of the section where the gate is attached (usually the heavy sections). It is so positioned that the emerging stream impinges on the opposite wall. In multiple cavity moulds, gates and runners also serve the functioning of balancing flow such that all cavities fill simultaneously. The polymer is cooled via the mould.

2.1.3. Glass Reinforced Plastics Processing

Glass reinforced plastics (GRP) possess certain inherent properties that are of interest in connection with fuel tanks:
(1) relatively high mechanical strength, combined with lightness;
(2) good resistance to a wide range of chemicals;
(3) ease of fabrication; and
(4) low mould cost.

Not many structural materials combine all the properties, and consequently, glass reinforced plastics can be considered as structural materials in their own right. The materials are used mainly for combinations of woven glass cloth, chopped strand mat, rovings with polyester and epoxide resins. Other resins, such as phenolics and silicones, have been used, but only to a limited extent.

Many applications in this field are concerned with manufacture of only a few articles. Wet lay-up processes are used or resin injection techniques where more articles are required.

Centrifugal moulding, although primarily applicable to pipes and tubes, has been extended to include cylindrical shaped vessels such as diesel fuel tanks. In this process, glass fibre mat of lengths of about 5 cm is fed into a rotating heated mandrel; the catalyst and resins are injected on to the glass mat and it is
alleged that this technique forces out all the air from the glass fibre and resin, resulting in a void free structure.

It is important to note that these materials are non-homogeneous and anisotropic, in contrast to many chemical engineering materials of construction, so that, from a design point of view, adequate safety factors must be provided.

The stresses in the wall of a vessel, caused by internal pressure, are represented by PD/4t for a sphere and PD/2t in the hoop direction, and PD/4t in the longitudinal direction, for a cylinder; where $P$ = internal pressure MN/m$^2$), $D$ = diameter (m), and $t$ is wall thickness (m).

For a sphere, the stress in the walls is the same in all directions, whereas for the cylinder, the stress in the hoop direction is twice that in the longitudinal direction. If the expected values and directions of stress, acting on a cylindrical container, are known, then the fibre orientation may be designed to allow for these. It is not always the case, however, that simple pressure loads only are operating as there are many requirements where additional external loads are applied such as bending, compression and longitudinal tension.

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Highly stressed reinforced plastics do not readily resist passage of fluids under pressure, and it is necessary to incorporate, in vessels of this type, a lining of impervious material. Metallic liners have been tried without success. One of the most useful lining materials is suitable synthetic rubber.

The main factor preventing the use of GRP fuel tanks is the difficulty of mass production.

2.1.4. Rotational Moulding

This is sometimes considered as a rival to blow moulding in the manufacture of plastics fuel tanks. Rotational moulded fuel tanks have been used in cars to date but the process is more commonly employed in the manufacture of articles where strength is not critical, e.g. water tanks.

Rotational moulding was, initially, a means of manufacturing articles from PVC resins. Later, polyolefin products were made by this means. Rotation moulding of polyolefins differs from other processes:

(a) it uses a resin powder instead of resin pellets;
(b) the powder is melted inside the mould, instead of being forced under pressure into
the mould;
(c) biaxial rotation of the mould is used;
(d) comparatively inexpensive moulds may be used, because of the simplicity (the system produces no pressure and there are no cooling channels in the mould).

Advantages of using rotational moulding include the following:

(a) moulds and tooling costs are low, especially for short runs;
(b) prototype moulds are inexpensive;
(c) secondary tooling is usually eliminated, as well as secondary operations;
(d) little waste or scrap;
(e) pieces, with undercuts and intricate contours, may easily be moulded;
(f) cross sectional deformation and warpage are at a minimum;
(g) relatively stress free items are produced, owing to a minimum of 'frozen in' stresses; and
(h) double wall construction feasible.

The resins for rotational moulding tend to have higher melt flow indices and lower molecular weights than those used in extrusion processes; this is to allow the molten material to move more freely in the rotating mould. Toughness, impact strength and resistance to low temperature brittleness are
decreased by an increase in the melt flow index. Low density resins, used in this process, produce articles of low stiffness and medium density resins are used where more stiffness is required.

Moulds are often simple and constructed from sheet steel, cast aluminium, or electroformed copper-nickel alloy.

Cope et al. 7 investigated rotational moulding of medium density polyethylene. Work was especially directed towards 'time to give a void free product' and also for 'onset of degradation'. The temperature range used was $220^\circ C - 440^\circ C$. Oven residence time could be decreased from 12 to 3 minutes at $220^\circ C$ and $440^\circ C$ respectively. This caused serious imbalance in cycle time, as oven residence time was significantly smaller than the cooling time. The critical factor in void dissipation was found to be the attainment of a temperature greater than $200^\circ C$. Mechanical properties were found independent of direction and moulding conditions. Morphology seemed to have little effect on mechanical properties.

Rotational moulded tanks are often, if not always, structurally weak. The microstructure exhibits clear evidence of voids, which have arisen because the process
is a low pressure one that does not mix the polymer very well. This structure leads to bad impact properties and high permeation, both of which would be undesirable in a fuel tank.
2.2. Blow Moulding

2.2.1. Blow Moulding - General

Blow moulding began during World War II. Until 1957, all blow moulding was in low density polyethylene (LDPE); squeeze bottle and fairly small containers were made. Since then, advances in machinery and introduction of HDPE have led to rapid development of the blow moulding industry \(8,9\).

Basically, blow moulding is used in the manufacture of hollow containers and consists of six well defined operations:

1) manufacture of homogeneous melt;

2) the production of the preform or parison;

3) the positioning of the mould in such a way as to surround and entrap the parison;

4) the operation of forming or calibrating the neck of the component if it is in the form of a container;

5) the introduction of air or other media to blow the parison to the shape of the mould cavity; and

6) the simultaneous cooling of the mould and
moulding.

In addition to these basic operations there are those that sever the parison from the parent body of the molten thermoplastic in the die, and eject the finished product from the mould. When it is considered that there are many ways of performing each of these operations, it will be appreciated that the number of permutations in the complete blow moulding process is considerable. Thus, because of the large number of possible permutations resulting from varieties of one or more of the process variables, the classification of equipment into clear cut types is virtually impossible.

Although injection moulding to produce the parison was the first to be used, an extrusion method of one form or another is now used by most blow moulding machine manufacturers (especially for large mouldings); there are basically two methods in use: firstly discontinuous extrusion; and secondly, continuous extrusion. The second method, with variations, is more widely adopted as it is applicable to the high-speed production of small to medium sized packs and containers in low density polyethylene, HDPE and polypropylene.

Continuous extrusion permits optimum
utilisation of extruder capacity and with suitable design of parison and mould transport mechanism, can provide very high speed production. Also the system can be used for unplasticised polyvinylchloride (uPVC), low and high density polyethylenes, and is suitable to the application of parison wall thickness control.

It is not necessary that an extruder should make parisons continuously. Two methods are available on present blow moulding machines: the accumulator system, which produces large diameter thick walled parisons for the blow moulding of components such as large jerry cans and drums; and reciprocating screw extrusion, which is really an extension of the system of intermittent extrusion; the extruder screw is stopped whilst the parison is blown, and a continuously rotating screw produce parisons at the required interval by the reciprocating action of the screw.

A large proportion of HDPE used in the UK goes into production of blow moulded containers. 10, 11

HDPE has inherent properties suited to blow moulding. It has a high viscosity at low stress, which means that parison sag is not as great as in other materials, also it is chemically inert to liquids. The material
has high heat stability. Blow moulded HDPE containers are tough, durable, rigid and have a high resistance to permeation.

The following four sections consider the important stages of blow moulding: mixing; formation of parison; parison blowing; and cooling.

2.2.2. Stage One, Mixing Mechanisms

Mixing is an important consideration in blow moulding: the material and temperature in the parison must be homogeneous; and pigment, and masterbatch must be well dispersed.

A mixture is a state formed by a complex of two or more ingredients that do not bear a fixed proportion to one another, and that, however comingled, are conceived as retaining a separate existence.

Mixing is an operation that is intended to reduce the non-uniformity of the mixture. This can be accomplished only by inducing physical motion of the ingredients. Two basic types of motion are involved in mixing. Brodkey\textsuperscript{13} calls these motions diffusions, and classifies them as molecular diffusion and bulk diffusion. Molecular diffusion is a process occurring spontaneously, and driven
by the concentration (chemical potential) gradient. It is dominant in gases and low viscosity liquids. In turbulent mixing, molecular diffusion is superimposed on the gross random eddy motion, which in turn, may occur within a larger scale of bulk diffusion or convective flow process.

In polymer processing, because of very high viscosities of polymer melts, eddy 'diffusion' is rarely reached and molecular diffusion almost insignificant, in that it occurs extremely slowly. Convection is the dominant mixing mechanism. It is the same for solid-solid, where convection is the only mixing mechanism, but only if one of the components is of low molecular weight (e.g. certain antioxidants, foaming agents, dyes used for fibres, slip additives), molecular diffusion may be significant.

Convection involves movement of fluid particles, blobs of fluid, or clumps of solid, from one spatial location in a system to another. Convection results in mixing, either if the interfacial area between the minor and the major component increases,\textsuperscript{14} or if the minor component is distributed throughout the major component without necessarily increasing interfacial area.\textsuperscript{15} The former criterion applies to liquid-liquid mixing, and the latter to solid-liquid and
solid-solid mixing.

Convection mixing can be achieved by a simple bulk re-arrangement of the material that involves a plug-type flow, and requires no continuous deformation of the material. Therefore, it can be termed bulk-convective mixing, or simply distributive mixing. Spencer and Wiley\textsuperscript{14} have referred to this kind of mixing as repetitive mixing, and McKelvey\textsuperscript{16} has used the term simple mixing.

This kind of mixing, through repeated rearrangement of the minor component, can, in principle, reduce non-uniformities to the molecular level. The repeated re-arrangements in distributive mixing can be either random or ordered. The former is the process that takes place, e.g. in V-blenders and many other solid-solid mixers, whereas the latter forms part of the mixing mechanisms in certain 'motionless mixers'.

Convective mixing can also be achieved by imposing deformation on a system through laminar flow. Hence we term this kind of convective mixing as laminar convective mixing.\textsuperscript{14} Others refer to it as streamline mixing, or simply laminar mixing.\textsuperscript{16} Liquid-liquid and liquid-solid mixing in processing are accomplished by laminar convective mixing through various types of
flow: shear, elongation (stretching), and squeezing (kneading). However, shear flows play the major role in processing.

We can generally state that if a liquid-liquid system is to be mixed by a laminar convective mechanism, permanent deformation of 'strain' in the context of laminar convective mixing does not include elastic or delayed elastic strains and certainly not rigid body rotation and translation. Furthermore, it should be obvious that for the interfacial surface to increase, both phases must undergo flow. Hence the viscosity ratio (as well as the viscoelasticity of the phases, which would bring about strain recover) plays a role in laminar mixing.

For all operations that do not involve materials that exhibit a yield point (and are miscible), the rate of application of stresses and strains plays no role and the decisive variable is the strain.\textsuperscript{17} In these cases, shear stresses are irrelevant as far as the degree of mixing is concerned (it is not irrelevant, of course, to power requirements). However, when a component is in operation that breaks only upon reaching a certain yield stress, the local stresses do not play a very decisive role in the mixing operation. Examples of such components are
carbon black agglomerates and viscoelastic polymer blobs. Moreover, with viscoelastic systems in particular, the rate of stress build up or local stress histories may be very important. This kind of mixing is referred to as dispersive mixing.

It is important to achieve homogeneity of temperature within the parison; hot spots could lead to uneven expansion upon blowing.

2.2.3. Stage Two, Formation of Parison

From both the product design and the economic point of view, the shape and the thickness of the parison throughout its entire length must be controllable.4,18,19

If the degree of inflation is independent of the position, the parison thickness must be uniform. It it varies, parison thickness should be increased where the degree of inflation is larger. Only under such conditions can acceptable product strength be obtained with minimum product weight. The parison diameter must also be controlled, not only because it contributes to product uniformity, but because of two additional reasons. First, its 'lay flat' width (π *D/2), should not exceed the mould diameter since this will interfere with mould closing. Second, if the blown product has a handle,
then at the axial height of the handle half of the 'lay flat' must be larger than the radial distance of the outer handle edge. This is because handle 'pinch off' occurs before any appreciable radial stretching of the parison.

From the discussion above it is concluded that because of the flow rate variation during parison formation and the presence of gravitational forces, the parison diameter and thickness are not easily controllable and are certainly not predictable from basic rheological measurements. Therefore practical solutions must be found and approximated analysis proposed.

The parison thickness, \( h_p(z) \), and radius, \( R_p(z) \), (see figure 2.1.), are related to each other and to the volumetric flow rate. For a parison die head extrusion angle \( \theta = 0 \), it is possible to estimate the parison thickness from extrudate swelling experiments with capillaries, at the same wall shear stresses. In this case, the following problems must be taken into consideration. First, the flow rate (thus shear stresses) varies with time, and second, only the leading portion of the parison is expected to achieve its full extrudate swelling value. Gravitational forces acting on the rest of the parison impose a constant tensile stress on it, which
Detailed cross-sectional representation of the die exit and the parison formed in the blow molding process.

Parison pleating, illustrating initially smooth parison becoming pleated with increased length.

Operating diagram for HDPE (A-60-70R). Arrows indicate regions of acceptable operation; heavy line is the allowable operating line for this combination of polymer, product, and machine conditions.
restricts swelling and thus causes axial deformation. Commercial HDPE used in blow moulding has a very high molecular weight to avoid sagging of the parison (i.e. to make the deformation more elastic).

When $\theta > 0$, the flow in the conical section of annular channel is not viscoelastic; thus capillary flow extrudate swelling results do not correlate with the observed $h_p(z)$. The parison radius $R_p(z)$ is an even more difficult quantity to predict, because it depends not only on the melt flow experience inside the die but also the forces acting on the parison, elastic strength, and probably elongational viscosity.

Cogswell et al. found that even with very large parisons, 70% of the 'sag' is elastic after 8 seconds. Furthermore, they offer a very approximate method of evaluating the cross sectional area and thickness reduction, and the accompanying reduction in parison length due to gravity. Finally, the problem of 'bounce', caused by the parison deceleration, is discussed in terms of the large inertial forces that are present, especially in large parisons. The problem of parison bounce is important in practice, because of the length of the parison at the moment of mould closing depends on it.
Schaul et al.\textsuperscript{22} discuss another problem related to parison formation, parison 'pleating' or 'curtaining'. The parison, upon exiting the die, is smooth, but at a given downstream distance (or certain time) it may form pleats (figure 2.2.) Pleating involves the buckling of the parison under its own weight. Thus the occurrence of pleating should be a function of parison wall thickness and should depend on the angle of extrusion (larger gravity component and a larger moment arm). From a melt property point of view, increased melt strength and higher extrusion rates (which makes the melt more elastic and allows less time for creep) alleviate pleating.

In the absence of the ability to analyse the parison formation problem quantitatively and to relate it to the fundamental rheological properties, Schaul et al.\textsuperscript{22} have approached it in an empirical fashion: four parison properties were evaluated at various levels of peak shot pressure and die gap, the two available process variables in reciprocating screw blow moulding. Response surfaces were experimentally obtained for the final parison diameter, product weight, severity of melt fracture, and pleating. By specifying minimum acceptable levels for each property (plotting the four 'acceptable' level curves on one graph), they were able to obtain
'operating lines' given in figure 2.3. These results agree specific to the polymer and the parison forming system used. The heavy line represents the acceptable range of shot pressure and die gap values to produce the specified product.

Ryan and Dutta\textsuperscript{23} attempted to model the length of parison as a function of time. They assumed that the final shape of the parison depended on the competing influence of two factors: influence caused by gravity and that caused by elasticity. Industrial blow moulding dies were assumed to have outer to inner radius ratios of less than three; curvature effects associated with the annular geometry may be neglected.\textsuperscript{24, 25}

Application of principle of conservation of mass gives,

\[ L_s(t) = \frac{V_e \cdot t}{S_d^2} \]  

2.2.3.(1)

\( L_s(t) \) is parison length as a function of time, subject only to swell. \( V_e \) is extrusion velocity, \( t \) is time, and \( S_d \) is the swell ratio. Thus, the parison length, subject only to swell, is less than the length corresponding to ideal extrusion and can only be ascertained from a knowledge of the swell

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ratio, S_d. From experimental data, the time dependent swell in the absence of gravitational effects may be represented as follows:

\[ S_d = 1 + (S_{deq} - 1) (1-\exp(-k_1 t)) \]

...2.2.3.(2)

\( S_{deq} \) is equilibrium swell ratio, and \( k_1 \) is a rate constant, both of which may be readily determined experimentally.25

As estimate of the influence of gravitational forces on the length and shape of the parison may be obtained by assuming that the axial velocity is of the form \( V_x = V(x,t) \), and that the process is isothermal. A schematic representation of the flow situation is shown in figure 2.4. The requirements that both shear and normal stresses must vanish along the free surface gives:

\[ T_{yy}N_y + T_{xy}N_y = 0 \]

...2.2.3.(3)

\[ T_{xy}N_y + T_{xx}N_x = 0 \]

...2.2.3.(4)

\( T_{ij} \) denotes total stress components. \( N_x \) and \( N_y \) are the components of the unit vector, normal to the free surface, and are given by the following equations:

\[ N_x = \frac{-dh}{dx} \left( 1 + \frac{d^2h}{dx^2} \right)^{-1/2} \]

...2.2.3.(5a)
\[ N_y = (1 + \frac{\partial^2 h}{\partial x^2})^{-1/2} \quad \ldots 2.2.3.(5b) \]

Equations 2.2.3.(3) and 2.2.3.(4) may be rearranged.

\[ T_{xy} = T_{xx} \frac{d h}{d x} \quad \ldots 2.2.3.(6b) \]

\[ T_{yy} = T_{xx} \frac{d^2 h}{d x^2} \quad \ldots 2.2.3.(6b) \]

Integrating equation of motion in the x direction with respect to y, from the centre line (\( y = 0 \)) to the free surface (\( y = h \), and making use of equation 2.2.3.(6) gives an expression:

\[ \frac{dV_x}{dt} + V_x \frac{dV}{dx} = \frac{1}{p} \frac{dT_{xx}}{dx} + T_{xx} \frac{d h}{d x} + g x \]

\[ \ldots 2.2.3.(7) \]

The deviatoric stress, \( t_{ij} \), is related to the total stress, \( T_{ij} \), as follows:

\[ T_{ij} = -P \ d_{ij} + t_{ij} \quad \ldots 2.2.3.(8) \]

Where

\[ P = -\frac{1}{3} T_{ij} \quad \ldots 2.2.3.(9) \]

The repeated subscript implies the adoption
Figure 2.4

Schematic Representation of Parison Subject Only to Drawdown
of the index summation convention. Assuming that the surface curvature is reasonably small \( \frac{dh}{dx} \ll 1 \), implies that \( T_{yy} = 0 \). Since \( T_{zz} = 0 \), equations 2.2.3.(8) and (9) imply that \( T_{xx} = \frac{3}{2} t_{xx} \). Therefore, equation 2.2.3.(7) becomes:

\[
\frac{dV_x}{dt} + V_x \frac{dV_x}{dx} = 3 \frac{dt_{xx}}{dx} + 3 \frac{t_{xx}}{dx} \frac{dh}{dx} + g \frac{dx}{dx} \tag{2.2.3.(10)}
\]

In addition, the movement of the free surface is governed by the following kinematic conditions:

\[
\frac{dh}{dt} = V_y - V_x \frac{dh}{dx} \tag{2.2.3.(11)}
\]

Integration of the continuity equation yields

\[
V_y = -y \frac{dV_x}{dx} \tag{2.2.3.(12)}
\]

Substitution of this result applied at the free surface into equation 2.2.3.(11) gives

\[
\frac{dh}{dt} + \frac{d}{dx} (hV_x) = 0 \tag{2.2.3.(13)}
\]

The following identity may also be written:

\[
\frac{dL_g}{dt} = V_x (L_g, t) \tag{2.2.3.(14)}
\]

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Equations 2.2.3.(10), (13) and (14), along with appropriate constitutive equations relating to the deviatoric stress tensor, \( t \), provide the mathematical description for the drawdown analysis. These governing equations represent a set of coupled, non-linear, partial differential equations. In addition, complication arises from the fact that the flow domain \((L_g, h)\) is not known a priori, but must be determined as part of the solution. Simple analytical solution to the above system of partial differential equations may be obtained by making additional assumptions with regard to the kinematics of deformation.\(^\text{25,26}\)

For example, if the convective terms in the equation of motion are neglected and, the surface profile is considered to be independent of axial location, integration of equation 2.2.3.(10) yields:

\[
T_{xx} = \frac{2}{3} \varphi g x (L_g - x) \quad \ldots 2.2.3.(15)
\]

Further, if the fluid is assumed to be described by a corotational Maxwell model, then

\[
T_{xx} + V_x L_0 \frac{dT_{xx}}{dx} = 2 \eta_0 \frac{dx}{dx} \quad \ldots 2.2.3.(16)
\]

Where \( L_0 \) and \( \eta_0 \) are rheological parameters.
Substitution of equation 2.2.3.(5) into (16) and solving for the axial velocity subject to the condition that $V_x(0,t) = V_e$ gives an expression:

$$V_x = V_e \exp(-a.L_0.x) + \frac{L_g}{L_0} \left(1 - \exp(-a.L_0.x)\right) - \frac{1}{a.L_0^2} (a.L_0.x + \exp(-a.L_0.x) - 1)$$

...2.2.3.(17)

where $a = \frac{p g_x}{3 \eta_0}$. Making use of equation 2.2.3.(17) in equation 14, enables a relationship between parison length and time to be derived. The equation is given as follows:

$$t = \int_{0}^{L_g} \frac{dl}{(1 - \exp(-a.L_0.L)) + (V_e - L/L_0) \exp(-a.L_0-L) \frac{a.L_0^2}{}}$$

The expression for the length contributions to swell and gravity may be combined in order to yield the resulting parison shape subject to these two competing influences. Figure 2.5. shows the calculation variation of the functions $L_s$ and $L_g$ with time. By adding the difference between pure drawdown and ideal behaviour, to the swell contribution, the actual parison length may be calculated as a function of time. A comparison is made with
Figure 2.5
Calculated and Experimentally Determined Parison Length as a Function of Time

Figure 2.6
The Brikum system of plunge neck blowing
experimental data obtained using a commercial blow moulding grade, high density polyethylene resin\textsuperscript{23} (Phillips Petroleum Company, Marlex EHM - 6006). Parameter values and material properties are summarised in Table 2.2.3.1.

Table 2.2.3.1. - Parameter values and material properties for Marlex EHM - 6006

\begin{tabular}{|l|}
\hline
S_{deq} = 1.92 \\
V_e = 0.86 \text{ cm/s} \\
k_q = 0.09684 \text{ /s} \\
\eta_0 = 3800 \text{ Pa s} \\
L_0 = 10 \text{ sec} \\
\rho = 964 \text{ kg/m}^3 \\
\hline
\end{tabular}

Although the theoretical model provides some useful insight on the influence of material properties and process parameters on the parison formation stage, it is evident that the model fails to describe accurately the growth of the parison especially at longer times. This failure may be caused by several possibilities, including the unrealistic nature of the many simplifying assumptions in the preceding analysis, the choice of constitutive equation for representing the rheological response of the material characterisation, and the assumed simple additivity of the contributions due to swell.
and drawdown. Shear viscosity is used in this model whereas sagging occurs in tension.

2.2.4. Stage Three, Parison Blowing

The function of the extruder and the die is to deliver consistently to a correctly designed mould set in a parison of the required diameter, wall thickness, temperature and viscosity. This parison, once it is positioned in the closed mould, is then expanded from a tubular form to an accurate reproduction of the surface of the mould cavity by the blowing. The parison is cooled sufficiently to be self supporting and to permit ejection. There are two basic blowing systems in common use: these are known as needle inflation and mandrel inflation.

2.2.4.1. Needle Inflation

The use of a hyperdermic needle or blow pin was an early method of inflating a parison and obviously can only be applied in blowing systems where the parison is trapped and sealed or to all intents and purposes trapped at both ends when the mould is closed. The needle is advanced to pierce the parison by compressed air; the needle then retracts, and the molten polymer seals the hole left by the needle.
2.2.4.2. Mandrel Inflation

Mandrel inflation as the name implies, is a system whereby a mandrel connected to a compressed air supply is inserted in the barrel of the molten tubular parison. In some cases the mandrel of the extrusion die itself has been used as a means of inflation. There are three common methods of mandrel inflation - bottom blow, top blow with and without calibration. There must be a device to produce a hole in the top for the mandrel to be inserted into.

