Powder injection moulding of steel–hardmetal graded structure composites

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POWDER INJECTION MOULDING OF STEEL-HARDMETAL
GRADED STRUCTURE COMPOSITES

by

Peter Lane

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University of Technology.

August 1991

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ABSTRACT

The powder injection moulding route has been evaluated as a fabrication method for the production of graded structure hardmetal coatings on steel substrates.

The experimental process route adopted involved placing a steel substrate within a mould cavity and sequentially injection moulding layers of hardmetal feedstocks over the substrate surface. There was a requirement to enlarge the cavity after successive moulding shots to create space for the next layer. The moulded composite was thermally debound and pressure sintered.

Key areas addressed during the study were: i) achievement of adhesion between the different layers, ii) transfer during debinding of the adhesive function from feedstock binders to the powders, iii) the accommodation of differential thermal shrinkages within the layers and iv) the design of suitable injection mould tooling.

Powder injection moulding feedstocks utilising a thermoplastic binder exhibited too large a shrinkage to form a stable bond with a steel substrate. An elastomeric binder system was developed which had a lower shrinkage, this system developed satisfactory adhesion. Each adhesion step in the process was individually validated. Initial attempts at moulding more than two layers of the multilayer structure were disrupted by distortion of the underlaying layers. After simple process modelling, graded process parameters were derived which reduced the forces associated with moulding the higher layers, enabling the complete structure to be sequentially moulded. The moulded units were successfully debound and consolidated by ceramic grain hot isostatic pressing.

A prototype three dimensional rock bit was fabricated to demonstrate the process and explore tooling practicalities.
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1.0 INTRODUCTION

Tool wear is a significant cost for many rock drilling and mineral refining activities [1,2]. A reduction of this cost would be welcome. Present day rock tools such as cutter chains and drill bits are fabricated from steel and tungsten carbide hardmetal [3]. The steel is used to fabricate the base structure of the tool and hardmetal is utilised to form the cutting surfaces. In this manner the best properties of the two materials can be exploited, the steel provides a tough shock resistant support for the hard wearing but brittle tungsten carbide. A typical steel would be a nickel rich alloy [4,5] such as AISI 4815, and the preferred hardmetal grade would be 6% cobalt + 94% tungsten carbide [6].

The joining of steel and hardmetal is problematic, the thermal expansion coefficient of hardmetal is about half that of steel and large interfacial stresses can be generated between bonded hardmetal/steel as a result of thermal exposure during service or fabrication [7,8]. Conventional metallurgical bonding techniques such as welding and brazing can only be used with difficulty because of the large thermal stresses generated and the damage that the processing temperatures can inflict on heat treatment conditions and carbon levels [3].

The difficulties of forming a steel-hardmetal bond have been overcome in modern rock drilling tools by use of button bits [6]. The hardmetal is formed in the shape of a button head with a shank which can be shrink or interference fitted into the steel body of the drill [3]. The button head is typically mushroom or cone shaped for percussive drills and chisel edged for rotary drills. The mechanical fitting eliminates the problems associated with brazing techniques but requires grinding of the hardmetal shank to a tight tolerance.
The button bit is limited in length because the hardmetal is brittle, the bit will snap off if the cutting edge of the button is allowed to protrude very far from the steel backing. In consequence bit designs are squat with low aspect ratios. This limit on bit dimensions places a limit on the depth of cut which is possible. Some drilling heads are produced which have steel cutting teeth, the toughness of the steel enables large teeth to be used which can take large cuts during drilling. However steel is a comparatively soft material and the service life of such drills can be limited. A button bit which could exhibit both the hardness of hardmetal and the toughness of steel would enable large and hard-wearing bits to be realised with consequent improvements in drilling performance. Possible approaches to this end, utilising existing coating technologies to coat a steel blank with hardmetal are not realistic in view of the limits of present technology. The coating layers possible are either too thin or too poorly adherent to be of significant value [9]. A possible way forward is to fabricate a structural composite with a hardmetal exterior and a steel core; in which the thermal property mismatch can be accommodated without recourse to the weak interlayers typical of present technology.

British Petroleum, (B.P.) has developed a graded structure technology [9] which enables such a composite to be fabricated. The composite comprises many material layers, the property differences between each layer are graded to limit the severity of the thermal expansion mismatch across each interface. In this manner the hardmetal can be joined to the steel using strong metallurgical welds without the presence of sharp and destructive discontinuities. The hardmetal layers form a large proportion of the composite structure and cannot be considered just as a coating but rather as "half" the composite.

The graded structure technology was developed as a powder
processing operation, because this is the only possible processing route for the hardmetal. Initial studies performed by B.P. utilised simple laboratory procedures which were not attractive as a commercial manufacturing method. A manufacturing system offering size and shape flexibility with appreciable levels of automation is essential to realise the potential of the graded structure composite.

A candidate manufacturing route is powder injection moulding, (PIM). The process offers the potential to shape and position powders with substantial freedom due to the plastic nature of the feedstocks used. It was proposed [10], that the layers of the graded structure could be moulded by PIM in three dimensional shapes and further that the multi layer structure could be built up by sequentially moulding the materials of the graded structure over a steel substrate. The first layer to be moulded would become the new substrate for the second layer and hence repetition could permit a multi layer injection moulding, (MLIM) process to be created.

The aim of this work was to examine the feasibility of using a MLIM procedure with PIM technology as a manufacturing route for the graded structure composite system.

Some specific objectives were identified: (a) to determine parameters for the PIM of the materials constituting the graded structure, (b) to determine conditions for interlayer adhesion between the layers of the graded structure, (c) to investigate the art of MLIM and (d) to develop experience with the design of injection mould tooling for MLIM using PIM feedstocks.

The progression of the project depended heavily on utilising existing science and technology; the subjects of particular importance to this study are discussed in chapter 2.
2.0 BACKGROUND THEORY AND TECHNOLOGY

2.1 POWDER METALLURGY

2.1.1 Introduction

This guide to powder metallurgy (P/M) is by necessity selective and is intended to provide only the essential background to this study. The guide is further biased in that the science and technology of steel and hardmetal, the materials of interest, is emphasised.

A comprehensive history of P/M is given by Cortezl [11] and the diversity of the P/M field has been considered by German [12], the American Society for Metals [13] and others [14,15,16].

In essence, the P/M process procedure is:

a) to mix or blend the powders;
b) to form a compact by filling a die with powder which is then pressurised to yield a shaped body with sufficient strength for handling;
c) to heat the compact to develop its strength via sintering reactions.

The primary question of P/M is, why process metal powders? There are many alternative methods available for the shaping of metals. There are three main reasons for the use of P/M, [17] firstly some materials can only be processed successfully by P/M, secondly the P/M process can demonstrate large economies with respect to competitive processes for part production and thirdly the use of powder processing can enable a wide range of technically unique and advantageous material systems to be fabricated.
The first reason is well illustrated by the refractory metals [18], in particular tungsten, molybdenum and tantalum. These metals are too hard and have melting points too high to be shaped by conventional methods. They can however be prepared as powders by chemical means and the powder compacted, sintered and hot worked.

The second reason for using P/M, that of economy, accounts for much of the industry's output. Detailed shapes can be formed in a single pressing stroke without the expense and waste of machining operations. Typical parts made for economic reasons include timing belt pulleys, oilpump gears and magnetic pole pieces.

The third reason, that of unique properties, is generating many new applications for the P/M process. P/M can permit greater control of microstructure than fusion processing, for example highly alloyed tool steel can be fabricated without the segregation problems of fusion techniques [19] and the hardening mechanism of oxide dispersion can be effectively utilised, because the P/M route can yield a uniform distribution of the two phases [20].

Powder metallurgy has developed into a modern industry and future growth is seen to come from the unique advantages offered when fabricating the new advanced materials such as the graded structure composite structure, which forms the basis of this study.

Properties of P/M materials depend heavily on the starting powder. Often the structure of the powder is not obliterated during the processing but rather is gradually changed at each step. In consequence a defect in the original powder can cause a defect in the finished article. This dependency of end properties on starting properties and the effects of gradual process transmutation has been described
systematically for ceramics by Messer [21] and Pask [22]. Powder characteristics are discussed below.

2.1.2 Powder Characteristics

An appreciation of powder characteristics is fundamental to understanding P/M process behaviour. Some of the characteristics of a powder are fixed by the materials' intrinsic properties and there is little scope for their modification by the powder metallurgist. For example, aluminium has a low specific gravity, and in consequence aluminium powders will exhibit a low bulk density. Determination of the extrinsic characteristics is shared between the powder manufacture and the end user. The powder fabrication route has a very strong influence on powder characteristics, but they can be modified by the end user to suit specific applications [23,24]. Characteristics of importance include: particle size and size distribution, particle shape, surface area, microstructure, flow properties and apparent density. Powder characteristics have been reviewed by Rhodes [25].

The measurement of powder characteristics is sensitive to sampling errors and many techniques [26,27] have been developed to ensure a representative sample is taken for characterisation. Particle size and size distribution is commonly measured by sieving methods [28]. A stack of sieves with increasing mesh sizes is prepared and a powder sample shaken down through the stack, each sieve traps all the oversize material. The proportions of the samples retained by each sieve can be used to plot a distribution of particle size. Sieving is not however practical for fine powders because the meshes required are very delicate and prone to clogging. Microscopy can be used for particle sizing as described in ASTM E20. Increasingly, modern microscopes are fitted with image analysis equipment to reduce the labour
intensive nature of this method. Other particle sizing techniques include sedimentation, light scattering and electrical conductivity [29]; these techniques can be applied to fine particles.

Particle size will influence the total surface area of a powder, this parameter is of importance in process reactions such as deoxidation and sintering. Particle surface area may be measured by gas adsorption using the B.E.T. method [30], or by permeametry, pycnometry and mercury porosimetry [31]. Particle size distribution will affect the packing efficiency of the powder, a broad distribution will give an improved packing density because the small particles can fit into the gaps between the large particles. It is possible to tailor make particle size distributions to optimise packing density. Typically three to five particle sizes are blended [32,33,34,35].

Particle shape can be qualitatively described according to type [36], for example, flake or dendritic. Many mathematical shape factors have been proposed and are becoming of increasing interest as computer based image analysis methods are improved, particularly with the use of fractals [37]. Particle shape will affect packing and flow properties.

Particle microstructure can strongly influence powder compressibility. An alloyed or quenched particle will exhibit more resistance to deformation than a pure annealed particle, so exhibiting a different response to the pressing operation [38].

Powder flow is an important consideration, the use of automatic die filling devices requires a free flowing powder. Flow can be assessed by timing the flow of a given weight of powder through a funnel, as described for the Hall
Flowmeter in ASTM B213. Flow is impaired by irregular particle shapes, fine particle sizes, low intrinsic density and high intrinsic friction coefficients.

The apparent density (AD) of a powder is the density of a freely poured powder. Determination of AD can be performed with the Hall Flowmeter and Cup as detailed in ASTM B212. The AD will determine the fill factor required in press tooling and the amount of compaction required to attain a desired density level. AD is decreased by particle irregularities, whereas spherical particles give the best packing. A wide particle size distribution can improve packing and hence raise AD. Fine particles pack poorly and tend to reduce AD. A powder with a low AD will require a great amount of compaction to achieve a usable density. This will yield a compact with good green strength but probably at the expense of a higher pressure requirement and reduced flow properties. In practice a balance between the conflicting characteristics is necessary.

2.1.3 Powder Manufacture

The powder manufacturing method influences powder characteristics. In consequence knowledge of a powder's origin is essential for an understanding of subsequent processing behaviour. Manufacturing methods can be divided into mechanical, chemical, electrodeposition and atomisation procedures. Their operation and effects on powder characteristics have been considered in detail by various authors [39] and only an overview will be presented here.

Mechanical Fabrication

Powder manufacture by mechanical processes is not a major fabrication route [40], the powder produced is typically coarse, work hardened and irregularly shaped, yielding an
unattractive set of characteristics compared to other powder fabrication processes. But some specialised utilisations of mechanically fabricated powder are performed.

Metal machining can be used to produce powder. [41] the technique is particularly useful for small scale production runs. Impact techniques can form powder production routes which are of particular value if the metal is brittle. The most common impact device is the ball mill. Other impact devices include vibratory mills and projection targets [42].

Chemical fabrication

Chemical powder fabrication is well illustrated by the sponge iron process [43]. This well established route utilises the solid state reduction of iron oxide with carbon powder to yield a porous agglomerate of iron particles. Iron oxide is sourcable from both ore and mill scale. The oxide is brittle and readily prepared as a powder by milling. A powder blend of iron oxide and carbon can then be mixed. The blend is furnaced, to cause reduction in a manner analogous to that of blast furnace chemistry. The product of furnacing is a cake of lightly bonded particles with a high void volume. The cake is broken up by grinding and then conditioned with an anneal to optimise the particle hardness and carbon level. Alternatively, metal oxides can be reduced via gas/solid reactions. For example, cobalt oxide is commercially reduced in a hydrogen or carbon monoxide furnace atmosphere [44].

Metal powder can also be fabricated by vapour phase techniques, typically those based on carbonyl chemistry [45]. Such processes are used commercially to produce iron and nickel powders.
Chemical precipitation of metals from solution can be practised \[46\], the resulting particles tend to be fine. It is possible to produce composite powders when one metal is used to nucleate the precipitation of the second \[47\].

**Electrodeposition**

Metal powders can be produced electrochemically in an aqueous cell \[48\]. The process is expensive and tight control of cell chemistry is required. In consequence the process is only used when the high purity levels attainable are essential. Powders produced as a sponge deposit include copper, silver and zinc; powders produced as a brittle deposit include iron and manganese. A major disadvantage of electrodeposition is that only elemental metals can be processed.

**Atomisation**

The atomisation process is the main powder fabrication technique \[50\], because it has the advantage of enabling almost any melt to be processed, in particular tightly specified alloys can be powdered. Further, through control of process parameters the powder characteristics can be manipulated with more flexibility than is possible under other manufacturing routes. Atomisation is, in essence, the break up of a liquid into fine droplets, this process requires a large energy input, the method used to provide this energy demarcates the different atomisation approaches.

The principle atomisation technique uses a high pressure fluid jet to disrupt a stream of molten metal \[51\]. Molten metal is poured through a nozzle into the top of a tower chamber, the resulting stream of metal is then impinged on by a pattern of fluid jets which break the stream up. The metal droplets fall in a widening cone, freezing during
passage. A model of the break up process is available [52]. Common atomising fluids are water, air and argon. Water provides a fast cooling rate and gives irregularly shaped particles. The heat transfer of gas atomisation is not so severe and spheroidisation of the droplets can occur yielding rounded particle shapes. Powder oxidation is caused during water atomisation, the oxidation levels produced by air atomisation can be acceptable if the air is dry, but for oxide free powder inert gases such as argon must be used.

An alternative to fluid jet atomisation is centrifugal atomisation [53]. The molten metal is rotated at high speed in a disk geometry and drops of the metal will break away from the disk's edge and form a spray of powder. A typical arrangement comprises a horizontally mounted disk rotating at speed, molten metal is poured from a crucible onto the disk and is "flung" off into a collecting volume. The particle size can be controlled to give near monodispersed powders. A rotating consumable electrode can be used to process refractory metals [54].

Metals can also be atomised by the soluble gas process [55]. A melt can be saturated with gas and then released into a vacuum, the gas expands in an explosive fashion breaking up the melt.

2.1.4 Powder Preparation and Lubrication

It is rare that a metal powder can be used directly; some precompaction preparation is usually required. The powder characteristics can be manipulated to optimise both the processing behaviour and end properties. There are however many different factors involved and many different approaches to achieving the best optimisation of the competing requirements. Each manufacturer will develop
process specific solutions. The main preparation steps are described below.

It may be desired to modify the particle size distribution [56], for example to increase the proportion of fines to aid sintering or to form a bimodal distribution to improve packing. To further this end powders can be classified into size fractions and then selectively reblended. Alloy materials can be advantageously prepared by mixing elemental powders [57], the alloy composition can be readily tailored and the comparative softness of the elemental powders utilised in compaction. Care must be taken not to over mix powders because this can lead to work hardening and consequent reduction of compressibility [57].

Lubricants are mixed with powders used in the traditional press and sinter manufacturing route [58]. The lubricant reduces friction effects in compaction tooling. If a die compaction tool is used without lubrication excessive wear and ejection forces will be experienced with tool seizure the probable outcome. Compaction can be performed without powder lubrication by applying lubricant to the tooling surfaces of a normal die. This latter option is however difficult to automate and is not in commercial use. Typical lubricants are materials such as stearic acid, zinc stearate and many waxes. These materials are all short chain molecules with some degree of surface specific interaction. The interaction may differ according to the metal and the optimal lubricant for one metal may be poor with another [58]. The lubricant can be over mixed with the powder to give less than optimal properties. If the lubricant is too well distributed over the particles surface, green compact strength and powder flow is reduced, and there is less free lubricant to lubricate the tooling surfaces [58].
Lubricants are typically used at loading levels of 0.5-2.0 weight percent [58]. This amount of lubricant will reduce the density of the pressing feedstock and, to a limit, the ultimate density achievable during compaction. High levels of lubricant can severely reduce compact green strength, but the reverse effect can be promoted with selected waxes to bond otherwise weak compacts [58]. Multi component lubricant systems may be needed to optimise powder flow, die lubrication and green strength [58].

The lubricant is burnt out of the compact prior to sintering. This process can be detrimental to sintered properties if an adverse residue is left. For example, metal oxides and carbon can be produced within the compact during burnout. Careful choice of lubricant and furnace atmosphere are required to achieve a complete burn out.

2.1.5 Powder Compaction

Powder compaction is performed by the application of pressure to the powder. The pressure has the effects of forcing the powder to conform to the cavity shape, increasing the packing density of the powder, promoting powder cohesion and the development of compact strength.

Compaction can be considered as a multi stage process [59,60]. Initial densification can be attributed to particle slippage or transitional restacking [61], the amount of densification attributable to this mechanism is believed to equate with the difference between apparent and tap densities [61]. The end point of this initial stage is believed to occur when a rigid network of point contacts is formed [60]. With increasing pressure the point contacts can flatten through plastic deformation to form areas of contact, at yet higher pressures bulk deformation of the particles may occur. The powder may also densify by
fragmentation, a metal forced to undergo large plastic deformation can become embrittled through work hardening. These stages or mechanisms of compaction do not necessarily take place in discrete sequence [60], but can act concurrently in differing proportions according to system properties. Further more some of the stages may not be exhibited by a particular powder as reported by Hardman and Lilley [62]. The densification produced by increasing pressure is subject to diminishing returns, as the metal progressively work hardens.

The development of compact strength, termed green strength, can be attributed to two mechanisms. Firstly, green strength can arise from the mechanical interlocking of particles, and secondly, from welding at the points of particle contact. It is problematic to investigate the action of the two mechanisms [63] and a clear demarcation of the mechanisms was not found in the literature. But it is believed that mechanical interlocking is the predominate mechanism for irregular particles at low compaction pressures and that point contact welding dominates for spherical particles at high pressures. [63] A low apparent density powder typically has an irregular particle shape which will promote the development of green strength through mechanical interlocking but the low starting density necessitates a high level of densification which provides many opportunities for welding. In commercial practice a roughly spherical particle shape is preferred for compaction. Such a shape leads to reasonable powder flow whilst retaining some potential for interlocking, and the mid range value of apparent density reduces the compaction work required to achieve a usable compact density.

The relationship between compact density and compaction pressure is of practical importance. The exact form of the relationship depends on powder characteristics, for example,
Fine powders require higher compaction pressures than coarse powders. Many empirical relationships are available for die compaction where the pressure distribution is complex [59]. Other workers as reported by Lenel [63] have studied compaction by isostatic means and have proposed pressure-density relationships founded on fundamental bases.

2.1.6 Powder Metallurgy compaction Tooling

In this section only tooling used in die compaction is described. Isostatic compaction tooling is described elsewhere [64,65]. The principle of die compaction tools is illustrated in Figure 2.1.6. Two punches, the upper and lower, operate in a die body. The punches are free to slide in the die body along the centre line. The pressing cavity is defined by the punch faces and die body wall. In operation the tool is opened by retracting the upper punch, powder is then admitted to the die body. The upper punch is returned to enclose the powder for pressurisation. The pressure is applied via the punches to the powder from an external press. To eject the compact the upper punch is retracted and the compact pushed clear of the die by action of the lower punch.

The die and punches are exposed to high stresses and abrasion. In consequence a typical tool set will have a die made of hardmetal inserted into a steel backing, and punches are made from tool steels such as D2 & H13. A standard working clearance for tooling is 0.0006 in/in. This high tolerance is required to prevent powder becoming trapped between the sliding surfaces of punch and die, the outcome of which is extreme wear and tool seizure. A tool set with the above specification [66] is expensive and it is possible to fabricate less expensive tooling in proportion to the life time, i.e. number of pressings, required.
Part design and tooling design interact and need to be considered together. The compaction process is subject to some limitations: reentrant features cannot be fabricated because ejection is impossible; the pressurised powder exhibits very little hydrostatic flow and as a result there is little horizontal powder movement in the die cavity and a uniform powder fill is essential; there are pressure losses as the compaction pressure is transmitted through the powder, this effect will produce a density gradient with highest density near the punches, a part height to width ratio of 3:1 is a limit beyond which this density gradient can cause problems [67].

Part shape will determine tooling shape, the shape must be chosen to meet both part requirements and tooling practicalities. Thin walled tooling is prone to failure and part shapes must avoid its use. Similarly feather edges on tooling associated with radii or chamfers will readily fail. Large angle chamfers with an end flat are preferred. Sharp corners can result in stress concentrations for both the pressurised die and the part. The part will expand slightly on ejection and a stress concentration may cause failure. A component with a thin section of large surface area is difficult to fabricate, achieving a uniform powder fill to avoid density variations is difficult, and the thin section is fragile and prone to crack when ejected.

When the compaction pressure is released from tooling the die and punches will exhibit elastic springback [66]. This elastic recovery must be balanced across the part dimensions to avoid part fracture, this effect becomes more important as part complexity increases.

Green part dimensions are controlled by tooling size, level of powder fill and compacting pressure. Tooling size is determined empirically to allow for sintering shrinkage,
tool elasticity and ejection expansion. The powder fill and compaction pressure act on part dimensions in a coupled manner, an increased powder fill will either result in a larger part or, if the pressure is raised, can result in a part of the original size but of higher density.

A compaction tool can be operated in three basic modes [66], single acting, double acting and floating die. In a single action system only one of the punches moves during compaction. Single action pressing is only used for thin parts. In double action systems both punches move in the die during pressing, this double ended movement reduces the density gradients in the part otherwise caused by poor pressure transmission through the powder. To further aid uniform part density a floating die system can be used. The die is free to move down over the lower punch during compaction.

The tooling is operated by a press which can cycle the tool through the filling, compaction, and ejection steps automatically. Such presses have been reviewed by Burns [66] and further aspects of tooling are described elsewhere [68,69].

2.1.7 Sintering and Consolidation

A powder compact prepared by die pressing is insufficiently strong for direct use. Sintering reactions can be used to increase compact strength and they are essential to the P/M process. In essence sintering is the phenomenon that occurs when a powder compact is heated to a temperature which does not exceed, but is a large fraction of, the metals' melting point. The compact gains strength and may shrink with consequential density gain. A compact is particulate in nature and contains a large amount of surface energy. It is this energy which is released to cause sintering. The
reduction of surface area is thermodynamically favourable and can be driven provided that the energy required to create the new grain boundaries is not too great. The processes of sintering take place by mass transport and the increase in compact temperature is required to overcome the kinetic barriers.

The transport mechanisms of sintering have been the subject of many studies [70]. Mechanisms which have been identified with confidence include:

a) surface transport by i) surface diffusion via vacancy movements, ii) evaporation-condensation,

b) volume transport by i) volume diffusion, ii) viscous flow, iii) plastic flow

The sintering process for a powder, (freely packed), can be described by three stages of microstructural change. Initially bridging necks form between the particles. This increases the contact area between the particles and leads to significant strength improvement. The intermediate stage of sintering is that of neck growth which takes the microstructure from that of open to closed porosity. At the end of this stage the particles are joined into a strong mass with pores distributed throughout the bulk. The final stage of sintering is associated with pore shrinkage by vacancy diffusion to the grain boundaries. During this stage the grain boundaries may break away from the pores in a process of grain growth, this isolation of the pores causes the end of densification.

Enough atomic diffusion can be present during sintering for blended powders to interdiffuse and form alloys. This effect can be utilised to fabricate bronzes [71].
During a commercial sintering operation the pressing lubricant is burnt out and the chemistry of the powder can be modified to control the carbon and oxygen contents. To achieve these aims manipulation of the furnace atmosphere is essential. The subject of furnace atmosphere chemistry and the gas-solid reactions which take place during sintering is extensively described by Nayer [72]. The practical importance of this aspect of sintering is illustrated by Wahling et al. [73] who report dimensional distortion of high speed steel parts if delubricated in an oxidizing rather than neutral atmosphere.

The solid state sintering process described above has two main disadvantages, the process is slow and stops short of full density. This has led to various approaches to enhance sintering by accelerating the mass transport mechanisms.

One simple method to promote sintering is to use a finer powder. The increased surface area will increase the amount of surface energy available in the system to drive the sintering process.

Other approaches to enhanced sintering can be divided into (i) activated sintering and (ii) liquid phase sintering. In the former the energy difference between particle surface energy and grain boundary energy can be increased to raise the driving force for sintering. Or alternatively the activation energy for atomic diffusion can be reduced. Examples include, phase stabilisation of body centred cubic crystal forms, the body centred cubic crystal packing arrangement is more open than face centred cubic and allows freer diffusion. The ferritic phase of iron can be stabilised by alloying additions [74]. Surface diffusion transport mechanisms can be facilitated by coating the particles with a mobile layer, a layer one or two atoms thick is adequate.
For example, tungsten can be sintered if treated with palladium [75].

Liquid phase sintering is possible in mixed metal systems, if one of the metals can form a liquid phase at sintering temperature. The liquid promotes rapid transport mechanisms and can lead to rapid and full densification. Liquid phase sintering exhibits three characteristic stages [76]. Initially the liquid enables rearrangement of the powder particles, the liquid can wet out the particle surfaces allowing movement. With continued heating the solid phase will dissolve in the liquid. If solubility is limited a solution and reprecipitation process takes place. If the solid has a high solubility in the liquid, the liquid phase may recross the solidus to give a transient liquid phase. This behaviour is useful if full densification is not desired. The liquid phase densification reaches a limit when particle-particle coalescence limits the particle centre movements and further consolidation occurs by solid state reactions. If sufficient liquid phase is present to occupy the void volume full density is achieved at this point. Increasing the proportion of liquid phase promotes rapid sintering to full density but the end properties of the compact may be unacceptably affected.

A theory of liquid phase sintering is given by Kingery [77] and the subject has been reviewed by Tendolkar & Sebastian [78] and others [79]. Many examples of liquid phase sintering are reported in the literature. Wang et al. [80] describe the use of copper based alloys for the liquid phase sintering of irons. McGinn et al. [81] describe liquid phase sintering of "Stellite" alloys.

The sintering routes cannot be guaranteed to remove all the porosity from a compact; this can limit mechanical properties and hence applications of the manufactured part.
In recent years a demand has arisen for methods of fully densifying compacts, especially for applications where liquid phase sintering is not applicable. A method of achieving further densification once the sintering mechanisms have reached their limit is to apply pressure in addition to heat. The pressure promotes vacancy diffusion to grain boundaries and free surfaces. Various techniques have been developed to transmit the pressure to compacts. The first approach developed was hot pressing. \[82\] the compact was placed in a compaction die set fabricated from heat resistant material such as graphite and then pressurised inside a furnace. This approach had the disadvantage that each compact shape required a unique die and only one compact could be processed in each furnace cycle unless intricate procedures and equipment were used. A more practical approach is to use a fluid pressure transmission medium. The choice of suitable fluids which can operate at the temperatures required is limited. The industry standard fluid is argon. The pressurisation can be operated in isostatic mode by filling a chamber with compacts and then pumping in argon until the desired pressure is attained. This is the basis of the Hot Isostatic Pressing, (HIP'ing), process which is in widespread commercial use. A theory of HIP'ing is given by others \[83\], application examples given by Lebas and Raisson \[84\] and the technology is treated at length by Price and Kohler \[85\]. HIP'ing can successfully remove the last traces of porosity from parts with significant improvements in mechanical properties. However HIP'ing with argon has the disadvantage that porous parts cannot be densified unless they are sealed in an evacuated container to prevent the build up of internal gas pressure. The container shrinks with the part during HIP'ing and is machined off afterwards. The closing step adds to the process cost. A further disadvantage of argon HIP'ing is that the compressed gas presents a
potential physical explosion hazard, and considerable safety management is needed.

An alternative pressurising media is ceramic grain [86,87]. The grains enable a porous part to be densified without canning and greatly reduce the explosion hazard associated with a gaseous media.

A modern trend to integrated consolidation equipment is emerging where delubrication, sintering and HIP'ing are all performed in the same chamber [88].

2.1.8 Hardmetals

Hardmetal is the name given to a range of cermet compositions comprising carbides bonded with a metal. The industry standard material is tungsten carbide bonded with cobalt. The powder route is essential to the fabrication of hardmetals. These materials are prepared by blending tungsten carbide powder with powder of the cementing metal cobalt. This process yields a uniform distribution of the binder phase which can "cement", by liquid phase sintering the tungsten carbide at temperatures considerably less than those required to sinter the pure material. Hardmetal technology has been extensively treated by others [89,90,91] who present more detail than can be given here.

Tungsten carbide is prepared by furnacing blended tungsten and carbon powders to promote their interdiffusion. Great care is needed to achieve the correct stoichiometry which is a prerequisite of good mechanical properties. A brittle eta phase can result from carbon deficiency and is a major production concern. The ballmilling route is used to fabricate tungsten carbide hardmetal. A ball mill consists of a cylindrical drum which is rotated with the longitudinal axis horizontal. The drum is filled with a charge of hard
balls, the powder and, in most cases, a fluid for wet milling. During the rotation the balls are carried to the top surface of the drum by the rotational velocity, at which point they fall to the bottom causing impacts. The ball milling process has the particular advantage that mechanical alloying and dispersion of the cobalt cementing phase is possible, a uniformly mixed powder of tungsten carbide smeared with cobalt can be produced. The tungsten carbide particle size is fine, a result of the chemical precursors utilised in its production and its fragmentation when milled. To assist powder flow the particles are spray dried after milling to form agglomerates with a large effective particle size.

The liquid phase sintering of hardmetal compositions is reported by Kingery et al. [92]. The tungsten carbide-cobalt system used can exhibit very rapid densification when the liquid phase forms, full shrinkage will occur in a few minutes. Carbon control during sintering is essential to avoid formation of the brittle eta phase. Spriggs [93] describes the reactions which must be controlled to prevent carbon loss.

2.1.9 Steels

Steel powders are almost exclusively made by atomisation procedures because the alloy compositions can be accurately prepared as melts. Argon atomisation can be used but the bulk of production is water atomised. A typical powder has an irregular shape and a quenched microstructure.

During the conventional press and sinter operation compact shrinkage is not desired because the dimensional accuracy of the part can be compromised [94]. In consequence a regime is operated were the powder is pressed to as high a density as practical, typically to 70-85% dense, this density is
comparable to the densification state of intermediate sintering. Then a sinter is performed, which because of the large area of contact between the particles will result in good mechanical properties. The sintering time and temperature are controlled to avoid volume shrinkage. This regime enables the accuracy of press tooling to be utilised but the residual porosity limits the level of attainable mechanical properties.

2.2 Polymer technology

2.2.1 Introduction

In the preceding section powder metallurgy was reviewed, in this section polymer technology, the second half of the powder injection moulding process, is surveyed. The subject coverage is very selective to meet the information needs only of this work. Polymer technology has been extensively treated by Brydson [95], Billmeyer [96] and Crawford [97], all of whom can be referred to for further detail.

2.2.2 Polymers

Polymers are chemically synthesised by joining many small organic units, monomers, to form a macromolecular chain. The chain may be formed from a single monomer type, producing a polymer or from several types, producing a copolymer. The chains can be produced in linear or branched forms. Chain structure can be ordered or random, for example, a copolymer with a monomer unit sequence of ABABA... is ordered and a chain with side branches attached chaotically has a random structure.

Polymeric material consists of many polymer chains. In a typical material a molecular weight distribution is present, with low, medium and high molecular weights corresponding to
low, medium and high chain lengths. A simple model of most polymeric materials is to liken the chains to a mass of spaghetti.

At melt temperatures polymer chains are mobile and the polymeric material has fluid like properties. When cooled, different behaviour will be exhibited according to the chain structure present. If the chains are ordered then crystallisation will result; the crystallisation is rarely complete and some amorphous material will be present between crystalline zones. Many polymers are classified as semicrystalline and have solidification microstructures shared between crystalline and amorphous material. The degree of crystallinity can be controlled by the degree of chain order, for example, low density polyethylene has a chain structure with many random side chains of differing lengths, [98] high density polyethylene has either no side chains or side chains with a narrow length distribution, [98] in consequence the latter material is more crystalline. If the polymer is disordered then it may exhibit glassy behaviour when cooled. If the glass transition temperature is above ambient the polymer will gain rigidity. examples of such polymers are poly methyl metacrylate (Perspex) and polystyrene. Both the above cases are thermoplastic polymers, named as such because the material can be repetitively cycled with temperature from solid to liquid to solid. If the glass transition temperature is below ambient the polymer will remain in a fluid like state. Some polymers such as atactic polypropylene are so disordered that properties of the material are those of a "gooey gunge". Less disrupted polymers of higher molecular weight form elastomers, the chains are joined by entanglements and can uncoil under stress to produce the large elastic deformations characteristic of elastomers.
Copolymers may span the complete range of behaviour, a copolymer predominantly comprised of monomer A may be a crystalline thermoplastic but when monomer B is the main component elastomeric behaviour may be exhibited instead. For example, a copolymer of ethylene and vinyl acetate is a crystalline thermoplastic at high ethylene contents but is an amorphous elastomer at high vinyl acetate contents.

Some polymeric materials can be fabricated from short chains containing reactive groups which can form chemical links with other chains. If many links are formed the material becomes rigid and unable to melt. Such materials are termed thermosets.

To achieve a particular material property it is often more convenient to alloy, or blend polymers rather than attempt synthesis of a new type [99]. However very few polymers are fully compatible and phase separations can be produced [100,98]. For example, olefinic and aromatic polymers are not compatible. Often usable levels of compatibility with otherwise incompatible polymers can be attained by aggressive mixing and control of thermal history. Many blends are semicompatible and the linkage at the phase boundaries allows scope for manipulation of physical properties.

2.2.3 Polymer Properties

Polymer mechanical properties are strongly influenced by molecular weight and the degree of crystallinity, increases of which improve strength and stiffness. Polymer response to stress is viscoelastic, both viscous and elastic behaviour are present in tandem. This means that elastic responses are damped by viscous mechanisms. For example the "snap back" after the release of a stress may be slowed down to a response time of many seconds. The viscoelastic nature of
polymers makes possible a large degree of stress relaxation. A stressed polymer can exhibit viscous creep with time. A continuously loaded polymer may eventually fail due to excessive creep.

It is possible to soften and toughen polymers by admixing small molecular species termed plasticisers. These molecules act by separating the polymer chains, hence reducing their interaction. This technique is widely applied to poly vinyl chloride.

Polymer rheology has been extensively treated by Brydson [101]. Flow behaviour is typically pseudoplastic rather than Newtonian and can be represented by a power law equation. The temperature dependence of viscosity follows, to a good approximation, an Arrhenius type relationship [102].

Polymer degradation is greatly accelerated in the presence of heat and/or oxygen. Two competing degradation processes operate in response to heat [103]; polymer unzipping, during which the polymer depolymerises into the constituent monomer units and random chain scission which cuts the chain into small segments. In the presence of oxygen an O2 radical can form which readily attacks the chain. Degradation of the polymer chain is often preceded by loss of any side groups, for example a hydroxyl group attached to an alkane chain can be removed on heating to produce a water molecule and leave an alkene unit in the chain. Polymers can be ranked according to their tendency to form carbonic soot and smoke during breakdown [103]. Saturated structures are the least prone to carbon formation. Unsaturated polymers such as polydienes and aromatic structures favour carbon formation. Increasing the length of side chains will also promote sootiness. Halides inhibit oxidation and tend to form unsaturated chars.
2.2.4 Injection moulding

The most commonly used polymers in injection moulding are the thermoplastics. The polymer is heated to form a melt; while in this plastic state the polymer is forced under pressure into a mould cavity, the polymer takes up the shape of the cavity and is stabilised by cooling which results in crystallisation and hence rigidity gain.

A typical injection moulder is shown in Figure 2.2.4. Polymer is transported along the barrel by rotation of the screw. The screw length is divided into several zones typically a feed zone, a compression zone where melting takes place and a metering zone where melt is homogenised. Further zones may be included for mixing or venting. Heat to melt the polymer is provided by barrel heater bands and by mechanical shear during transport along the screw length. A reservoir of melt is present at the screw tip; injection is performed by applying pressure to the stationary screw length. It is also possible to design machines with a plunger type barrel in which the screw is replaced with a piston, but such machines are rare. The potential for mixing and heat transfer are limited in a plunger type barrel. Further the injection pressure is transmitted via a length of melting polymer and the effective pressure at the nozzle may not be stable. Injection machines are reviewed in detail by Johannaber [104].

An injection mould is built in two halves. The two halves can be held, closed together by hydraulic force to form the cavity shape and after moulding, the mould can be opened to release the moulding. It is usual to provide a set of ejector pins which act during mould opening to push the part free of the cavity. The mould split line is normally vertical.
Melt is transferred to the mould cavity via runner channels cut in the mould. Flow along a runner will cause a pressure drop due to wall friction effects and momentum loss at corners. Heat is lost from the melt to the mould bulk which can be thermally stabilised by circulating a fluid heat transfer medium through channels inside the mould. After mould filling the nozzle is retracted from contact with the mould and the runner channels solidify along with the moulding. Both are removed from the mould together and then mechanically separated. It is possible with sophisticated tooling to avoid this awkward step but this is not always practicable. Injection mould design has been treated at length by Pye [105] and Riley [106] who give more detail than can be presented here.