2.2.4.3. Top Mandrel Inflation

The mould is mounted in the 'neck up' position, but the blowing mandrel actually enters the open parison, to size the internal neck diameter, and the cutting action between the mandrel and the top of the mould removes excess material, thus producing a finished container. However, it must be borne in mind that the mating at the top of the mould with the mandrel does not necessarily constitute a perfect cutting means and some manual removal of excess may also be required particularly if the moulds have become badly worn.

An extension of this system, known as plunge neck blowing was developed by other manufacturers. In this system the blowing
mandrel is in two parts, one of which was to calibrate the internal diameter of the neck and the other part, being in effect a sliding sleeve to the calibrator, which descends after blowing, to form the top rim of the bottle and to cut off any excess material (see figure 2.6.).

2.2.4.4. Air Requirements for Blowing

In general there are two basic requirements for good inflation.

(1) The parison must be inflated as quickly as possible in the early stages so that the parison mass is subjected to a minimum of cooling prior to contacting the mould surface.

(2) The inflated parison must be held under pressure in intimate contact with the mould surface, which may contain embossed decoration during the cooling period.

There are two variables that control the volume of air passed into the mould; air pressure (i.e. the compressed air line pressure), and the diameter of the air inlet orifice. For a given line pressure, a large diameter orifice will give a greater volume of air than the small orifice in a given time.
High air velocity can have undesirable effects on the parison during the blowing process, particularly in the early stages of blowing, therefore the air inlet orifice is made as large as possible so the volume of air is sufficient but the velocity is low.

The second stage of inflation requires that the air pressure must be sufficient for the inflated parison to develop surface detail. The precise pressure required will depend on the wall thickness and effective diameter of the moulding and on the mould and parison temperatures.

2.2.5. Stage Four, Cooling of Blow Moulded Objects

Cooling of a moulding can be achieved from both the internal and external surface to the mould and via the internal surface by the circulation of air or by other means. In practice, at present, the metal mould is maintained at low temperature by circulating a cold liquid (water, water/ethylene glycol, or brine) through channels within the mould. Heat from the polymer is carried away by the circulant. The efficiency of heat transfer can be changed by using metals of different conductivities for the mould, and by altering the arrangement of cooling channels. Forced convection is the process by which heat is transferred, and is dependent on the
geometry of the cooling channels, the physical properties of the coolant, and flow rate.

Ideally, heat transfer is high when the temperature difference between molten polymer and coolant is great; refrigeration units are often used to produce coolant at low temperatures. The lower limit for mould temperatures is governed by mould sweating (temperature below dew point); this problem can be reduced by internal cooling, i.e. cooling through the inside surface of the polymer. A number of techniques have been applied:30-33

(1) circulation of air in the gas space;
(2) injection of liquid carbon dioxide after a short blow with air;
(3) injection of high pressure moist air;
(4) use of low temperature air; and
(5) cyclic addition and exhaust of cold air.

In the cooling process of crystallising polymers from the molten to the solid phase, a large amount of latent heat is evolved. The problem of cooling, with this latent heat term included, has been investigated.34-40
Dussinberre\textsuperscript{34} viewed the solidification of polymer where latent heat ($H$) evolved is accounted for by the use of a variable specific heat ($C_p$).

\[
H = \int_{T_{lm}}^{T_{um}} C_p \, dT \quad \ldots 2.2.7.(1)
\]

$T_{um} =$ upper limit of melting range; $T_{lm} =$ lower limit of the melting range.

Guttfinger et al\textsuperscript{35} considered a polymer melt initially at $T_0$, being held between two plates, at a lower temperature $T_w$ (below solidification temperature of the polymer). The set of equations describing the solidification of the melt is as follows:

\[
\rho C_p \frac{dT}{dt} = \frac{d}{dz} (K \frac{dT}{dz}) \quad \ldots 2.2.7.(2)
\]

\[
T(z,0) = T_0
\]

\[
\frac{d}{dz} \left(0,t \right) = 0
\]

\[
T(h+,t) = T_w
\]

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Here $z$ is the coordinate measured from the
centre line and $h^+$ is the distance from the
centre line to the wall.

The above set of equations was applied to the
solid, as well as the molten phase. Within
the solidification range, the latent heat of
solidification ($H$) is included in the
specific heat term as in Dussinberre's
method.

Horsefield\textsuperscript{36} solved the heat equation for
crystallising polymers by assuming specific
heat to be constant over small ranges.

Sifleet et al\textsuperscript{38} have used crystallisation
kinetics in the heat conduction equation as a
heat generation term.

\[
\frac{dT}{dt} = \alpha \frac{d^2 T}{dx^2} + \frac{Q}{\rho C_p} \quad ...2.2.7.(3)
\]

where $Q = \rho H \frac{d\lambda}{dt}$ and $\frac{d\lambda}{dt}$ is the rate
of change of crystallinity with time; $\alpha$ is a
constant; $H$ is the latent heat; and $\rho$ is
density. The Avrami equation\textsuperscript{40} represents
crystallisation kinetics:

\[
\lambda = 1 - \exp \left( -Z_n t^n \right) \quad ...2.2.7.(4)
\]

$\lambda$ is the degree of crystallinity; $t$ is the
time when crystallisation begins isothermally;
$Z_n$ is a kinetic parameter; and $n$ is an
integer function for the type of crystallisation and nucleation occurring.

In all the three previous approaches, the specific heat is taken to be continuous function of temperature; it is much less temperature dependent in the solid region than in the melt region. Various techniques have been developed to reduce cooling time and increase productivity. 31-33,41-43

Edwards et al 44 investigated the use of carbon dioxide as an internal coolant; results are presented from an experimental blow moulding rig and from industrial machines. Additionally, the data are interpreted using a theoretical model of cooling and solidification during the blow moulding process. The material used was high density polyethylene (manufactured by Dow Chemicals). Temperature gradients were found to occur across the wall thickness; the bottle is usually cold on the outside and reheats, when removed from the mould. 45,46 Once this reheat temperature reaches a maximum there are no appreciable temperature gradients across the wall thickness. Edwards et al 44 use maximum reheat temperatures as a common basis for all the cooling tests. The reduction in cooling time achieved by injecting liquid carbon dioxide was 45%
compared with air circulation, and 65% compared with single shot air injection.

Edwards et al\textsuperscript{44} use half bottles with thicknesses in the range 3 - 7 mm; the effect of carbon dioxide flow rate on cooling time for these bottles can be seen in figure 2.7. At high levels of cooling rate, the cooling time remains constant; this indicates a region of diminishing returns. Figure 2.8. shows a comparison between cooling by air and carbon dioxide. Figure 2.9. shows that changing the mould temperature, within the limits 5 - 15°C, did not affect the reduction of cooling time obtained by using liquid carbon dioxide injection. It was also found that pulsing of injection can lead to reductions in the usage of carbon dioxide, for the same cooling times.

2.3. \textbf{Welding in Blow Moulded Products}

For economical reasons the main processes used in joining injection moulded parts are the heated tool butt welding, ultrasonic welding and friction welding.\textsuperscript{47-50} Literature reports on the interdependence of the main parameters in these welding processes and on the way they affect seam quality. In addition, the details are given of the influence of prior processing history on the seam quality of the injection moulded parts.
Figure 2.7

Effect of CO₂ flow-rate on cooling time.
Comparison of CO₂ cooling with air circulation.
(a) Cooling time versus half-bottle thickness; (b) cooling time versus half-bottle weight. (●) Air circulation; (○) CO₂ cooling (nozzle R0).

Figure 2.8

Effect of CO₂ flow-rate on cooling time.

Figure 2.9
Hot tool welding has been used on the fuel tanks investigated in this thesis. It is reported\textsuperscript{50} that in hot tool welding, the flow velocity during the joining process has a considerable influence on the seam strength. The flow velocity is a function of prior history, i.e. the melted zone width, $L$, the viscosity, $\eta$, and the welding pressure, $P_s$.

It is possible to define a specific minimum velocity below which the seam strength can no longer be increased, i.e. optimum seam strength lies below this flow velocity.

The weld line resistance of PP/EP rubber blends and of PP filled with inorganic particles has been investigated by Savadori et al.\textsuperscript{51} In the case of opposing flows, specimens of PP/EP rubber blends just fail at the yield point and yielding of the material is locally distributed along the weld-line without any necking.

The strength, $O_w$, (of the welded specimens), decreases with rubber content. The $O_w/O_y$ ratio, where $O_y$ is the yield stress of the unwelded specimens, can be considered as an index of welding resistance and decreases with increasing rubber content and decreasing rubber molecular weight. In the case of filled PP alone, brittle fracture of the specimens occurs before yielding and the strength; and the failure mode depend on the content and the shape factor of the filler.
This behaviour, which does not seem to be influenced by moulding parameters or by removing the surface crack produced by compressed air escaping, is completely absent in the case of parallel flows, once the surface notches, which are eventually formed, are removed. This phenomenon has been examined and discussed according to the most recent hypothesis about weld line strength.51

Injection moulded fittings have to be attached to the fuel tank to form a leak proof seal; the common method of joining is hot plate welding. Consideration of welding is important as weld failures in fuel tanks have been observed.

In hot plate welding, the two objects to be welded are brought into contact with a hot plate; the plate is removed after a specified heating time; the two objects are then brought together and welded under axial pressure.

Surface quality of hot plate is of fundamental importance.52,53 It is usually made from corrosion resistant materials with good thermal conductivity. Hot plates for welding temperatures up to 300°C are mainly made from aluminium; at higher temperatures (up to 350°C) aluminium bronze is used. All hot plates are heated electrically. To prevent sticking of polymer to the hot plate, the surface of three dimensionally shaped hot plates are coated with poly tetrafluoroethylene (PTFE) or covered with glass fibre reinforced PTFE film (in the case of flat hot
Figure 2.10.
A. BUTT WELDED SEAM

B. CONCEALED ON ONE SIDE

C. CONCEALED ON BOTH SIDES

D. CORNER WELD WITH CONCEALED SEAM

E. WELDING OF THREE PARTS WITH CONCEALED SEAM
plates.)

The regions to be welded may be designed to enhance desirable properties (see figure 2.10.): high mechanical joint strength; attractive appearance; and absolute tightness of the weld joint.

Strength of the weld is commonly expressed as a weld factor (%); this is the ratio of the strength of the weld to the unwelded material. Factors influencing weld factor are heating time, welding temperature, welding time (time for which pressure is applied), and welding pressure; the influence of these factors is investigated in this thesis.

Alignment of welding surfaces may also be a factor; this is considered in the literature\textsuperscript{54}.

2.4. Permeability of Blow Mouldings

Containers with low permeability for storage of food and chemicals are prepared by the HILS-BM method\textsuperscript{55} in which a high barrier layer, e.g. poly(vinyl alcohol) is laminated between two olefin layers. The permeability to O\textsubscript{2} is reduced by a factor of \textgreater 80 and that of N\textsubscript{2} and CO\textsubscript{2} by a factor of 800 compared with polyolefins containers of the same wall thickness. The permeability to organic solvent is greatly reduced.\textsuperscript{55}
The blow moulding of polyolefin containers with a 0.5 - 5\% fluorine in nitrogen mixture will reduce the permeation of many solvents\textsuperscript{56}. The process can be easily adapted to standard blow moulding machines and involves the addition of three separate systems: the gas blending system, the blow gas delivery system and the blow gas exhaust system. The controlled reaction of polyethylene with fluorine produces a fluor-carbon layer approximately 150 Å thick. Weight loss tests for 11 days at 40°C showed improvements in the permeation of non-polar solvents. Correlation of permeation data with solubility parameters showed the fluorinated containers to be effective for solvents with solubility parameters less than 18.4 (MJ/m\textsuperscript{3})\textsuperscript{0.5} and greater than 20.4 (MJ/m\textsuperscript{3})\textsuperscript{0.5}. Commercial solvents such as petrol, paint, turpentine, motor oil, and varnish were effectively contained in fluorinated containers.

A recent development to improve permeation resistance has been the introduction of laminated containers, where 2 or 3 layers of different materials are coextruded to form a container\textsuperscript{57}.

2.5. Process Variables

Glyde's paper\textsuperscript{58} was a cornerstone in the development
of blow moulding, and discusses the effect of variables and the difference between the two types of processes - extruded parison and preform moulding.

The main product responses are six, in four groups: shrinkage and distortion, strength and stiffness, strength of pinch welds and surface appearance. There are at least 11 parison, machine and mould variables and many interact. Nearly all of these variables affect the strength of the pinch welds. Process factors are important mainly by virtue of their influence on rate of polymer crystallisation, pressure/time relations and parison tension.

2.6. **Blow Moulding of Large Containers**

The range of blow moulded products extends to 900 litres and shot weights of up to 40 kilogrammes. All the processing plant of this calibre is of the extrusion blow moulding category. For successful quantity production high performance plasticising, repetition of extrusion conditions and parison thickness control are essential.

Accumulator designs may be split up into three types: Crosshead ram type, annular piston type and reciprocating screw type (see figures 2.11, 2.12 and 2.13.)

Holzmann reports that larger containers differ from small containers in that they are less sophisticated to manufacture and the blowing unit is not mobile;
therefore the production of consistent parisons is more difficult.

Large containers require longer cooling times - the parison pushing out time is not equal to the total cycle time as in smaller articles. The parison has to be extruded and moulded as fast as possible to prevent lengthening and the accumulator should be emptied completely at each stroke. Accumulator heads are established as preferable to individual accumulators, particularly with high molecular weight polyethylene.

Materials must have a high resistance to thermal degradation, high melt strength, a broad range of temperatures for which they are molten and resistant to melt fracture. Such properties are available in most thermoplastics and the polyolefins have an economical advantage. Moulds are frequently made of aluminium with rear wall cavity cooling. The design of a product is invariably a compromise between the major requirements of overall specification and those of economics, handling and storage requirements and chemical compatibility.

The two principal requirements of performance are resistance to chemical attack and to physical damage. Drop testing is the usual method adopted by container users; environmental stress cracking, the most commonly met chemical hazard is not so simple. A recently developed method covering both aspects is to establish reversion performances of a complete
Figure 2.11
Crosshead-ram accumulator

Figure 2.12
Annular piston accumulator

Figure 2.13
Reciprocating screw accumulator
container when immersed in bath of water and anionic detergent at 80°C.

2.7. Notes on Design

Fuel tanks require low surface area to volume ratios, for important reasons: evaporation of fuel is lessened; and minimum surface area may lead to a reduction in thickness variation. The geometry with the highest volume to surface area ratio (V/A) is the sphere; V/A is \( \frac{r}{3} \) (\( r \) is radius).

For a cylinder, it can be shown that the minimum surface area is obtained when \( r = \frac{(V/2)^{1/3}}{3} \) this occurs when \( r = \frac{h}{2} \); V/A ratio for cylinder is \( \frac{r \cdot h}{2(r+h)} \) (\( r \) and \( h \) are radius and height of cylinder).

A right-angled object has minimum surface area when all sides are equal, i.e. a cube; V/A ratio is \( \frac{a}{6} \) (\( a \) is length of one side of cube). At constant volume and minimum surface areas for the following geometries V/A sphere > V/A Cylinder > V/A cube.

These calculations are relevant when considering the design of a tank. The tank, however, is usually designed to fit in the car, and consequently is irregular in geometry.
3. HIGH DENSITY POLYETHYLENE

3.1. Introduction

The first commercial ethylene polymer was branched polyethylene, commonly designated as low-density or high pressure material to distinguish it from the essentially linear high-density polyethylene. High-density polyethylene (HDPE) can be produced in several ways, including coordination polymerisation of ethylene, and polymerisation with supported metal oxide catalysts. Commercial production of linear polyethylene, using these routes, began in 1952. Typical linear polyethylenes are highly crystalline polymers containing less than one side chain per 200 carbon atoms in the main chain. Melting point is above 127°C (typically about 135°C), and density is in the range 940 - 970 kg/m³.

Most of the differences in properties between branched and linear polyethylenes can be attributed to the higher crystallinity of the latter polymers. Linear polyethylenes are significantly stiffer than the branched material, and have a higher crystalline melting point, and greater tensile strength and hardness.

The production of bottles and other containers by blow moulding accounts for over 40% of the linear
polyethylene made. Linear polyethylene is ideal for blow mouldings as it has low parison sag, is highly inert, and offers a high degree of stiffness per unit wall thickness.

About 20% of the linear polyethylene is produced in the injection moulding of housewares and toys. Other major uses of linear polyethylene include pipes, film and sheet and extrusion coated laminates.

3.2. Molecular Weight

3.2.1. General

Many distinctive properties of polymers are a consequence of the long chain lengths, which are reflected in the large molecular weights. Polymers exhibit polydispersity, and the degree of accuracy of measurement of molecular weight is much lower than for simple monodisperse molecules; the molecular weight is an average, at best dependent on the particular method of measurement used. Measurement of the molecular weight of a polymer system is of considerable importance, as the chain length can be a controlling factor in determining solubility, elasticity, tear strength, and impact strength in many polymers.61

Molecular weights of polymers can be determined by chemical means or by physical
methods of functional group analysis, by measurement of the colligative properties, by light scattering, by ultracentrifugation, or by measurement of viscosity of solution or melts. All these methods, except the last, are absolute. Viscosity methods are not, however, direct measures of molecular weight; the value lies in the simplicity of the techniques.

Since typical polymers consist of mixtures of many molecular species, molecular weight methods yield average values. The measurement of the colligative properties, in effect, counts the number of moles of solute per unit weight of sample. This number is the sum over all molecular species of the number of moles, $N_i$, of each species present:

$$\sum_{i=1}^{\infty} N_i$$

The total weight, $w$, of the sample is similarly the sum of the weights of each of the molecular species,

$$w = \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} N_i \cdot M_i$$

The number average molecular weight ($\bar{M}_n$) is
given as

\[ \bar{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i = \sum_{i=1}^{\infty} M_i \cdot N_i / \sum_{i=1}^{\infty} N_i} \]

= Total Mass / Total number of molecules

Colligative methods measure number average molecular weight. The weight average molecular weight is measured by light scattering and is given as

\[ \bar{M}_w = \sum_{i=1}^{\infty} N_i \cdot M_i^2 / \sum_{i=1}^{\infty} N_i \cdot M_i \]

\( \bar{M}_w \) is always greater than \( \bar{M}_n \) except for monodisperse systems. (See figure 3.1) The ratio of \( \bar{M}_w / \bar{M}_n \) is a measure of the polydispersity of the system. \( \bar{M}_w \) is more sensitive to the presence of high molecular weight species.

Intrinsic viscosity measurement leads to the viscosity average molecular weight, defined by the equation

\[ \bar{M}_v = \sum_{i=1}^{\infty} w_i \cdot M_i^a \cdot \frac{1}{a} \]
FIGURE 3.1. A TYPICAL MOLECULAR WEIGHT DISTRIBUTION
a is an exponent constant $\bar{M}_v$ depends on 'a' as well as on the distribution. For $a = 1$, $\bar{M}_v = \bar{M}_w$.

Viscosity and melt flow index are highly dependent on molecular weight, as shown previously; in fact the most important structural variable determining the flow properties of polymers is molecular weight, or alternatively chain length, $Z$ (the number of atoms in a chain). Flory\textsuperscript{62} suggested that $\log \eta$ was proportional to $Z^{1/2}$; it has since been observed by Fox\textsuperscript{63}, for essentially all polymers that, for values of $Z$ above a critical value $Z_c$,

$$\log \eta = 3.4 \log Z_w + k$$

Where $k$ is temperature dependent. This equation is valid only for shear stresses sufficiently low ($10 - 100 \text{ N/m}^2$). The weight average chain length, $Z_w$, is usually assumed to be the appropriate average for the above conditions.

While the Newtonian melt viscosity is determined by $\bar{M}_w$, the dependence of viscosity on shear rate also depends on the molecular weight distribution. The drop in melt viscosity below its Newtonian value begins at a lower shear rate for polymers with broader molecular weight distributions. At
sufficiently high shear rates, the melt viscosity appears to depend primarily on $\bar{M}_n$ rather than $\bar{M}_w$. Qualitative information, at least, about the molecular weight distribution can be obtained from melt viscosity-shear rate studies.

3.2.2. Molecular Weights of High Density Polyethylenes

Rough values for molecular weights (g/mol) from Gel Permeation Chromatography for the following Rigidex grades are:

- 002-55 and 002-47 - 155,000;
- 006-60 - 130,000;
- H060-45P - 250,000;
- and H020-54P - 290,000.

The properties of HDPE polymers are directly related to the molecular weight and density of the individual grades. Increases in molecular weight improve impact strength and resistance to environmental stress cracking, but flow properties are deteriorated. Melt index is used as a measure of molecular weight. A low melt index indicates high molecular weight whereas a high index is related to a low molecular weight.

Typical melt flow indices and molecular weights used in blow moulding grades of linear polyethylenes are around 6.5 g/10 minutes (190°C, 216 kg load), which corresponds to a molecular weight of 250,000.
3.3. Morphology and Microstructural Interfaces

3.3.1. Introduction

Polyethylene, like many other polymers is partially crystalline; linear polyethylene and branched polyethylene are about 7.0% and 50% crystalline respectively; the most direct evidence is provided by x-ray diffraction studies. The x-ray patterns of crystalline polymers show both sharp features associated with regions of three dimensional order, and more diffuse features characteristic of molecularly disordered amorphous phases. Additional evidence comes from polymer properties, such as density, which is intermediate for those calculated for completely amorphous and crystalline species.64,65

Crystallisability has long been recognised to be associated with structural order. Typical crystalline polymers are those whose molecules are chemically and geometrically regular. Occasional irregularities, such as chain branching in polyethylene, limit the extent of crystallisation.
The fully extended planar zigzag is the conformation of minimum energy for an isolated section of a hydrocarbon chain. Fully extended chains are found in crystal structures of polyethylene; it is to be expected that these conformations will be favoured in crystal structures.

Except for end groups, the arrangement of chains in the crystal lattice is essentially the same as that in crystals of linear paraffin hydrocarbons containing 20 - 40 carbon atoms. The unit cell of polyethylene is orthorhombic (see figure 3.2.) with dimensions $a = 0.741$ nm, $b = 0.494$ nm, $c = 0.255$ nm ($c$ is the chain repeat distance, and is identical with the fully extended zigzag repeat distance). The positions of the hydrogen atoms are not detectable by the x-ray method but have been calculated assuming tetrahedral bonds and a C-H distance of 0.11 nm.

The fringed-micelle model (see figure 3.3.) accounts for elasticity in polymers, an individual molecule is likely to pass through different regions of order and disorder. The concept of two kinds or order (though only a first approximation) has been, and continues to be, very useful in providing the basis of an explanation for the variable densities,
FIGURE 3.2. POLYETHYLENE UNIT CELL

FIGURE 3.3. FRINGED-MICELLE MODEL
melting points, etc., shown by crystallised polymers. The fraction of material supposed to be fully crystalline is known as the degree of crystallinity of a sample.

The textural scale of the fringed-micelle model was believed, primarily on the basis of crystallite sizes estimated from the widths of x-ray diffraction rings, to be on the scale of a few tens of nanometres (nm). Such dimensions were not then observable. Not until 1945 was it appreciated, first for polyethylene, and subsequently for other polymers, that there was additional ordering on a larger scale. This is due to the prevalent crystallisation of high polymers as spherulites.

The 'shish kebab' is a morphology that was recognised early in the study of polymer systems. It comprises a narrow central thread (typically about 30 nm in diameter) strung with small platelets (see figure 3.4.). A shish kebab may be regarded as nucleation of fibrils followed by epitaxial over growth of lamellae sharing a common chain axis orientation along the fibre. The fibre itself results from strain-induced crystallisation, i.e. from distorted molecular conformations in which chains have been brought and maintained parallel for long enough to nucleate crystallites. This type
FIGURE 3.4.

THE SHISH KEBAB MORPHOLOGY

FIGURE 3.5.

SPHERULITE STRUCTURE
3.3.2 Spherulites

Spherulites are micro-spheres and have diameters usually in the range 0.5 - 100 μm (see figure 3.5); they are characteristic of polymers that have crystallised from the melt in the absence of significant stress or flow. A spherulite is characterised by a radial growth of fibres from a central nucleus. The radial fibres may simply diverge, and fail to fill space. Only if they branch, creating more fibrils at greater radial distances, will space be uniformly filled. The fibres comprise twisted crystal lamellae.