Injection moulders can be automatically cycled through the moulding procedure, the normal cycle is described below: mould closure, pressurisation of the melt, injection to fill the mould, pressure hold on during which the moulding cools, pressure release, mould opening, and part ejection. The cooling moulding will shrink, this means that the cavity shape is not faithfully reproduced. The hold on pressure is used to alleviate this problem, extra polymer can be packed into the cavity to fill the space created by shrinkage.

Injection moulding has been extensively treated by Crawford [97] and Rosato [107] who can be referred to for additional information.

2.2.5 Elastomer technology

Elastomers are rarely used in a pure state, but rather mixed with fillers and oils. The fillers can act as cheapeners and reinforcing agents, the oils can provide internal lubrication necessary to reduce the elastomer viscosity for processing. The presence of fine, sub micron particulate
fillers can provide a large increase in strength resulting in fracture strengths above that of the pure elastomer. To provide dimensional stability elastomers must be crosslinked, cured. In practice chemical links between the chains are formed at a level of about one per 100 monomer units. To further crosslinking chemical agents are added to the mix and reactive sites included in the chain structure. The crosslinking is temperature activated; during injection moulding, a heated mould is used to perform the reaction. Further aspects of elastomer technology are comprehensively treated by Blow and Hepburn [108].

2.3 Powder Injection Moulding

2.3.1 Introduction

Powder injection moulding (PIM) is a process route for the shaping of powdered materials; the technique was used in the 1930's in the production of ceramic spark plug insulators [109] but the wider potential of the process was not realised until the mid 1970's when Wiech [110] applied it to metallic powders. Development of the process has since taken place as described by Erickson and Wiech [111], Gutjahr and Pearse [112], Billiet [113], Haworth and James [114], Evans [115] and German [116]. The process utilises powder technology, powder metallurgy, polymer science and injection moulding techniques; it is a multi disciplinary subject.

A powder can be mixed with polymeric material to form a plastic composition, a plastisol, which can be shaped by injection moulding in a fashion analogous to that of normal polymers. After moulding, the polymer can be removed by various debinding procedures to leave a powder compact available for consolidation by conventional processes. Different approaches to the powder injection moulding

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The prime attraction of PIM is that the net shape - any shape capabilities of injection moulding can be applied to inorganic materials. A further attraction is that the hydrostatic nature of mould filling offers the potential for uniform part density across complex geometries [117]. These features enable the PIM process to overcome the geometry limitations inherent in powder die compaction and provides an extension to the shape capabilities of powder metallurgy and ceramic fabrication.

The PIM process can be divided into four key areas: (i) plastisol formulation, (ii) injection moulding, (iii) debinding and (iv) consolidation. These areas are described below.

2.3.2 Plastisols

A plastisol is a polymer-powder mixture. The plastisols utilized as injection moulding feedstock in the PIM process are widely developed and the subject of many patents: for example, Wiech [118], Rivers [119] and Farrow & Concictori [120]. Empirical experience has found that a plastisol composition of fine particle sized powder, 10 microns or less, [112,121,122,123] mixed with a low molecular weight olefin polymer, will give acceptable performance. This simple benchmark composition has been used to investigate plastisol properties at Loughborough University of Technology [124,125] and elsewhere [126,127].

There is a need to mix the plastisol with as high a level of powder as is possible, too little powder and the moulding will disintegrate when the polymeric binder is removed, and be difficult to densify. An empirical guide is that 50
volume percent is the minimum powder content which can be successfully used [128]. High powder loading also generates other advantages: sintering densification and debinding are promoted, part density gradients are reduced and the potential for debinding distortions is reduced. Much work has been performed on polymer-powder mixtures at lower loading levels as reported by Bhattacharge [129], but little work is published concerning the higher loading levels. A question of prime importance is, how high a loading can be mixed with the polymer? This question is decided by particle packing limits, the maximum random packing density for monodisperse spherical particles is 63.7% [128], at this point a network of interparticle contacts forms and the polymer is unable to fully coat the particles. This packing maximum is an important feature of PIM because at this powder loading plastisol viscosity tends to infinity [127], a real process limitation. The exact packing maximum for a specific powder will be influenced by particle shape and particle size distribution. An empirical equation to calculate critical powder loading in terms of tap density, pycnometer density and particle sphericity is given by Warren and German [130]. An experimental determination of the packing maximum is possible if a plot of plastisol density versus volume fraction powder loading is made. The density peaks at the packing maximum [127]. Alternatively the mixing behaviour can be observed, and the transition from a smooth melt to a "dry" lumpy composition taken as the point of the powder loading maximum [126]. In addition torque rheometry can be utilised to determine the powder packing maximum [131].

The dependency of viscosity on powder loading can be represented by many equations as reviewed by Edirisinghe and Evans [132]. Practical PIM systems are typically formulated with a volume powder loading 2-5% less than the maximum possible to give a usable viscosity [133,134]. At this
loading level there is sufficient binder present not only to fill the interparticle voids, but also to provide a particle coating which can prevent direct particle contact and perform a lubrication function. The polymer matrix will also influence plastisol viscosity and high melt flow index (BS3412) polymer grades are used, which are less viscous than conventional injection moulding grade material. The use of standard injection moulding grade polymers for the plastisol binder results in a very viscous melt, the viscosity increasing effect of the powder addition must be balanced by reducing the binder viscosity. Martyn et al. [124] report that hardmetal plastisols formulated with high molecular weight polymer exhibit too high a viscosity to permit practical mixing operations. This difficulty was resolved by utilisation of low molecular weight waxes in the plastisol compositions.

There is much interest among practitioners of PIM to increase powder loadings while maintaining a low plastisol viscosity: approaches to this end include blending particle size fractions to improve inherent particle packing [123], use of smooth spherical particles which can exhibit flow above the "maximum" loading level, selection of polar binder components which can interact with the particles [124] and utilisation of surface active additions to the polymeric binder to enhance the formation and adherence of a lubricating film on the particles [126,135,136]. The success of such systems is proprietary knowledge and is not openly published.

The rheological concepts developed for polymers have been found to translate to PIM. The rheological behaviour of plastisols is not Newtonian, but typically is pseudoplastic [123,137], flow curves can exhibit good experimental fit with the power law equation. Dilatant flow can arise above a critical shear rate for high powder loadings [117],
dilatancy is avoided by most practitioners unless very high powder loading levels are essential. Some plastisols, particularly those fabricated with sub micron powders, can exhibit a yield point for flow as reported by White [139].

Plastisol rheology is strongly influenced by the powder-binder interaction, if a large proportion of binder is immobilised at the surface of the particles then plastisol viscosity will be raised [140]. Addition of surface active substances can effect rheology of plastisols as reported by Plynshch and Siezko [135], and the powder-binder interaction can be investigated by rheology [140]. The interaction can be considered for the cases of complete particle wetting or nonwetting and consideration given to the effects of coupling agents as discussed by Bigg [126].

The role of powder binder interactions has been extensively studied for carbon black filled rubber compounds as reviewed by Blow [141].

In addition to acceptable flow properties a plastisol must exhibit some mechanical strength after moulding, the injection moulded material must gain rigidity in the cavity to survive ejection and handling stresses. This strength is normally provided by crystallization of part of the binder at mould temperature.

The plastisol formulation needs to fit the requirements of every stage of the PIM process, in the next sections further features of plastisol formulation pertaining to the individual process stages are detailed.

2.3.3 Injection Moulding

The injection moulding technology used in PIM is taken almost directly from conventional polymer injection moulding experience with the requirement of only a few modifications.
In essence injection moulding is a process where plastic material is heated to lower its viscosity and then pressurised to force the material into a shaped cavity in which the material gains strength and can be removed as a solid part. The process is discussed in section 2.2.4.

The high powder content of a plastisol raises its thermal conductivity above that of a pure polymer [122], in consequence the heat transfer within an injection moulder is improved and short screw lengths will provide satisfactory heating [112]. The raised thermal conductivity will also increase cooling rates, in practice this results in a limited flow length/time through unheated runners and mould cavities. In consequence flow paths are kept as short as possible and mould filling times are reduced as far as practicable, to ensure moulding is complete before the plastisol freezes. The high thermal conductivity of plastisols renders the nonisothermal nature of mould filling of particular importance [117]. Predictions of mould filling based on isothermal viscosity measurements are difficult to interpret because of the rapid cooling experienced within the mould cavity. A practical assessment of mouldability can be performed with a spiral mould [142,143], plastisol formulation and moulding conditions can be manipulated to yield the longest possible flow path under the nonisothermal state. For example, it has been found by Martyn et al. [117] that spiral moulding tests of hardmetal/wax plastisols are more temperature than pressure sensitive. Further aspects of "real" moulding conditions can be evaluated with a zig zag cavity [144]. Increasingly this problem can be solved by computer modelling [145] utilising packages such as "Mold Flow" [146]. A plastisol is more viscous than the polymer equivalent and runner and gate dimensions are enlarged proportionally [122]. Further enlargement and careful positioning of the gate can be performed to prevent jetting. Mould filling under conditions of jetting is believed to generate internal flaws in the moulding because of poor
adhesion at the weld lines created and the entrapment of air \([117,145]\). This problem can be avoided if conditions of plug like mould filling are used. Moulding defects may also be created if the plastisol binder exhibits a large and abrupt cooling shrinkage, such as that exhibited by highly crystalline materials with a narrow melting range \([117]\). Plastisol mouldings are not as strong as a normal polymer part and the inmould cooling shrinkage is greatly reduced leading to a tighter part fit in the injection cavity. In consequence a plastisol part may break when ejected from the mould, unless large taper angles are present on the cavity and large, well sited, ejector pins are used.

From the work of others \([117,127]\) it is possible to derive an empirical benchmark specification for plastisol flow and mouldability. Non dilatant flow must be exhibited up to shear rates of \(1000 \text{ s}^{-1}\) with an apparent viscosity not exceeding 2000 Pa s.

PIM feedstocks can be very abrasive and significant wear of injection machinery and in particular mould gates is a feature of the process, repairs and replacements are needed with a frequency not experienced when moulding normal polymers.

### 2.3.4 Debinding

After moulding, the binder must be removed from the plastisol to leave a powder part. This process is called debinding. It is necessary for some mechanism to be present or to be developed within the material to retain powder cohesion after polymer removal. Exactly how the powder coheres is uncertain, possible mechanisms include powder interlocking, adhesion from polymer chars and the onset of sintering reactions.
The most widely used debinding route is thermal [147], the moulding is heated in a gaseous atmosphere and the polymer is removed by evaporation. Some low molecular weight material may evaporate directly, but the binder will often need to be broken down by degradation reactions before evaporation can take place. Degradation by random chain scission is the expected behaviour. Consideration of the expected breakdown products can be a useful guide to polymer selection, if highly conjugated (carbon precursors) or toxic structures are the likely outcome an alternative polymer can be chosen. If debinding occurs too rapidly the gaseous products will raise the internal pressure of the moulding causing bloating, blistering and cracking. Such damage is prevented by use of controlled heating rates which limit the rate of binder breakdown and by use of multi component binders which can be progressively removed [148]. Optimization of thermal debinding to remove the binder as quickly as possible whilst avoiding part damage is of great commercial interest. At Loughborough University of Technology the results of thermal gravimetric analysis have been used to design debinding time-temperature profiles which take into consideration the temperatures at which the binder weight loss rate is at a maximum and reduce the heating rate in proportion to preserve part integrity [149]. Another approach to optimization is to debind under conditions of constant weight loss rate, a rate chosen which is "safe" and eliminates part damage. Systems to achieve this by monitoring in furnace weight are reported by Carlstrom [150] and Vago [151]. Issitt [152] has developed an experimental system which can derive time-temperature profiles to produce a specified mass loss rate. German [147] has outlined a theory of thermal debinding which may promote a more fundamental approach to debinding optimization. Pragmatic methods to reduce debinding times include use of high powder volume loadings as reported by Martyn et al. [124] and restriction of the process to parts with thin (a
few mm) cross sections. The approach used to design debinding profiles during this work is given in section 4.3.3. Thermal debinding is usually complete at 500°C but parts are often taken to higher temperatures to promote sintering which provides additional cohesive strength for handling purposes. Hardmetal parts can be strengthened in this way by cobalt diffusion to form a "brown" moulding [124].

Debinding in an inert atmosphere can result in a large carbon residue [124], debinding in the presence of oxygen allows burning of the binder with oxidative scission of polymer but can cause severe oxidation of metal powders, debinding in a hydrogen rich atmosphere can promote binder breakdown by hydrogenation reactions [153,154]. The gas flow rate through a debinding furnace can effect debinding performance, below a critical rate polymer cracking to carbon will occur [155] but a detailed understanding of this subject area is not at present available. Atmosphere control can have a large effect on carbon control; after debinding, the level of residual carbon left in the compact must be sufficiently low to avoid detrimental effects and this is a major process concern particularly for hardmetal parts.

During debinding part distortion can occur because the powder "floats" in the liquified binder and the shrinkages associated with removal of inter particle binder are not guaranteed to be isotropic [156]. Martyn et al. [117] has found that mouldings fabricated from plastisols with a low powder loading slumped during debinding unless supported with an alumina packing powder. Kipphut and German [157] recommend use of powder with a high compacted angle of repose to resist debinding distortions due to viscous creep. After debinding part size depends on the balance between, thermal expansion during the temperature rise experienced by the part and contractions caused by binder removal.
Debinding can be promoted if the part is packed in a fine porous media, low molecular weight binder components will be drawn out of the part by capillary action [158]. Solvents can be used to extract binder from parts, as described by Wiech [159]. Kennedy [158] and Finn [160] report the successful use of vacuum to promote debinding.

An alternative class of binder systems has been developed where the major component is water, as described by Rivers [119], and Schuetz [161]. Such binder systems are amenable to very rapid debinding but care is required to maintain feedstock stability and corrosion of powders and process equipment can occur.

To achieve very clean debinding without any residue it is proposed to use unzippable polymers, which can thermally degrade into monomer units [162].

2.3.5 Consolidation

The consolidation of PIM parts is not intrinsically different from the consolidation of P/M parts, discussed in section 2.1.7, except that the typical starting density is lower. In consequence, the use of some sintering enhancement, such as fine particle sizes [163] and/or high temperatures [164], is required to achieve full density.

2.4 Adhesion

2.4.1 Adhesion Theory

The proposed multi layer injection moulding process is an adhesion process; inter layer adhesion is an essential process requirement.
Adhesion can be defined as the ability of two bodies when brought into contact to resist separation. The process of adhesion may be interpreted in terms of firstly, the specific interactions between materials and secondly, how inter material contact is achieved. The specific interactions of adhesion can be attributed to the following well known mechanisms acting in isolation or more commonly two or more acting in collusion:

1) Mechanical interlocking, for example, the "Velcro" touch close fastener.

2) Dispersive forces i.e. Van der Waals and hydrogen bonding interactions.

3) Diffusion, either molecular or atomic, for example inter diffusion of polymer chains in heat sealed films, or atomic inter diffusion in the case of diffusion bonded metals.

4) Chemical bonding, bridging the interface between the adhering bodies with chemical bonds. For example, the silane glass/epoxy coupling agents.

5) Electrostatic attraction resulting from unlike charge interactions.

Before any of the above mechanisms can come into play, the two bodies, between which adhesion is desired, must come into contact with each other. This requirement is hindered by the presence of surface roughness. A normal surface is on the microscopical scale composed of a "mountain and valley" texture. When overlaid such surfaces are only in physical contact over the area of the mountain tops [165], this is a small fraction of the projected area and greatly limits the adhesive potential between the two bodies. The high degree
of contact required can be attained by wetting out the surfaces with a liquid, i.e. an adhesive, the liquid can fully explore the surface topography. The wetting process is governed by the surface thermodynamics and any external pressure or shear stress applied to the adhesive. This is described for a planar surface by the Young Equation [166].

\[ \gamma_{sa} = \gamma_{sl} + \gamma_{la} \cos \theta + \pi \]

As shown diagrammatically in Figure 2.4.1.

\[
\begin{align*}
\gamma &= \text{surface energy} \\
\gamma_{sa} &= \text{surface-air energy} \\
\gamma_{sl} &= \text{surface-liquid energy} \\
\gamma_{la} &= \text{liquid-air energy} \\
\theta &= \text{wetting angle} \\
\pi &= \text{spreading pressure}
\end{align*}
\]

For a liquid to wet a surface \( \gamma_{sa} \) must be greater than \( (\gamma_{sa} + \gamma_{la} \cos \theta) \). Hence the higher the energy of a surface the more readily it can be wetted. For example, metals, with their high surface energies, are readily wetted out by low surface energy materials such as polymers.

During practical adhesion processes the adhesive is not allowed to spread solely by thermodynamic wetting, external pressure and shear are also involved. Pressure will aid penetration of the surface roughness and so increase the effective area of contact. Shear can be detrimental to wetting even though it may be essential to spread the adhesive, because the higher dynamic wetting angle will be present [167]. In some cases however, shear thinning of the adhesive will occur and the reduced viscosity will further assist wetting.

In many adhesion systems a multi component adhesive is utilised, where the wetting and interaction functions are
split between the separate components; in this manner both functions can be optimised. For example, a hot melt adhesive [168] may be formulated from a low surface energy, low viscosity wax, which provides good wetting, and a polar polymer which can interact via hydrogen bonding.

Even when good wetting and adhesion mechanisms are present poor bonding can be caused by the presence of a weak boundary layer. In the context of this study machine oil, mould release agents, P/M pressing lubricants or loose powder could constitute a weak boundary layer. Adhesive failure due to a weak boundary layer can be prevented if the layer can be removed by cleaning operations such as shot blasting and solvent degreasing.

The rough nature of real surfaces will affect the wetting behaviour of an adhesive. A liquid may spread over a surface along pores, scratches and other inhomogenieties even though it may not spontaneously wet a planar surface [167]. It has been found that surface capillaries will wet out in advance of the bulk adhesive, and their presence can increase wetting rates [167].

A surface with pores and pits which can be filled with adhesive could exhibit significant mechanical keying and the preparation of porous surface textures is widely investigated as a means to enhance adhesion. To achieve good pore penetration low viscosity, low wetting angles and small pore radii are preferred [167]. Regrettably, penetration into inkwell type pits is poor compared with that into cylindrical shaped pores, [167] an inkwell pore would give very good keying from the wedge effect.

The adhesion to a substrate which has open porosity through out its thickness will be affected not only by surface roughness but also by capillary suction into the body of the
substrate [169]. This effect can be deleterious to adhesion if too much of the adhesive is drawn into the substrate, leaving the interface deficient in material needed to provide adhesion. This problem is commonly prevented by adding fillers to the adhesive [170]. A plastisol is highly filled and hence this effect is unlikely to be exhibited during the proposed MLIM procedure.

Surface texture can aid the adhesion of pastes and other granular materials, when the two textures are matched they can interlock to form a mechanical bond, as reported by Budweit [171] and in the Surveyor [172]. A similar pattern of behaviour is exhibited by powders adherent to a rough surface, maximum adhesion is present for either a smooth or a macroscopically rough surface and minimum adhesion is present when the roughness is less than the particle size [173]. The adhesion of a particle resting on the "mountain tops" of a surface texture is less than that of a particle resting in a "valley", because in the latter case the area of contact is greater [173].

Further aspects of adhesion are described by Wu [174], Brews and Briggs [175], Kinlock [167], Bikerman [176], Wake [177] and Owens [178].

In this study the particular adhesion cases of interest are i) polyolefins to steel, ii) polyolefins to polyolefins, iii) metal powders to other metal powders, and iv) inmould adhesion during injection moulding. These cases are discussed below. The effects of differential expansions/contractions of bonded materials on adhesion are discussed in Section 2.5: Coatings.
2.4.2 Polymer-metal Adhesion

Application of polyethylene (PE) as a melt to metal surfaces does not tend to yield good values of adhesion. PE is a low surface energy material and should readily wet high energy metal surfaces but even when wetted out the PE-metal interface lacks strength. PE is a nonpolar, relatively inert material and can only interact via dispersion forces which are weak. This may be an inherent cause of poor bonding but other factors may be in play. Bikerman and Huang [179] have suggested that PE bond failure takes place due to cohesive failure of the PE near the interface, (PE has a low cohesive energy), or that failure may be due to a weak boundary layer formed by low molecular weight material rejected from the bulk polymer during crystallisation.

PE-metal adhesion could be improved by treating the metal surface to raise its surface energy. This approach would raise the adhesion level achieved by thermodynamic wetting. The adhesion can also be improved by incorporation of a polar group into the PE material; such groups can interact more strongly with the metal than the PE.

Bigg et al. [180] have shown that adhesion of PE is promoted by oxidation, and it has been further shown that the oxidation is catalysed by iron [181]. In consequence good adhesion to steels is possible if the PE is subject to heat during bonding. No clear explanation of the effect of oxidation has been found in the literature, but the following factors are considered to play a part: i) the temperatures used to cause oxidation will lower the polymer viscosity and aid wetting, ii) the oxidation may introduce polar groups into the polymer, and iii) the oxidation can cause crosslinking of the PE; this local increase in material modulus may raise the work required for dehesion.
It has been found [182,183] that the cooling rate of a PE-metal bond can influence the adhesion level achieved. A quench will produce polymer material of lower crystallinity which will undergo greater deformation during fracture, hence raising the bond strength.

Polymer-metal adhesion can be improved by texturising the metal surface, for example surfaces with a fibrous or spiky texture exhibit enhanced adhesion [184,185]. It is believed [184,185] that the improved adhesion is due not only to an increased area of contact, but also that the small radii associated with the texture create stress concentrations which induce extensive yielding in the polymer during bond failure. The involvement of an increased volume of polymer in bond failure requires an increased amount of work hence raising adhesion levels.

Bair [186] has proposed that incomplete wetting of a metal surface which produces a bubble rich interface can increase adhesion, this has been found to be the case for a model system by Adam et al. [187] A model of the imperfect wetting of a rough surface which could give rise to such a structure is discussed by Timsit [188]. It is believed [186] that the bubbles give rise to a stress distribution near the interface which extends polymer yield during debonding into the polymer bulk so increasing the work for dehesion. It is possible that this situation may occur during this work if a porous P/M substrate is over moulded, each surface pore may act in a manner analogous to a surface bubble.

2.4.3 Polymer-Polymer Adhesion

Adhesion between polymer melts is good, but the adhesion between a solid polymer and a melt tends to be poor. Polymers have low energy surfaces and in consequence the thermodynamic wetting energy is small. As a result,
achieving adequate wetting out can be problematic. The unaided adhesion values for polymer solid - melt bonding are low, particularly for polyolefins were only dispersion interactions are present. This is illustrated by the limited types of adhesives which are effective on polyolefinic surfaces [189].

The adhesion of a polyolefin melt can be improved if the polymer is chemically modified to introduce polar groups into its structure, for example by carboxylation [189]. Similar effects can be achieved by blending a polar polymer with the polyolefin [168]. The increased polarity raises the level of interaction across the bond interface. A further route to improved adhesion is to treat the surface of the solid polyolefin to raise its surface energy. PE can be treated with acids or electrical discharge to form a more wettable surface.

A polymer surface can be texturised to promote mechanical interaction. Funke and Zorll [190] report a technique whereby a polymer film can be prepared with open surface porosity, this porosity can be filled when over coated by a polymer melt, the mechanical keying produced can enhance bond strengths.

The good adhesion between polymer melts is attributed to interdiffusion of the polymer chains [191]; this yields mechanical interlocking on a microscopic scale. For interdiffusion to occur there must be some degree of compatibility or miscibility between the polymers and significant chain motion must be present. The chain mobility required can be produced by heat or use of solvents. It is found that the melt fronts in multi gated injection mouldings will join satisfactorily provided they meet at a sufficiently high temperature [194]. Dissolving the polymer in a solvent will permit great chain mobility and rapid
interdiffusion. After bonding, the solvent can be evaporated away from the interface. This step however limits the technique to thin films such as paints. Some rubber compounds exhibit a property known as autotack [192]; two pieces of rubber can be overlaid and adhesion will spontaneously develop between the two. This behaviour is utilised in the manufacture of laminated products such as tyres and belting. The autotack is believed to arise from interdiffusion of very mobile segments of the rubber compound. The process does not need the assistance of pronounced heating.

2.4.4 Metal Powder Adhesion

The adhesion of metal powders can be considered on two levels, the adhesion of particles and the adhesion of powder bodies.

The pressure bonding of particles to form powder compacts is discussed in Section 2.1.5. Particles may also be bonded by a second phase such as a hard wax [58] or a thermosetting resin [193]. The bonding of particles by sintering reactions is discussed in Section 2.1.7.

Direct adhesion between powder bodies is possible, with the application of pressure and heat, if good matching of the surface textures is present, or if the particles of one powder are sufficiently mobile to conform to the surface of the second body. However, these requirements are rarely met and the use of interlayers is required. The interlayer can be generated as part of a brazing or welding operation. Alternatively the technology of diffusion bonding can be applied to P/M bodies, as discussed in Section 2.6.2. This provides an effective route to adhesion. A powder body is often a manufacturing process intermediate and further densification is desired. This allows the bonding operation
to occur in an environment of consolidation which greatly widens the potential for adhesion. Bonding of powder monoliths is discussed further in Section 2.6.2.

2.4.5 Inmould adhesion

The success of the multi layer injection moulding (MLIM) procedure proposed in Chapter 1.0 depends on achievement of inmould adhesion between the different layers. MLIM is not a conventional process and there is no known utilisation analogous to that proposed, but elements of the process are commercially exploited in some product specific applications, as described below.

Inmould welding of polymers routinely occurs when melt fronts in multi gated cavities join. It is found that high melt temperatures and pressures aid good bonding [194].

Thermoplastics can be moulded around metal inmould inserts, for example, a thread insert. Adhesion is promoted by mechanical texturising of the insert surface and by compressive forces generated across the interface by cooling shrinkage of the polymer [195]. The same procedure can be performed with epoxy resin moulding [196].

A prototype car body panel has been produced by inserting a shaped steel sheet into an injection mould and moulding a web of polymeric stiffening into the section [197]. It was discovered that the cooling shrinkage of the polymer produces residual stresses in the panel, these were reduced by selection of semicrystalline polymer.

Maskus and Gehniler [194] have examined inmould welding as a joining technique for polyamides. The study involved over moulding monolithic polyamide with a polyamide melt. They found that high melt temperatures were required to achieve good adhesion.
Polyester windows in cassette tape bodies can be incorporated by encapsulation in the bulk material as an inmould process [198]. Multi colour light units for car light clusters can be moulded on multi colour machines [98].

The bonding of rubber to metal inserts is a large industry [199] and much of the production is by injection moulding. Products such as car engine mounts and flexible couplings are produced. For effective bonding the metal surface must be clean, free from loose dirt, grease or oil. Often the surface is shot blast to provide a mechanical key for adhesion. The surface is further prepared for adhesion by coating with an adhesive primer. During the injection moulding cycle the rubber is maintained at temperature and pressure within the mould to allow rubber crosslinking reactions to occur; these conditions also allow the development of a chemical bond at the metal-rubber interface.

A survey of in-house experience reviewing the very wide range of materials processed within the Institute of Polymer Technology and Materials Engineering, found that inmould adhesion to an injection mould cavity was a rare occurrence. This "problem"; from the view point of normal moulding, was only experienced when high mould temperatures were used or if the polymer was very polar.

Some pointers for successful inmould adhesion to a mould insert can be summarised. Adhesion is promoted by (i) careful surface preparation, (ii) use of a surface primer, (iii) polymer polarity and (iv) provision of high melt temperatures. The presence of residual stresses at the interface due to polymer shrinkage must be recognised.
2.5 Coatings

2.5.1 Introduction

This study embraces many aspects of coating science. The graded structure is an attempt to extend the use of wear resistant hardmetal beyond the limits of its use as a coating, but the proposed fabrication route of multi layer injection moulding takes the form of placing many individual coating layers to form the composite structure. The placement of each layer can be treated as a coating event. In this section the basic criteria for a successful coating, features of multi layer coatings and aspects of wear resistant coatings are discussed.

2.5.2 Coating Principles

For the purposes of this study a coating can be defined as a thin layer of material adherent to a massive substrate. This combination of substrate-interface-coating can be described as a coating system.

A coating will only adhere and remain coherent if the stresses arising from any differential expansions-contractions between coating and substrate are limited. This aspect of coating science is of fundamental importance and has been investigated for solvent cast polymer films [200,201] and evaporated metal films [202]. Differential dimensional changes between coating and substrate have two principle causes: firstly the method used to place the coating may create an initial size differential, and secondly, if present, a difference between the thermal expansion coefficients of coating and substrate will give rise to stresses during thermal cycling. A "perfect" coating system is free from stresses at the interface or in the coating. This can be achieved by matching the coating
and substrate characteristics, but in real systems some residual stresses are present, resulting from the placement procedure, thermal expansion coefficient mismatches and differential temperature response of the coefficients.

If the adhesive bond and coating material are strong significant stresses can be accommodated, but there are limits. If the stresses are too high coating failure will occur. The failure behaviour exhibited will depend on whether the coating stress is compressive or tensile and the strength of adhesion. When good adhesion is present a compressed coating will peel to form adherent petal shapes while a coating under tension will craze to form a network of cracks around islands of adherent coating [203]. This behaviour is most clearly displayed by brittle coatings. If the interfacial adhesion is weak compared to the strength of the coating material then any significant stress will cause the coating to separate from the substrate as a whole. The presence of a coating stress imposes a thickness limit on a coating. As coating thickness increases the total energy in the system, in the form of strain energy, increases until it exceeds the adhesive energy and debonding occurs [201].

The requirements of a matched thermal expansion coefficient coating system are amply illustrated by the pottery glazes [203]. Glazes are applied to the surface of ware in a powder form. The powder matures during firing to form a glass coating. At firing temperatures the glassy nature of the glaze allows the coating to exhibit fluid behaviour and interfacial stress build up is prevented. However, when the ware is cooled the glaze falls below the glass transition temperature and becomes "solid like". From this point down to ambient temperature careful matching of the glaze and pottery body is necessary to ensure "fit" of the glaze [204]. Throughout the cooling the interfacial stress must be kept within bounds. The "fit" between glaze and pottery
body at ambient temperatures is such that the glaze is maintained in light compression during normal use.

A second approach to the "perfect" stress free coating is to provide a mechanism whereby the mismatch stresses can be relieved. In many cases the residual stresses produced by the placement of the coating can be released by annealing operations [205,206]. Some polymer coatings can be formed from elastomeric materials, for example, polyurethane paints and varnishes. The elastomeric nature of the coating allows it to conform to the dimensional changes of the substrate with the inducement of only low stresses.

2.5.3 Multi Layer Coatings

The use of multi layer coating systems can overcome many of the adhesion difficulties inherent in systems where the substrate and coating are dissimilar materials. The use of interlayers between the substrate and the external coating surface can enhance adhesion by providing chemical/physical compatibility.

For example, the adhesion of PVC to steel is poor because the halogenated nature of PVC reduces its reactivity and the presence of plasticisers can form a weak boundary layer [207]. Adhesion can be improved by use of a primer on the steel [208], typically an acrylate material. The primer is chosen to simultaneously bond to the steel and PVC, hence forming a bridging phase between the otherwise incompatible materials. Careful choice of primer chemistry is essential to find functional groups which meet the requirements of both materials.

Interlayers can also be used to enhance mechanical adhesion between materials. For example, the metallising of ceramics can be assisted by providing a porous polysilicate
interlayer which can bond to the ceramic through chemical compatibility and form a mechanical bond with the metal coating [209].

An interlayer can also be used to control the stress distribution in a coating system. If a desired coating is bonded directly to the substrate the stresses generated may be too great for bond stability. However if bonding is through an interlayer the stress levels at each interface can be reduced by grading the material properties to limit the differential associated with each interface in the system. For example, most paint systems use this approach [210] and a "buffer" layer is a feature of many hard-facing systems [211].

Some of the most developed multilayer coating systems are those used to coat metal cutting tools, ceramic layers can be laid down in sequence by chemical vapour deposition to build up complex structures [212]. A second generation coating system comprises of (i) a substrate, (ii) a backing layer which ensures coating smoothness and adhesion to an substrate, and (iii) an interlayer to bond the backing to the outer active layer, comprised of a stack of wear resistant materials chosen to act synergistically to meet the demands of the many wear mechanisms experienced.

2.5.4 Wear Resistant Coatings

The use of coatings to reduce wear is widely practised and can result in large economic benefits. The material most frequently protected is steel, and this technology is extensively developed [213]. A well established method to improve wear resistance is hardening the surface layer of the steel by, for example, nitriding, carburizing or case hardening. Vororoshin et al. [214] reports a technique to form a surface layer by diffusion. This allows a high degree
of alloying and carbide formation with elements such as chromium, zirconium, titanium, vanadium, niobium, and molybdenum.

Thicker and potentially longer lasting wear coatings can be placed by a variety of technologies. Tungsten carbide can be plasma sprayed [215,216], titanium nitride can be deposited by physical vapour decomposition [217], alumina is deposited by chemical vapour deposition. These coatings give useful performance and are adequate for many purposes, but the coating thickness is limited, typically to a few microns, and the coatings are not suited to mechanically aggressive environments such as rock drilling.

To cope with the wear problems of rock and earth tooling the technology of hard facing has been developed [218,219,220]. The technology uses weld deposition to lay down very thick coatings. The coating material has a steel matrix which is filled with carbides, the steel permits weldability and the carbides provide wear resistance. The difficulty of the thermal expansion coefficient mismatch between steel and the ceramic carbides is reduced by use of the steel matrix for the coating. In some cases use of a "buffer" interlayer is required to accommodate the property mismatch, as mentioned above [211].

The coating methods described attempt to place layers of hard ceramic materials over steel. The methods are limited by either low coating thickness, required to accommodate the thermal property mismatch, or by comparatively low effective hardness in the case of hard-facing. Technologies to overcome these limitations for tungsten carbide coated steel are discussed below.
2.6 Steel-Hardmetal composite structures

2.6.1 Concepts

Many workers [7,9,221,222] have realised the potential benefits of simultaneously utilizing the toughness of steel and the hardness of hardmetal within single components. The approaches taken to this end are not targeted to produce a homogenous feedstock but rather targeted at producing composite components with the steel and hardmetal distributed where toughness or hardness is required. However fabrication of such composite components is not a simple operation, two prime difficulties are present. Firstly, hardmetal has about half the thermal expansion coefficient of steel, this mismatch can cause large and destructive thermal stresses to arise at the interface between bonded hardmetal and steel. Secondly, the difference in carbon level between the two materials is about 40 atomic %. If the hardmetal loses carbon a brittle eta phase will form at the interface and if the steel gains too much carbon it can melt, at fabrication temperatures, due to depression of the solidus. Hence control of carbon diffusion across the steel-hardmetal interface is essential.

The joining technique used to fabricate steel-hardmetal composites is of prime interest to practitioners in the field and attempts to develop improved bonding are perceived as the route to advance this product area.

2.6.2 Joining technologies

The joining procedures for steel-hardmetal composite structures can be roughly divided into those starting with monolithic shapes and procedures which coprocess the materials in powder form, as illustrated below. No
A generalised joining method has been developed, but rather a collection of product type and shape specific processes.

Mechanical joining can be used; clamps, wedge mounting, screws and hold down plates are commonly utilised as described by Northrop [31]. Hardmetal inserts can be shrink fitted inside steel cases, this procedure gives the advantage that in service the brittle hardmetal is held in compression.

Brazing is an established joining technique [3], especially for cutting tools, the low temperatures associated with brazing limit the thermal strains induced during cooling of the joint. A thin brazed joint is the strongest but is the least able to resist the shear stresses developed on cooling, the thickness of a brazed joint cannot be increased greatly except by introducing an interlayer. Typically a copper interlayer is used, the copper provides extra thickness through which the thermal expansion coefficient mismatch can be accommodated by shear. Sufficient brazing strains may be produced to distort a composite unit if the adherents are thin sectioned.

Attempts to weld hardmetals to steel using conventional gas or arc welding are not successful [3]. Success has however been achieved with electron and laser beam welding [222], where the energy beams cause very localised heating of the materials, greatly reducing both the potential for carbon transfer and the presence of cooling stresses. Similar results can be achieved with friction welding [223]. Success has been claimed for pressure welding in a ceramic grain HIP'ing bed [4].

A widely publicised method of joining dissimilar materials is diffusion bonding [224,225,226], its application to bonding steel-hardmetal is reported by Samoilov [227],
The use of an interlayer at the joint interface is generally found to be essential to accommodate the thermal strains generated by bonding. Nickel is the normal choice for the interlayer material. It has been found that if the diffusional activity of the interlayer is enhanced the consequential broadening of the bond interface increases joint strength [8]. Almond, Cottenden & Gee [229] and Cottenden & Almond [230] have studied the metallurgy of hardmetal–steel diffusion bonds and report that a key to producing a good bond is the avoidance of decarburization of the hardmetal at the interface. This can be achieved by priming the mating surfaces with graphite prior to bonding or by using an interlayer metal with a relatively high carbon content.

A possible method of fabricating steel–hardmetal composites is by compaction of the materials in powder form. A two layer powder compaction process is described by Schreiner [231] and fabrication of an annular P/M composite is described by Lee [232], however no reported application of these approaches to steel–hardmetal bonding was found in the literature.

Coextrusion of powders can be used to fabricate composite bodies, billet preforms for hot extrusion can be fabricated by coisostatically pressing P/M material around a steel blank [233] or by coisostatically pressing powders [221]. The extruded composite can be used to fabricate articles such as bars and shank end mills. The coextrusion of powder plastisols is reported by Plvushch et al. [234].