The structure of spherulites causes light to be scattered. Spherulites are associated with, and believed to be due to, the segregation of molecular species in a sample. For example, shorter molecules are likely to predominate in interspherulitic boundaries, and give these regions different mechanical properties leading, in certain circumstances, to preferential crack growth between spherulites.

The fringed-micellar arrangement of molecules at the 20 nm level did not really fit in with
the idea of spherulites, two orders of magnitude larger in scale, particularly in view of the fact that the molecular chain is generally tangential in spherulites instead of radial as had been expected.

Two major features are common to all variants of spherulites: the microstructure of spherulites all contain equivalent radial elements; and the isothermal growth rate constant is independent of the radial distance. Keith and Padden presented a semiquantitative theory of these properties in terms of general crystal growth mechanisms. There were two problems of spherulitic crystallisation, according to the authors: the development of radial fibrils; and the explanation of the proliferation of fibrous units to fill space uniformly, and maintain spherical symmetry. The latter they describe as small-angle, non-crystallographic branching.

Crystal growth is usually governed by diffusion, either of heat or matter, yet the solution of the diffusion equation for an expanding sphere is known to give a surface area increasing linearly with time. If diffusion is the dominant process, therefore, the implication of constant growth rate is that local conditions are not changing with time. Keith and Padden noted that, in certain
systems, the melt left between growing fibrils was never crystallised on subsequent cooling; they concluded that the condition of the melt was inhomogenous; and they formulated a theory based on diffusion of impurities away from growing crystal surfaces.

A polymer sample is polydisperse with respect to molecular weight; it may contain branched or entangled molecules. All of the elements will lead to variations in growth rate among different species. The less easily crystallised will tend to build up in numbers at a growing interface, i.e. act as effective impurities, and then diffuse away to regions of lesser concentration.

Nucleation can be heterogeneous in origin, the growth occurring on particles dispersed in the matrix polymer. The normal method of nucleation, in the absence of such particles, is termed homogeneous nucleation, occurring within the matrix polymer itself. Heterogeneous nucleation results in crystallisation starting at a higher temperature.

Keith and Padden's theory assumed an equilibrium concentration of impurities, C_{oo}, in a supercooled polymer melt, within which crystallisation was proceeding at a finite
rate. The impurities were at a distance, $\delta$, from a hypothetical planar crystal surface growing in the melt; $\delta$ is given by $D/G$, where $D$ is the diffusion coefficient for 'impurities', and $G$ is the rate advance of the surface (see figure 3.6.)

The build up of impurities on further crystallisation depresses the equilibrium melting temperature below that which it would otherwise be. The effective supercooling and thermodynamic drive for crystallisation are reduced. A protuberance developed on the interface would find itself growing in a low impurity concentration region; the supercooling would be greater than at the interface, although the temperature would be the same. The protuberance would therefore be stable, and one sees that a planar interface growing under these conditions is inherently prone to break up into an array of protrusions. This leads to fibrillation; the 'diameter' of these 'fibres' is also likely to be approximately equal to $\delta$ because this is the scale of the diffusion field at each growth tip, which sets an approximate dimension to the adjacent units.

In addition to fibrillation there must be small-angle branching to give the spherulites their spherical symmetry. Principally, small-angle branching becomes more diffuse.
FIGURE 3.5.a.
SCHEMATIC DEPENDENCE OF IMPURITY CONCENTRATION, C, WITH DISTANCE AHEAD OF GROWING CRYSTAL SURFACE

FIGURE 3.5.b.

$T(x)$ Ambient temperature
$T_L(x)$ Liquidus
$\Delta T(x)$ Supercooling $= T_c - T$

Solid

Liquid

$c(x)$
the thinner the fibrils.

Keith and Padden proposed that the correlation of finer fibres and more frequent branching is consistent with new fibrils initiating at misaligned surface nuclei, near tips of existing units. A fibril will only survive if it has a 'diameter' near $\tilde{a}$; smaller ones will disappear, and larger ones break up. As the requisite size becomes larger, the chance of the existence of a suitable nucleus must decrease, so that for smaller $\tilde{a}$ there should be more branches and a finer texture, in the manner found. 67-69

The outward growth of the fibrils is termed primary crystallisation; secondary crystallisation is growth filling the interstices.

More complicated spherulites may contain concentric extinction rings (zero birefringence) indicating that at the location of the rings, the molecular axis (c) is parallel to the illumination. The maltese cross seen between crossed polars may degenerate into a zigzag of connecting bands; and a consequence of the radial units being inclined to the plane of a non-diametral section.

Zigzags of larger amplitude may also occur in
simpler, unbanded spherulites when 'the crystallographic directions of the twisted fibrils are such that optic axes are prevented from falling in tangential directions'.74

Spherulites are observed as birefringent structures in the polarising microscope, possessing a dark maltese cross pattern; the maltese cross occurs when the principal optical direction of the radial units fall parallel to the polarised light vibration directions.

3.3.3. Crystallinity in Polymers

Individual polymer crystals were discovered grown from dilute solutions of polyethylene in xylene75; the idea of polymer molecules forming single crystals was alien to the fringed-micelle model.

Keller75 deduced that molecules, typically 5 - 10 \( \mu \text{m} \) long, lay in the crystals with their lengths across the thin dimension of lamellae (12nm). The inescapable conclusion was that chains must fold back on themselves repetitively at each crystal surface alternately, a phenomenon known as chainfolding.

The amorphous or disordered material is
assumed to lie between the fold surface of the lamellae. Lateral discontinuities between lamellae must also be considered when mechanical properties are taken into account.

Evidence for lamellae in bulk, melt crystallised polymers has accumulated mostly by comparison with the similar behaviour of solutions grown crystals using a variety of techniques; examples are small-angle x-ray scattering, thermal measurements and molecular mass measurements of chemically degraded materials, as instrumented facilities have become available.76

It is worthwhile to recognise the existence of defects in crystal polymers just as in any other poly-crystalline material. Among them are the following:

1) Point defects, such as vacant lattice sites, interstitial atoms, and chain ends;

2) Dislocations, primarily screw and edge dislocations;

3) Two dimensional imperfections;

4) Chain disorder effects; and

5) Amorphous defects, defined as large
enough to disrupt the lattice surrounding their own immediate area by forcing other atoms out of the normal lattice positions.

The effect of all these defects is to provide both localised amorphous regions, contributing to diffuse x-ray scattering, and deformed or distorted lattices termed paracrystalline.77

Experimental observations of the development of crystallinity in polymers are of two types; a property, such as specific volume is observed as a function of time at constant temperature, and the rate of formation and growth of spherulites is observed directly with the microscope.

Crystallinity development in polymers is not instantaneous. The time for complete crystallisation is indefinite; it is customary to define the rate of crystallisation as the inverse of the time needed to obtain one-half the total volume change. The rate increases as the temperature decreases, reaches a peak, then decreases as the molecules become less mobile, and crystallisation becomes diffusion controlled.

If data for specific volume as a function of
time during crystallisation are plotted against log time, all the curves have the same shape, and can be superimposed by a shift along the time axis. This behaviour is also typical of the crystallisation of low molecular weight substances, and curves of this type can be fitted with an equation due to Avrami:

\[ \ln \left( \frac{V_\infty - V_t}{V_\infty - V_0} \right) = -\left(\frac{1}{W_C}\right) k t^n \]

where \( V_\infty, V_t \) and \( V_0 \) are specific volumes at the times indicated in the subscripts, \( W_C \) is the weight fractions of material crystallised, \( k \) is a constant describing the rate of crystallisation, and \( n \) is an exponent varying with the type of nucleation and growth process.

Quantitative aspects of the Avrami equation are not completely satisfactory; it is not always possible to determine \( n \) or to ascertain whether \( n \) is constant throughout the crystallisation process; and it is generally found that crystallisation continues in polymer systems for much longer than the equation predicts.

The disappearance of a polymer crystalline phase at the melting point is accompanied by changes in physical properties: the material becomes a viscous liquid, with discontinuous
changes in density, refractive index, heat capacity, transparency, and other properties. Measurement of any of these properties may be used to detect the crystalline melting point, $T_m$. Polymers exhibit melting ranges, and the value of the crystalline melting point may be determined by the sensitivity of the method used.

Almost all measurements of $T_m$ are made by differential thermal analysis. Other methods that could be used to detect $T_m$ are x-ray diffraction, and infrared and NMR spectroscopy.

Small crystals will tend to melt at lower temperatures than large ones due to a higher surface free energy of small crystallites. The temperature interval for fusion decreases with increasing molecular weight, and also it broadens with increasing breadth of molecular weight distribution.

The crystallinity of a material may be given in terms of $\rho$, $\rho_c$, and $\rho_a$, the densities of the bulk, crystalline, and amorphous material respectively.

\[
\begin{align*}
\text{Total volume } V &= V_c + V_a \\
\text{Total weight } W &= W_c + W_a \\
\text{Crystalline fraction by weight,}
\end{align*}
\]
\[
X_c = \frac{W_c}{W} = \frac{P_c \cdot V_c}{P \cdot V} \quad (1)
\]

but \( \frac{V_c}{V} = 1 - \frac{V_a}{V} \quad (2) \)

also \( P \cdot V = P_c \cdot V_c + P_a \cdot V_a \)

whence \( \frac{V_a}{V} = \frac{1}{P_a} (P - P_c \cdot \frac{V_c}{V}) \quad (3) \)

Combining (2) and (3) and solving for \( \frac{V_c}{V} \)
\[
\frac{V_c}{V} = \frac{P_c}{P} \left( \frac{1}{P_a} - \frac{P_c}{P_a} \right)
\]

This method relies on \( P_a \) being independent of size of amorphous regions and of orientation; \( P_a \) is very difficult to measure with some materials.

When a polymer is subjected to an external stress, it undergoes a rearrangement of the crystalline material. Changes in the x-ray diffraction pattern suggest that the polymer chains align in the direction of applied stress and a shish kebab morphology may form. If a polymer was highly crystalline before orientation, there will not be a large subsequent increase in crystallinity; however, polymers of low crystallinity may become significantly more crystalline.

3.3.4. Effect of Crystallinity on Properties

The level of crystallinity in polymers affects many properties. An increase in crystallinity increases modulus (stiffness), and yield strength, but tends to make a plastic more brittle. Stiffness and yield stress are relatively independent of
molecular weight and can be expressed as single valued functions of degree of crystallinity. The degree of crystallinity decreases with temperature during approach to the melting temperature ($T_m$); stiffness and yield stress decrease correspondingly. The factors often set limits on the temperature at which a plastic is useful for mechanical purposes.

Impact behaviour of a polymer is determined by the relation between the yield stress and the tensile strength in brittle failure (or brittle strength). If the yield stress or strength is lower than the brittle strength then the polymer is tough at the given level of strain rate. If the brittle strength is lower, brittle failure takes place on impact.

The major effect of a crystallite in a sample is to act as a cross link in the polymer matrix. This makes the polymer behave as if it was a cross linked network, but as the crystallite anchoring points are thermally labile, they are destroyed as the temperature approaches the melting temperature, and the material undergoes a progressive change in structure beyond $T_m$, when it is molten. Thus crystallinity has been aptly described by Bawn\textsuperscript{78} as a form of 'thermoreversible crosslinking'.
Crystallinity decreases the solubility of polymers markedly; properties related to solubility are often functions of crystallinity, relatively independent of molecular weight. Permeability, the product of solubility and diffusivity, is similarly dependent on crystallinity.

3.3.5. Microstructural Interfaces

Large blow moulding systems classically incorporate a chilled mould to reduce cycle time. For a crystalline polymer, e.g. HDPE, contact time with the cold mould results in a quenched layer of polymer of lower crystallinity and different texture compared with the bulk of the moulding. The morphological interface between these two regions, some 150 - 200 μm inside the moulding, has been found to form a weak point for failure by a variety of tests.

A low mould temperature (6°C) was found to lead to low crystallinity near the outside wall compared with uniform crystallinity across the wall thickness for a half bottle made using a 40°C mould (see figure 3.4.). Brittle impact strength and yield stress were found to be approximately maximum at 40°C mould temperature (see figure 3.5.).

The use of a warm mould at 40°C was found to
FIGURE 3.4.

Outside Impact Strength (J) as a Function of Mould Temperature

Brittle Impact Strength
Yield Stress

FIGURE 3.5.
produce a moulding with no quench zone and therefore no interface. The presence of a microstructural interface is more damaging, potentially, than the presence of a zone of different crystallinity and texture. When under stress, different elastic characteristics of each phase dictate that the stress system at the interface is complex (usually involving shear) and may lead to delamination, e.g. under thermal cycling. Internal cooling by forced air circulation has been shown to increase the cooling rate, and thus allow the use of a warm mould economically. For thick mouldings (>4mm) cooled in a warm and forced air cooling, no significant increase in cycle time is found, theoretically or in practice over that for a chilled mould with forced air cooling, provided that the mould is opened immediately after the internal surface is crystallised.79,80

Using simple heat transfer considerations, an increase in cooling time would be inevitable for an increased heat sink (mould) temperature; the lower crystallinity region, however, produced as a consequence of low mould temperature, has reduced thermal conductivity (reduced by lower crystallinity); this will compensate the higher mould temperature to an unknown extent.
Use of a warm mould (40°C) allows the manufacture of blow mouldings that are free from elastic strain. Products made using a higher mould temperature will be less distorted.
CHAPTER 4

4. EXPERIMENTAL MATERIALS AND METHODS

4.1. Materials

The three main materials used were linear high density polyethylenes with high molecular weights; namely Rigidex H060-45P (BP Chemicals), Lupolen 4261-A (BASF), and Marlex MS 201 A (TPI France). Data for the polymers were obtained from their respective suppliers. Rigidex H060-45P is

<table>
<thead>
<tr>
<th>TABLE 4.1. Materials Used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melt Flow Index (MFI)</strong></td>
</tr>
<tr>
<td><strong>(21.6 kg load) at 190°C</strong></td>
</tr>
<tr>
<td>Units</td>
</tr>
<tr>
<td>Rigidex HD60-45P</td>
</tr>
<tr>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td>Marlex MS 201 A</td>
</tr>
<tr>
<td>Rigidex 002-55</td>
</tr>
</tbody>
</table>
TABLE 4.2. Use of Materials in Experimental Work

<table>
<thead>
<tr>
<th>Product</th>
<th>Use of Material</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Half Bottles</td>
<td>Impact Testing</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td>Peugeot</td>
<td>General</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td>Talbot 309</td>
<td>Investigation</td>
<td>(Diesel)</td>
</tr>
<tr>
<td>Fuel Tanks</td>
<td></td>
<td>Marlex MS 201A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Petrol)</td>
</tr>
<tr>
<td>Ford Triton Fuel Tank</td>
<td>General</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td></td>
<td>Investigation</td>
<td>Rigidex HD60-45P</td>
</tr>
<tr>
<td>Ford Sierra Fuel Tank</td>
<td>General</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td></td>
<td>Investigation</td>
<td>and Rigidex HD60-45P</td>
</tr>
<tr>
<td>International Harvester</td>
<td>General</td>
<td>Rigidex HD60-45P</td>
</tr>
<tr>
<td>Fuel Tanks</td>
<td>Investigation</td>
<td></td>
</tr>
<tr>
<td>Welded</td>
<td>Hot Plate</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td>Tensile Bars</td>
<td>Welding</td>
<td>and Rigidex HD60-45P</td>
</tr>
<tr>
<td>Black Chemical Container</td>
<td>Welding</td>
<td>Rigidex HD60-45P</td>
</tr>
<tr>
<td></td>
<td>Investigation</td>
<td></td>
</tr>
<tr>
<td>25 Litre Chemical Container</td>
<td>Failure</td>
<td>Rigidex 002-55</td>
</tr>
<tr>
<td></td>
<td>Analysis</td>
<td></td>
</tr>
<tr>
<td>Injection Moulded Specimens</td>
<td>Petrol</td>
<td>Lupolen 4261-A</td>
</tr>
<tr>
<td></td>
<td>Immersion</td>
<td></td>
</tr>
</tbody>
</table>
a copolymer, and consequently has a lower density than the corresponding homopolymer; Rigidex copolymers have slightly lower rigidity, tensile strength, and resistance to elevated temperatures than the homopolymers. They are designed for use in applications where the maximum resistance to stress cracking is required.

A minor material used was HDPE Rigidex 002-55; the information for this was also supplied by the manufacturer.

4.2. Work on Half Bottles

Half bottles were blow moulded using a modified blow moulder; this rig allowed monitoring of the temperature on the inside and mould-side of the blow moulding during production (see figure 4.2.1.); mould temperatures were controlled: high was 55°C, intermediate temperatures were 33°C and 46.5°C, and the lowest was 10°C. All other variables were kept constant: melt temperature at 210°C; cooling time at 180 sec. The material used was HDPE Lupolen (BASF 4261-A). Three bottles were produced at each temperature.

Further work included changing internal cooling from static to 700 litres a minute \((1.7 \times 10^{-2} \text{ m}^3/\text{s})\); mould temperature was kept constant at 30°C. Three half bottles were produced at each circulation rate (static, 160 litres/min = \(2.67 \times 10^{-3} \text{ m}^3/\text{s}\) and 700 litres/min = \(1.17 \times 10^{-2} \text{ m}^3/\text{sec}\).
FIGURE 4.2.1. MOULD FOR HALF BOTTLE

Mould for half-bottle formation.
Specimens for impact testing were cut from areas on the curved surface of the half bottles; the specimen size was approximately 50 mm square, and the specimen was struck on the outer (mould side) surface. About 8 specimens could be obtained from each half bottle. The diameter of the indentor used was 20 mm. The details of the impact testing, using a Rosand Instrumented Falling Weight Tester are given later in this chapter (4.4.1.).

Results were compared using a t-test for two independent means; also used was the GENSTAT statistical program on the Multics computer (see Appendix 1 on the treatment of results).

Initially, two conditions were compared: high mould temperature (55°C) with low mould temperature (10°C). The first set of results represents this comparison. Later on, the rest of the data were included to investigate the nature of the relationship between mould temperature and impact peak force; it was not certain whether the relation was a peak effect or correlation. Finally, the effect of air circulation on peak force was investigated.

The screw extruder used for producing the half bottles consists of a screw rotating in the heated barrel or cylinder; plastic pellets are fed from the feed hopper through the feed throat into the channel of a screw (see figure 4.2.2.). The screw rotates in the barrel and conveys plastic forward for melting and delivery. A drive motor provides the power for
the controlled rotation of the screw, which can vary from 0 - 120 rpm. The mechanical motor is connected to the main drive shaft of the extruder with flexible coupling to ensure uniformity in rotational speed. The speed of the screw is an important variable; it controls the movement of material and heat generated by friction. The screw is divided into three zones: the feed section, which conveys polymer pellets forward in the solid state; the transition zone, where pressure compression and melting occur; and the metering section, which develops pressure, and controls the uniformity of the output rate. The ratio of the feed depth to metering flight depth (compression ratio) is approximately 3 : 1. The screw has a constant flight pitch with L/D ratio (barrel length/barrel diameter) of 25 : 1.

The die used is a fishtail or coathanger.24,81,82 This die changes the shape of the flow channel from cylindrical to that of a flat sheet (see figure 4.2.3.). The function of the die is to produce an extrudate of the required dimensions; also back pressure develops in the extruder. The inside surfaces of the flow channel, the fish tail and the distributing section were smoothed to prevent accumulation (and eventually degradation) of the plastic flowing over these surfaces.83

The breaker plate produced enough pressure in the screw of the extruder to enable the material to be well mixed. Its thickness was 40% of the barrel diameter (which was 3.81 cm) and it was drilled with
FIGURE 4.2.3.

DIE HEAD ARRANGEMENT FOR FLAT SHEET EXTRUSION
4.7 mm diameter holes. The holes were counter sunk to avoid 'dead spots' between them. The spiral flow pattern from the screw end was broken up with the breaker plate.

The start up procedure was as follows:

1) the cooling water supply for the extruder was turned on;

2) the extruder and die heaters were set to give the required temperature, and three hours were allowed for warming up;

3) any condensation in the air filter was drained, then the air supply was turned on, and the pressure regulator adjusted to give the required blow pressure; and

4) the cooling water supply for the mould was turned on, and the flow rate adjusted as required.

The following describes an experimental run.

1) The Data Transfer Unit (DTU) was set to record the thermocouple output of mould temperature and air temperature at predetermined time intervals. These data were recorded.

2) The pyrometer and the chart recorder were
switched on.

3) The extruder motor was started, and the screw speed set for the required extrusion rate.

4) Once the sheet of the required length had been formed, the extruder motor was disengaged with an external footswitch.

5) The toggles to lock the mould into place were set; the sheet trapped between the mould halves.

6) The air supply for sheet inflation was started, and the stopwatch started.

7) Steps 3 - 6 were repeated, using mould temperatures of 10°C, 33°C, 46.5°C, and 55°C; also at constant mould temperature (30°C), with varying internal air circulation rate at three levels (static, 160 litres/min = 2.67 x 10^{-3} m^3/s, and 700 litres/min = 1.17 x 10^{-2} m^3/s).

4.3. **Welding**

Hot plate welding was used to join HDPE injection moulded tensile bars (Lupolen 4261-A and Rigidex H060-45P) and an extruded sheet (Rigidex H060-45P). A simple welding rig was used, without using stops.

The procedure for the welding operation was as
follows.

1) Tensile bars were cut into two equal halves; the rough surfaces were polished to a smooth surface, and cleaned with acetone.

2) Having loaded the jig with the prepared specimen, the weights required to give the desired loading pressures were prepared.

3) The tensile bars, in the rig, were aligned, and the clock started.

4) The two ends of the tensile bars were brought into contact with the hot plate for a specified time.

5) The upper clamp was raised and the hot plate was withdrawn, and simultaneously, the two bar ends were brought into contact under the welding pressure (this occurred within 3 seconds).

6) After a specified welding time, the weights were removed and the assembly was allowed to cool down to room temperature.

4.4. Testing Methods

4.4.1. Impact Testing

Plastics fuel tanks must pass several tests
in order to be legal in this country; amongst these is a sub-zero temperature impact test. Impact properties of plastics fuel tanks are given a high priority in this thesis. The following section is a summary of the use of instrumented falling weight impact testing to date.

Instrumented falling weight impact testers have been developed recently. Other research on impact testing is reported in the literature.

Turner et al. used injection moulded plates of HDPE (Rigidex 075-60N) to observe the effect of geometry on impact properties. Specimens were freely supported on a raised ring, 40 mm internal diameter, and impacted at the centre by a striker with a hemispherical end of diameter 20 mm. The apparatus used was a CEAST Advance Fractoscope System MKS, the primary output of which is force versus time (which may be integrated into energy), velocity and displacement as functions of time, and force as a function of displacement. The operating temperature was approximately 21°C.

Turner et al. remark on the association between the force-time graphical output and the type of failure observed: in the Rigidex 075-60N an undersized hole is formed upon
impacting; the initial peak corresponds to the tear development; a flap is left when the tear stops short of the full circle. The tail of the curve corresponds to frictional resistance and is not genuine constituent of impact energy.

Jones et al \(97\) used high speed photography technique for interpretation of the force-time curves; the first main peak was associated with crack initiation in brittle materials, and yield in ductile materials.

It seems probable that the peak force \(P\) is associated with a shear failure mechanism.\(^96\) If the rupture site coincides with the whitened rim, the shear stress will be

\[
\frac{\text{peak force}}{\text{circumferential rim area of whitened zone}} = \frac{P}{\pi Dh} \quad \text{N/mm}^2
\]

where \(h\) = thickness and \(D\) is diameter, which corresponds to the diameter of the whitened zone.

The quoted tensile yield stress used by Turner et al was 32.5 MPa, and by assuming that shear stress,
\[ \sigma_s = \sigma_y / \beta \]

where \( \sigma_y \) is tensile yield stress

\[ P/h = D.58.95.N/mm \text{ thickness} \]

Turner et al did not find that there was a truly linear relationship between peak force and thickness as predicted by this model. Peak force, gradient, energy to first peak, and energy to complete penetration were found to be proportional to thickness raised to the respective powers of 1.4, 1.3, 1.75 and 1.57. Other data from the literature show the impact energy was roughly proportional to thickness to the power 1.71 for several different polymers.\(^98,99\)

Toughness determination in plastics is used for tasks ranging from quality control to detailed research.\(^100\) It has been found that an instrumented falling weight method has advantages over others and that the instrumented version giving a record of the force and deflection during impact would be advantageous.

Two reasons are responsible for recent research activity in this field:

1) relatively inexpensive to process large amounts of data using a dedicated
computer system; and

2) the technical understanding of toughness in thermoplastics remains imperfect.

In the falling weight type impact tester, impact energy is transferred to the specimen by a free, but guided, fall of an impactor nose, coupled to a force transducer. Energy is determined by $mg\cdot h$ and impact velocity is $(2gh)^{0.5}$ where $m =$ impact mass, $g =$ acceleration due to gravity, and $h$ is drop height. The equipment is commonly used as an excess energy device, and it can be shown that when the available energy is five times the energy absorbed by the specimen, the retardation of the impactor during impact is negligible.

A transient recorder is triggered by the falling nose just prior to impact: force-time data during deformation and fracture are stored (see figure 4.4.1.); the excess energy condition allows these data to be transformed into force-deflection data because time will be proportional to deflection of a specimen. The force-deflection data may be graphically displayed on an oscilloscope screen and passed to a dedicated computer system for analysis. Transfer of data to a larger computer database is advantageous where data
FIGURE 4.4.1. INSTRUMENTED FALLING WEIGHT IMPACT TESTER
can be statistically analysed.

The available types of machine cover a large range of test speeds. The energy ranges are up to about 10 joules, 40 to 130 joules, and up to 600 joules; these achieve practical impact speeds in respective ranges 1 to 3 m/s, 2 to 5 m/s, and 2 to 7 m/s.

Impact tests are carried out over a wide range of temperatures; some of the apparatus is constructed with an environmental chamber, which allows choice of temperature in the range -100°C to +100°C.

Testing, in this work, was carried out using a Rosand Falling Weight Impact Tester; this was especially useful since it had a wide range of operational variables, and output could be stored and analysed to extract relevant information.

When the striker did not completely penetrate the specimen, the measurements were regarded as invalid; any such results obtained were set aside. The calculations rely on small change in velocity during impact. Velocity at impact was estimated using a simple motion equation: \( v^2 = u^2 + 2as \) (\( v = \) final velocity, \( u = \) initial velocity, \( a = \) acceleration due to gravity, \( s = \) distance). Velocity, as the striker approached the specimen, was
monitored by sensors, and calculated accurately.

Peak force, energy to the peak, and total failure energy were noted for each specimen; mass of striker was 25 kg; velocity at impact was 4 m/s. \(\text{(Test temp. } = 23^\circ\text{C)}\)

Specimens for impact testing were cut from areas on the blow moulding; the specimen size was approximately 50 mm square, and the specimen was impact tested on the outer (mould side) surface; thickness measurements were made as near as possible to the point of penetration. The striker used had a semi-circular end with diameter of 20 mm.

4.4.2. Thickness Distributions

Thickness measurements of fuel tanks were usually made at 10 mm intervals, using callipers; measurements were in mm to one decimal place. Thickness distribution plots using 0.5 mm class interval widths.

4.4.3. Etching and Microscopy Techniques

Etching was used to highlight structural features in specimens taken from the fuel tank walls (see Chapter 6). The specimens were then observed under a scanning electron microscope.
Two techniques have transformed the possibilities of investigating melt crystallised morphologies with the electron microscope: these are chlorosulphonation and permanganic etching. The latter was used in the experimental work as it was less hazardous to perform. Etchants may be nitric acid, but this tends to be too strong a treatment. A weaker acid, however, was used comprising potassium permanganate dissolved in sulphuric acid to a concentration of 5%. The specimen was etched at 70°C for an hour, cleaned, and then gold coated (to increase contrast) before observation in the electron microscope. The etchant removes 1 to 2 µm selectively from polyethylene in typical treatments. It attacks interlamellar material preferentially, but does not penetrate too far into the specimen. The sample is not embrittled and can be handled relatively easily.

The specimens that were etched were from the fuel tanks, while welded tensile bars were observed using the light microscope between crossed polars (to show orientation). The carbon black pigmented fuel tanks and associated welds were not easily observed using a light microscope.

The following describes the procedure used for hot stage microscopy in Chapter 8.
The equipment used included a Mettler hot stage and temperature controller, and a Reichert Biovar microscope, with crossed polars, and a plan 10 times objective lens.

A thin section of about 8 micrometres was microtomed and placed on a half slide with a cover slip and placed on the hot stage.

The hot stage was initially at 70°C; the temperature was increased at 3°C a minute to 150°C; decreased again to 100°C at the same rate; the sample was observed continuously.

4.4.4. Melt Flow Index Measurements

Study of the flow behaviour of molten polymers is essential to establish the feasibility of any process involving melting. An ideal test would predict thermal stability, ease of processing, and quality of mouldings. Processibility can be controlled by altering parameters such as average molecular weight and molecular weight distribution of polymer, and by incorporating various types of quantities of plasticisers, lubricants, and stabilisers.\cite{102}

Detailed consideration of flow behaviour of polymers is a science in itself: Bernhardt,\cite{24} for instance, studies the subject in relation to common processing
techniques, while Cogswell provides a comprehensive study of modern concepts of the subject as a whole.

Brydson, Paul, and Wissbrun have carried out studies of the rheological properties of polymer melts, and their relationship to processibility.

The determination of melt flow index (MFI) is one of the most widely used tests for flow characterisation in thermoplastic materials. The test exists in a number of variants according to polymer type and molecular weight. Although widely used, the test has limitations; while it is of particular value as a control test on thermoplastics having relatively low melt viscosities, it does not necessarily indicate uniformity of other properties of polymers of the same type, but made by other manufacturers, nor is MFI a fundamental polymer property.

In method 720A of BS2782 (1979), three variants are described corresponding to ISO R292 (1967). These two standards refer specifically to 'The Determination of Melt Flow Index of Thermoplastics'.

The principle employed is that of determining the rate of flow of molten polymer through a closely defined extrusion plastometer.
The procedure used in the experimental work for testing of MFI was as follows. The cylinder, piston and die were kept thoroughly cleaned by treatment with solvents and wiping with lint-free cloths. The cylinder was maintained at 190°C for 15 minutes, and then charged with between 4 and 8g of sample (in less than a minute) and the unloaded piston reinserted. Four minutes later, the weight was added and molten material began to extrude through the die. The rate of extrusion was measured by cutting off the extrudate every two minutes. Several such cut-offs were taken up to 15 minutes after insertion of the sample, and these all had to be taken when the piston head was between 50 mm and 20 mm above the upper end of the die (as marked by lines on the piston). The first cut off, and any containing bubbles, were discarded; the remainder (at least 3) were weighed, and the average mass was calculated. The highest and lowest sample masses had to be within specified tolerances, otherwise the result was discarded, and a further test was performed on a fresh portion of the material. The melt flow index was calculated as the weight (g) extruded in a reference time (600 seconds).

4.4.5. Measurement of Density

The determination of the density of solid
plastics is detailed in ISO R1183 (1970),\textsuperscript{108} which gives four methods according to the nature of the plastics materials. The British equivalents are contained in BS2782, methods 620A and 620E (1980),\textsuperscript{109} which closely follows the present ISO format. American standards are to be found in ASTM D792 (1966)\textsuperscript{110} and D1505 (1968).\textsuperscript{111}

Method D of ISO R1183 is the Density Gradient Method. It is suitable for sheet, rod, tube, and moulded articles, the density being determined at one of the standard laboratory temperatures of 20°C, 23°C, and 27°C (23°C was used in this work).

A specimen that had smooth surfaces, and was free from crevices was cleaned and placed in a small bottle of the denser of the two solutions, which were used to make up the density column. The two solutions were made from isopropanol and water, the latter being denser.

1 litre of solution B was placed in vessel 2, and one litre of solution A in vessel 1 (see figure 4.4.2.) with the taps kept closed.

The magnetic stirrer was started in vessel 1; this agitated enough to mix but not as much as to form bubbles; the connecting tap was opened, and the denser solution started to
FIGURE 4.4.2.

DENSITY COLUMN
flow into the vessel containing the less dense solution. After hydrostatic equilibrium had been achieved, the right hand tap was adjusted so as to allow a column to be filled in about 2 hours. Finally the filling tube, with the upper end closed, was removed carefully and slowly (see also Payne and Stephenson).112

The density range achieved in the column was 920 - 960 kg/m³. The temperature was controlled accurately at 23°C. The mixed liquids had no effect on the materials under test, were transparent, of low volatility, and low viscosity. The tube was calibrated with spherical glass floats, about 5 mm in diameter, the densities of which had been previously measured.

At least 24 hours after the floats were gently lowered into the column, the height of each above a reference level was determined with a cathetometer. The measured heights were plotted against density, and a smooth curve without discontinuities resulted.

At least two specimens of the material to be tested were cut into identifiable shapes, and lowered carefully into the column; after at least 1 hour, the height of the centre of gravity of each specimen was measured; the corresponding density was arrived at using
the calibration plot.

The clearing of the column was performed using a wire gauze basket, drawn upwards through the column at a uniform rate not exceeding 10 mm/min, after which the basket was returned to the bottom of the column, which was the recalibrated.\textsuperscript{102, 113}

4.4.6. Tensile Testing

Tensile testing was carried out on JJ tensile testing machines at room temperature (23°C), and at 40 mm/min extension rate. The stress to yield (or brittle failure) was noted in MN/m\(^2\).

4.4.7. Thermal Analysis

Part A describes the procedure used in Chapter 7 for investigation of thermal oxidative stability: Part B is the procedure used in Chapter 8 for ascertaining which materials were present, and their quantities.

A) The following describes the procedure used to ascertain thermal oxidative stability of materials with relation to welding.

A 10 - 15 mg sample was heated in a DSC cell at 10°C a minute under nitrogen.
When the temperature reached 200°C, an air flow was substituted for the nitrogen, and timing on the chart started. The onset of oxidation was recorded as an exothermic departure from the base line as the oxidation reaction set in (the sample being maintained at 200°C).

B) The Differential Scanning Calorimeter (DSC) was used to determine the melting points of crystalline species present, as well as the location of the crystallisation peaks. Baselines were approximated and the size of the peaks were calculated; quantities of materials present were estimated. The procedure was as follows: the specimen was weighed to as near to 15 mg as possible, and placed in a pan lid, and then into the cell, which was then covered. The cooling attachment (MCA) was clamped into place on the cell, and also covered. The MCA was switched on 10 minutes beforehand to enable it to be used.

The initial rate of increase of temperature was 10°C per minute up to 200°C. The pen sensitivity was set to 10 mV/cm.
The test was commenced and when 200°C was reached, it was held for five minutes at this limit. The instrument was set to cool at 5°C per minute to 0°C; it was then heated up again to 200°C at 10°C a minute.

The second heating was carried out to clarify the definition of melting peaks.
5. WORK ON HALF BOTTLES

5.1. Experimental Method

5.1.1. General

In blow moulding the use of a warm mould at 40°C has been found to produce a moulding with no quench zone, and therefore no morphological interface, with better mechanical properties than a moulding produced with a mould temperature of 10°C. Improved internal cooling by forced air circulation has been shown to increase the cooling rate, and thus allow the use of a warm mould economically. For thick mouldings (>4mm) cooled in a warm mould, and forced air cooling, no significant increase in cycle time has been reported, theoretically or in practice over that for a chilled mould with forced air cooling, provided that the mould is opened immediately after the internal surface is crystallised.

This work examines the effect of changing mould temperature on impact properties of blow moulded half bottles; low mould temperatures should lead to a weaker product owing to the quenching effect (details of...
impact testing are given in section 4.4.1. It is suggested that higher mould temperatures do not lead to significantly longer cooling times; slight increases may be offset by circulating internal cooling medium.

Calculation of cooling behaviour was carried out using a blow moulding model developed at Bradford University by Edwards et al.\textsuperscript{45} Cooling times could then be predicted as a function of air circulation rate and mould temperature, other parameters being kept constant. Contour plots for predicted cooling times and impact peak force dependent on the two given variables may be evaluated; optimum conditions can then be chosen.

Half bottles were blow moulded using a modified blow moulder (see section 4.2.); this rig allowed monitoring of the temperature on the inside and mould-side of the blow moulding during production mould temperatures were controlled (from 10°C to 55°C). All other variables were kept constant: melt temperature at 210°C; cooling time at 180 sec. The material used was HDPE Lupolen (BASF 4261-A). (See section 4.2.)
5.1.2. **Effect of Air Flow Rate and Mould Temperature on Cooling**

Bradford University's cooling model\textsuperscript{45} was used to predict the effect of air flow rate and mould temperature, during blow moulding, on the cooling time (see Appendix 2).

Sixteen calculations were made, with the following variables kept constant:

- Parison temperature 210°C
- Polymer thickness 5 mm
- In the mould cooling time 180 seconds
- Ambient air temperature 23°C
- Ambient air heat transfer coefficient 5 W/m\textsuperscript{2}K. (for natural convection)

Four mould temperatures (0, 20, 40 and 60°C) at four air flow rates (160, 200, 250 and 300 litres a minute) represented the conditions for the sixteen calculations. The flow rates had been chosen following work carried out at Bradford University by Georghiades.\textsuperscript{45} Above 300 L/min, the heat transfer coefficient was shown to remain constant. The following heat transfer coefficients were used, corresponding to the above air flow rates respectively: 30, 45, 60 and 66 W/m\textsuperscript{2}K.

Present work at Bradford, using higher flow pressures (6.6 bar as opposed to 2.8 bar used by Georghiades) suggests that the values of
heat transfer coefficients used in these calculations may be slightly low.

The output of the calculations (see Appendix 3) was examined; the time taken for the polymer (in theory) to reach complete crystallisation from 210°C was approximated for each graph (time to change in slope). This time was thought to closely represent that at which mouldings could safely be removed from the mould without distortion. A contour plot of this cooling time as a function of air flow rate and mould temperature was drawn; further, an equation was fitted to this contour plot so that points beyond the given variable limited could be extrapolated, and tested for accuracy.

5.2. Results

5.2.1. Comparison of Impact Properties Between High and Low Mould Temperature Specimens

Total energy to failure was found to change significantly with changing mould temperature: a higher mould temperature resulted in a higher total energy to failure.

For a 10°C mould temperature, the mean failure energy was 132.3 J; mean failure energy of specimens made with mould
temperature at 55°C was 159.3 J; mean thicknesses were 6.55 and 5.39 mm respectively.

Table 5.1. Showing Data Obtained from Impact Testing at High and Low Mould Temperatures.

<table>
<thead>
<tr>
<th>THICKNESS, MM</th>
<th>TEMP, C (MOULD)</th>
<th>FORCE, N</th>
<th>ENERGY TO PEAK, J</th>
<th>FAILURE ENERGY, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>10</td>
<td>6164</td>
<td>60.4</td>
<td>122.5</td>
</tr>
<tr>
<td>5.7</td>
<td>10</td>
<td>4020</td>
<td>36.2</td>
<td>65.6</td>
</tr>
<tr>
<td>6.1</td>
<td>10</td>
<td>5944</td>
<td>65.4</td>
<td>97.4</td>
</tr>
<tr>
<td>6.3</td>
<td>10</td>
<td>7145</td>
<td>71.7</td>
<td>133.1</td>
</tr>
<tr>
<td>6.4</td>
<td>10</td>
<td>7429</td>
<td>82.0</td>
<td>146.0</td>
</tr>
<tr>
<td>6.4</td>
<td>10</td>
<td>7214</td>
<td>73.6</td>
<td>132.6</td>
</tr>
<tr>
<td>6.5</td>
<td>10</td>
<td>7717</td>
<td>75.5</td>
<td>136.4</td>
</tr>
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<td>10</td>
<td>7243</td>
<td>73.7</td>
<td>152.0</td>
</tr>
<tr>
<td>6.8</td>
<td>10</td>
<td>5866</td>
<td>57.1</td>
<td>116.6</td>
</tr>
<tr>
<td>7.8</td>
<td>10</td>
<td>8039</td>
<td>73.3</td>
<td>176.2</td>
</tr>
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<td>10</td>
<td>8860</td>
<td>85.4</td>
<td>176.4</td>
</tr>
<tr>
<td>3.3</td>
<td>55</td>
<td>6232</td>
<td>67.4</td>
<td>114.1</td>
</tr>
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<td>55</td>
<td>6774</td>
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<td>55</td>
<td>6984</td>
<td>72.7</td>
<td>148.9</td>
</tr>
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<td>80.3</td>
<td>144.2</td>
</tr>
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<td>4.7</td>
<td>55</td>
<td>6056</td>
<td>54.1</td>
<td>103.3</td>
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<td>5.2</td>
<td>55</td>
<td>6921</td>
<td>63.6</td>
<td>219.3</td>
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<tr>
<td>5.6</td>
<td>55</td>
<td>7658</td>
<td>74.3</td>
<td>148.3</td>
</tr>
<tr>
<td>6.6</td>
<td>55</td>
<td>6955</td>
<td>76.9</td>
<td>153.7</td>
</tr>
<tr>
<td>6.7</td>
<td>55</td>
<td>9641</td>
<td>97.7</td>
<td>217.9</td>
</tr>
<tr>
<td>7.0</td>
<td>55</td>
<td>8547</td>
<td>96.1</td>
<td>191.9</td>
</tr>
<tr>
<td>7.1</td>
<td>55</td>
<td>8093</td>
<td>86.7</td>
<td>168.3</td>
</tr>
<tr>
<td>7.7</td>
<td>55</td>
<td>10300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.8</td>
<td>55</td>
<td>10460</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The calculated t-value for energy means was 1.81; 5% significance value for 20 degrees of freedom is 1.73; calculated value > 5% significance value; the null hypothesis can be rejected that results have arisen purely by chance; it is highly likely that mould temperature affects failure energy; a higher mould temperature leads to a higher failure energy.

5.2.2. Effect of Thickness and Mould Temperature on Peak Force

Thickness, temperature and force values for static internal cooling were processed using GENSTAT; this suggested that the force was proportional to the square root of thickness; this relationship was used in further processing and an equation for force as function of temperature and square root of thickness was arrived at; the effect of temperature was found to be significant (using 0.1% F-distribution tables); the usual significance level used is much less stringent at 5%.

The following is the summary of output from the GENSTAT program (which was used to fit peak force as a function of thickness and mould temperature).
### Regression Coefficients

<table>
<thead>
<tr>
<th>Y-VARIATE</th>
<th>Standard Estimate</th>
<th>Standard Error</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>-3261.298</td>
<td>972.541</td>
<td>-3.35</td>
</tr>
<tr>
<td>square root thick</td>
<td>3908.788</td>
<td>387.260</td>
<td>10.09</td>
</tr>
<tr>
<td>temp</td>
<td>34.180</td>
<td>7.200</td>
<td>4.75</td>
</tr>
</tbody>
</table>

Calculated formula for force as function of thickness and temperature:

\[
\text{force, N} = 3908.8 \times (\text{thickness, mm})^{0.5} + 34.2. \\
(\text{temperature, °C}) - 3261.3
\]

The F-value, indicating significance of effect of mould temperature on peak force, is obtained from the analysis of variance table on the following page; the CHANGE in mean squares (MS) is divided by the corresponding residual.

\[
F = \frac{17470582}{775296} = 22.5
\]

For an F distribution with \(v_1 = 1\), \(v_2 = 21\) the F values at their respective significance levels are as follows: 4.35, 5%; 8.10, 1%; 14.82, 0.1%. F value calculated has to be greater than F value from table; the calculated value of 22.5 is greater than all three F values given. This means that a relationship between the temperature and the
peak energy is very probable.

*** Analysis of Variance ***

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
<td>8.249E 7</td>
<td>41243420</td>
</tr>
<tr>
<td>RESIDUAL</td>
<td>6.435E 7</td>
<td>775296</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1.468E 8</td>
<td>1727487</td>
</tr>
<tr>
<td>CHANGE</td>
<td>-1.747E 7</td>
<td>17470582</td>
</tr>
</tbody>
</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 55.1

DF is degrees of freedom, SS is sum of squares (related to variance) and MS is SS/DF.

Also the following equations were fitted (see Appendix 3):

peak energy, $J = 39.7 \cdot (\text{thickness, mm})^{0.5} + 0.36 \cdot (\text{temp, } ^\circ \text{C}) - 30.25$

failure energy, $J = 82.0 \cdot (\text{thickness, mm})^{0.5} + 1.1 \cdot (\text{temp, } ^\circ \text{C}) - 80.6$

Air circulation rate was shown to have no significant effect on impact properties within the range used (0 to 700 litres a minute).

Figure 5.1 - 5.4 are output graphs from the Rosand impact tester; these show the effect
FIGURE 5.1
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 0
Sample: HDPE18
Details: G
Date: 25/04/86
Time: 11:38:36
Mass: 25 Kg
Temp: 20°C

Half Bottle; Mould Temperature 10°C,
Thickness 6.1 mm

PEAK INFORMATION
Force=5944. N
Deflection=0.013 m
Energy=36.46 J

FAILURE INFORMATION
Deflection=0.029 m
Energy=97.38 J

N  Force-Distance
ROSAND INSTRUMENTS IMPACT TEST SYSTEM

Drive: 1
Sample: HDPE15
Details: E
Date: 21/05/86
Time: 10:07:32
Mass: 25Kg
Temp: 20°C
Half Bottle; Mould Temperature 33°C,
Thickness 5.9 mm

PEAK INFORMATION
Force=6559. N
Deflection=0.028 m
Energy=75.56 J

FAILURE INFORMATION
Deflection=0.042 m
Energy=136.0 J

---

*Figure 5.2*
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: HDPE10
Details: B
Date: 20/05/86
Time: 09:53:18
Mass: 25Kg
Temp: 20'C

PEAK INFORMATION
Force=7199. N
Deflection=29.16 mm
Energy=83.19 J
Gradient=15.47 KN/m

FAILuRE INFORMATION
Deflection=45.76 mm
Energy=153.3 J

Half Bottle; Mould Temperature 46.5°C,
Thickness 5.8 mm
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: HDPE2
Details: D
Date: 28/04/86
Time: 08:56:34
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=7658. N
Deflection=0.019 m
Energy=74.25 J

FAILRE INFORMATION
Deflection=0.037 m
Energy=148.3 J

Half Bottle; Mould Temperature 55°C,
Thickness 5.6 mm
of mould temperature on the shape of the curve. Generally, the failure mode of each specimen was consistent; a tear was formed that made a partial ring, the material yielded, corresponding to the peak on the force-distance graph; a tab was formed, which held the circular portion formed during tearing to the main body of the specimen. The hole, now in the specimen as a result of the tearing, was smaller in dimensions than the striker body; also the striker was being pushed through the specimen after the main impact had occurred; the resulting friction was manifest in the tail of the force distance curve. This resistance energy did not contribute to the real impact strength, and was excluded when calculation of the impact properties was carried out.

Figure 5.5. and 5.6. are Rosand output graphs showing that air circulation rate has little effect on the force-distance curve.

Figure 5.7 is a contour plot for peak force (N) as a function of air flow rate (L/min) and mould temperature (°C); the weak effect of air flow rate on impact peak force (within the experimental limits) can be observed.

5.2.3. Cooling Curves

The cooling curves showed that a higher mould
FIGURE 5.5

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: HDPE23
Details: E
Date: 04/06/86
Time: 10:48:41
Mass: 25 Kg
Temp: 20°C

Half Bottle; Mould Temperature 30°C,
Thickness 5 mm, Air Circulation Rate 160 L/min

PEAK INFORMATION
Force = 6906 N
Deflection = 0.020 m
Energy = 71.21 J
Gradient = 32.52 KN/m

FAILURE INFORMATION
Deflection = 0.040 m
Energy = 143.1 J
FIGURE 5.6

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: HDPE28
Details: E
Date: 04/06/86
Time: 10:19:17
Mass: 25Kg
Temp: 20°C

Half Bottle; Mould Temperature 30°C,
Thickness 5 mm, Air Circulation Rate 700 L/min

PEAK INFORMATION
Force=6833 N
Deflection=0.022 m
Energy=71.73 J

FAILURE INFORMATION
Deflection=0.038 m
Energy=131.7 J
**FIGURE 5.7**
Contours Represent Peak Impact Force (N)

**FIGURE 5.8**
Contours are Cooling Time (Sec)
temperature led to increased cooling time; experiments with the circulation rate of the internal coolant as the variable showed that, with sufficient air circulation rate, extra cooling time arising from high mould temperature could be minimised.

5.2.4. The Cooling Model

The time to complete crystallisation from the processing temperature is shown as a function of air circulation rate and mould temperature in the contour plot (figure 5.8); this model applies only to mouldings that are 5 mm thick.