2.6.3 Graded structure composites

The joining techniques described above are limited by either the presence of a sharp discontinuity of properties at the interfaces or by the presence of a comparatively weak
interlayer. These limitations can be overcome by use of a graded interface as reported by Begg, Brown and Charman [9], who have developed the graded structure composite which this project seeks to fabricate with PIM technology. An interface comprised of several layers where the property mismatch between the steel and hardmetal is bridged in a stepwise fashion is utilised to accommodate thermal stresses whilst enabling strong metallurgical bonds to be utilised. The graded structure composite [9] is fabricated by P/M, during consolidation, care is required to limit diffusion, otherwise the graded layers will homogenise as described for titanium carbide cermets by Kitaai et al. [235]. Control of carbon diffusion across the interface is provided by a layer of BO1 tool steel. Detail of the graded structure is presented in Figure 2.6.3. A similar approach to joining materials has been recently revealed in Japan under the name of functionally graded materials [236].

However, fabricating such a multilayer composite is difficult, particularly if the constituent powders need to be shaped in three dimensions. Development work has been performed by HIP'ing a stack of canned powders [237] and the use of laser sintering is reported for fabrication of multilayer structures [238]. Both of these methods are expensive and limited with respect to the shapes that can be produced. It is hoped that the multilayer injection moulding technique of this work will provide a flexible and attractive fabrication method, capable of producing three dimensional graded structure parts.
3.0 PROCESS ANALYSIS AND EXPERIMENTAL DESIGN

3.1 Process Analysis

3.1.1 Adhesion Approach

The fabrication of the multilayer graded structure by multilayer injection moulding, as described in chapter 1.0, can be considered as an adhesion problem. For successful fabrication adhesion must be present at each interface and be maintained throughout the processing. There is also a need for the adhesive function to be transferred between different interaction mechanisms as fabrication is progressed. Initial adhesion is expected to be attributable to the polymeric binder. When the binder is "burnt out" the adhesive function must be transferred to the powders. On consolidation the interpowder bonding must be developed into a metallurgical weld.

The adhesion processes can be analysed as a group of interfaces, a set of adhesion requirements and a set of adhesion transfer operations, as detailed in Table 3.1.1.

It was decided to evaluate the adhesion at each of the interfaces in isolation as a preliminary to attempting fabrication of the whole graded structure. The determination of processing conditions for each adhesion step was seen as a prerequisite to attempting full manufacture, because coupling effects in a full graded structure would impede interpretation of the systems adhesion behaviour, and confuse interfacial and composite behaviour. Once each individual adhesion step was validated in isolation it was believed that fabrication of the whole graded structure could be undertaken with confidence.
The adhesion processes are fundamental to the fabrication procedure and can be used as a reference point when designing the process, each option or parameter can be considered with view to the effect on adhesion.

3.1.2 Differential shrinkages

The adhesive bonding of the graded structure composite could be destroyed by differential shrinkages of the layers in the structure, if the interfacial stresses generated become too large and overcome the bond strength.

The following fabrication steps were identified as potential causes of differential shrinkages:

a) Cooling shrinkage of injection moulded plastisol when bonded by over moulding to other layers of the composite structure.

b) Shrinkages associated with plastisol debinding, the binder removal may cause a reduction of particle centre separations.

c) The different layers of the composite may exhibit differential sintering rates and hence cause a mismatch of shrinkage-temperature-time patterns during thermal processing.

d) The presence of different sintering mechanisms; for the steel, solid state sintering and for the hardmetal, liquid phase sintering; this may cause a shrinkage differential during consolidation.

e) Cooling of the composite structure from consolidation temperatures will induce a large differential shrinkage between the steel and hardmetal, but this should be
accommodated by the developed grading technology incorporated into the graded structure composite by B.P. [9].

A representation of the possible differential shrinkages present after cooling of a moulded plastisol coating layer can be developed as below:

If: $\alpha = \text{linear thermal expansion coefficient}$
- $\rho = \text{density}$
- $V = \text{volume loading of powder}$
- $P = \text{numerical proportion}$
- $\Delta s = \text{differential shrinkage}$
- $T = \text{temperature (\degree C)}$
- $s = \text{substrate}$
- $w = \text{wrought}$
- $p = \text{plastisol}$
- $WC = \text{tungsten carbide}$
- $Co = \text{cobalt}$
- $poly = \text{polymer}$
- $a = \text{ambient}$
- $m = \text{mould}$
- $i = \text{injection}$

Then the linear thermal expansion coefficient of a steel powder metallurgy substrate can be written as:

$$\alpha_s = \alpha_w (\rho_s^{1/3})$$  [Ref 239]  3.1.2.1

And the linear thermal expansion coefficient of a plastisol can be simply written using the linear mixture equation [240] as below:

$$\alpha_p = V [ P \alpha_{WC} + (1-P) \alpha_{Co} ] + (1-V) (\alpha_{poly})$$  3.1.2.2

N.B. equation 3.1.2.2 does not include a term for any crystallization shrinkage of the binder.
Thus the differential shrinkage between substrate and over moulded plastisol is:

\[ \Delta s = -\alpha_m (p_s^{1/3})(T_a - T_m) + \alpha_p (T_i - T_a) \] 3.1.2.3

Equation 3.1.2.2 could be used to ensure that all the different plastisols layers in the graded structure have matched thermal expansion coefficients.

Equation 3.1.2.3 describes the effect of plastisol formulations and moulding temperatures on the shrinkage mismatch between the steel substrate and plastisol layers. Decreasing plastisol injection temperature and increasing mould temperature should reduce \( \Delta s \). In the ideal case \( \Delta s = 0 \) but it is expected that in practice \( \Delta s \gg 0 \) and the interface will be stressed. Some of this stress might be relieved if the plastisol exhibits stress relaxation behaviour. If \( \Delta s \gg 0 \) then a cooled graded structure moulding will contain a residual stress distribution within the plastisol, with fully constrained material at the steel substrate-plastisol interface and semiconstrained / unconstrained material at the free surface. A question of interest is, what is the residual strain energy in the plastisol? This is the energy available to overcome the adhesion or cause cracking.

If: 
- \( E = \) residual strain energy 
- \( R = \% \) stress relaxation 
- \( h = \) plastisol thickness 
- \( \sigma = \) stress 
- \( \varepsilon = \) strain

Then it is possible to simply write:

\[ E = \frac{1}{2R} \int_0^h (\sigma \varepsilon) \, dh \] 3.1.2.4
Regrettably $\sigma = f(h)$ and $\varepsilon = f(h)$ are not simple expressions and no reliable forms have been found in the literature.

3.1.3 Injection moulding transients

Injection moulding is a nonsteady state process and many transient effects are present. It was considered valuable to examine some of the transients which might prove damaging to the multi layer injection moulding process. In particular the effects of temperature, shear and pressure.

A) Heat transfer

The injection moulded plastisol must be cooled in the mould cavity to stiffen the melt, and thus provide sufficient strength for part ejection. The heat is lost to the mould walls and to the substrate material of the graded structure. The cooling requirements of the mould can be maintained by water cooling and bulk mould temperature kept constant. However the surface temperature of the cavity will fluctuate. A question of interest is, to what extent would a plastisol layer be heated when over moulded with the next layer in the graded structure? Heating of a substrate plastisol layer could have beneficial effects at low levels of temperature rise and penetration. The thermal energy could aid adhesion through promotion of polymer interdiffusion and an increase in surface conformability. At higher levels of heating the plastisol could soften and become more prone to distortion in response to injection stresses. It can be further speculated that heating of the substrate plastisol could form a diffuse thermal interface below the physical interface which would broaden the thickness of material resisting the presence of any cooling shrinkages, in effect grading the thermal shrinkage mismatch.
through bulk plastisol rather than leaving it concentrated at a narrow interface.

An upper bound level for the heat transfer to layers of plastisol over moulded with a subsequent layer can be determined by considering the cavity as firstly, a three body problem of a material sheet sandwiched between two infinite bodies, and secondly as a semi-infinite body instantly coated with a fluid, as described by Rohesnow and Choi [241].

If: $T =$ temperature
\[ \alpha = \text{thermal diffusivity} \]
\[ K = \text{thermal conductivity} \]
\[ h = \text{surface heat transfer coefficient} \]
\[ t = \text{time} \]
\[ a, b = x \text{ axis coordinates} \]
\[ i = \text{initial} \]
\[ f = \text{fluid} \]
\[ \text{erf} = \text{error function} \]
\[ \text{erfc} = \text{complementary error function} \]

Then:

\[ \frac{T - Ta}{T_a} = \frac{1}{2} \left[ \text{erf} \left( \frac{b - x}{\sqrt{at}} \right) - \text{erf} \left( \frac{a - x}{\sqrt{at}} \right) \right] \quad 3.1.3.1 \]

And:

\[ \frac{T - Ti}{Ti} = \text{erfc} \left( \frac{x}{\sqrt{at}} \right) - \exp \left[ \frac{xh}{2} + \frac{at}{K} \right] \left[ \left( \frac{K}{h} \right)^{1/2} \right] \] \[ \text{erfc} \left( \frac{x}{\sqrt{at}} \right) \quad 3.1.3.2 \]

Equation 3.1.3.1 enables surface time-temperature calculations to be performed and equation 3.1.3.2 gives information on the depth of heat penetration.
B) Strain energy input

During the multi layer injection moulding process the graded structure composite is formed from plastisol layers moulded over a steel substrate, injection of the higher layers may stress the preplaced layers below. The incoming plastisol will be forced over the surface of the previous layer, the friction at the interface will transfer a shear force to the material below. If the plastisol is free to deform by simple shear, as shown in Figure 3.1.3.1, then a strain energy transient will be generated in the material, this energy could be released by plastic deformation of the material or by dehesion from the substrate; hence the magnitude of the strain is of interest.

For a condition of plane strain:

If: 
\[ E = \text{strain energy in underlying layers} \]
\[ f = \text{shear force} \]
\[ y = \text{shear strain displacement} \]
\[ K = \text{a constant} \]
\[ n = \text{number of plastisol layers placed} \]
\[ h = \text{layer thickness} \]

Then: 
\[ E = \frac{fy}{2} \] 3.1.3.3

And: 
\[ y = Knh \] 3.1.3.4

Hence the effect of injecting sequential layers on the strain energy transient is as below:

\[ n = 0 \quad E/Kh = 0 \quad \text{strain of steel substrate is negligible} \]
\[ n = 1 \quad \Rightarrow 1/2fy \quad \Rightarrow 1 \text{ energy unit (Nm)} \]
\[ n = 2 \quad \Rightarrow fy \quad \Rightarrow 2 \text{ units } \]
\[ n = 3 \quad \Rightarrow 3/2fy \quad \Rightarrow 3 \text{ " " } \]
\[ n = 4 \quad \Rightarrow 2fy \quad \Rightarrow 4 \text{ " " } \]
Moulding the second layer produces an energy transient of 1 unit, moulding subsequent layers gives rise to increases of 100%, 50%, and 33% for layers 3, 4, and 5 respectively. Even though the strain energy transient per unit volume of plastisol increases in a linear manner the total strain energy in the system increases very abruptly with placement of the third layer. This implies that placement of the third plastisol layer could be a crucial process step.

C) Pressure transient

During an injection moulding cycle an incoming melt will exert a pressure on the plastisol layer(s) already placed. It is reasonable to expect this pressure to cause elastic and possibly plastic compression of the underlying plastisol. Such a displacement would give rise to a step in the plastisol surface, just in advance of the incoming melt front, as depicted in Figure 3.1.3.2. If the melt "got behind" the step a mechanism to produce rucking distortion of the interface would be created. Increasing the number of layers increases the expected step height in the percentage ratios calculated for the strain energy transient.

3.1.4 Graded parameter processing

The considerations of section 3.1.3 suggest that the successful moulding of layers in the graded structure composite will become less favourable as the number of layers placed is increased. In consequence, some design whereby the effects of injection temperature, shear and pressure could be graded to compensate for the increasing vulnerability of the plastisol composite to physical damage during moulding, as the number of layers rises, may be a requirement of the multi layer injection moulding process.
3.2 Experimental Design

3.2.1 Methodologies

This study was aimed at developing a process technology, the prime aim was to find a way of fabricating the graded structure by powder injection moulding, rather than to study the fundamentals of the materials or processes involved. The project was purposely pushed towards the goal of part production to validate the original concepts. In consequence the experiments were directed towards part fabrication and matters of purely scientific interest were noted but left unexplored unless directly on the path of process development. It would have been possible to expend much effort understanding the early stages of the proposed fabrication process in depth, only to find that subsequent steps were blocked and inviable, rendering the initial work of little value to the project aims.

A need to cover the many staged and multi disciplined nature of the fabrication process led to the adoption of economical experimental approaches. Experiments were designed as far as possible to give "yes or no" answers without recourse to numerical data gathering. The approaches taken included testing extremes, determining upper and lower bounds and working with attributes.

3.2.2 Organisation

The experimental work followed the progression of process steps necessary for the fabrication by multi layer injection moulding of the graded structure composite. The organisation of experiments was ruled by the necessity of validating each fabrication step in sequence to provide a foundation for the next, the series of steps investigated is presented in Chapter 5.0.
4.0 EXPERIMENTAL MATERIALS AND METHODS

4.1 Materials

4.1.1 Metal powders

The metal powders used during this work are listed below:

- **sponge iron**: median particle size 100\(\mu\)m, tap density 50\%, internal laboratory standard

- **AISI 4815 steel**: a nickel–molybdenum steel, median particle size 90\(\mu\)m, size distribution given in Figure 4.1.1.1, tap density 46\%, apparent density 34\%, water atomised, with a rough irregular shape illustrated in Figure 4.1.1.2, fabricated by Powdex for B.P.

- **BOI tool steel**: a high carbon steel alloyed with chromium and tungsten, three batches were used
  a) median particle size 110\(\mu\)m,
  b) a sub 100 mesh (sub 177\(\mu\)m) batch with median particle size 85\(\mu\)m
  c) a sieved fraction of sub 100\(\mu\)m material with median particle size 47\(\mu\)m

The particle size distributions are given in Figure 4.1.1.3, this powder was water atomised and the particle morphology is shown in Figure 4.1.1.4, the powder was fabricated by Powdex for B.P.
4.1.2 Polymers

The polymers used in this work are listed in Table 4.1.2 under the headings of thermoplastics, waxes and elastomers.

4.1.3 Process aids

a) Haftolat, an ethylene – propylene monomer solution supplied by Kettlitz-Chemie GmbH & Co. KG
b) Sufacid, grade U-115, a fatty acid supplied by Jahres Fabrikker, Norway.
c) Hoechst wax C micropowder, a fine particle sized hard amide wax, developed as a P/M pressing lubricant, supplied by Hoechst UK.
d) Zinc stearate SLR supplied in fine powder form by Fisons.
e) Release agents, many propriety systems including: Release agent type A81760, developed for g.r.p. moulding by K & C Mouldings, this is a wax in a solvent solution which can be brush or spray applied to leave a hard, buffable, wax coating. 'Antiquia' wax polish, this material is a liquid which can form a fluid surface coating. Release agents supplied in aerosol form based on silicones, dioctylphthalate (DOP) and PTFE.
4.1.4 Other materials

Alumina cement, Alcem 101 supplied by Refractory Mouldings and Castings Ltd.
Carbon black, sulphur free.
Gas mixtures supplied by BOC special gases i) 25% H₂ Balance N₂  ii) 6% H₂ Balance N₂. % = atomic percent.
Titanium sheet.
SLR grade laboratory chemicals, such as solvents and acids.
Metallographic materials as supplied by Struers.
Hardmetal etchant: 10% potassium hydroxide, 10% potassium ferricyanide in water.

4.2 Process tooling

4.2.1 Powder metallurgy compaction dies

(A) Compaction die set for block substrates: This tool was used to make powder metallurgy blocks 12 by 15 by 28mm for use as graded structure substrates. The blocks were intended for use in the MLIM test mould. The die was double ended, and is shown in Appendix 1.

(B) Compaction die set for rock bit substrates: This tool was designed to produce substrates for a prototype rock bit, the tool was double acting and a cavity was recessed into the end of one punch to shape the substrate tip. The die is shown in drawings RBT 3 & 4 in Appendix 1.

4.2.2 Injection moulding tools

These tools were designed to operate with a horizontal split line. Tools A & B were single sided and operated with a blank top plate. The tools contained internal channels for the circulation of cooling water.
(A) Impact test bar mould: This mould was used either as designed or modified by a cavity insert for the coating of wrought steel substrates and simple MLIM lamination experiments. The mould and modifying insert arrangement are shown in Appendix 1.

(B) MLIM Test mould: The mould was designed for the evaluation of the multi later injection moulding process in a two dimensional geometry. Block powder metallurgy substrates could be positioned inside the mould cavity and lowered by adjusting a shim pack to permit moulding of sequential plastisol layers. The mould is shown in Appendix 1.

(C) Rock bit mould: The mould is shown in drawings RBT 5, 6 & 7 in Appendix 1. This mould was double sided, the rock bit substrate was positioned in the lower half and a cavity formed in the upper half. The mould was gated through the upper half, placing the runner system in the mould body rather than on the split line as was the case for the other moulds. The cavity was formed from an epoxy insert which could be changed to enlarge the cavity and hence create space for sequential moulding of plastisol layers. The epoxy inserts were fabricated by casting resin around machined blanks. The blanks and casting mould are shown in drawings RBT 8 & 9 in Appendix 1.

4.3 Process methods

4.3.1 Preparation of steel substrates from wrought stock

Wrought steel substrates were prepared for use in a blanked off impact test bar mould. The substrates were cut from bright drawn, EN3B (BS907) steel stock, to dimensions of 28 by 12 by 3mm. The upper surface of the substrate was subject to the various treatments described below:
(A) Leaving the surface as ground; surface roughness average value (Ra) 0.33μm.

(B) Polishing the surface to a "mirror finish" with 1200 grade grit.

(C) Shot blasting the surface to (Ra) values of 0.90μm or 1.25μm.

These three treatments were followed by ultrasonic degreasing in xylene.

(D) Electroplating the surface with nickel. Plating conditions given in the Canning Hand Book on Electroplating [242] were used. After plating, the substrates were washed in distilled water and hot air dried. Plating thickness was determined by weight gain. Thicknesses in the range 18 - 22μm were produced, the surface Ra value was 1.25μm.

(E) Coating the surface with solvent cast EVA rubber. Levapren 500 rubber was dissolved in chloroform and applied with a dropper to the substrate surface. The unit was then dried under an infra red lamp for 30 minutes. Coating thickness was determined by weight gain. Thicknesses in the range 20 - 100μm were produced.

Treatments D & E were applied to both ground and shot blast (Ra = 0.90μm) surfaces.

(F) Preheating the substrate. The substrates were placed in a muffle furnace maintained at a temperature in the range 300 - 400°C and removed after 10 minutes for injection moulding use. The furnace was flooded with nitrogen, it was not possible to use a reducing atmosphere for safety reasons. The short heating time and protective atmosphere did not completely prevent surface oxidation, and visible
blueing of the steel was present. The muffle furnace was positioned next to the injection moulder and a standard transfer time from furnace to mould of five seconds and an inmould time prior to injection of five seconds was established and used throughout the experimental studies. The substrates experienced a temperature fall of about 100°C prior to mould cavity filling.

4.3.2 Powder Metallurgy Procedures

Powder compaction was performed using material testing machines as presses. Three machines were used during the course of the project; an Instron machine model TT-DM-L with a 10 ton capacity, an ESH servohydraulic machine with a 25 tonne capacity and a Denison machine model T42B4 with a 50 ton capacity.