The following quadratic equation was accurately fitted to the cooling time contour plot.

\[
\text{cooling time (sec)} = 166.39 - 0.44560A + 0.86461B + 7.3359 \times 10^{-4}AA + 1.0938 \times 10^{-2}BB - 2.4763 \times 10^{-3}AB
\]

A implies that the constant should be multiplied by air flow rate (L/min); B that it should be multiplied by mould temperature (°C). This model fits the data quite well, e.g. at 160 litres/min air flow rate, and 0°C mould temperature, the given cooling time was 114 sec; the value arrived at using the
quadratic was 113.95 sec.

5.3. Discussion

The F test and analysis of variance methods used are valid and indicate a high positive correlation between temperature and peak force during impact testing. More data could have been used to obtain a more accurate equation relating force, thickness, and temperature; however, the amount of data was sufficiently large to validate a comparison of means.

The exact effect of thickness was unknown before the experiment; the program was written to find the effect of thickness on the force. The effect of both thickness and temperature on force was then examined. The force seemed to be proportional to thickness with logarithm around 0.5; this exponent value, may have been affected by mould temperature but was not investigated further. The results for peak force as a function of mould temperature and thickness raised to the power 1 are given in Appendix 3.

This exponent value (0.5), to which the thickness is raised, seems a little low. Turner et al\textsuperscript{96} found peak force, gradient, energy to first peak, and energy to complete penetration to be proportional to the thickness raised to the respective powers 1.4, 1.3, 1.75, and 1.57 (HDPE Rigidex 075-60N). The low exponent values found in this experiment may have arisen because the effect of mould temperature could have been confounding the thickness effect. Thicker
specimens often tend to embrittle more when impact tested since a higher straining rate occurs on the surface in tension. However, the trend observed was increasing impact strength with increasing thickness, at a less than linear rate showing that the pure geometric effect dominates the blow-moulded HDPE. The main aim of this particular experiment was to determine whether mould temperature affected the impact properties; a significant effect was found. Perhaps, a more accurate equation relating impact properties, mould temperature and thickness of blow mouldings could be obtained using equipment that could be well controlled; this cannot really be said about the Bradford blow moulding rig; variation of thickness between mouldings was high, and so effect of mould temperature could not be investigated independently of thickness. The thickness power of 0.5 used here, could possibly have been changed to 1 without greatly affecting the accuracy; however the independent effect of thickness is investigated later, using specimens from a Peugeot Talbot 309 tank (see Chapter 6).

The mode of failure in these HDPE Lupolen 4261-A specimens was the same as reported in the literature for HDPE Rigidex 075-60N.96 Most of the impact failures observed in the specimens were of the tearing variety; yielding corresponded to the peak on the force-distance graph. Frictional resistance at the tail of the curve arose from the hole having a smaller diameter than the striker; this resistance was not included in the impact strength.

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Those specimens not failing in the described manner were too thick for tearing to occur; only yield took place.

The points of interest concerning cooling behaviour include the following:

a) the effect of increased mould temperature on cooling time; and

b) whether internal air circulation will give higher mould temperature mouldings similar cooling times to those of mouldings manufactured with low mould temperatures.

Results have shown that air circulation does not affect impact properties significantly, within the range 0 to 700 litres a minute; this is useful to know; if impact properties had been affected, then it would possibly be a waste of time introducing internal air cooling.

The cooling model from Bradford University seemed to be sufficiently accurate, based on inspection of the cooling curves from production of the half bottles in this experiment. Figures 5.7 and 5.8. should be compared, to arrive at optimum conditions for blow moulding (a balance between low cooling time and high impact peak force). It should be noted that these contour plots apply only under the conditions of the calculation: namely, a parison temperature of 210°C,
polymer thickness 5mm, and ambient air temperature of 23°C. A good thickness distribution within the specified product is also important (impact properties were shown to be highly dependent on thickness); this would also lead to a good heat distribution and better cooling pattern in the blown parison.
6. BLOW MOULDED PLASTICS FUEL TANKS

6.1. Introduction

6.1.1. General

The following reports an investigation of several high density polyethylene fuel tanks; the problems associated with the tanks have been investigated and compared.

The Peugeot-Talbot 309 fuel tank, shown in figures 6.1 and 6.2 is now in production; the petrol tank, made in France, weighs 5.6 kg, and is made from Marlex MS 201 A; the diesel tank, manufactured by Willamot, weighs 7.14 kg, and is made from Lupolen 4261-A. Structural aspects of the tank were examined (welds together with other features of the tank) and the effect of pinch-off and thickness on impact properties was investigated. Experimental methods used are described in chapter 4.

Features of the tanks were observed under the microscope: pinch-offs; texture (a section through the wall of the tank was etched in potassium permanganate/sulphuric acid
FIGURE 6.1  PEUGEOT TALBOT 309 FUEL TANK
CR Compressed Region
PO Pinch-Off
FIGURE 6.3  FORD TRITON FUEL TANK

SECTION 2

SECTION 1(A)

SECTION 1(B)

SECTION 1(C)

PINCH-OFF

FILLER NECK AT TOP END OF TANK
solution at 70°C); welds; and pigment dispersion. Good sections of the tanks were hard to obtain owing to the filler present this problem was found with all the black fuel tanks.

A production tank (mass 7.0 kg) made by Ford for the Triton or Transit van was also analysed (made from Lupolen 4261-A): thickness distributions, texture, density, MFI values and welds were examined. (See figure 6.3)

The Ford Sierra tank, weighing 5.9 kg, was experimental; it was made from both Lupolen 4262-A and Rigidex H060-45P, a tank made of the former material was investigated.

Left hand (4.5 kg) and right hand (6.9 kg) International Harvester tanks (both Rigidex H060-45P) were in production. Thickness distributions, texture, pigment dispersion, and MFI values were investigated.

A calculation was also performed to ascertain the approximate internal air cooling flow rate needed for a 7 kg mass tank.

6.1.2 Effect of Thickness and Pinch-Off on Impact Properties

Plastics fuel tanks must pass several tests
to be acceptable (see Appendix 4); among these is an impact test. The impact behaviour of plastics fuel tanks is therefore an important area, and so it is investigated here.

Flat areas on a Peugeot Talbot 309 petrol (Marlex MS 201A) and a diesel tank (Lupolen 4261-A) were cut into sizes suitable for impact testing on a Rosand impact tester. A standard striker, with 25 kg load falling at 4 m/s was used; peak force, peak energy and failure energy were recorded (see section 4.4.1); a relationship between impact properties and thickness was fitted using GENSTAT (see appendix 1). The impact properties were fitted in the following manner:

\[ \log (\text{impact property}) = A + B \log(\text{thickness}) \]

where A and B are constants. The constant B is the exponent value by which the thickness has to be raised to be proportional to the impact property (peak force, energy to peak, failure energy).

Impact failure values for pinch-off regions were compared with those from normal areas.
6.2 Results

6.2.1 Thickness Distributions

The mean wall thickness of the Peugeot Talbot 309 petrol tank (manufactured in France) was calculated as just above 5mm; data were obtained from the sections shown in figure 6.2. Considering the angular shape of the tank, the thickness range was narrow (see figure 6.4).

The two heavier (7.14 kg) diesel tanks (manufactured by Willamot) had mean wall thicknesses of 6.0 and 6.2 mm.

The most marked change in thickness was noticed at the kiss-offs; figure 6.5 shows a cross-section through the larger kiss-off in the petrol tank. The cross-sectional area of the weld region of kiss-off was approximated at 750 mm$^2$; the least cross-sectional area of the wall of the kiss-off was much lower (estimated at 400 mm$^2$); this shows a serious imbalance; failure will occur earlier in the wall.

The Ford Triton tank (Lupolen 4261-A) was examined at sections at right angles to the long axis of the tank; this was in order to assess the amount of material in the tank as a function of distance from the top of the
Figure 6.4 Thickness Distribution on P-T Fuel Tanks

FIGURE 6.5 THICKNESS DISTRIBUTION ON KISS-OFF
parison; this is shown at the top of the tank in figure 6.3.

Cut (l)b of the Ford Triton tank (see figure 6.3) was the narrowest section, and had an average thickness 5.4 mm; the standard deviation was 0.82 mm, and the measured periphery was 1.42 m. Section (2) was a wider section, having a mean thickness 5.7 mm and a standard deviation 1.3 mm; the measured periphery was 1.79 m. Section 1 (a) had a mean thickness of 5.7 mm, standard deviation of 0.675 mm and periphery 1.46 m. Section 1 (c) had a mean thickness 5.7 mm, a standard deviation 0.8 mm and a periphery 1.45 m. Thickness measurements were taken every 20 mm on the sections of this tank.

Sections 1 (a), (b) and (c) show that amount of material in cross section is consistent throughout length of tank.

The average thickness of the whole Triton tank wall was just under 5.7 mm.

Identical cuts were made on another Triton tank; the above results were repeated.

Distribution (from first tank)

<table>
<thead>
<tr>
<th>Thickness, mm</th>
<th>&lt;4</th>
<th>4-4.5</th>
<th>4.5-5</th>
<th>5-5.5</th>
<th>5.5-6</th>
<th>6-6.5</th>
<th>6.5-7</th>
<th>7-7.5</th>
<th>&gt;7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>10</td>
<td>11</td>
<td>47</td>
<td>20</td>
<td>15</td>
<td>36</td>
<td>16</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>
Figure 6.6  Thickness Distribution on Ford Triton Fuel Tank

Figure 6.7  Textural Interface on Section Through Wall of Triton Fuel Tank (100 Times) 0 100 200 μm
This shows bimodality (see figure 6.6)

Distributions of right hand Harvester and 2 Sierra tanks are shown in figure 6.8 (average thicknesses were 8.85 mm and 5.35 mm respectively).

6.2.2. Pinch-offs

The pinch-offs (where the mould compresses the parison, and impedes inflation) showed some interesting features under a low power microscope: in the Peugeot Talbot 309 petrol tank strands of polymer were seen to cross the pinch-off; holes could be seen, in some places, underneath the strands; this effect is shown in figure 6.10. (magnification 10 times). An investigation was made to check the hole penetration: a section, perpendicular to the pinch-off line was cut; 20 µm surfaces were repeatedly removed using a microtome; the surface near the pinch-off was observed for cracks; a number were observed (see figure 6.11). The positions of the pinch-offs in the Peugeot Talbot 309 tanks is shown in figure 6.2.

The pinch-off region, in the Ford Triton tank, indicated in figure 6.3, occurs at the 'top' and 'bottom' of the moulding only. The initial parison was approximately circular in cross section and was impinged at the 'top'
Figure 6.8 Thickness Distribution Comparison

Figure 6.9 Textural Interface on Ford Sierra Fuel tank (100 Times) 0 100 200 μm
Figure 6.10  Holes in Pinch-Off 0 1 2 mm
(10 Times)

Figure 6.11  Perpendicular Section to That Above 0 1 2 mm
(10 Times)
and 'bottom', at the pinch-offs.

The pinch-offs on the Ford Sierra experimental tank, and on the left and right International Harvester tanks were less well defined than on the Ford Triton tank, but were still significant.

6.2.3. Texture

An interface was observed 150-200 μm from the mould wall side in the Peugeot Talbot 309 petrol tank (Marlex MS 201 A), Ford Triton Tank (Lupolen 4261-A), and the Ford Sierra tank (Lupolen 4261-A); these are shown in figures 6.12, 6.7, and 6.9. This results from a cold mould (employed to reduce cycle times); the texture in the wall is finer on the mould wall side, and there is a distinctive jump to coarser spherulite size (from about 15 μm to 40 μm diameter); this demarcation zone may be a crack nucleation site.

6.2.4. Welds and Other Observations

White tabs, in both the Peugeot Talbot tanks, which act as cable constraints, are spot welded to the tank body; these welds, under close examination, proved not to be satisfactory. Using a low powered optical microscope, holes were clearly visible along
Figure 6.12  Etched Section through Tank Wall 0 100 200 μm (100 Times)

Figure 6.13  Mounted Cross Section of Bent Elbow Weld (.5 Times) 0 3 4 mm
weld lines; little material diffusion was observed.

Other welds, in the Peugeot Talbot Tanks, were investigated; most marked defects are shown in the angled spout weld; sections of the weld showed that the injection moulded spout had a distinct skin. The weld bead produced by the spout was small compared with that produced by blow moulded material. Figure 6.13. shows a mounted cross-section of this weld; the internal weld bead is visible; this is possibly large enough to disrupt fuel flow in the spout aperture. Further investigations show blow moulded and injection moulded materials (from the Willamot tank) to have melt flow indices 0.43 and .21 g/10 min respectively (10 kg, 190°C, 2 mm die); the blow moulded material had a higher density. The injection moulded spout was badly made; this is shown by the presence of a skin. The higher MFI of the blow moulded material is borne out by the larger weld bead it produced.

The MFI range for material from the Triton tank (Lupolen 4261-A) was 0.165-0.170 g/10 min. (190°C, 10 kg load, and 2 mm die).

The density of a section from the Triton tank wall was 941 kg/m³. Density differences between outside and inside of wall were
investigated; outside 936 kg/m³, inside 943 kg/m³. This signifies that the inside is of higher crystallinity than the outside. This would result from a quenching effect where the mould, in contact with the outer side, is cold.

In the Ford Triton tank, cracks were visible in welds (a) and (c) (see figure 6.3), extending along weld lines and of order of 10 mm long. This shows that welding conditions were not optimised.

All of the following MFI values are for high density polyethylene at 190°C, using 10 kg load and 2 mm die.

Table 6.1.

<table>
<thead>
<tr>
<th>Description</th>
<th>MFI g/10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH Harvester</td>
<td>.46</td>
</tr>
<tr>
<td>Filler neck</td>
<td>.70</td>
</tr>
<tr>
<td>RH Harvester, main tank</td>
<td>.59</td>
</tr>
<tr>
<td>Injection moulded charpy specimen</td>
<td>.74</td>
</tr>
<tr>
<td>Injection moulded tensile specimen</td>
<td>.31</td>
</tr>
<tr>
<td>Weld on RH Harvester, tank</td>
<td>.41</td>
</tr>
<tr>
<td>Sierra main tank</td>
<td>.41</td>
</tr>
</tbody>
</table>
The density of the Sierra and Harvester tanks was 945 kg/m³.

A large number of service failures of welds on the Harvester tanks were caused by maltreatment; adding to this was the observation that welding conditions of injection moulded fittings to the main tank were not satisfactory; orientation in the moulding was found to be high.

Dispersion of carbon black in the blow moulded material of all the tanks investigated was poor; black striations were observed; dispersion in the injection moulded material, used in the attachments, was little better.

The Sierra tank had lines of blemishes on inside wall which were found to be gelled HDPE.

6.2.5. Cooling Calculation

The following is an approximation for the rate of air flow necessary to cool a plastics fuel tank internally.

The inside of a blow moulding may be cooled by circulating air. The mass of the tank is 7 kg; it is assumed that half the cooling is to be achieved via the inner surface and that the parison temperature is at 210°C.
Density of air at NTP is 1.243 g/litre; specific heat 1.017 kJ kg\(^{-1}\) K\(^{-1}\). Initial temperature of air is 20°C.

For a cooling time of 180 seconds, and a blowing pressure of 6 bar, and making a reasonable assumption about removal of moulding from the mould, the air flow necessary may be calculated.

Removal is assumed to take place immediately after crystallisation (100°C). Enthalpy data, as a function of temperature, are used to determine the latent heat contribution (LH). Enthalpies for a Dow HDPE are as follows: 584.2 kJ/kg at 195°C; 415.1 kJ/kg at 125°C (referred to 20°C).

Let \(Q_1\) be the heat evolved in changing the temperature (T) from 210°C to 100°C (minus LH); this is 220 kJ. \(Q_2\) is the LH (assumed evolved at 100°C) and is 175 kJ. For half the weight of the tank to be cooled internally (3.5 kg), \(q_1\) is 770 kJ; \(q_2\) is 612.5 kJ.

\[
770,000 = V_1 \times 1.243 \times 1.017 \times (147.5 - 20) \\
(147.5 \text{ is the average of 195 and } 100. ) \\
V_1 = 4,777.4 \text{ litres} \\
612,500 = V_2 \times 1.243 \times 1.017 \times (100 - 20) \\
V_2 = 6,056.5 \text{ litres}
\]

- 122 -
Total volume of air required is 10,833.9 litres; for 180 seconds, at 6 bar, the air flow rate must be 10.0 litres a second.

Figure 6.14. and 6.15. show the effect of changing melt temperature and blowing pressure, respectively, on the required air flow rate.

6.2.6. Impact Testing

Strong dependences of impact properties on thickness were found. For the Peugeot Talbot petrol tank (Marlex MS 201A),

peak force, \( N = 1057.5 \times \text{(thickness, mm)}^{1.17} \)
peak energy, \( J = 6.0 \times \text{(thickness, mm)}^{1.48} \)
failure energy, \( J = 10.9 \times \text{(thickness, mm)}^{1.58} \)

For the diesel tank, (Lupolen 4261-A),

peak force, \( N = 1390.8 \times \text{(thickness, mm)}^{1.03} \)
peak energy, \( J = 11.6 \times \text{(thickness, mm)}^{1.12} \)
failure energy, \( J = 17.0 \times \text{(thickness, mm)}^{1.32} \)

(see Appendix 3)

Pinch-offs caused a marked deterioration in all impact properties; brittle failure was observed along pinch-off lines (see figure - 123 - ).
Figure 6.14  Effect of Melt on Cooling

Figure 6.15  Effect of Pressure on Cooling
6.16). The failure mode of the specimens was consistent; originally, tearing took place, followed by yield corresponding to peak in the force displacement curve); the tear formed an incomplete circle, which was joined to the main body of the specimen by a tab. Force displacement curves for both petrol and diesel tanks at five different thicknesses are shown in figures 6.17 - 26. Graphs for pinch-offs on each tank are shown in figures 6.27 - 30.

Table 6.2. shows a comparison between pinch-off impact values on the two types of tank.

Table 6.2 Comparison of Pinch-Off Impact Results

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Peak Force, N</th>
<th>Peak Energy, J</th>
<th>Failure Energy, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>2994</td>
<td>27.03</td>
<td>52.6</td>
</tr>
<tr>
<td>6.6</td>
<td>3590</td>
<td>33.60</td>
<td>60.6</td>
</tr>
<tr>
<td>8.5</td>
<td>9270</td>
<td>107.70</td>
<td>193.2</td>
</tr>
</tbody>
</table>

Peugeot Talbot Petrol (Marlex MS 201A)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Peak Force, N</th>
<th>Peak Energy, J</th>
<th>Failure Energy, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>6247</td>
<td>47.85</td>
<td>92.6</td>
</tr>
<tr>
<td>5.0</td>
<td>6984</td>
<td>61.67</td>
<td>128.8</td>
</tr>
<tr>
<td>5.0</td>
<td>7346</td>
<td>65.99</td>
<td>124.9</td>
</tr>
<tr>
<td>6.0</td>
<td>7546</td>
<td>71.41</td>
<td>119.9</td>
</tr>
<tr>
<td>8.3</td>
<td>7810</td>
<td>70.94</td>
<td>130.6</td>
</tr>
</tbody>
</table>

Peugeot Talbot Diesel (Lupolen 4261-A)
Pinch-Off from Peugeot Talbot 309 Petrol Tank, having undergone Impact Testing; Brittle Failure along Weld Line is Conspicuous (10 Times) 0 1 2 mm
FIGURE 6.17.

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT14
Details:
Date: 09/07/86
Time: 10:12:16
Mass: 25Kg
Temp: 20'C

PEAK INFORMATION
Force=4606. N
Deflection=0.025 m
Energy=37.37 J
Gradient=36.23 KN/m

FAILURE INFORMATION
Deflection=0.039 m
Energy=81.24 J

Peugeot Talbot Petrol Tank, Thickness 3.7 mm
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT1
Date: 09/07/86
Time: 09:27:06
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=6149. N
Deflection=0.024 m
Energy=57.74 J

FAILURE INFORMATION
Deflection=0.037 m
Energy=115.2 J

Peugeot Talbot Petrol Tank, Thickness 4.5 mm
FIGURE 6.19.

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT26
Details:
Date: 09/07/86
Time: 10:38:116
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=6691. N
Deflection=0.019 m
Energy=66.84 J

FAILURE INFORMATION
Deflection=0.032 m
Energy=130.5 J

Peugeot Talbot Petrol Tank, Thickness 5.3 mm
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT3
Details:
Date: 09/07/86
Time: 09:33:43
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force: 8210. N
Deflection: 23.31 mm
Energy: 78.94 J
Gradient: 10.49 KN/m

FAILURE INFORMATION
Deflection: 39.61 mm
Energy: 177.4 J

Peugeot Talbot Petrol Tank, Thickness 5.7 mm
FIGURE 6.21

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT30
Details:
Date: 09/07/86
Time: 10:44:55
Mass: 25Kg
Temp: 20°C

Peugeot Talbot Petrol Tank, Thickness 6.2 mm

PEAK INFORMATION
Force=9094. N
Deflection=21.77 mm
Energy=85.40 J

FAILURE INFORMATION
Deflection=39.17 mm
Energy=201.8 J
FIGURE 6.22

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 17
Date: 21/07/86
Time: 11:11:33
Mass: 25 Kg
Temp: 20°C

Peugeot Talbot Diesel Tank, Thickness 4.7 mm

PEAK INFORMATION
Force = 6759 N
Deflection = 0.026 m
Energy = 62.59 J

FAILURE INFORMATION
Deflection = 0.041 m
Energy = 132.9 J
FIGURE 6.23

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 8
Date: 21/07/86
Time: 10:53:07
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=7204. N
Deflection=0.026 m
Energy=68.29 J

FAILURE INFORMATION
Deflection=0.043 m
Energy=144.9 J

Peugeot Talbot Diesel Tank, Thickness 5.3 mm
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 16
Date: 21/07/86
Time: 11:12:31
Mass: 25 Kg
Temp: 20°C

Peugeot Talbot Diesel Tank, Thickness 5.8 mm

PEAK INFORMATION
Force=8347. N
Deflection=0.026 m
Energy=85.14 J

FAILURE INFORMATION
Deflection=0.038 m
Energy=158.1 J
FIGURE 6.25

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 18
Date: 21/07/86
Time: 11:16:35
Mass: 25Kg
Temp: 20°C

Peugeot Talbot Diesel Tank, Thickness 6.4 mm

PEAK INFORMATION
Force=9.983 KN
Deflection=25.71 mm
Energy=108.9 J

FAILURE INFORMATION
Deflection=39.95 mm
Energy=215.7 J
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 14
Date: 21/07/86
Time: 11:07:10
Mass: 25 Kg
Temp: 20°C

Peugeot Talbot Diesel Tank, Thickness 7.0 mm

PEAK INFORMATION
Force = 10.07 KN
Deflection = 18.35 mm
Energy = 101.6 J

FAILURE INFORMATION
Deflection = 23.56 mm
Energy = 151.6 J
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1  
Sample: PT6  
Details: PIN  
Date: 09/07/86  
Time: 09:44:04  
Mass: 25Kg  
Temp: 20°C

PEAK INFORMATION
Force=2994. N
Deflection=0.019 m
Energy=27.03 J
Gradient=63.54 KN/m

FAILURE INFORMATION
Deflection=0.033 m
Energy=52.65 J

Peugeot Talbot Petrol Tank, Pinch-Off Thickness 6.4 mm
FIGURE 6.28

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 1
Sample: PT13
Details: PIN
Date: 09/07/86
Time: 09:48:38
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=3902. N
Deflection=0.018 m
Energy=27.36 J
Gradient=33.73 KN/m

FAILURE INFORMATION
Deflection=0.032 m
Energy=60.57 J
ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 21P
Date: 21/07/86
Time: 11:24:14
Mass: 25Kg
Temp: 20'C

PEAK INFORMATION
Force=7810. N
Deflection=0.0211 m
Energy=70.91 J
Gradient=52.60 KN/m

FAILURE INFORMATION
Deflection=0.039 m
Energy=130.6 J
Figure 6.30

ROSAND INSTRUMENTED IMPACT TEST SYSTEM

Drive: 3
Sample: PTB
Details: 22P
Date: 21/07/86
Time: 11:26:14
Mass: 25Kg
Temp: 20°C

PEAK INFORMATION
Force=7546. N
Deflection=0.025 m
Energy=71.41 J

FAILURE INFORMATION
Deflection=0.040 m
Energy=119.0 J

Peugeot Talbot Diesel Tank, Pinch-Off Thickness 6.0 m
Looking at figure 6.16, it can be seen that the failure mode is not the same as that for a specimen containing a pinch-off, in which the failure is brittle, and this can be seen in the relevant graphs; the specimen has not yielded, and failure has occurred early, along the pinch-off line. A significant drop in peak force accompanied impact testing at a pinch-off, compared with testing of a normal area.