Compaction dies were double ended as described in Section 4.2.1, and operated as follows. The die and lower punch were set up on the lower platen of the press, the die supported on spacer pieces. A weighed amount of powder was poured into the die and manually levelled. The upper punch was then inserted into the die and the die cavity pressurised at 30 MPa. This prepressure was then released and the supportive spacers removed from the now self supporting die. Pressure was then reapplied up to the compaction level desired. Compact ejection was performed using the lower punch, the tool was inverted on top of the spacers and machine pressure used to drive the compact out. This operating sequence is shown in Figure 4.3.2.1. It was possible to replace the spacers with a spring if desired.

Lubrication was provided during pressing by premixing lubricant with the powder. Mixing was performed in a double cone mixer. Both zinc stearate and Hoechst wax C were mixed with the powder, singly and in combination. A powder mix
with 1% zinc stearate was adopted as a standard pressing feedstock.

Sintering was performed in laboratory tube furnaces supplied by Lenton Thermal Designs, two furnaces were used: one wire wound with an operating limit of 1200°C and one equipped with silicone carbide elements with an operating ceiling of 1600°C. The tubes had fitments to enable use of a controlled atmosphere or vacuum. The layout of the required ancillary equipment is shown in Figure 4.3.2.2. Standard sintering procedures were adopted for steel and hardmetal as detailed in Table 4.3.2. HIP'ing operations were performed by B.P. using a novel ceramic pressurising medium, with pressure and temperature set at 200MPa and 1300°C respectively.

4.3.3 Powder Injection Moulding Procedures

A) Plastisol Preparation. Plastisol formulations were mixed in a one step operation; the binder was not premixed, the binder components were mixed together to form the binder whilst simultaneously mixing with the powder. Small, 30cc, batch mixes of plastisol were produced from a Brabender Plastograph torque rheometer fitted with a W30H mixing head, a plastisol was considered effectively mixed when the measured torque reached a plateau level [124]. Larger scale mixing was performed with a Baker Perkins batch mixer, the mix state produced by this machine was checked by remixing samples in the Brabender plastograph and observing if torque stability was present. Both mixers were preheated and then incrementally filled during an initial 10 minute period before running under the conditions given in Table 4.3.3. These conditions were used throughout the project except whilst mixing BO1 tool steel plastisols as described in Section 5.6.
B) Moulding. Moulding was performed with a Fox and Offord injection moulding machine. The machine was equipped with a plunger type barrel and had a horizontal platen split line.

C) Debinding. When designing a debinding schedule a question of interest is, what starting temperature can be tolerated? i.e. what is the maximum temperature the mouldings can be taken to before debinding begins? Full utilisation of the rapid temperature rise possible up to the start of debinding weight loss can significantly reduce debinding times. In this work the start of debinding was assessed by placing mouldings in a preheated oven for two hours at progressively higher temperatures until the onset of binder loss, as indicated by weight loss or colour change, caused by a change from wetted powder to dry powder.

A second question of interest is, is the weight loss rate during debinding constant with a given temperature ramp or does the binder predominantly "burn out" at various trigger temperatures? This latter case is the norm. The results of thermogravemetic analysis (TGA) can be used to detect critical temperatures at which the weight loss rate peaks. It is empirically found that the critical temperatures for debinding are reduced if the heating rate is decreased [243]. This effect must be allowed for when applying the results of TGA to the design of debinding schedules, because the heating rates experienced in part debinding are greatly less than those used for TGA. For the conditions of this work a correction factor of 20°C was required [243].

If a constant temperature ramp was used for debinding it would need to be very low to avoid the destructive internal pressures associated with rapid weight loss at the trigger temperatures. A more practical approach was to tailor the temperature ramp with reference to temperature to suit the nonlinear weight loss characteristics, ensuring that
excessive weight loss rates were not experienced and also enabling weight loss to be accelerated near the end of debinding when the danger of internal pressure build up was reduced.

The role of gas flow during debinding was to protect the powders from oxidation and to remove the debinding volatiles from the part vicinity, the gas may also act to assist polymer scission\[153\]. Gas is expensive and it is customary to use as little as possible, a minimum flow rate can be determined by progressively lowering the flow rate until carbon deposition occurs. The acceptable flow rate will however be influenced by the heating rate, a low gas flow coupled with a high heating ramp will promote carbon deposition. The tube furnace used in this work was tilted to assist the relatively dense debinding volatiles to flow away from the heated zone towards the gas exit.

Thermal debinding was performed in a laboratory tube furnace with a controlled atmosphere and time-temperature profile. The atmosphere comprised of 25 % hydrogen, 75 % nitrogen, fed at a flow rate of 100 - 250cc/min through a tube diameter of 75mm. A Eurotherm 818P programmable logic controller was used to impose a time-temperature profile, up to eight independent ramp/plateau/dwell segments were available. Mouldings were supported on alumina powder during debinding. Hoops of titanium sheet were positioned in the hot zone upstream of the mouldings to act as a getter of any moisture and oxygen not completely removed by the dryer-deoxidation system, detailed previously in Table 4.3.2.2. During the experimental work appropriate debinding profiles were developed as detailed in Appendix 3.

D) Consolidation. The procedures described in Section 4.3.2 were applied to debound mouldings.
4.3.4 Multi Layer Injection Moulding Methods

A) Impact test bar mould: As shown in the drawings mentioned previously, in Section 4.2.2, a wrought substrate was mechanically placed in the lower half of the blanked off cavity, just below the mould gate. Plastisol was then moulded over the top surface of the substrate and the substrate-coating unit ejected. If plastisol was moulded over a smooth substrate it was possible to peel the plastisol free and place it in the mould as a substrate which could be over moulded to produce two layer plastisol laminates. The layer thickness was 3mm.

B) MLIM test mould: Substrates were positioned by adjustment of a shim pack to permit over moulding of 1mm thick plastisol layers. After moulding of one layer the substrate-layer unit was lowered in the cavity by removing shims, to create space for the moulding of a further layer.

c) Rock bit mould: There was a need to align the substrate prior to mould closure, firstly to prevent a "crunch" between the substrate tip and epoxy insert, and secondly to ensure equally distanced substrate-cavity wall clearances. After each moulding shot it was necessary to clear out the runner system.

4.3.5 Graded structure compositions

Two slightly different graded structure compositions were utilised. Composition A was used for investigation of individual process steps and fabrication of MLIM geometry graded structure units. Composition B was used to fabricate the prototype rock bit.
### Layers of composition A:

<table>
<thead>
<tr>
<th></th>
<th>Steel</th>
<th>AISI 4815</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tool steel</td>
<td>BO1</td>
<td></td>
</tr>
<tr>
<td>Hardmetal</td>
<td>30% Co Balance WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>20% Co WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>16% Co WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>14% Co WC</td>
<td></td>
</tr>
</tbody>
</table>

% = weight percent

Design geometry AISI 4815 substrate 15mm thick topped with five 1mm thick layers.

### Layers of composition B:

<table>
<thead>
<tr>
<th></th>
<th>Steel</th>
<th>AISI 4815</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tool steel</td>
<td>BO1</td>
<td></td>
</tr>
<tr>
<td>Hardmetal</td>
<td>28% Co Balance WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>20% Co WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>15% Co WC</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>12% Co WC</td>
<td></td>
</tr>
</tbody>
</table>

% = weight percent

Design geometry AISI 4815 substrate 20mm height topped with five 1.1mm thick layers.

### 4.4 Analytical Methods

Many analytical methods were utilised including:

Rheological assessments performed with both Davenport and Instron capillary rheometers. The abrasive nature of the plastisols can result in damage to a pressure transducer if sited by the capillary entrance, in consequence the pressure was measured by a load cell between the piston and drive mechanism.
Thermal analysis was performed using Du Pont apparatus. Differential scanning calorimetry, DSC, dynamic mechanical analysis, DMA, and thermal mechanical analysis, TMA, were exploited. Also, thermal gravimetric analysis, TGA, was performed using a Stanton thermorecording balance, model HT-F26418 and a CI Electronics microbalance.

Density measurements were made according to ISO 3369 practice.

Microhardness was measured with a Reichert microhardness tester.

Surface texture parameters [244] were measured with a Talysurf 10 supplied by Taylor Hobson in accordance with BS1134.

Mechanical testing was performed with a J.J. Lloyd tensometer, type T5002.

Optical metallography was performed with a Reichert MEF3 microscope.

Cambridge 2A, Cambridge stereoscan 360 and Jeol-100CX electron microscopes were used to examine powders and material surfaces.
5.0 EXPERIMENTS AND RESULTS

5.1 Powder injection moulding technology

5.1.1 Introduction

The research proposal [10] which initiated this project contained the implicit assumption that powder injection moulding (PIM) technology was an established technique; but in fact PIM is still an immature technology; and much of the information gained about the subject is not published for commercial reasons. In consequence the experimental work started with an exploration of PIM processing to establish an appropriate benchmark technology, as a foundation for the broader experimental investigation.

At Loughborough University of Technology in-house PIM experience was available, Issitt [152] had developed a procedure utilizing a thermoplastic binder for the moulding of iron powders and Martyn et al. [117,124] had developed a wax based binder for hardmetal powders.

It was decided to perform the initial studies with hardmetal powder because this material constitutes the major component of the proposed multi layer injection moulding (MLIM) process. It was further decided to use a 6% cobalt 94% tungsten carbide grade of hardmetal for this initial work so that results could be compared with available in-house knowledge.

The project opened with a study of binder technology. The objective was to produce a workable benchmark plastisol formulation adequate for exploration of the MLIM process.
5.1.2 Binder and Plastisol formulation

Trial polymer binder blends were mixed, using a Brabender Plastograph, as described in Section 4.3.3, spanning the range from single component thermoplastic polymer through multi component polymer/wax combinations to pure wax systems. The formulations are given and numbered in Table 5.1.2.

Blends (No.'s 1, 3, 9, 11 & 12) were chosen for mixing with powder as trial plastisols, the choice was made on criteria of (i) low shrinkage, (ii) low viscosity as indicated by mixing torque, (iii) the need for some toughness, and (iv) the degree of adhesion to the Brabender mixing chamber. The critical volume powder loading was evaluated by mixing plastisol batches at 50, 55, 60 & 65 volume percent powder with binder No.11 chosen, because the formulation was central within the formulation ranges. It was found that the plastisol loaded with 65 volume percent hardmetal powder exhibited no flow in the Davenport capillary rheometer. The plastisol formulated with 60 volume percent powder only exhibited flow at low shear rates. At 55 & 50 volume percent adequate flow for injection moulding was present, as specified in Section 2.3.3. The chosen blends were mixed at a level of 55 volume percent powder loading. The inclusion of ethylene vinyl acetate (EVA) in a blend markedly reduced mixing torque and the incidence of material throw back from the mixer's throat. A rheological assessment was performed to check that adequate flow properties and feedstock cohesion were present.

Thermoplastic type binders were found to mix satisfactorily with the hardmetal powder and form a rheologically acceptable plastisol. It was discovered that use of the high molecular weight polymer was unnecessary, it was not required to give cohesion to the plastisol mix or to achieve
good flow properties. EVA was effective when in low molecular weight form as a viscosity reducing component. The use of waxes in the plastisol mixes could cause beneficial reduction of plastisol viscosity but a waxy surface was produced on plastisol even at low wax contents. The findings above greatly narrowed the field of prospective binder formulations, as discussed in Section 6.1, and pointed to the use of a two component system of medium molecular weight polymer with a low molecular weight EVA. Such a plastisol was mixed and found to have good flow properties. It was found possible to increase the powder volume loading to 57% and still retain adequate flow characteristics. The developed formulation is detailed below:

| Escorone LD655 | 50 |
| Escorone UL40028 | 50 |

100 parts per hundred by weight

This was mixed as a plastisol with 57 volume percent hardmetal powder, 6% cobalt 94% tungsten carbide.

This formulation was accepted as the benchmark plastisol and utilised for injection moulding trials.

The linear thermal expansion coefficient of the plastisol was measured by thermal mechanical analysis and found to lie in the range 30 - 40*10^-6 at 57 volume percent powder loading. The expansion coefficient was found to be a function of powder loading as shown in figure 5.1.2.

It was discovered during DSC measurements that when mixed as part of a plastisol the crystallinity of low density polyethylene was reduced by 2%.
The use of electrical conductivity measurements as a plastisol quality control test was investigated. It was possible to distinguish between mixes at different powder volume loadings and to detect the presence of EVA but the results were very sensitive to surface condition and contact pressure. The findings are detailed in Appendix 2.

5.1.3 Injection moulding

Trial mouldings were produced in an impact test bar mould, as described in Section 4.2.2. The process was trouble free and the plastisol composition behaved satisfactorily, resulting in complete mouldings with a smooth surface finish. Moulding conditions of barrel temperature 160°C, nozzle temperature 180°C, mould temperature 25°C, pressure 2000 psi and hold on time 10 seconds were successfully used and were accepted as a benchmark standard. Use of mould release agents was unnecessary. The mouldings exhibited sufficient strength for ejection and handling, even though their modulus of rupture in a three point bend test was only 2N/mm² compared with 100N/mm² for abraded glass.

N.B. Jetting behaviour was exhibited during cavity filling if the melt temperature was reduced below 140°C, as shown in Figure 5.1.3.

5.1.4 Debinding and sintering

The next major step in establishing a benchmark PIM technology was to develop a suitable debinding regime. To avoid powder oxidation it was decided to debind in a hydrogen rich atmosphere. For reasons of laboratory practicality a tube furnace was chosen to form the debinding chamber, as described in Section 4.3.3. The debinding time-temperature profile was generated following the procedure also described in Section 4.3.3. TGA analysis of the bench
mark plastisol revealed a weight loss peak at a trigger temperature of 450°C and complete weight loss above 525°C. The debinding profile, as assessed by TGA, was wide, this profile was wider than expected because the EVA degraded in two stages. Firstly at a low temperature, the side groups were stripped then secondly, at a higher temperature the main chain underwent scission, as shown by the TGA profile in Figure 5.1.4.1. An initial debinding profile, total time 36 hours, was applied with disastrous results, extensive part cracking and bloating was caused. A much longer profile, total time 72 hours was then applied with success, this time was reduced to 66 hours and this profile was accepted as a standard for further experimental work. The profiles are detailed in Appendix 3.

During debinding the mouldings were supported on a bed of alumina powder, the powder provided support to the moulding, raised the part clear of the impervious furnace furniture and provided scope for wicking mode removal of mobile degradation components during debinding.

Sintering of the 6% Cobalt hard metal was performed at 1450°C in vacuum (1mm Hg), a blended alumina/carbon packing powder (7 weight percent C) was used to achieve carbon balance. 30 minutes at temperature was sufficient to produce fully dense material free of eta phase and carbon inclusions, as shown in Figure 5.1.4.2. Some severely cracked specimens were present, as shown in Figure 5.1.4.3, and these defects were traced to incomplete mould filling in cases when the hold on pressure was not maintained during the moulding cycle.
5.2 Lamination of thermoplastic plastisol with wrought steel substrates

5.2.1 Substrate positioning

This series of experiments was performed using the blanked off impact test bar mould, with substrate blanks machined from wrought stock, as described in Sections 4.2.2 and 4.3.4 respectively. The developed thermoplastic plastisol was used throughout this series of experiments.

There was concern that the substrate might be displaced by the incoming plastisol because the substrates were loosely placed, rather than positively secured, in the injection cavity. It was found that if the machining tolerance on the substrates was tight, so that the gap between the substrate edge and the cavity wall was small, then the substrate positioning was stable and the over moulded plastisol formed a mirror image coating layer, as shown in Figure 5.2.1. If the machining tolerance was poor, plastisol filled the gap between substrate and cavity wall. This behaviour could be tolerated, but if the gap was very large then plastisol could get underneath the substrate and lift it away from the cavity base, producing irregular laminates. Fortunately a plastisol is very viscous compared with a normal polymer and correspondingly large tolerances were possible. Substrate/cavity gaps of 0.25mm were not explored by plastisol and gaps up to 0.50mm could be tolerated, i.e. the limit on substrate / mould wall tolerance was plus 0.00 minus 0.25 mm.

During the above test of substrate positioning, no inmould adhesion by the plastisol to either the cavity walls or to the substrates was observed. It was recognised that adhesion to the substrate but not the cavity wall was a process requirement. Hence a series of surface differentiation
methods was investigated with the aim of promoting adhesion selectively to the substrate surface.

5.2.2 Substrate surface differentiation

The first differentiation method assessed was to clean the substrate surface, as described in Section 4.3.1 and to leave the cavity dirty. However, the cleaning proved insufficient to achieve adhesion.

The second differentiation approach taken was to modify the substrate surface by polishing, shot blasting and nickel electroplating, as described in Section 4.3.1. Micrographs of the modified surfaces are presented in Figure 5.2.2. However, none of these surface treatments effectively promoted adhesion under the established moulding conditions.

The next approach taken to the adhesion problem was to preheat the substrates to temperatures between 200°C and 300°C. Adhesion to the substrates was excellent when ejected from the mould but on cooling to room temperature the adhesion was lost. Adhesive failure was by delamination or cracking, as shown in Figure 5.2.3. An annealing experiment was performed by cooling mouldings overnight in an oven to find out if the gradual cooling cycle might provide a mechanism whereby the interfacial stress could be relieved by creep behaviour. However, this annealing method did not prevent adhesive failure.

The above behaviour raised the question, is the plastisol cooling shrinkage too large to be accommodated? This conclusion was reached, for reasons discussed in Section 6.2.

It was possible to mould substrate-plastisol coating units in which the plastisol coating was hooked over the gated end
of the substrate. This enabled the length difference between the cooled plastisol and substrate, i.e. the shrinkage mismatch, to be measured with a travelling microscope, at the end of the unit opposite the gate, as shown in Figure 5.2.4. The mean differential shrinkage was found to be 0.7 %.

Surface texture assessments of substrate surfaces and the corresponding debonded plastisol coatings were performed. It was found that the plastisol exhibited good replication of the substrate surface roughness but exhibited reduced slope angles, as detailed in Table 5.2.1.

5.2.3 EVA interlayer

A possible means of accommodating the plastisol shrinkage would be to place a compliable interlayer between the plastisol and the steel. The interlayer material would need to maintain adhesion whilst experiencing shear deformation caused by the shrinkage mismatch. A candidate material was EVA rubber, this material is very polar and tacky and, in an uncrosslinked state, is capable of supporting plastic shear strains. Some substrates were coated with EVA rubber layers in the range of 20-100 μm thickness, as described in Section 4.3.1, and overmoulding trials were performed.

An initial concern was that the EVA layer would be scraped off the substrate by the incoming plastisol. This fear was however unfounded; the interlayer stayed in place and was successful as an adhesion intermediary. Stable adhesion to a substrate was consistently achieved without the need for substrate preheating.