6.3. Discussion

Wall thickness distributions in the Peugeot Talbot tanks are satisfactory. Kiss-off regions, where thickness was the least were found to be possible weak points. Kiss-offs result from protrusions on both mould halves that almost meet, and form a weld of opposite parison walls. The reason for the inclusion of the kiss-offs in the design was to prevent serious creep deformation at high temperatures (say 40°C).

The thickness distribution of the Triton tank was narrow and the amount of cross sectional material was consistent within the tank.

Thickness distributions were reasonable in all tanks; the Harvester tanks could have had better distributions if their shapes were less angular; this would also lessen surface
area to volume ratio.

The higher average wall thickness in the Harvester tank (8.85 mm) than in the Sierra tank (5.35 mm) means that more material goes into making the Harvester tank (it is about 1 kg heavier). This seems a waste of material for tanks of the same capacity. The extra material allows for the thickness at the sharp corners in the Harvester tank; the corners are found to be relatively thin; the thickness may be as low as 3 or 4 mm compared with the maximum observed thickness in the tank of 13 mm. The problem could be remedied with an improved tank design.

The white tabs, which are spot welded at various locations on the Peugeot Talbot tanks, are not satisfactory; it would be better to use a hot melt adhesive suited to use with HDPE.

The welds, on the Triton tank appear to be unsatisfactory, a result, possibly, of unsuitable welding conditions (see welding report, Chapter 7). Also, weld and tank materials may not be suited to each other.

Welding on the Sierra and Harvester tanks was not satisfactory; recommended conditions for Lupolen 4261-A and Rigidex H060-45P are given in Chapter 7. A skin was observed on most of
the injection moulded fittings, for all the
tanks examined: this arose from bad moulding
conditions. This skin is thought to add to
the problem of poor welds as cracks may start
from the skin.

The Peugeot Talbot (Lupolen 4261-A) had a
similar MFI value to the Ford Sierra 4261-A),
but Ford Triton fuel tanks (Lupolen 4261-A)
had a much lower MFI value. Other MFI values
observed show the polymer that has been
injection moulded into fittings for the
Harvester tank (Rigidex H060-45P) has an
unusually low MFI (0.46 g/10 min) compared
with the expected at least 1). There are two
main reasons for this: the moulding cycle
times are too short; and the melt
temperatures are too high, and this leads to
degradation, which would obviously be
detrimental to product properties.

The blow moulded part of the Harvester tank
had a higher MFI value of 0.7 g/10 min. The
same polymer grade is used in making the tank
and the injection moulded attachments.

The Lupolen 4261-A powder has a high MFI of
1.45 g/10 min, and the injection moulded
tensile specimen (also of Lupolen 4261-A)
has a value of 0.74 g/10 min., which roughly
equals that of the blow moulded Harvester
tank, and is greater than the MFI of the

- 127 -
filler neck; this would suggest that the moulding conditions are better in the case of the tensile specimens.

The injection moulded Charpy specimen had a lower MFI than the tensile specimen.

Flaws observed in the Sierra tank could be removed by improved mixing and temperature control in the barrel. Pigment dispersion in all the tanks could be improved. Mixing is dispersive and distributive in this case. Increased homogeneity in the mix can be achieved by use of a breaker plate in the extruder; this will serve to increase back pressure, which will increase the shear and mixing. Increased screw speed will have the same effect.

The investigation of effect of thickness on impact properties produced exponent values that were not too different from those in the literature. The value of the exponents are also found to increase from peak force, through energy to peak, to failure energy. The overall values in the literature tend to be a little higher, however; the methods used there, for calculating the exponent values were by log-log paper; the method used here was less subjective.
Using the fitted equations, the expected peak force for a 5 mm thick part of a petrol tank is 6951 N; that for a diesel tank is 7298 N, confirming the initial observation that the tank made by Willamot was superior.

Pinch-off lines contain possible crack starters; pinch-offs were later shown to lower impact strength significantly; these features should be minimised in the design of the tank. The Willamot tanks had stronger pinch-offs than in the French tanks.

The pinch-offs are regions where unsatisfactory bonds are often formed. They may be compared with welds where the best joints are found to form at temperatures around 250°C, and for 30 seconds heating. In practice, the parison temperature is significantly less than this; this is assumed to be the reason for the weakness at the pinch-off.
7. **WELDING**

7.1. **Introduction**

The materials used in this programme were Lupolen 4261-A (BASF) and Rigidex H060-45P (BP Chemicals). (See section 4.1.)

Tensile bars were injection moulded, and cut in half; the halves were then hot plate welded together. (See section 4.3.)

The moulding conditions for the materials were as follows: all materials were injected in the range 2 to 3 seconds; hold-on times in all cases were 14 seconds. Further cooling occurred in about 50 seconds.

Both materials were moulded, with a melt temperature of 230°C and a mould temperature of 60°C, into standard tensile bars. The Rigidex H060-45P grade was also moulded under a second set of conditions (melt temperature = 250°C and mould temperature 60°C).

The aim of the programme was to produce, by factorial design, a set of welds from each material, and to use the GLIM statistical package to arrive at an 'optimum weld' within practical limits.
The design of the experimental procedure was factorial, which entailed coding the four factors as follows.

Table 7.1.

<table>
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<th>CODE</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
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<tr>
<td>CONDITIONS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOT PLATE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEMP. °C</td>
<td>220</td>
<td>245</td>
<td>270</td>
<td>295</td>
<td>320</td>
</tr>
<tr>
<td>HEATING TIME (SEC)</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>WELDING TIME (SEC)</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>PRESSURE ON WELD (BAR)</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The order of welds was as given in Table 7.2 in the GLIM program: the first column is level of weld temperature (-2 lowest, 2 highest), column 2 heating time, column 3 weld time, and column 4 weld pressure. For example, -2 in the first column corresponds to
**FIGURE 7.1.A.**

RIGIDEX HD60-45P CHEMICAL CONTAINER

**FIGURE 7.1.B.**

WELDS JOINING EXTRUDED SHEET TO INJECTION MOULDED ENDS

NEGATIVE MISALIGNMENT

POSITIVE MISALIGNMENT
weld temperature of 220°C; 2 in column 3 signifies 30 seconds welding time.

The values of yield stress obtained on tensile testing the welds (at 40 mm/min. and 20°C) were divided by the mean yield stresses of 3 unwelded tensile bars tested under the same conditions. The welds were tested in random order to minimise systematic variations. Weld beads were not removed.

Calculation of weld factor:

\[
WF = \frac{\text{Yield stress of welded bar}}{\text{Mean yield stress of unwelded bar}}
\]

One centre point bar from each batch was not tested, and this was sectioned and observed under the microscope between crossed polars. Differences in the orientation in the bar and weld bead, and size of the weld bead were the main features to be compared by microscopy. Data for 35 welds from each of the three moulding conditions were separately fed into the GLIM computer program given in Table 7.2.

The GLIM program enabled an equation to be calculated to best describe the effect of the factors chosen on the weld factor (WF).\textsuperscript{115, 116} The program uses a quadratic of the following form:

\[
WF = g_0 + A.(\text{Weld temp.}) + B.(\text{Heat time}) + C.(\text{Weld time}) + D.(\text{Pressure}) + AA.(\text{Weld temp.} \times \text{Weld temp.})
\]

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TABLE 7.2. (RIGIDEX, MELT TEMPERATURE = 230°C)

By comparing the standard errors in the second column of output in Table 7.3 with the estimates of coefficients the significance of the latter may be gauged as follows:

\[
\text{if } \frac{\text{Estimate}}{\text{Standard error}} > 2, \quad \text{then the coefficient can be said to be significant.}
\]

The differences between the fitted and the observed data can be seen in Table 7.3, the values being given in the column headed 'residuals'.

A plot of fitted data vs. residuals is given in Table 7.3. If these points are randomly arranged then there are apparently no systematic variations. If
## TABLE 7.3.

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<tr>
<th>cycle</th>
<th>deviance</th>
<th>df</th>
<th>estimate</th>
<th>s.e.</th>
<th>parameter</th>
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<td>0.8264</td>
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<td>a</td>
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<td>20</td>
<td>0.7000E-01</td>
<td>0.1348E-01</td>
<td>b</td>
</tr>
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<td>0.2333E-01</td>
<td>0.1348E-01</td>
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<td>d</td>
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<td>0.5909E-02</td>
<td>0.1176E-01</td>
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<td>20</td>
<td>0.7265E-02</td>
<td>0.1176E-01</td>
<td>ad</td>
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<tr>
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<td>0.6000E-01</td>
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<td>0.6000E-01</td>
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<td>bc</td>
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### unit observed

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<th>residual</th>
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<td>0.1990E-01</td>
</tr>
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<td>0.8004</td>
<td>0.1990E-01</td>
</tr>
<tr>
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<td>0.6927</td>
<td>0.2773E-01</td>
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<td>0.1750E-02</td>
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<td>0.3434E-01</td>
</tr>
<tr>
<td>33</td>
<td>0.8000</td>
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<td>0.2634E-01</td>
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<td>35</td>
<td>0.8600</td>
<td>0.8264</td>
<td>0.3304E-01</td>
</tr>
</tbody>
</table>

## Note

- A table showing the results of a statistical analysis, with columns for cycle, deviance, df, estimate, s.e., and parameter.
the residual value is less than 10% of the fitted coefficient then the coefficient can be used with a high level of confidence.

Using the quadratic equation with the relevant coefficients, other values may be extrapolated and interpolated and a contour plot may be obtained.

Microscopy and photomicrography were also used in the search for optimum welding conditions.

From the results it was hoped to draw some conclusions on the effect of moulding conditions, material, and residual orientation on the weld factor.

A container for chemicals was also investigated in connection with welding; the chemical container consisted of a black sheet extruded body, welded vertically, with white injection moulded end fittings, which were welded to the main body (see figure 7.1). The polymer used in the container was Rigidex H060-45P high density polyethylene.

Failure of the tank occurred twice at sub-zero (-18°C) temperatures during testing. In both cases, failure was observed at the welds. One occurred at the sheet-to-sheet weld, and the other at the sheet-to-top end fitting joint.

The aim of this programme was to find out why such failures were occurring. The effectiveness of the
sheet-to-sheet weld was considered by comparing 'weld factors' from data obtained in a factorial experiment; weld temperature, heating time, weld time, and weld pressure, were varied. The general geometry of both the sheet-to-sheet and sheet-to-end moulding welds was examined, and any misalignment noted. The size of the welding beads was also recorded.

A factorial design of experiment was used with 35 individual hot plate weld operations, including 11 centre point conditions.

The welding was carried out as with previous welding experiments. The ranges of the four factors used were welding temperature between 220°C and 320°C, heating time between 10 and 50 seconds, weld time between 10 and 30 seconds, weld pressure between 1.5 and 3.5 bar.

The tensile bars were machined from the black sheet along a direction perpendicular to the sheet-to-sheet weld line, so that the original sheet-to-sheet welding could be simulated as far as possible.

Testing of the bars was also carried out as described in the previous welding experiments, at 40 mm/minute and 20°C.

The GLIM statistical package was used to fit a quadratic to the results of the factorially designed experiment. The GLIM program used, which includes weld factor values obtained, is given in Table 7.4.
TABLE 7.4.

\$c
\$c
\$c
\$c
\$c
\$units 35
\$data A B C D WF
\$read
1 1 1 1 .96
1 1 1 -1 .98
1 1 -1 1 1.06
1 1 -1 -1 .90
1 -1 1 1 .85
1 -1 1 -1 .91
1 -1 -1 1 .98
1 -1 -1 -1 .76
-1 1 1 1 .95
-1 1 1 -1 1.01
-1 1 -1 1 .99
-1 1 -1 -1 .96
-1 -1 1 1 1.02
-1 -1 1 -1 .95
-1 -1 -1 1 1.12
-1 -1 -1 -1 .97
2 0 0 0 1.01
-2 0 0 0 .87
0 2 0 0 .95
0 -2 0 0 .84
0 0 2 0 .94
0 0 -2 0 .90
0 0 0 2 .92
0 0 0 -2 1.01
0 0 0 0 1.02
0 0 0 0 .93
0 0 0 0 1.03
0 0 0 0 .89
0 0 0 0 .95
0 0 0 0 .90
0 0 0 0 .91
0 0 0 0 .94
0 0 0 0 .97
0 0 0 0 1.00
0 0 0 0 .95
\$calc AA= A*A
\$calc BB= B*B
\$calc CC= C*C
\$calc DD= D*D
\$calc AB= A*B
\$calc AC= A*C
\$calc AD= A*D
\$calc BC= B*C
\$calc BD= B*D
\$calc CD= C*D
\$mac quad
\$fit A,B,C,D,AA,BB,CC,DD,AB,AC,AD,BC,BD,CD
\$d e r $ $\$cal R = %yv - %fv$
\$plot R %fv $ $\$endmac$
\$return
The GLIM output containing the coefficients of the quadratic, predicted weld factors, and a residuals plot, is given in Table 7.5.

The container was examined critically for any stress concentrations that might occur owing to design features. Misalignment at the weld was quantitatively measured around the rim of the container, both at the top and bottom (see Table 7.6.).

6 injection moulded tops and 6 bottoms were measured across diameters (see Table 7.7).

7.2. Results

7.2.1. General

The values of the coefficients for each tensile bar moulding condition can be seen in Table 7.3. In all four sets the factors C and D (corresponding to weld time and weld pressure) are much less significant than the coefficients A and B (weld temperature and heating time). Hence for simplicity, the contour plots were drawn at the centre points of C and D.
<table>
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<tr>
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<table>
<thead>
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<th>s.e.</th>
<th>Parameter</th>
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<td>3</td>
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<td>0.1146E-01 BB</td>
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<td>0.1313E-01 D</td>
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**TABLE 7.5.**

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<th>Unit observed</th>
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<td>1.023</td>
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<td>.9900</td>
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<tr>
<td>5</td>
<td>.8500</td>
<td>.8817</td>
</tr>
<tr>
<td>6</td>
<td>.9100</td>
<td>.0071</td>
</tr>
<tr>
<td>7</td>
<td>.9800</td>
<td>.9604</td>
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<td>.8063</td>
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<tr>
<td>9</td>
<td>.9500</td>
<td>.9950</td>
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<td>10</td>
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<td>11</td>
<td>.9900</td>
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<td>35</td>
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scale parameter taken as 0.4941E-02
### TABLE 7.6. BOTTOM END

<table>
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<tr>
<th>Angle (deg.)</th>
<th>Misalignment (mm)</th>
<th>Weld bead size (cm) Black sheet</th>
<th>White end</th>
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<tbody>
<tr>
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<td>1.5</td>
<td>0.75</td>
<td>0.68</td>
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<td>60</td>
<td>1.0</td>
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<td>120</td>
<td>-2.0</td>
<td>0.65</td>
<td>0.56</td>
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<tr>
<td>180</td>
<td>1.0</td>
<td>0.62</td>
<td>0.80</td>
</tr>
<tr>
<td>240</td>
<td>1.0</td>
<td>0.65</td>
<td>0.91</td>
</tr>
<tr>
<td>300</td>
<td>1.5</td>
<td>0.70</td>
<td>0.84</td>
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### TOP END

<table>
<thead>
<tr>
<th>Angle (deg.)</th>
<th>Misalignment (mm)</th>
<th>Weld bead size (cm) Black sheet</th>
<th>White end</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>3.5</td>
<td>0.60</td>
<td>0.61</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>0.65</td>
<td>0.60</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
<td>0.70</td>
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<td>0.67</td>
<td>0.73</td>
</tr>
<tr>
<td>240</td>
<td>1.5</td>
<td>0.60</td>
<td>0.80</td>
</tr>
<tr>
<td>300*</td>
<td>2.5</td>
<td>0.70</td>
<td>0.97</td>
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</table>

* Denotes failure region.
### Table 7.7: End Fittings

#### Bottom end

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<th>w1 (cm)</th>
<th>w2 (cm)</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>26.4</td>
<td>26.6</td>
</tr>
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<td>26.4</td>
<td>26.6</td>
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<tr>
<td>26.5</td>
<td>26.7</td>
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</table>

#### Top end

<table>
<thead>
<tr>
<th>w1 (cm)</th>
<th>w2 (cm)</th>
<th>w3 (cm)</th>
<th>w4 (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.8</td>
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<td>26.7</td>
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<td>26.5</td>
<td>26.8</td>
</tr>
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</table>
Table 7.8.

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield stress of original bar (MPa)</th>
<th>Mean weld factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lupolen 4261-A</td>
<td>30.00</td>
<td>96.33</td>
</tr>
<tr>
<td>Rigidex H060-45P (melt temp. = 230 °C)</td>
<td>37.00</td>
<td>82.64</td>
</tr>
<tr>
<td>Rigidex H060-45P (melt temp. = 250 °C)</td>
<td>36.2</td>
<td>83.99</td>
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</tbody>
</table>

All the contour plots in figures 7.2 - 7.4 tend to show good weld factors at high heating times, weld temperature also play a strong role in the determination of weld factors. Lupolen 4261-A produced weld
FIGURE 7.2. LUPOLEN WELD FACTOR CONTOUR PLOT

(at centre point weld time and pressure)
FIGURE 7.3. RIGIDEX (MELT TEMPERATURE = 230°C) WELD FACTOR CONTOUR PLOT, WITH CENTRE POINT WELD TIME AND PRESSURE
FIGURE 7.4. RIGIDEX (MELT TEMPERATURE = 250°C) WELD FACTOR CONTOUR PLOT, WITH CENTRE POINT WELD TIME AND PRESSURE
FIGURE 7.5. RIGIDEX SHEET WELD FACTOR (%) CONTOUR PLOT AT CENTRE POINT WELD TIME AND PRESSURE
factors generally higher than the Rigidex H060-45P, and the Rigidex H060-45P moulded at the higher melt temperature produced a higher weld factor than the lower melt temperature Rigidex H060-45P. The weld factor appeared to have an inverse relation to the yield stress of the corresponding tensile bar perhaps indicating that orientation in the as-moulded bars is a deleterious factor. Weld factors are only relative to the properties of the as-moulded bars.

The residual values for all three experiments were low and the scatter plots fairly random, so this showed that the fitted model was appropriate.

In the Lupolen 4261-A set, the weld number 18 produced at centre point conditions except for 200°C weld temperature produced a weak bond (WF = 36.5%) and no bead was visible. All the welds of Lupolen 4261-A with the first two factors at -1 and -1 gave brittle welds with small weld beads (WF = 60%). Higher heat times of 40 sec, but same temperatures, produced much stronger bonds that had a good bead size and that were much more ductile (average weld factor = 95%).

At a temperature of 296°C, the quality of the welds increased again with heat time (WF at heat time = 10 sec was 77% and when heat
time was 50 sec, WF = 98.9%.

The higher heating time also improved bead size and ductility of the welds at failure. The highest weld factor occurred in one of the centre points, which in general produced the high results.

In most respects, the trends shown in the Lupolen 4261-A were also observed in the two sets of welds in Rigidex H060-45P, but the weld factors for Rigidex H060-45P were lower overall.

Heating times and weld temperatures were again important. Both Rigidex H060-45P sets showed reasonably ductile welds produced at centre point conditions. Larger weld beads were generally produced at high welding temperatures and heating times. Ductility increased with welding temperature and heating time, although, at the highest temperatures (320°C) brittle failure was noted. Ductile welds failed by yielding.

Weld bead size was satisfactory at the centre point conditions and decreased with a decrease in weld temperature and heating time, to be almost non-existent at the lowest temperature (220°C). The lower temperatures and lower heat times tended to produce brittle welds, which were weak. Brittle
failures were characterised by cracking, and an absence of any gross plastic yielding.

The two Rigidex H060-45P sets had to be welded at much higher temperatures than the Lupolen 4261-A set of welds, in order to effect a good weld (see contour plots in figures 7.2. - 7.4.).

Figure 7.5. shows the contour plot of the weld efficiency of the Rigidex H060-45P sheet. The contours represent weld factor values (%). The irregular pattern that arises in the central area of the plot is a result of the welds not failing, the failure occurring away from the weld. This should show a random variation as it is not affected by weld temperature or heating time. Optimum conditions seemed to be around the centre points chosen.

The following welds (experiment numbers) failed away from the weld: 1, 3, 4, 9, 10, 11, 15, 17, 18, 21, 24, 25, 28, 33 and 35. The following failed in a brittle manner: 2, 5, 13, 16, 19, 23 and 32. Weld number 20 failed because of insufficient melting resulting in a small weld bead. The remaining welds failed in a manner somewhere between brittle and ductile. The welding produced, in general, very good specimens and the welding is recommended to
take place at about the centre point conditions. The only bad areas observed (see figure 7.5.) were at low heating times and extremes of temperature.

Weld number 20 was made at low heating time and, as noted above, was not satisfactory. The centre point welds stated above are those with numbers greater or equal to 25. The conditions for welding of the other numbers can be referred to in Table 7.4. Welds from the original container were found to be of the same strength as those made at centre point conditions.

The results in Table 7.6. show that there is a high misalignment on the top end at 60° and 360° round the rim. This corresponds to the region near the filler hole. This coincided with a failure region observed on the container having undergone a sub-zero temperature impact test. Observation of the orientation near the hole shows a break in the flow, and an internal weld line where the two flows meet again after the break. The system is gated at the centre. The hole is placed exactly above the sheet-sheet weld line.

The bottom end seems to be well aligned throughout the rim. The top end has slight ovality (see Table 7.7). The direction
perpendicular to the diameter containing the hole is about 1% shorter than the other diameters. This may arise from the obstruction to flow at the hole.

Microscopy (see figures 7.6. to 7.8.) showed that Lupolen 4261-A welded tensile bar produced a highly stressed weld, in which a 'skin' produced by the injection moulding process, formed a continuation into the weld bead. In the Rigidex H060-45P there was no continuation of this 'skin' into the weld bead. The batch at the higher melt temperature (250°C) produced a less highly orientated situation in the tensile bar, as expected, and also lowered the yield stress but raised weld factors. The orientation in the lower melt temperature Rigidex H060-45P was comparable with that shown in the Lupolen 4261-A, but the yield stress of the Rigidex H060-45P was significantly higher.

7.2.2. Thermal Oxidation Test Results

A new method was investigated for evaluating the thermal oxidative stability of polyolefins; this is particularly relevant for components that are to be welded, since poor stability might be expected to contribute to a low weld strength. (See section 4.4.7 on thermal analysis).
Figure 7.6 Centre Point Weld for Lupolen (20 Times)

Figure 7.7 Centre Point Weld for Rigidex (Melt Temp = 230°C)
Centre Point Weld for Rigidex (Melt Temp = 250°C)
0.1 mm (20 Times)
The results obtained for thermal oxidative experiments are tabulated below.

Table 7.9.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TIME FOR OXIDATION, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propathene H5E110 (Polypropylene) high heat stability</td>
<td>35+</td>
</tr>
<tr>
<td>Lupolen 4261A</td>
<td>9</td>
</tr>
<tr>
<td>Lupolen 4261A - Moulded tensile bar</td>
<td>10</td>
</tr>
<tr>
<td>Lupolen 4261A - Part of weld on tensile bar</td>
<td>9</td>
</tr>
<tr>
<td>Lupolen 4261A - Moulded impact specimen</td>
<td>9</td>
</tr>
<tr>
<td>Rigidex 002-55 - Date of delivery to RB, 12 July '84</td>
<td>6</td>
</tr>
<tr>
<td>Sample from Harvester fuel tank</td>
<td>27</td>
</tr>
<tr>
<td>Moulded filler neck, Harvester fuel tank</td>
<td>43</td>
</tr>
<tr>
<td>Rigidex H06045P - Sample from Sierra fuel tank</td>
<td>26</td>
</tr>
</tbody>
</table>

7.3. **Discussion**

Lupolen 4261-A welds produced higher weld factors than those of Rigidex H060-45P. The unwelded bars of Lupolen 4261-A had a lower mean yield stress (30.0 MPa) than either of the Rigidex H060-45P sets (37.0 MPa for melt temperature at 230°C, and 36.2 MPa for melt temperature at 250°C). The difference in yield stresses of the two materials may have arisen because
of a slight difference in moulding conditions, which was not registered on the injection moulding machine; this may, in turn, have led to a changed weld factor (weld strength / yield strength or stress); as the denominator of the equation would be lower for the Lupolen 4261-A, a higher weld factor would result.

Lupolen 4261-A had to be welded at lower temperatures than Rigidex H060-45P to achieve an optimum (see figures 7.2. - 7.4.). The optimum conditions for welding of Lupolen 4261-A, with time saving in mind, are weld temperature = 245°C, heating time = 20 sec (at least), welding time = 20 sec, and weld pressure = 1.5 bar.

The optimum conditions for welding Rigidex H060-45P, moulded with a melt temperature of 230°C are weld temperature = 280°C, heating time = 30 sec (at least), welding time = 20 sec, and welding pressure = 2.5 bar.

Optimum conditions for the welding of the 250°C melt temperature Rigidex H060-45P were very similar to the 230°C set, but values of weld factor were generally higher.

A higher melt temperature produced less orientation in the specimen (see figures 7.6 to 7.8).

The optimum weld for Lupolen 4261-A (see figures 7.6 to 7.8) is comparable with the more highly stressed of the two Rigidex H060-45P welds shown. The Lupolen
4261-A has a significant difference in that the skin produced on injection moulding appears to continue into the weld bead.

The polymer melt enters the cold injection mould, and makes contact with it. A layer is formed near the mould that has low orientation and low crystallinity. The adjacent layer has high orientation and low crystallinity. The adjacent layer has high orientation caused by the molecular chains being 'dragged' over the surface of the solidified polymer. In the core of the moulding the region is thermally protected by the outer layers, and crystallinity is high, as dense spherulites can grow; the orientation is relatively low.

The welding produced in the black Rigidex H060-45P sheet, in general, very good specimens and the welding is recommended to take place at about the centre point conditions. The only bad areas observed (see figure 7.5) were at low heating times and extremes of temperature.

Brittle failures were generally recorded for welds produced with low heating times. Brittle failure occurs when the yield strength is higher than the fracture strength. Factors affecting the mode of failure are crystallinity and molecular weight of material, temperature and rate of testing. Welds fail in a brittle manner if tested at a fast rate, and low temperature; this is because the relaxation times of polymers are relatively long under these conditions.
conditions. Crystallinity and molecular weight increases resulting in corresponding yield strength increase; ductility also increases.

Short molecules can easily segregate on crystallisation, and accumulate between spherulites; fracture will occur at spherulitic boundaries; this effect can be reduced with a narrower molecular mass distribution.

It is suggested that the side of the top end should be rotated 180° in order that two stress concentrations are not coincident (filler hole and sheet-to-sheet weld).

This investigation was useful in that it pointed out the drawbacks of extruding a plastics sheet and further welding it, in an attempt to produce an impermeable seal. The welding will always be a limiting factor. Blow moulding does not encounter this problem and thus seems a better process for the manufacture of fuel tanks.

In the thermal oxidative tests, the results seem to fall into two distinct groups, with onset times for oxidation of 5 to 10 min. and 25+ min.; we question whether the former are really adequate. Rigidex H060-45P has a higher thermal oxidative stability than the Lupolen 4261-A; this is shown in the hot plate welding experiments as good Rigidex H060-45P welds can be made at higher temperatures than those of Lupolen 4261-A.
The oxidation of polyethylene is thought to occur preferentially at chain fold surfaces and possibly chain ends.
CHAPTER 8

8. Failure of a 25 Litre HDPE Chemical Container

8.1. Introduction

This chapter describes an investigation of the failure, in service, of a HDPE (Rigidex 002-55) chemical container. The container is shown schematically in figure 8.1.

The failed part of the assembly on top of the container, had pulled away, leaving a hole in the top, some 30 mm by 80 mm. The most significant fact about this hole apart from the occurrence itself, was the very brittle nature of the crack surface for about one third of its periphery, a type of failure not characteristic of high molecular weight polyethylene. The problem devolves therefore into finding out what has induced the brittleness in what is usually a very ductile material.

The masterbatch material used was a green pigment in a low density polyethylene (LDPE) carrier.

8.2. Experimental Method

8.2.1. Microscopy

Photomicrographs were taken at 10 and 40 times magnification, between crossed polars,
DIAMETER = 304 MM

25 LITRE CONTAINER
MADE BY
WILLAMOT
IN RIGIDEX 002-55
to show the microstructure at different levels of resolution. Hot stage microscopy was also used to examine the melting behaviour of the material (see section 4.4.3.)

8.2.2. Thermal Analysis

The Differential Scanning Calorimeter (DSC) was used to determine the melting points of crystalline species present, as well as the location of the crystallisation peaks. Baselines were approximated and the size of the peaks were calculated; quantities of materials present were estimated (see section 4.4.7. part B.)

8.3. Results

8.3.1. Microstructure

Figure 8.2. (10 times magnification) shows the light coloured streaks present in a green pigmented matrix. Figure 8.3. (40 times magnification) shows the pigment dispersion in the form of dark spots or dark clumps of spots. Light spots are assumed to be titanox. Distinct white striations were apparent at very low magnifications.

Under higher magnification, pigment dispersion was seen to be bad, this is shown
Figure 8.2  Light Coloured Streaks in Green Pigmented Matrix (20 Times) 0 1 mm

Figure 8.3  Pigment Dispersion in the form of Dark Clumps (40 Times) 0 0.25 0.5 mm
in figure 8.3. There were areas of green organic pigment observed.

The white striations were assumed to be badly mixed LDPE, but this was later shown to be a wrong assumption; there was a lack of pigment in the striations; not possible if the original masterbatch added to HDPE was LDPE plus pigment.

The green matrix started to melt first at 117°C and was completely non-birefringent at 125°C. The white streaks didn't melt until 134°C. It was thus concluded that HDPE made a large part of the white streaks.

8.3.2. Thermal Analysis

T_m peaks were noted at 115°C and 135°C, showing, as expected, that both HDPE and LDPE phases were present.

Crystallisation peaks occurred at 120°C and 100°C corresponding again to HDPE and LDPE.

Peak sizes were approximated in both cases and a rough 50 : 50 ratio of HDPE : LDPE was calculated.

8.4. Discussion

Possible sites for failure were frequently observed.
The most likely type of failure is that due to striations of HDPE: these are the largest and most distinguishing features on the specimen that could originate the brittle failure observed.

The main cause of trouble was, undoubtedly, poor mixing, coupled with excessive amounts of masterbatch and quality of the recycled HDPE. The white streaks are assumed to be made from the recycled HDPE, and this recycle does not appear to mix very well. The masterbatch polymer carrier accounts for some of the LDPE, it is difficult to account for the rest.

The reason for the poor mixing may be that the low density branched carrier polymer does not blend with the linear high density base polymer. The base polymer crystallises in an orthorhombic form by chain folding, and appears as spherulites. The branched chains of the low density polymer will prevent alignment with the linear chains, thus suppressing crystallisation and causing phase segregation.

Also back pressure in the extruder may be insufficient to create enough dispersive and distributive mixing in the melt; a breaker plate will increase back pressure. Increased screw speed will also increase shear and mixing; pre-compounded stock should be used.

The reason for inclusion of a masterbatch into the base polymer is to make the product material less
expensive (at present HDPE costs about 600 pounds/tonne, and LDPE costs 400 pounds/tonne). A more compatible material to masterbatch with HDPE would possibly by a linear LDPE (this costs 380 pounds/tonne); this possibility, however, was not investigated.
9. Petrol Immersion and Stress Relaxation Tests

9.1. Introduction

Lupolen 4261-A is an important material when considering blow moulding of fuel tanks. Fuel tanks have to pass impact tests in order to be acceptable by EEC standards (see Appendix 4). As well as impact testing this chapter describes experiments on petrol immersion, and stress relaxation.

9.2. Experimental Method

50 sharp notched impact specimens and 30 tensile specimens (HDPE Lupolen 4261-A) were immersed in petrol for four weeks and were then tested and compared with non-immersed specimens.

Ten impact specimens were subjected to temperatures of -20°C and -2°C (10 petrol immersed and 10 non-immersed) and to ambient conditions (26°C). Impact tests were carried out using a pendulum impact tester and units were arbitrary.

Two tensile specimens were extended to 5% strain on a JJ tensile tester at 40 mm/min. One tensile bar had been previously immersed in petrol for four weeks, the other remained non-immersed. The relaxation of stress was measured as a function of time up to 500
9.3. Results

The results in Table 9.1. show the effect of petrol immersion on impact energy.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average Impact Energy (arbitrary)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrol Immerged for Four Weeks</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>0.6456</td>
</tr>
<tr>
<td>-2</td>
<td>0.6294</td>
</tr>
<tr>
<td>-20</td>
<td>0.6048</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Non-Immersed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.5070</td>
</tr>
<tr>
<td>-2</td>
<td>0.4793</td>
</tr>
<tr>
<td>-20</td>
<td>0.4480</td>
</tr>
</tbody>
</table>
Table 9.2. shows stress relaxation data for immersed (4 weeks) and non-immersed HDPE specimens.

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Non-Immersed Stress (MPa)</th>
<th>Four weeks Immersed Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.16</td>
<td>10.8</td>
</tr>
<tr>
<td>10</td>
<td>9.45</td>
<td>9.25</td>
</tr>
<tr>
<td>20</td>
<td>8.80</td>
<td>8.50</td>
</tr>
<tr>
<td>50</td>
<td>8.35</td>
<td>8.05</td>
</tr>
<tr>
<td>100</td>
<td>7.65</td>
<td>7.40</td>
</tr>
<tr>
<td>300</td>
<td>6.85</td>
<td>7.10</td>
</tr>
</tbody>
</table>

(See figure 9.1.)

Table 9.3. gives the yield stress measurement of petrol immersed specimens.

<table>
<thead>
<tr>
<th>Tensile Specimen</th>
<th>Yield Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (immersed)</td>
<td>26.91</td>
</tr>
<tr>
<td>2 (immersed)</td>
<td>26.07</td>
</tr>
<tr>
<td>3 (immersed)</td>
<td>26.19</td>
</tr>
<tr>
<td>Average (immersed)</td>
<td>26.39</td>
</tr>
<tr>
<td>Non-Immersed</td>
<td>30.00</td>
</tr>
</tbody>
</table>
FIGURE 9.1.

Stress MPa

Non-immersed

Petrol Immersed 4 Weeks

TIME, SEC.
Table 9.4. Dimensional changes

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After 4 weeks Petrol Immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Length</td>
<td>181.5</td>
<td>193.5</td>
</tr>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gauge width</td>
<td>12.7</td>
<td>12.8</td>
</tr>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>3.2</td>
<td>3.34</td>
</tr>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9.5. Weight Changes After Four Weeks Petrol Immersion

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Initial Weight (g)</th>
<th>Final Weight (g)</th>
<th>Change (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.437</td>
<td>9.045</td>
<td>0.608</td>
</tr>
<tr>
<td>2</td>
<td>8.467</td>
<td>9.100</td>
<td>0.633</td>
</tr>
<tr>
<td>3</td>
<td>8.498</td>
<td>9.154</td>
<td>0.656</td>
</tr>
<tr>
<td>4</td>
<td>8.472</td>
<td>9.132</td>
<td>0.660</td>
</tr>
<tr>
<td>5</td>
<td>8.568</td>
<td>9.205</td>
<td>0.637</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.639</td>
</tr>
</tbody>
</table>
9.4. **Discussion**

From the results, it can be seen that petrol enhances the impact strength of the HDPE specimens; as expected, lower temperatures lead to lower impact strengths. Some constituents of petrol may act as a kind of plasticiser; the practical significance of this is that the tank will have less chance of leaking on a heavy impact if it has had petrol in it for a while. This increase in impact strength with increased petrol uptake is obviously a desirable property.

Table 9.2. shows that the non-immersed specimen maintains a higher stress at 5% strain. Therefore, it has a higher relaxation modulus. Petrol from the immersed specimen evaporates after about 300 seconds, and this is manifest in a positive deviation from linearity.

The immersion in petrol for four weeks lowers the yield stress of a tensile specimen from 30 MPa to 26.4 MPa; although it is desirable to have a high yield strength, the benefit from increase in impact properties after immersion seems to far outweigh the decrease in yield strength.

As can be seen in Table 9.4, the most significant dimensional increase, after immersion, is in the total specimen length. The length is increased by about 10 mm (5.5%) whereas the cross sectional area increased only by about 6.9%. The total volume
increase was approximately 12.7%.

Weight changes were consistent throughout the five specimens; the average weight increase was 7.5%.

The increase in dimensions in the longitudinal direction can be attributed to differences in swelling caused by orientation. It is therefore advisable for the manufacturer to take this effect into account when designing the tank (it is also important that only the inner side of the tank will be subject to immersion, in use). The tank may be designed to expand in certain directions after several months of service so that it fits well into the allocated space in the car.

Diffusion of petrol into the specimens is dependent on crystallinity. Normally crystallised polymers will swell less in comparison with amorphous regions; there is less free volume between the molecules of an ordered region in which the relatively small petrol hydrocarbon molecules can move. Some part of the petrol acts as a plasticiser, this part will diffuse between the polymer chains (more easily in amorphous regions) and interfere with interchain bonding; chains that can move independently will lead to a material that can absorb shocks without cracking. This interference of interchain bonding leads to a lower yield stress, as observed.

The textural organisation of semi-crystalline polymers imposes some chemical consequences. The
interlaminar or amorphous regions provide diffusion channels through which suitable reagents can permeate more easily; chemical reactions tend to occur preferentially at or near fold surfaces. The fold surfaces may also be more accessible to the small reagent molecules, thus reinforcing the chemical reactivity in these regions. In polyethylene, gauche bonds are present in the folds but not in the fold stems (these bonds are more reactive). End groups may be concentrated at or between fold surfaces, and as they are chemically different from the basic monomeric unit, they may bring specific and localised chemical reactions to these areas.

The interlamellar amorphous regions and fold surfaces are the areas penetrated by part of the petrol, in the permeation tests. In the stress relaxation experiments, some molecules in the petrol acted to plasticise the amorphous regions, thus allowing chain segments to slip more easily, thus promoting subsequent stress relaxation.

Brittle materials do not possess mechanisms of blunting adventitious cracks; in crystalline polymers, crack blunting is connected with intercrystalline regions.

Crystalline polymers that are stressed (internally or externally), when brought in contact with chemicals, may be subject to two consequences. Chemicals admitted to the crucial interfacial regions may, if present for a prolonged period, plasticise the local
volume so that high stresses cannot be withstood. Secondly, the amount of interlamellar crosslinking depends on the ratios of molecular length to crystallite thickness, which needs to be sufficiently large to maintain ductility. Lower molecular mass material is more vulnerable to cracking for a given thickness; this material crystallises from the last remaining melt pockets, and is thus segregated, leading to concentration of the material most at risk in particular localities. The performance is improved by the removal of lower molecular mass polymer.
10. Structure of a Rotational Moulding

10.1. Introduction

Rotational moulding is possibly an alternative manufacturing method for plastics fuel tanks. Typical materials in use are the Stamylex polyethylenes (DSM), which have medium molecular weights, and high melt flow indices. Rotational moulding has the advantage of using only thin-walled, inexpensive moulds. The process involves the partial filling of the heated mould with polyethylene powder; the mould is then rotated about two perpendicular axes. The powder is distributed on all the walls of the mould. The mould may be cooled by quenching in cold water.

This investigation examines the microstructure of products made by this low pressure process, and questions whether the mixing is adequate.

10.2. Procedure

The morphology of the polyethylene was examined for gold coated prepared specimens, with a Cambridge 'Stereoscan' scanning electron microscope.
10.3. Results

Figures 10.1. and 10.2. are of a plane surface, prepared with a glass knife, and representing a through-the-thickness section of the moulding.

Figure 10.3. and 10.4. are of a similar surface after etching for 30 minutes in permanganic acid at 70°C.

Figure 10.1. (x23). General view of surface of a section through the wall, showing faults, (holes).
Figure 10.2. (x300). Better view of skinning caused by smearing the surface.

Figure 10.3. (x380). Etching on the surface of a hole.

Figure 10.4. (x18). Some parts of the moulding are reminiscent of Gruyere cheese.

The overall picture obtained from viewing these rotation moulding sections is that the structure would be entirely unsuitable for a fuel tank.

10.4. Discussion

The electron micrographs shown are proof of the inferior structure of rotational moulded products: holes would lead to easy nucleation of cracks and brittle failure; high permeation and evaporation of the contents of the tank.
Figure 10.1 General View of Surface of CAT Rotational Moulding (23 Times) 0 435 870 μm

Figure 10.2 View of Skinning Caused by Smearing the Surface. (300 Times) 0 33 67 μm
Figure 10.3 Etching of a surface Hole in CAT Rotational Moulding (380 Times) 0 26 53 µm

Figure 10.4 Etched Section Showing Holes In Rotational Moulding (18 Times) 0 0.55 1.11 mm
The medium density material used in rotational moulding will have lower crystallinity than that used in blow moulded fuel tanks. The decrease in density and crystallinity will lead to higher permeation, which is undesirable in fuel tanks.

The process relies on a low pressure generated during the rotation. The acceleration toward the centre of the mould is given by \( w^2 r \) or \( v^2 / r \), where \( w \) = angular velocity of rotation of mould, \( r \) is the radius, and \( v \) is the velocity at this radius; force = mass.acceleration; this force is usually less than one gravity, and hence the material will tend to come away from the mould when it is rotated onto the top side, i.e. it will tumble. A remedy would possibly be to use a faster rotation speed (centrifugal moulding) or a larger axis of rotation; this would place more shear force on the polymer and possibly increase mixing. However, equipment would be more expensive; the main advantage with rotation moulding is the cheapness of equipment.
Conclusions

Much of the investigation reported in this thesis had evolved from the regulations given in Appendix 4, which specify the quality of plastics fuel tanks in use in EEC countries. The tank must pass an impact test, this aspect was thoroughly investigated. Also important is the effect of extent of permeation of petrol into the walls of the tank; petrol immersion tests were also performed. Strength of hot plate welds, although not specifically mentioned in the regulations, is examined; welds had previously caused frequent failures in production tanks (e.g. International Harvester tank).

The following sections conclude the results.

1. Cooling Effects in Blow Moulded Tanks

A microstructural interface appears in all of the fuel tanks examined. It has been shown in other work that the interfaces arise from the use of a cold mould in the blow moulding operation. This is often the case in practice as the shortest possible cycle time is sought. Work on the half bottles (Chapter 5) showed that low mould temperatures (10°C) in blow moulding lead to poor impact properties. This interface typically occurs at about 150 μm from the outer surface of the wall; quenching occurs adjacent to the cold mould, and crystallinity is
lower compared with the rest of the thickness. The interface marks a boundary between low and high crystallinity, and fine and coarse texture. Keith and Padden's theory of spherulite growth implies that the process relies on diffusion of impurities away from a growing tip of a fibril. The diffusion activation energy will consist of two parts: energy of migration of the impurity; and energy of formation of a vacant site into which the impurity can go. The cold mould may cause an adjacent region to be at insufficient temperature to reach the required diffusion activation energy. Once the temperature is adequate, the diffusion may not restrict spherulitic growth, and the texture will be correspondingly coarse, and crystallinity high. The fine structure observed adjacent to the mould is formed rapidly at low temperature, with little opportunity for diffusion. Also, more nuclei will be formed at a low temperature, on the mould-side; this will result in higher nucleation and smaller spherulites.

Apart from lowering impact properties, this interface results in a lower heat extraction rate as the low crystallinity region has a lower thermal conductivity; this means that only limited reductions in cycle times are obtained from lowering the mould temperature during blow moulding. We have observed that half bottles made using a mould temperature of 55°C had much better impact properties. No real peak effect was observed for the impact properties, within the experimental temperature range, although it does
seem sensible to assume that there is an optimum temperature; in any case, as the temperature of the mould is increased, there must be an effect on cooling time; the mould temperature must be a compromise. The work on half bottles did not demonstrate the type of relationship between mould temperature and impact properties. Further work, with more reliable equipment, should be carried out to ascertain the nature of this relationship accurately.

Increasing internal air flow rate during cooling in blow moulding was shown not to affect impact properties significantly. An increase in air flow rate, however, significantly lowers the cooling time needed. This means that a high mould temperature can be used, which leads to better impact properties, compensated for cooling times if internal cooling is employed. This will be viable if the engineering costs of installing an internal cooling system are not too high; the preferred coolant is air (ambient temp.); carbon dioxide may be more effective but it is also more expensive.

When blow moulded articles are removed from the mould, the surface which has been in contact with the mould heats until it reaches an equilibrium level; this is called the re-heat temperature.

The cause of re-heat is the high heat transfer coefficient at the cold mould/polymer interface. When the moulding is removed from the mould, the
Surface heat transfer coefficient becomes negligible and the thermal gradient within the wall moves towards an equilibrium; the temperature throughout the wall will be approximately constant. The same can be said of internal cooling; a high internal air flow rate will result in a high heat transfer coefficient; when internal cooling is stopped, the heat transfer coefficient on the inside of the moulding, will become negligible.

(2) Geometric Effects

Pinch-offs were deteriorating features of almost all the tanks examined; they were associated with voiding, which penetrated into the wall of the tank. Pinch-off areas were later shown to be detrimental to impact properties; brittle failure usually occurred on the pinch-off line after impact. It was noted, however, that above a certain thickness, the effect of the pinch-off in lowering impact properties was not so great, and a more ductile failure can occur. More work should be carried out on these features to ascertain the best conditions for making a pinch-off that is not a weak point on the tank.

Thickness distributions were investigated on all the blow moulded fuel tanks. The most uniform appears to be in the Peugeot Talbot 309 tank. The knowledge of thicknesses is important as it will affect impact and permeation properties, both of which are critical in fuel tanks (see Appendix 4). The effect of thickness on impact properties was investigated in this work.
It was found that the peak was almost directly proportional to the thickness. Energy to the first peak, and failure energy were proportional to thickness raised to a power greater than 1. The relationship varied from tank to tank; this may have arisen from experimental variation, but other factors too e.g. the manner in which the tank was made, and material used may be influenced. It is obvious that an optimally processed tank will lead to higher impact properties; whether this affects the exponent or the multiplying constant is as yet, unknown.

Little can be found in the literature concerning what affects thickness; a model was discussed in the literature review but this does not seem to be sufficiently accurate. More work needs to be carried out on this subject before thickness can be controlled satisfactorily. If fuel tanks are always to be made to be fitted into the car rather than the car to be fitted around the fuel tank, than the parison will have to be thickened in places that are to be expanded more during blowing. Despite the Peugeot Talbot tank being very angular, the thickness distribution is reasonable. The kiss-offs are possibly weakening features as thicknesses near these areas are sometimes small; the parison should be preferentially thickened corresponding to where the kiss-off will be. Preferential thickening should be used at the pinch-offs, also, to balance the detrimental effect of these features.
(3) **Structure and Physical Properties**

Pigment dispersion in the blow moulded fuel tanks was found to be bad, in general. Poor processing conditions and masterbatching techniques, using low density polyethylene (LDPE) as carrier polymer are thought to be responsible for this.

Failure modes of specimens in impact testing were quite consistent; the impact striker formed a hole in the specimen, made by tearing the material at the periphery of the hole until a tab was formed; this joined this circle of material to the main body of the specimen. The hole formed was too small for the striker to pass through without resistance; this resistance energy was not considered as a true part of the total failure energy. Brittle failure, during impact testing, was only observed on pinch-offs.

Most of the welds examined on the fuel tanks were not satisfactory. Microscopy was the main tool used for examination; orientation in the welds could be observed by using a polarising microscope. The observation of the tank welds was difficult because of carbon black pigmentation. Weld failures are common in fuel tanks. The weld joins injection moulded fittings to the main body of the fuel tank; the seal must be both strong and impermeable to fuel. Heating times were found to be too short and welding temperatures too high; this leads to degradation of material near to the weld. The reason for the use of short heating times was economy. The materials to be
welded should have similar MFI values (rarely the case), should not be degraded and orientation should be controlled. Injection moulded fittings were, sometimes, found to be badly moulded; orientated skins were often observed on the moulding; also orientation was conspicuous on section of the fittings. Good dispersion of pigment in the main blow moulded tanks is also important.

Viscosity and melt flow index are highly dependent on molecular weight which is possibly the most important structural variable affecting flow properties. The zero-shear melt viscosity is determined by the weight average molecular weight, and the dependence of viscosity on shear rate depends on the molecular weight distribution. The drop in melt viscosity below its 'Newtonian' value begins at lower shear rate with polymers with broader molecular weight distributions. It is thus important for HDPE components that are welded together to have similar MFI and molecular weight distribution values.

A welded extruded sheet container was also examined. This has disadvantages: it is not very easy to obtain complex shapes using this method; the welding is not easy and could easily be faulty if the sheet were not properly aligned; and the weld is a potential weak point on the container.