The bonded units produced were debound. It was found that after debinding the adhesion was lost. No bond was developed between the steel and hardmetal.
5.3 Elastomeric Binder

5.3.1 Introduction

After the adhesive success of the elastomeric EVA interlayer the idea of mixing a powder with an elastomeric binder was explored. Replacement of a thermoplastic binder with elastomeric material was expected to reduce plastisol shrinkage because of the absence of a crystalline phase. It was also believed that the semirigid nature of the elastomer might promote plastic/elastic accommodation of shrinkage mismatches throughout the coating bulk by stress relaxation and creep. Four binder formulations, an EVA system and three EPM systems (Mk 1, 2 & 3) were investigated, and are detailed in Table 5.3.1. The plastisols were mixed with hardmetal powder, 6% cobalt balance tungsten carbide, all binders except the Mk3 were mixed with 57 volume percent powder loading.

5.3.2 Processing Behaviour

The plastisol mixed with EVA rubber proved to be too viscous and tacky. The plastisol exhibited rheology just inside the criteria given in Section 2.3.3 but only "short" mouldings could be produced. Incomplete EVA elastomeric plastisol coatings are shown in Figure 5.3.2.1.

During mixing of the EPM based elastomeric plastisol the mixing torque did not show the gradual rise exhibited by a thermoplastic plastisol, the rise was disturbed by a discrete jump in torque level after a few minutes of mixing, as shown in Figure 5.3.2.2.

The Haftolat process aid was found to volatilise readily and above 200°C a pronounced vapour was produced. The plastisol could be mixed at a minimum temperature of 150°C, below this
temperature dispersion of the elastomer was poor. It was found that mixing in the Brabender plastograph mixing head produced a plastisol which was "drier" than an identical formulation mixed in the larger Baker Perkins mixer. Calculation of plastisol powder volume loading from debinding weight losses revealed polymer losses during mixing of 1 and 4 volume percent for the Baker Perkins mixer and the Brabender respectively. The amount of Haftolat in mix formulations was increased to correct for this loss.

The injection moulding conditions developed for the thermoplastic plastisol were applied to the elastomeric plastisol with the exception that the "melt" temperature for injection moulding was reduced to 150°C. Hence barrel temperature was set at 140°C and nozzle temperature set at 150°C.

The Mk1 binder formulation, EPM elastomer blended in a 1:1 ratio with processing aid resulted in a plastisol which moulded well and adhered to everything, including the injection mould cavity wall. This adhesion was stable and withstood cooling to room temperature. The adhesion to the cavity as well as the substrate made ejection from the mould impracticable unless release agents were selectively applied to the cavity walls but not to the substrate surface. It was found that the choice of release agent was important, silicones & DOP agents were mobile and migrated onto the substrate surface, wax based release agents were found to stay in place on the cavity walls and leave the substrate surface clean. The mechanical properties of this plastisol were low, the plastisol could at best be described as soft. Distortion and surface damage often accompanied ejection from the mould.

A Mk2 plastisol formulation was mixed containing semicrystalline EVA (28% VA groups). This composition was
stiffer and less tacky than the previous plastisol. Under the standard moulding conditions and without application of release agents, the composition did not adhere to the mould cavity walls but did adhere to the shot blast and nickel plated substrates, forming a stable bond which survived cooling to ambient temperature. The adhesion to the nickel plate was greater than that to the shot blast steel.

The effect of moulding parameters on part density was investigated, it was found that increases of melt or mould temperature decreased density. It was also found that increased pressure hold on times increased part weight but reduced part density. The findings are shown in Figure 5.3.2.3.

A debinding cycle was developed for the elastomeric plastisol using the approach described in Section 4.3.3. The TGA trace of the Mk2 EPM elastomeric plastisol is shown in Figure 5.3.2.4. The onset of weight loss was assessed to occur at 70°C, using the method described in Section 4.3.3 (C). The cycle was 87 hours long and is detailed in Appendix 3.

5.3.3 Elastomeric Plastisol Characteristics

A survey of elastomeric plastisol characteristics was performed to enable the formulation to be optimised and to increase understanding of factors which could play a role in the MLIM process.

A minimum proportion of 23% elastomer was found to be required in the binder formulation to prevent dilatant flow behaviour in the shear rate range 0 - 1000 s⁻¹. It was found to be possible to raise the powder volume loading of the elastomeric plastisol to 58%, a 1% increase over the level
possible with a thermoplastic plastisol, whilst maintaining acceptable rheology.

These findings generated the Mk3 elastomeric plastisol formulation. Elastomer content was reduced to 25%, lowering viscosity and the powder loading was increased by 1 volume percent.

Plastisol viscosity ($\eta$) was found to have a linear relationship with the proportion of elastomer in the binder, in the range 25-45% elastomer. The relationship is shown in Figure 5.3.3.1 and can be expressed for a Mk3 formulation as below:

$$\eta = 1.11 \times \text{elastomer} - 22.75$$

Where the percentage is a weight fraction of the binder components. A plot of plastisol viscosity as a function of temperature was derived as shown in Figure 5.3.3.2.

Plastisol viscosity was also affected by elastomer molecular weight. Increasing elastomer molecular weight increased plastisol viscosity, as shown in Table 5.3.3. The EPM plastisols could be broken up by solvent swelling, indicating that crosslinking of the elastomer was not a feature of the mixing process.

The hardmetal powder was found to act as a reinforcing filler, increasing the tensile properties of the plastisol beyond those of the binder material by a factor of two. Fracture strengths and modulus of the elastomeric binder and plastisol were 0.42, 0.46 and 0.80, 1.25 N/mm² respectively. Failure was characterised by strands of elastomer drawn across a gap of torn matrix as shown in Figure 5.3.3.3.
Plastisol and binder stress relaxation behaviour was assessed, with injection moulded tensile bars, strained to 50% of the failure strain. Both materials exhibited partial relaxation. Relaxation reached a plateau level after about 20 minutes, with the binder and plastisol losing about 25% and 33% of the load level respectively.

Plastisol hot strength was limited as shown by the DMA trace in Figure 5.3.3.4. Above 80°C strength and stiffness was lost. DSC traces were taken from the binder constituents and the Mk3 plastisol. The Keltan 740 EPM and the plastisol showed negligible endotherms but the Escorene UL40028 EVA did show an appreciable endotherm.

Debound mouldings exhibited a post debinding expansion - contraction of less than 0.005 volume percent.

5.4 Plastisol/Plastisol Laminates

The next stage of the multi layer injection moulding process to be investigated was the lamination of plastisol layers.

Plastisol substrates were prepared as described in Section 4.3.4 and over moulded in the impact test bar mould, as for the wrought steel substrates. The layer thickness was three mm. A 6% cobalt 94% tungsten carbide hardmetal was used throughout this experiment.

The lamination of thermoplastic plastisol was investigated, but the laminates failed on cooling with extensive cracking.

Over moulding a substrate of the Mk1 elastomeric plastisol was not viable. The plastisol was too soft causing the substrate layer to be rucked up and pushed to the end of the cavity by the incoming material, as shown schematically in Figure 5.4.1.
Lamination of the Mk2 elastomeric plastisol was more successful; stable interlayer adhesion was achieved. A slight distortion of the substrate layer occurred, in which the layer became inclined as shown in Figure 5.4.1. Cooling the mould to 15°C prevented this distortion enabling mirror image laminates to be produced. The cooling shrinkage of the over moulded layer was expressed in two ways. The laminate could curl, or a non square end was produced; both behaviours are shown schematically in Figure 5.4.2. The observed behaviour was typically a mix of the two responses. Elements of the behaviour are visible in Figure 5.8.2.

Debound laminates had excellent adhesion in what was a "brown" process stage. The laminates could be broken by a sharp tap against a bench top but exhibited no preferential fracture along the plane of bonding.

Laminates were sintered as described previously in Section 4.3.2. Many of the sintered laminates were found to be cracked. Both inter and intra lamina cracks were present, as shown in Figure 5.4.3. A long debinding cycle of 108 hours duration (detailed in Appendix 3) was applied to the mouldings without reducing the incidence of cracks. Mouldings of laminates and monoliths of matched geometry were prepared under identical processing conditions, and it was found that the laminates cracked whilst the monoliths remained whole. Thin slices of laminates were taken and debound-sintered, these samples were crack free, with nearly invisible weld lines. Increasing the moulding pressure hold on time to 15 seconds was found to eliminate interlaminate cracking, but intralamina cracks were still present. The Mk2 elastomeric plastisol was replaced by the Mk3, which had lower viscosity and a higher powder loading. This eliminated the intralamina cracking. The crack free specimens produced exhibited an hourglass cross section normal to the injection direction. The hourglass distortion corresponded to a 2-4%
linear sintering shrinkage variation across the moulding dimensions. It was noted that this hour glass distortion was exhibited by both crack free laminate and monolithic mouldings.

The conditions for successful plastisol lamination can be summarised; mould cooling, extended pressure hold on during moulding and use of the Mk3 elastomeric plastisol.

The use of ultrasonic nondestructive testing techniques was evaluated as a method to detect cracks in the sintered laminates and the procedure was found not to be successful. It was believed that the dense tungsten absorbed too much energy to permit distinction between good and bad samples [245].

5.5 Powder Metallurgy substrates

Powder metallurgy substrates were prepared by die compaction using the die set described in Section 4.2.1, and operated as detailed in Section 4.3.2. The die cross section was 28 by 12 mm and a target compact height of 15 mm was set to complete the substrate shape. The die set geometry matched that of the MLIM tool and the substrates were intended to be used directly in the tool without any post compaction machining or coining. The pressing feedstock was a 4815 AISI steel powder mixed with 1% zinc stearate. Substrates were pressed to densities in the range 55 - 70 volume percent, corresponding to pressures in the range 80 - 385 MPa.

A powder compressibility curve was derived, and is shown in Figure 5.5.1, the corresponding curve for a sponge iron powder was also determined for comparison purposes, and is also shown in Figure 5.5.1. The hardness of the 4815 powder was determined by Vickers micro hardness; a value of 325 Hv was measured.
It was necessary to produce substrates with controlled density and size. This required selection of paired die fill and pressure parameters - size control by pressure control was not acceptable because this approach would leave compact density uncontrolled. The paired pressure - die fill parameters were determined by iteration.

Substrate green strength was poor. Substrates compacted to 60 volume percent density crumbled when subjected to injection moulding stresses. An amide wax lubricant was substituted for the zinc stearate, but produced only slight improvement in green properties. Substrates compacted to 70 volume percent density had a green strength which was almost sufficient to withstand the injection moulding cycle but some cracking and spalling occurred. The substrates could be strengthened sufficiently for injection moulding by a presinter at 1000°C for 30 minutes. The shrinkage during the presinter was negligible, and a clean, bright surface was produced. Substrates prepared under this regime were accepted for use in multi layer injection moulding trials. A micrograph of a typical substrate surface is shown in Figure 5.5.2.

The surface roughness of the pressed substrates was found to decrease with increased density, as depicted in Figure 5.5.3. At 60 and 70 volume percent density the surface roughness average was \( 3.5 \mu m \) and \( 2.6 \mu m \) respectively.

5.6 BOI Tool Steel Plastisol

The plastisol produced by mixing the Mk3 elastomeric binder with BOI steel powder (size 110\( \mu \)m) had different properties and behaviour than the hardmetal plastisol mixes. Mixing schedules two to three times longer than those used with hardmetal plastisols were required to obtain a cohesive mix. The BOI plastisol produced was, in comparison to the
hardmetal plastisols, very soft and weak; the plastisol surface was glossy when compared to the hardmetal plastisol, and free powder was occasionally present on the surface of mouldings, particularly at areas distant from the injection point. The scope for re-use of BOI plastisol feedstock scrap was limited, the flow properties were lost after a short time-temperature history and the heated plastisol developed a repugnant smell. The BOI plastisol was too soft to support over moulded plastisol layers. Attempts to over mould this plastisol resulted in push off and rucking defects, as described previously in Section 5.4.

The plastisol formulation parameters of powder particle size and proportion of elastomer in the binder were investigated with a view to improving plastisol properties. Trial plastisols were formulated as detailed in Table 5.6.1. Values of room temperature (25°C) shear modulus and the limit of hot strength were determined by DMA and are given in Table 5.6.2. Use of a "fine" particle sized powder of (47µm) produced a large improvement in plastisol properties. Increasing the proportion of elastomer in the binder also improved plastisol strength.

A further method investigated to improve plastisol properties was to substitute the 740 EPM elastomer with high viscosity, high molecular weight elastomer. Plastisols were formulated, as detailed in Table 5.6.1, and their mechanical properties were determined by DMA, as reported in Table 5.6.2. It was found that incorporation of high viscosity elastomer raised plastisol properties, improving both shear modulus and hot strength. Some very high viscosity elastomers, such as Royalene 400, are supplied preblended with a process oil, the use of such elastomers in the binder formulation did not yield the expected improvement in properties. The amount of Haftolat process aid in the binder formulation was reduced to allow for the oil added with the
elastomer, so that the total proportion of process aid/oil in the binder was maintained at 50 volume percent.

A BOI plastisol formulated with a Mk3 elastomeric binder was mixed with 2 weight percent fatty acid, Sufacid U-115. This greatly reduced the mechanical properties of the plastisol and the fatty acid bloomed on the plastisol surface.

A modified plastisol composition with medium sized (85µm) powder mixed with a binder containing 50 weight percent elastomer was accepted for use in the MLIM procedure, for the practical reasons discussed in Section 6.3. This composition was more difficult to mould than the standard hardmetal plastisol, a 10°C increase of melt temperature and a heated mould, temperature 40°C, was required to mould the 1mm thick layer needed for fabrication of the multilayer structure. This BOI plastisol was adequate for the production of mouldings and was sufficiently strong to be overmoulded in lamination trials, but the level of mechanical properties was less than that of the hardmetal plastisols.

5.7 Process adhesion steps

The aim of this experiment was to try in isolation each adhesive step - both interfacial bonding and adhesion transfer - necessary for success of the MLIM process route. If each step was found viable then attempts to put all the steps together to form the MLIM procedure could be undertaken with increased confidence, as described in Section 3.1.1.

Test laminates of each interface in the graded structure were fabricated using the impact test bar mould and MLIM test mould, using the procedures described in Section 4.3.4. The interfaces investigated were previously listed in Table
3.1.1. Hardmetal plastisols mixed with the Mk3 elastomeric binder and a B01 tool steel plastisol, formulated as detailed in Section 5.6 were used during the investigation; debound with the schedule described in Section 5.3.2 and sintered at 1300°C as noted in Table 4.3.2. The laminates were processed through the route of moulding, debinding and sintering and their adhesion behaviour observed, as reported below.

4815 steel / B01 tool steel This interface was moulded in the MLIM injection mould using a powder metallurgy substrate compacted to 70 volume percent density and presintered. Satisfactory plastisol/substrate adhesion was produced in the green state. It was found that when the laminate was forcibly separated, a surface coating of plastisol was left on the substrate surface. On debinding, adhesion was established between the two materials. When sintered this bond was strengthened. The steels did not undergo more than 1% linear shrinkage during the sinter, leaving the laminate with a high porosity level.

B01 tool steel / 28% cobalt - 72% tungsten carbide hardmetal

This laminate was moulded in the impact test bar mould. Good adhesion was present in the green and debound states. However, after sintering the hardmetal peeled away from the steel, in the manner shown in Figure 5.8.4 for a MLIM geometry graded structure unit.

28% / 20%, 20% / 16% & 16% / 12% cobalt, balance tungsten carbide hardmetal

All these interfaces exhibited similar behaviour. In the green state good adhesion was present and it was not found possible to forcibly separate the laminate along the interface. The laminates tended to curl, as shown in Figure 5.7.1, and this behaviour matched that exhibited during the
lamination of 6% cobalt 94% tungsten carbide hardmetal plastisol, described in Section 5.4. The adhesion in the debound state was excellent and when sintered a good bond was developed.

NB: A few steel substrates were directly coated with hardmetal. When sintered, the steel was severely attacked and the surface melted, affirming the need for control of carbon diffusion across the composite interface.

The post debinding dimensional change associated with these graded structure powders was measured and found to be, on average, a linear expansion of 1.4%.

5.8 Multi layer injection moulding of the graded structure

The aim of this experiment was to assess the multi layer injection moulding (MLIM) process. An injection tool was designed for the process, as described in Section 4.2.2. The operation of the tooling is described in Section 4.3.4. It was found that the height of the shim pack exceeded the sum of individual shim thicknesses and the substrate height was reduced by 0.2 mm to compensate. Coatings were successfully produced with the tool, a 1mm thick plastisol layer could be moulded over a substrate, as required for the intended graded structure geometry. The ejector pin in the gate area of the mould was occasionally jammed by plastisol seepage into the ejector pin / mould body clearance.

Placement of the first injection moulded layer of the graded structure, the B01 plastisol, was established during the testing of individual interfacial adhesion, as reported in Section 5.7, hence the investigation started with placement of the first hardmetal layer to produce a three layer composite. This was achieved directly without need to modify
any of the standard process conditions, a typical three layer unit is shown in Figure 5.8.1.

Placing the third injection moulded layer was not possible under the standard process conditions. Attempts to do so resulted in distortion of the underlying two plastisol layers. The distortion occurred in the modes described in Section 5.4, namely push off and rucking. Distorted specimens are shown in Figure 5.8.2.

Placement of the third moulded layer (fourth layer of the composite) was attempted with use of progressively higher melt temperatures to reduce plastisol viscosity. At a temperature of 220°C the placement was successful, yielding distortion free four layer units. The use of plastisol melt temperatures above 220°C was investigated but it was found that substantial binder volatilisation occurred within the injection moulder and plastisol properties were impaired.

Attempts were made to fabricate the multilayer structure in two stages, by first moulding three plastisol layers, then debinding the unit to raise its strength before moulding the remaining two layers. This approach was not successful because of very poor adhesion between the debound plastisol surface and the over moulded material.

It was noted that the range of plastisol viscosity achievable by manipulation of melt temperature was limited, the useable temperatures were bracketed by the minimum temperature for mould filling, 140°C and the temperature above which plastisol decomposition was significant, 220°C. It was discovered previously that a greater range of plastisol viscosity could be created by controlling the elastomer content of the binder, as reported in Section 5.3.3. This extra flexibility was sufficient to allow a trial of graded processing parameters derived from the
simple process modelling detailed in Section 3.1.4. A set of plastisol feedstocks were prepared with graded binder elastomer contents, as specified in Table 5.8.1. The gradations corresponded to plastisol viscosity reductions in the ratios derived in Section 3.1.3. The viscosity of the higher layers in the structure was reduced to lower the shear force expected to be transmitted to the under lying layers during injection moulding.

Direct use of the graded viscosity feedstocks with the standard injection moulding conditions was not a success. Distortion defects were present in many mouldings of the third plastisol layer and the moulding of higher layers was dominated by distortions. It was found that the use of graded injection pressures was also required. The injection pressures were reduced in parallel to the plastisol viscosity gradations, as detailed in Table 5.8.2. Under these conditions all five plastisol layers could be moulded without distortion to form a complete composite unit, as illustrated in Figure 5.8.3. Occasional specimens were distorted and it was found possible to prevent this by slightly raising the melt, i.e. injection temperature, by 5-20°C as and when required during operation of the injection moulder. After overmoulding by the four hardmetal plastisol layers the BO1 plastisol layer was compressed and visibly oozed out of position over the edges of the substrate, this effect was not gross, the thinning of the BO1 layer was not greater than 0.2 mm.