A test on thermal oxidative stability of polymers was investigated, which identified the polymers suitable for welding. Polymers that degraded after a few
minutes at 200°C in air were considered to be unsuitable. Rigidex H060-45P was found to have a higher thermal oxidative stability than Lupolen 4261-A, and was thus better suited to welding at higher temperatures. This was because of inclusion of antioxidants in Rigidex H060-45P

(4) Additional Studies

Tests showed that petrol immersion is not detrimental for impact properties, although yield stress is lowered. Weight changes are of the order of 7.5% after a 4 week immersion period. Dimensional increase is dependent on orientation; tensile bars have significant length increases along the main axis of the bar (6.61%); the width of the bar increases by less than 1%; the thickness of the bar was initially too small to be able to detect increases in dimension accurately. These immersion tests were carried out using HDPE Lupolen 4261-A, which is characterised by high molecular weight; grades of polyethylene used in blow moulding tend to be similar. Rotational moulding used medium or lower molecular weight resins; these should theoretically have higher permeation.

At present, blow moulding is the most suitable method for production of plastics fuel tanks. Rotational moulding was briefly investigated and found not to be satisfactory; the microstructure tends to be porous and this leads to increased permeation and poor impact properties. The microstructure arises because
the process operates at low pressure, and little mixing or shearing occurs. The medium density polymers used in rotational moulding leads to lower crystallinity in the product. Permeation, a product of diffusivity and solubility, is increased with decreasing crystallinity. The product will also be less stiff and be more susceptible to creep deformation.
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This section describes statistical tests and procedures used in the project.

T-Test

The t-test is a parametric test of the difference between two means of two independent samples. The test assumes that the two sets of scores come from normal populations with equal variance, but the test is not affected by minor violations of these rules. It is also assumed that measurements are on an interval scale.

Although both the Z and t-tests are parametric two-sample tests, the t-test is specially adapted for small samples (where one or both samples are smaller than thirty) and is less powerful than the Z test.

In essence the t formula measures the size of the difference between the means of two samples and converts them into a standard measure of deviation. Hence a large value of t signifies a marked difference between the sample means and, correspondingly, a low probability that the samples vary purely by chance. If this probability falls below 0.05, the chance hypothesis may be rejected in favour of the alternate hypothesis that there is a genuine reliable difference between the levels of performance in the two experimental conditions.

Unlike the Z test, the t statistic cannot be converted into a probability without taking into account the sample sizes, or more precisely, the degrees of freedom of the test.
In calculating the standard deviation of a set of $N$ scores, $N-1$ will be free to vary; the $N$th score is fixed to give the whole set the predetermined mean; there are two sets of scores; $N_1 + N_2 - 2$ degrees of freedom.

\[
t = \frac{(\bar{X}_1 - \bar{X}_2) \sqrt{\frac{2}{N_1 N_2}}}{\sqrt{\frac{(N_1 S_1 + N_2 S_2)}{(N_1 + N_2)}}}
\]

$S$ and $\bar{X}$ denote variance and mean respectively.

GENSTAT

GENSTAT is a computing language for data manipulation and statistical analysis. Procedures are frequently required and may be written, stored, and subsequently retrieved for use by a few simple instructions. GENSTAT can handle many sets of data in one computer run: a feature that can be very useful when results obtained from one set of data are needed to control operations on a subsequent set.

All the commonly occurring experimental designs can be analysed, e.g. all orthogonal designs with one or more error terms, and designs with balanced or partially balanced confounding. Output includes the analysis of variance table, tables of means and effects of standard errors. The model is simply and concisely specified using model formulae. Missing values are allowed and analysis of covariance is provided. Treatment terms can be partitioned into polynomial (linear, quadratic, etc) or other, user-defined contrasts.

Linear regression analysis can be carried out for weighted or
unweighted data. By adding or dropping variables from the regression model, a sequence of analyses is easily obtained. Automatic selection of variables is also available. Analyses can be produced for several dependent variables simultaneously. Output includes analysis of variance tables, regression coefficients with standard errors and variance covariance matrix, and fitted values with residuals. The results of analyses can be saved in standard GENSTAT data structures for further analysis or display.

Users are not restricted to the use of classical regression models based on the Normal distribution; for example, log-linear models based on the Poisson distribution are available for analysis of contingency tables. When the data are proportions, models based on the Binomial distribution can be used.

The following is an example of a GENSTAT program to fit an equation

\[
\log (\text{force}) = A \cdot \log (\text{thickness}) + B \cdot \log (\text{temperature})
\]

where \(A\) and \(B\) are constants.

`refe'Polymer
`unit'$34
`vari'thickness,temp,force
`read'thickness,temp,force
`calc'logforce=log(force) : logthick=log(thickness)
`terms/prin=c'logthick,temp,logforce
`y'logforce
`fit'logthick
`add'temp
`run'
The simplest first order linear regression model in one variable \( X \) is
\[
Y = B_0 + B_1.X + \text{error}(e)
\]

The straightforward analysis can be neatly expressed in matrix terms. Usually more complex models are needed: more than one independent (or predictor) variable is necessary to explain results.

Matrix analysis may be applied to the following linear model:
\[
Y = B_0.X_0 + B_1.X_1 + B_2.X_2 + e
\]

- \( Y \) = response; \( X_0 \) = dummy variable, whose value is always unity; \( X_1 \) & \( X_2 \) are independent variables; \( Y \) is \([ n*1 ]\) vector; \( X \) is \([ n*3 ]\) vector; \( B \) is a \([ 3*1 ]\) vector; and \( e \) is a \([ n*1 ]\) vector \( (n\) is the number of data points.

The least squares estimates of \( B_0, B_1 \) and \( B_2 \) are given by
\[
b = (X'X)^{-1}X'Y
\]

where \( b \) is the vector of estimates of the elements of \( B \), provided that \( X'X \) is nonsingular. \( X' \) means that columns and rows are interchanged; \( X \) signifies the inverse of \( X \).

- \( b_0 \)!
- \( b_1 \) is obtained and hence the following equation:
- \( b_2 \)
\[
Y = b_0 + b_1.X_1 + b_2.X_2
\]

In reality, when these matrix calculations are performed
by a computer routine, they are not carried through in precisely the same manner; one reason for this is that large rounding errors occur when this sequence is followed; coding and decentralisation are employed.

Use of GLIM Program

GLIM is similar to GENSTAT; GLIM was used in the welding experiment to fit a polynomial of the following form:

\[
\text{response} = b_0 + b_1 M + b_2 F + b_{11} M^2 + b_{22} F^2 + b_{12} M F + \text{error}
\]

To estimate a model involving squared terms, it is necessary to carry out runs at three levels of each variable; a particularly useful set of designs for estimating second degree polynomials is Central Composite Rotatable Design. This is formed by taking a two level factorial experiment and supplementing it by centre points (at which all variables are set to their mid ranges), and star points (at which one variable is set at the greatest or least and with remaining variables set to the middle of the range). The design has at least two advantages over the conventional:

- it allows the investigation of interactions between the separate factors;
- even if there are no interactions, the factorial approach makes more economical use of the experimental material.

GLIM is preferred to other similar programs for the following reasons:

1) it can handle any combination of qualitative factors, and it provides a simple, concise way of specifying complex factorial experiments;
2) unexplained variations, not normally distributed, can be handled;

3) facilities are provided for drawing graphs of the residuals, i.e. the differences between the observed values and those predicted by the fitted model; examination of the residuals can often help to assess the adequacy of the fitted model.
APPENDIX 2

The following are the results from the calculations carried out on Bradford University's computer. They predict cooling behaviour as a function of air flow rate and mould temperature during the blow moulding process.

<table>
<thead>
<tr>
<th>RUN NUMBER</th>
<th>AIR FLOW RATE (L/Min)</th>
<th>AIR HTC W/m K</th>
<th>MOULD WALL TEMP, °C</th>
<th>TEMP 4 MIN FROM START, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>INSIDE</td>
<td>MIDDLE</td>
</tr>
<tr>
<td>1</td>
<td>160</td>
<td>30</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
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Cooling times were approximated from the following time-temperature curves: the slope of the curve is initially at a constant negative value; the slope levels at the start of crystallisation; when crystallisation is complete, the slope resumes the same negative slope. The time to resume this slope from the initial parison temperature is the nominal cooling time.

An equation was fitted to predict these times as a function of air circulation rate and mould temperature, in the results. The following are predicted values.

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<td>105</td>
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<tr>
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PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data
+++++ Inside surface
***** Outside surface

TEMPERATURE (°C)

TIME (h)

0 24 48 72 96 120 144 168 192 216 240
PLOT OF TEMPERATURE vs POSITION
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (−)
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

***** Inside surface
***** Outside surface

TEMPERATURE (°C)

0 20 40 60 80 100 120 140 160 180 200

TIME (h)

0 24 48 72 96 120 144 168 192 216 240
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.
Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION

- 200 -

TEMPERATURE (°C)

- 0 -

0 0.001 0.002 0.003 0.004 0.005

POSITION (m)

---

t = 20s
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)

- t= 20s

---

RUN...
PLOT OF TEMPERATURE vs TIME

- Inside surface
- Middle
- Outside surface

Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION
PLOT OF TEMPERATURE vs TIME

- Inside surface
- Middle
- Outside surface

Experimental Data

Inside surface
Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

0  0.001  0.002  0.003  0.004  0.005

- 20  40  60  80  100  120  140  160  180  200

t = 20s

---
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

- Inside surface
- Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

0  0.001  0.002  0.003  0.004  0.005

t = 20s
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)

$200$
$180$
$160$
$140$
$120$
$100$
$80$
$60$
$40$
$20$
$0$

$0.001$
$0.002$
$0.003$
$0.004$
$0.005$

$\uparrow t = 20s$
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

+++++ Inside surface
++++++ Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)

-100  -90  -80  -70  -60  -50  -40  -30  -20  -10  0  10  20  30  40  50  60  70  80  90  100

-0.001  -0.002  -0.003  -0.004  -0.005
PLOT OF TEMPERATURE vs TIME

- Inside surface
- Middle
- Outside surface

Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)
PLOT OF TEMPERATURE vs TIME

- Inside surface.
- Middle.
- Outside surface.

Experimental Data

+++
Inside surface

+++ 
Outside surface
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (C)

POSITION (m)
PLOT OF TEMPERATURE vs TIME

- Inside surface
- Middle
- Outside surface

Experimental Data

+++++ Inside surface
***** Outside surface
PLOT OF TEMPERATURE vs POSITION.

-temperatures vs position graph with different lines indicating temperature at different positions.
PLOT OF TEMPERATURE vs POSITION

TEMPERATURE (°C)

POSITION (m)
PLOT OF TEMPERATURE vs TIME

- Inside surface
- Middle
- Outside surface

Experimental Data

- Inside surface
- Outside surface

TEMPERATURE (°C)

TIME (s)
APPENDIX 3

Statistical Analysis of Results of Impact Tests

This section shows the raw data from the impact work; also shown is the statistical analysis of these data. The data are analysed using the GENSTAT program (see Appendix 1). Tables of output from the GENSTAT program are given. The program used to analyse the data precedes the tables; the program lines are numbered. A correlation matrix indicates the strength of relation between two factors; 0 is weak, and 1 or -1 is strong. Regression coefficients and analysis of variance tables are explained in Chapter 5.

Impact Results for Half Bottles

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<th>Thickness, Mould Temp, C</th>
<th>Air Circ Rate, L/min</th>
<th>Peak Force, N</th>
<th>Peak Energy, J</th>
<th>Energy, J</th>
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## Program for GENSTAT

```plaintext
1 'refe'Polymer
2 'unit'$86
3 'vari'thickness,temp,flow,force
4 'read'thickness,temp,flow,force
5 'calc'thick2= (thickness)
6 'terms/prin=c'thick2,temp,force
7 'y'force
8 'fit'thick2 (thick2 is thickness)
9 'add'temp
10 'run'
```

### Correlation Matrix

```
***** CORRELATION MATRIX *****

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DF = 84
***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: force

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<th>T</th>
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S.E. is standard error, T is Estimate/ S.E.; if this is greater than 2 then the estimate is significant.

*** ANALYSIS OF VARIANCE ***

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<td>-6.723E7</td>
<td>67231647</td>
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</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 45.1 (the higher this value the better the fit)

***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: force

<table>
<thead>
<tr>
<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>1125.419</td>
<td>552.127</td>
</tr>
<tr>
<td>thick2</td>
<td>863.998</td>
<td>83.612</td>
</tr>
<tr>
<td>temp</td>
<td>33.532</td>
<td>7.085</td>
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</table>

*** ANALYSIS OF VARIANCE ***

<table>
<thead>
<tr>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
<td>8.415E7</td>
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</tr>
<tr>
<td>RESIDUAL</td>
<td>6.269E7</td>
<td>755267</td>
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<tr>
<td>TOTAL</td>
<td>1.468E8</td>
<td>1727487</td>
</tr>
<tr>
<td>CHANGE</td>
<td>-1.692E7</td>
<td>16917604</td>
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</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 56.3 (reasonable fit)
Peugeot Talbot Petrol Tank Impact Results

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Peak Force (N)</th>
<th>Peak Energy (J)</th>
<th>Peak Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>4606</td>
<td>37.37</td>
<td>81.24</td>
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<td>4.0</td>
<td>5514</td>
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<td>100.2</td>
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<td>4.0</td>
<td>5509</td>
<td>46.46</td>
<td>100.0</td>
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<td>98.58</td>
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<td>107.0</td>
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<td>5671</td>
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<td>106.6</td>
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<td>54.66</td>
<td>113.2</td>
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<td>4.3</td>
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<td>111.0</td>
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<td>5915</td>
<td>54.12</td>
<td>107.6</td>
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<td>57.72</td>
<td>112.2</td>
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<td>6496</td>
<td>60.17</td>
<td>120.4</td>
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<td>6525</td>
<td>61.85</td>
<td>128.2</td>
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<td>4.8</td>
<td>6369</td>
<td>68.11</td>
<td>131.6</td>
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<td>5.2</td>
<td>7394</td>
<td>68.82</td>
<td>135.9</td>
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<td>6691</td>
<td>66.84</td>
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<td>67.17</td>
<td>156.9</td>
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<td>168.7</td>
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<td>8689</td>
<td>87.5</td>
<td>189.3</td>
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<tr>
<td>6.2</td>
<td>9094</td>
<td>85.4</td>
<td>201.8</td>
</tr>
</tbody>
</table>

Analysis of Impact Force

A program to fit force = constant*(thickness) (all of the following programs have been written to fit this type of relationship).

1 'refe'Polymer
2 'unit'$24
3 'vari'force,pen,fen,thickness
4 'read'force,pen,fen,thickness
5 'calc'thick2=log(thickness):lg=log(force)
6 'terms/princ'thick2,lg
7 'y'lg
8 'fit'thick2
9 'run'

MN is mean, MIN is minimum value, and MAX is maximum value.

<table>
<thead>
<tr>
<th>Force</th>
<th>MIN MIN MAX</th>
<th>6489.6667</th>
<th>4606.0000</th>
<th>9094.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pen</td>
<td>MIN MIN MAX</td>
<td>60.7429</td>
<td>37.3700</td>
<td>87.5000</td>
</tr>
<tr>
<td>Fen</td>
<td>MIN MIN MAX</td>
<td>127.9800</td>
<td>61.2400</td>
<td>201.8000</td>
</tr>
<tr>
<td>Thickness</td>
<td>MIN MIN MAX</td>
<td>4.7167</td>
<td>3.7000</td>
<td>6.2000</td>
</tr>
</tbody>
</table>

- 226
***** CORRELATION MATRIX *****

    DF = 22

log(thickness) 1  1.0000
lg            2  0.9731  1.0000
              1  2

***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: lg

<table>
<thead>
<tr>
<th></th>
<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>6.9637</td>
<td>0.0912</td>
<td>76.37</td>
</tr>
<tr>
<td>log(thickness)</td>
<td>1.1678</td>
<td>0.0589</td>
<td>19.82</td>
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</table>

*** ANALYSIS OF VARIANCE ***

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
<td>1</td>
<td>0.64300</td>
<td>0.642999</td>
</tr>
<tr>
<td>RESIDUAL</td>
<td>22</td>
<td>0.03601</td>
<td>0.001637</td>
</tr>
<tr>
<td>TOTAL</td>
<td>23</td>
<td>0.67901</td>
<td>0.029522</td>
</tr>
<tr>
<td>CHANGE</td>
<td>-1</td>
<td>-0.64300</td>
<td>0.642999</td>
</tr>
</tbody>
</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 94.5 (good fit)

Analysis of Peak Energy

Program

1 'refe'polymer
2 'unit' $24
3 'vari' force,pen,fen,thickness
4 'read' force,pen,fen,thickness
5 'calc' thick2=log(thickness):lg=log(pen)
6 'terms/prin=c' thick2,lg
7 'y/lg
8 'fit' thick2
9 'run'

***** CORRELATION MATRIX *****

    DF = 22

log(thickness) 1  1.0000
lg            2  0.9731  1.0000
              1  2

- 227 -
***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: $\log$  

<table>
<thead>
<tr>
<th></th>
<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>1.7981</td>
<td>0.1255</td>
<td>14.33</td>
</tr>
<tr>
<td>$\log(\text{thickness})$</td>
<td>1.4830</td>
<td>0.0811</td>
<td>18.28</td>
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</table>

*** ANALYSIS OF VARIANCE ***

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
<td>1</td>
<td>1.03693</td>
<td>1.036934</td>
</tr>
<tr>
<td>RESIDUAL</td>
<td>22</td>
<td>0.06823</td>
<td>0.003101</td>
</tr>
<tr>
<td>TOTAL</td>
<td>23</td>
<td>1.10517</td>
<td>0.048051</td>
</tr>
</tbody>
</table>

CHANCE  -1 -0.36934 1.036934

PERCENTAGE VARIANCE ACCOUNTED FOR 93.5 (good fit)

Analysis of Failure Energy

1 'refe'Polymer
2 'unit' $\$24$
3 'vari'force,pen,fen,thickness
4 'read'force,pen,fen,thickness
5 'calc'thick2=$\log(\text{thickness})$; $\log = \log(fen)$
6 'terms/prin=c'thick2,$\log$
7 'y'$\log$
8 'fit'thick2
9 'run'

***** CORRELATION MATRIX *****

DF = 22

$\log(\text{thickness})$  1  1.0000
$\log$  2  0.9752  1.0000

1  2

***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: $\log$  

<table>
<thead>
<tr>
<th></th>
<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>2.3927</td>
<td>0.1182</td>
<td>20.23</td>
</tr>
<tr>
<td>$\log(\text{thickness})$</td>
<td>1.5784</td>
<td>0.0764</td>
<td>20.66</td>
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</tbody>
</table>
### Analysis of Variance

#### ANOVA Table

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<tr>
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<td>1.1746</td>
<td>1.1746</td>
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<tr>
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<td>0.0606</td>
<td>0.0028</td>
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<tr>
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<tr>
<td>Change</td>
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</tr>
</tbody>
</table>

Percentage variance accounted for 94.9 (good fit)

---

Impact Results for Peugeot Talbot Diesel Tank

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Peak Force (N)</th>
<th>Peak Energy (J)</th>
<th>Failure Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>6759</td>
<td>62.59</td>
<td>132.9</td>
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<tr>
<td>4.8</td>
<td>7624</td>
<td>79.71</td>
<td>162.7</td>
</tr>
<tr>
<td>5.2</td>
<td>7350</td>
<td>65.32</td>
<td>122.4</td>
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<tr>
<td>5.3</td>
<td>7204</td>
<td>68.29</td>
<td>143.8</td>
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<tr>
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<td>7507</td>
<td>69.04</td>
<td>151.3</td>
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<td>8659</td>
<td>88.99</td>
<td>158.4</td>
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<td>8508</td>
<td>87.49</td>
<td>178.7</td>
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<td>158.1</td>
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<td>83.72</td>
<td>169.9</td>
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<td>211.9</td>
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<td>90.22</td>
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<td>108.9</td>
<td>215.4</td>
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<tr>
<td>7.0</td>
<td>10005</td>
<td>97.18</td>
<td>213.1</td>
</tr>
</tbody>
</table>

Analysis of Peak Force

1 'repe' Polymer
2 'unit' $17$
3 'var' 'thickness,force,pen,fen'
4 'read' 'thickness,force,pen,fen'
5 'calc' 'thick2=log(thickness):logf=log(force)
6 'terms/prin=c' 'thick2,logf'
7 'y' 'logf'
8 'fit' 'thick2'
9 'run'
***** CORRELATION MATRIX *****

\[ \begin{array}{ccc}
\text{log(thickness)} & 1 & 1.0000 \\
\log f & 2 & 0.7902 & 1.0000 \\
\end{array} \]

***** REGRESSION ANALYSIS *****

Y-VARIATE: logf

<table>
<thead>
<tr>
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<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
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</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>2.4491</td>
<td>0.3921</td>
<td>6.25</td>
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<tr>
<td>log(thickness)</td>
<td>1.1197</td>
<td>0.2242</td>
<td>4.99</td>
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</table>

*** ANALYSIS OF VARIANCE ***

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
<td>1</td>
<td>0.2219</td>
<td>0.221939</td>
</tr>
<tr>
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<td>15</td>
<td>0.1335</td>
<td>0.008900</td>
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<tr>
<td>TOTAL</td>
<td>16</td>
<td>0.3554</td>
<td>0.022215</td>
</tr>
<tr>
<td>CHANGE</td>
<td>-1</td>
<td>-0.2219</td>
<td>0.221939</td>
</tr>
</tbody>
</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 59.9 (reasonable fit)

Analysis of Failure Energy

1 'refe'Polymer
2 'unit'\$17
3 'vari'thickness,force,pen,fen
4 'read'thickness,force,pen,fen
5 'calc'thick2=log(thickness):logf=log(fen)
6 'terms/prin=c'thick2,logf
7 'y'logf
8 'fit'thick2
9 'run'

***** CORRELATION MATRIX *****

\[ \begin{array}{ccc}
\text{log(thickness)} & 1 & 1.0000 \\
\log f & 2 & 0.8337 & 1.0000 \\
\end{array} \]

- 231 -
***** REGRESSION ANALYSIS *****

*** REGRESSION COEFFICIENTS ***

Y-VARIATE: logf

<table>
<thead>
<tr>
<th></th>
<th>ESTIMATE</th>
<th>S.E.</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.8342</td>
<td>0.3945</td>
<td>7.19</td>
</tr>
<tr>
<td>log(thickness)</td>
<td>1.3193</td>
<td>0.2256</td>
<td>5.85</td>
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*** ANALYSIS OF VARIANCE ***

<table>
<thead>
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<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>REGRESSN</td>
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<td>0.308095</td>
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<tr>
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<td>0.009009</td>
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<tr>
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<td>0.4432</td>
<td>0.027701</td>
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<tr>
<td>CHANGE</td>
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<td>0.308095</td>
</tr>
</tbody>
</table>

PERCENTAGE VARIANCE ACCOUNTED FOR 67.5 (reasonable fit)

Comparison of Pinch-Off Impact Results

---

PT Petrol

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Peak Force, N</th>
<th>Peak Energy, J</th>
<th>Failure Energy, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.4</td>
<td>2994</td>
<td>27.03</td>
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</tr>
<tr>
<td>6.6</td>
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<td>60.6</td>
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<tr>
<td>8.5</td>
<td>9270</td>
<td>107.70</td>
<td>193.2</td>
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</tbody>
</table>

PT Diesel (Manufactured by Blagden Industries)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Peak Force, N</th>
<th>Peak Energy, J</th>
<th>Failure Energy, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8</td>
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<td>124.9</td>
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<td>119.9</td>
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<tr>
<td>6.3</td>
<td>7810</td>
<td>70.94</td>
<td>130.6</td>
</tr>
</tbody>
</table>
Summary of Annex 5 of EEC Regulations Concerning Fuel Tanks

(Regulation number 34, December 1979)

1) The tank must pass a pendulum test at (within 2 °C of) −40 °C; mass of pendulum is 15 Kg and radius of rotation is 1m. The energy of the pendulum should not be less than 30 Nm.

2) Cracking or leaking should not occur when the tank is subject to a pressure test at (within 2 °C of) 53 °C. The tank is filled to capacity with water and is pressurised at 0.3 bar for 5 hours.

3) The maximum permissible average loss of fuel shall be 20g in a 24 hour testing period. The tank shall be filled to half capacity, stored, and hermetically sealed. Storage temperature is within 2 °C of 40 °C.

4) After having been subject to 3, tests 1 and 2 should be passed.

5) A fire resistant test should be passed.

6) The tank is filled to half capacity with water at 20 °C, and is subject to a temperature of within 2 °C of 95 °C for one hour. The result of the test should be considered satisfactory if the tank does not subsequently leak or is seriously deformed.