Adhesion was maintained during debinding of the multi layer units with the occasional exception of the top two layers. These layers occasionally arched away from their interfacial position, as shown in Figure 5.8.3.

On sintering, the hardmetal layers were found to shrink whilst the steels retained their original dimensions. This
resulted in the hardmetal layers peeling away from the steels, as shown in Figure 5.8.4. This behaviour matched that experienced when testing the individual adhesion steps as reported in Section 5.7. The steel was not densified sufficiently by sintering to close the porosity. Debound composite units were consolidated by ceramic grain HIP'ing to yield physically integral compacts.

5.9 Multi layer injection moulding of a graded structure rock bit

5.9.1 Introduction

The aim of this experiment was to try to extend the moulding of the graded structure from the simple rectangular geometry of the MLIM mould to a three dimensional shape of commercial interest. The design chosen for fabrication was a rock bit insert. The part shape and dimensions were provided by B.P. [246]. The part volume was divided into the layers of the graded structure to form a composite unit. The geometries are shown in Drawings RBT 1 & 2 presented in Appendix 1.

5.9.2 Substrate fabrication

The substrate shape was cylindrical with the addition of a truncated cone with diametrically opposite hyperbolic sections absent, protruding from one end face. The cone base radius was \( \frac{2}{3} \) rd\# that of the cylinder, the "conical" tip was shaped to form a chisel edge, as shown in Drawing RBT 2. A compaction die was made to press this shape, as described in Section 4.2.1. The cylindrical shank of the substrate was formed by the die wall and the "conical" tip formed by a cavity recessed in the end of one punch. Initial pressing was performed using a ESH servohydraulic testing machine and the standard powder feedstock. The pressing procedure is detailed in Section 4.3.2.
Compaction at a pressure of 385 MPa, as used to produce substrates for the MLIM mould, was not successful. The substrate tip was retained within the punch cavity and was found to break off the cylindrical shank. The tip left in the punch cavity could only be removed by mechanically breaking it up in situ. The surface roughness of the punch cavity was measured and found to have a roughness average of 0.67 µm. Pressing feedstock was prepared with a new lubricant system, 1.75% Wachs and 0.75% Zinc stearate. Use of this feedstock did not prevent substrate fracture. The compaction die was transferred to the larger capacity Denison testing machine and the compaction pressure was progressively raised. The higher the compaction pressure the greater the tip height produced. At a compaction pressure of 700 MPa, corresponding to a density of 82 volume percent, complete substrates were produced, but the tip extremity was weak and friable. To develop sufficient strength in this region a presinter was required. The roughness average of the tip surface was 2.7 µm.

The compaction die was operated in floating mode with the die body spring supported. This produced a 0.5-0.75% increase in powder compressibility but this was insufficient to improve tip strength. It was observed that tool wear was pronounced over the radius at the punch cavity entrance. The surface roughness of the punch cavity was remeasured after 40 pressings and found to be 0.59 µm. The high pressures found necessary to produce whole substrates gave rise to correspondingly high densities. Conditions of 700 MPa pressure, density 82%, fill weight 95 gm, and a presinter were accepted as a working standard. Control of the fill factor was required to control substrate height and the presinter conditions were manipulated to control shank diameter. A typical presintered substrate is shown in Figure 5.9.2.
5.9.3 Operation of injection mould tooling

The mould parts and design is shown in drawings RBT 5-9 presented in Appendix 1. It was found that the epoxy insert would crack under injection pressures unless closely supported by the mould body - a tight fit was necessary. The substrate shank was very closely fitted in the bottom mould (tolerance +0.00 - 0.05mm) in light of the experience with the impact test bar mould, to prevent plastisol seepage between mould and substrate.

Initial moulding of the BO1 plastisol layer was disrupted by preferential adhesion to the cavity rather than the substrate. It was noted that the surface finish of the epoxy cavities was not high. It was possible to smooth the epoxy surface by coating it with a glaze of unfilled liquid epoxy resin. The plastisol adhesion to the glazed cavities was greatly reduced and part removal was possible.

The orientation of the substrate within the bottom mould had to be correct before mould closure to avoid unintentional mechanical contact between substrate and cavity. Use of the positional lock built into the bottom half of the mould was found to be unnecessary because once positioned, the substrate was not found to rotate out of alignment when over moulded.

Part ejection was not directly provided for in the mould via a conventional ejector pin assembly. The ejection procedure intended with the tool design was two staged: firstly to part separate the injection machine bolsters to open the mould without engagement of the ejector pin assembly, during this movement the substrate shank would be locked in the bottom mould half causing the injection moulded region of the part to be drawn out of the cavity; the second stage of ejection would be performed after unlocking the substrate, when full separation of the bolsters would engage the
ejector pin assembly pushing the substrate clear of the mould bottom. This procedure did work when the weak BOI tool steel plastisol was used, the moulding and runner separated by necking at the gate region. The procedure did not work when the hardmetal plastisols were used because the moulding was too well attached to the runner and detachment from the runner did not occur, consequently ejection resulted in torn mouldings. It was found necessary to eject the runner and moulding as a whole. It was found possible to achieve ejection if the substrate was unlocked before mould opening, and then the injection pressure reapplied to the opened mould to force the runner, and hence the moulding, out of the mould top. The mould operating procedure adopted in response to the initial moulding trials is listed in flow form below:

a) substrate placement and orientation in bottom mould
b) mould closure
c) injection
d) pressure hold on, (15 seconds)
e) mould opening
f) reapplication of injection pressure
g) part removal
h) clearing of runner channel, and
i) cavity cleaning.

5.9.4 Injection moulding results

It was not found possible to mould a 1mm thick plastisol layer over the rockbit substrate. In consequence, the layer thickness was increased to 2mm, at which complete layers could be moulded. This reduced the possible number of layers that could be placed, using the prepared cavity inserts, from five to three.
It was decided to mould the first three layers of the graded structure to form a composite within the limit imposed by the necessity of increased layer thickness for moulding. The BO1 layer was successfully moulded, as were hardmetal layers using the graded processing parameters. This is illustrated in Figure 5.9.4. Three dimensional rucking type defects were experienced if the graded processing parameters were not applied. Oozage of the BO1 plastisol layer out of position after placement of the hardmetal layers was experienced, as found previously with the composite units fabricated with the MLIM tooling.

5.9.5 Debinding and consolidation

Debinding was successful and adhesion was maintained. Slumping of the units resulted if debound horizontally and this orientation was avoided. Consolidation by ceramic grain HIP'ing was performed.
6.0 DISCUSSION

6.1 Powder injection moulding technology: Thermoplastic plastisols

The need for progressive debinding necessitated the use of a binder formulation which was a polymer blend of several components, as discussed in Section 2.3.4. Further a multi component binder was considered favourable with respect to the development of controlled adhesion, as discussed in Section 2.4.1. It was decided to select the components with the view of ensuring polymer compatibility, because of evidence suggesting that incompatible polymer phases in PIM feedstocks may, on solidification, form particle free zones, to the detriment of part homogeneity [247]. Also the presence of incompatibility would increase the complexity of interpreting plastisol behaviour. The polymers used would also have to be easily "burnt out" and this would limit the choice of materials, as detailed in Section 2.3.4 and discussed in Section 2.2.3. To enable flexibility in the binder formulation the polymers would have to be available in a range of molecular weights and forms. The above requirements were most easily met by the polyolefins, which were subsequently chosen for this work.

A pure wax binder system was not considered a suitable system for the proposed use because such a system has a waxy surface and the cooling shrinkage is large. These characteristics were considered unfavourable to the adhesion requirements of the project. It was also considered that inclusion of plasticisers, though beneficial to flow properties, could be detrimental to adhesion because of their tendency to bloom on surfaces [207].

When considering binder formulation it was convenient to divide the thermoplastic polymers into three classes: i) low
molecular weight material i.e. the waxes, ii) medium molecular weight material, and iii) high molecular weight material, i.e. material such as injection moulding grade polymer. Use of a three component blend of low, medium and high molecular weight polymer emerged as a minimal formulation, no appreciable changes to blend properties were experienced when further components were added. It was found that inclusion of high molecular weight polymer was not essential for the maintenance of flow or strength properties. This finding, considered with the inherently high viscosity of such material and the great amount of chain breakdown required in its debinding, resulted in the decision to avoid its use.

The inclusion of EVA in the binder blend was advantageous because the material was compatible with the olefinic base and the two stage thermal degradation of the EVA widened the debinding weight loss profile. These positive attributes, considered along with the improvements in mixing caused by EVA and its reputation as an adhesive, led to the decision to include some in the final formulation. N.B. The Escorene UL40028 EVA with 28% VA groups is at the limit for compatibility with olefinic polymers [248].

Waxes were rejected for use as a component in the thermoplastic binder because their waxy properties were exhibited even when greatly diluted by other material. This may have been due to the waxes blooming at the plastisol surface. This behaviour was not considered favourable for adhesion.

The powder loading level achieved for thermoplastic plastisol of 57 volume percent was slightly lower than was hoped for; higher values are reported in the PIM literature [112, 114, 127]. The low value may have arisen because the irregular morphology of the hardmetal powder may have
resulted in a predisposition to dilatancy. Similar binder systems mixed with spherical particles can be formulated with higher powder loadings [126]. It was probable that the lack of highly interactive material which can form binder–particle interactions may also have reduced the attainable powder loading level. Martyn has found that inclusion of such material in a binder can greatly increase the useable powder loading level [124].

Plastisol rheology and moulding behaviour were as expected, in that the behaviour matched that described in PIM literature, as detailed in Section 2.3. The moulding thickness of 6mm used whilst investigating PIM technology was thick in both conventional injection moulding and PIM terms, and was making a large demand of the technology. The large thickness increased the difficulty of compensating for feedstock shrinkage. In Section 2.2.4 the disadvantages of a plunger type injection moulder were discussed. These disadvantages were reduced when using PIM feedstocks because their increased thermal conductivity off set the inherently poor heat transfer of such machines.

The prime concern when debinding hardmetal was to produce a crack free part and the removal of all carbon was of secondary importance. Unless a gross carbon imbalance is produced the imbalance can be corrected during sintering by manipulation of the sintering atmosphere [249]. Consequently the debinding profiles were aimed at achieving crack and bloat free parts as a first priority. The large thickness of 6mm raised the danger of bloating and cracking during debinding. The debinding cycle accepted for use with the thermoplastic plastisol had a duration of 66 hours, this would be considered undesirably long for commercial exploitation but the cycle was accepted as adequate for the exploitation of MLIM procedures, which was the central objective of this study.
A debinding shrinkage of a few percent was expected. The plastisol was loaded with 57 volume percent powder, six percent less than the proportion of powder required for attainment of the density maximum for random packed powders. On removal of the binder phase it was expected that the particle centre separations would be reduced raising the powder packing density towards that of complete packing. However the hardmetal plastisol did not exhibit any appreciable debinding shrinkage, this may have been due to the very fine size and irregular shape of the particles promoting a high level of mechanical interlocking, thus preventing particle contractions into the voidage left by the removed binder.

6.2 Initial coating experiments: Thermoplastic plastisol and wrought steel substrates

These experiments addressed two process requirements of multi layer injection moulding. Firstly, the question of whether or not a substrate loosely placed within a mould cavity would retain positional stability when over moulded, and secondly, how adhesion to the substrate, but not the mould cavity walls could be achieved.

The wrought steel substrates coated during these experiments were not positively constrained within the impact bar mould cavity. The low height of the substrate limited the potential for lateral restraint by the cavity walls allowing the substrate to be flipped out of position in the cavity bottom, such behaviour was not acceptable. Concern that such a displacement might be the result of the sudden transmission of pressure and shear forces to the substrate during mould filling proved to be unfounded. However it was found that injected plastisol could explore the substrate-mould wall tolerance and infill the substrate-mould bottom gap, displacing the substrate upwards. At the extreme end of
this behaviour the substrate was in effect "floated" away from the cavity bottom by plastisol. For this to occur the plastisol pressure below the substrate must have exceeded the pressure of the plastisol above. A possible source of such a pressure differential could be that the plastisol coating the substrate top surface had a larger volume available to expand into and hence experienced a larger pressure drop than the plastisol which had entered into the restricted nether regions of the cavity. Fortunately this behaviour could be prevented by reducing the substrate-cavity wall gap to a level which was not explored by the injected plastisol. The large gap of 0.25mm that was acceptable was indicative of the inherently poor flow characteristics of PIM feedstocks in comparison to pure polymeric materials. These results gave confidence that the process requirement of inmould substrate positional stability was achievable without the need for any special procedures, such as use of clamping or dowelling.

The approach taken to achieve adhesion of moulded plastisol to the substrate surface, but not to the mould walls, was to differentiate the surfaces, promoting preferential adhesion to the substrate. No attempt was made to reduce the adhesive potential of the mould surfaces because they were polished by the plastisol feedstock during moulding. A hardmetal plastisol can be likened to a grinding paste. It was considered that any special surface preparations applied to the mould, such as, for example a PTFE coating, would be quickly worn away rendering this method unattractive. Consequently the differentiation process was focused on increasing the adhesive potential of the substrate.

Surface contamination with dust, moisture and grease may prevent adhesion, as discussed in Section 2.4.1, hence the first surface differentiation investigated was to clean the substrate surface and leave the cavity "dirty". Also surface
roughness may promote adhesion, as also discussed in Section 2.4.1, and hence substrates were prepared with shot blast surfaces.

After negative results using these surface preparations a calculation was performed to estimate the amount of free binder available in the plastisol. Assuming the hardmetal particles to be spherical, the available polymer could produce an individual coating thickness of 7nm. It was considered reasonable to assume that the plastisol surface would exhibit a similarly limited polymer coverage. The high loading of powder may be conceived as "drying up" the plastisol by binding the polymer. It was possible that during injection moulding a powder/binder separation [117] may have taken place with surface enrichment with polymer but no evidence for this was observed during this work. The plastisol surface was examined by scanning electron microscopy (Figure 5.2.2) and found to be not a smooth polymer surface but rather a surface rich in particles i.e. insufficient free binder was present to form a polymeric skin on the plastisol. In view of this limited polymer availability at the interface substrates were prepared with polished surfaces because it was thought that such surfaces might be effectively wetted out by a very limited amount of polymer. However, the results of this approach were also negative.

It is widely known that oxidation of polyolefins can promote adhesion, as discussed in Section 2.4.2. Substrates were prepared with a coating of electroplated nickel in the hope that this catalytically active metal [250] would promote oxidation and hence adhesion under moulding conditions. This did not happen, possibly because the melt temperatures used were too low.
The lack of success achieved with the physical surface differentiation methods discussed above led to the idea of heating the substrate. The heat could promote adhesion: (a) by delaying plastisol cooling enabling a lower viscosity state to be effective during bonding, and (b) by promoting polymer oxidation. This option had been resisted because of the considerable practical inconvenience inherent in its adoption. Adhesion to the heated substrates was excellent but the adhesion was not stable. When cooled to room temperature, the plastisol either peeled away from the substrate or cracked.

Plastisol delamination as a whole indicated that the adhesion was weaker than the coating. Cracking of the plastisol coating indicated that the adhesion was stronger than the plastisol. In this case further increase in adhesion levels would not aid coating cohesion because, in the cracked units the adhesion had exceeded the strength of the plastisol and was still insufficient to contain plastisol shrinkage. Besides the macro shrinkage of the plastisol the measurements of surface topography revealed a possible micro shrinkage at the interface. The delaminated plastisol surface exhibited a lower slope angle than the substrate surface it was replicating. Such an effect may have been caused by incomplete wetting of the surface, but could have also originated from a retraction of shrinking plastisol from the interface; this would be an additional factor acting with the shrinkage stresses against adhesion. It was interesting to note that the level of substrate surface replication by the plastisol coating was good irrespective of whether or not the substrate was preheated. Unless the interfacial adhesion is dependant on fine scale wetting effects beyond the resolution of the surface parameter measurements it can be concluded that the improvement in adhesion with use of a heated substrate was
not due to improved wetting but can be attributed to oxidation mechanisms.

A question of interest was, could the shrinkage of the plastisol be reduced sufficiently to enable stable adhesion to be developed? This would mean reducing the thermal expansion coefficient of the plastisol to the same order as the steel and limiting the crystalline shrinkage present when the binder was frozen.

There were two obvious routes to lower the thermal expansion coefficient of the plastisol; firstly to raise the powder loading and secondly to use a binder with a low expansion coefficient. However the first option is limited by the need for plastisol flow, the powder loading can not be increased above the maximum for good flow behaviour. The simple linear mixture equation (LME) [240] was used to model the theoretical thermal expansion coefficient of the plastisol, following Equation 3.1.2.2. The value calculated was $40 \times 10^{-6}$ K$^{-1}$ which was in close agreement with the measured value of $30-40 \times 10^{-6}$ K$^{-1}$. The observed agreement suggested that it would be valid to use the LME to calculate the value of binder thermal expansion coefficient that would be required to form a plastisol of thermal expansion coefficient equal to that of the steel substrate. This can be diagrammatically represented as shown in Figure 6.2.1, where a plot of experimental and calculated data of thermal expansion coefficient as a function of powder volume loading is shown and the process window for a matched plastisol expansion coefficient is delineated. It can be seen that, in spite of the very high powder loading used in plastisols, to match the thermal expansion coefficient value of steel a low polymer thermal expansion coefficient value would be required. The value was calculated to be $60 \times 10^{-6}$ K$^{-1}$, such a value is within the property range for polymers. This can be illustrated by listing the thermal expansion coefficients of
some common polymers. rigid PVC has a value of $55 \times 10^{-6}$ K$^{-1}$, polystyrene $70 \times 10^{-6}$ K$^{-1}$, polyethylene low and high density $250 \times 10^{-6}$ K$^{-1}$, paraffin wax $110 \times 10^{-6}$ K$^{-1}$, polyisoprene $220 \times 10^{-6}$ K$^{-1}$ and polypropylene $62 \times 10^{-6}$ K$^{-1}$, data from the "Science data book" [267]. The required value of polymer thermal expansion coefficient is however near the limit of the range of values exhibited by polymers. A plastisol was mixed with polypropylene and a thermal expansion coefficient of $20 \times 10^{-6}$ K$^{-1}$ was measured. This value approaches the value for EN3B steel $12-13 \times 10^{-6}$ K$^{-1}$ [269] but fell short of creating a plastisol of matched thermal expansion coefficient and indicates that the agreement between experimental and LME values of thermal expansion coefficient was not exact. The potential to create a plastisol with a thermal expansion coefficient less than that of the steel was considered very remote.

Reduction of binder crystallisation shrinkage was considered possible if noncrystalline i.e. amorphous polymer was selected. However the range of available amorphous thermoplastics is limited to materials such as polystyrene, polycarbonate and poly methyl metacrylate. The debinding prognoses for these materials was not considered good for the reasons discussed in Sections 2.2.3 & 2.3.4 and the latter two materials are expensive.

Formulation of a low thermal shrinkage plastisol was limited by the need to use a binder comprised of a polymer blend. The low molecular weight material essential to lower plastisol viscosity and broaden the debinding weight loss profile, has a greater shrinkage than high molecular weight material because of the greater number of chain ends. It was doubted that the thermal expansion coefficients listed above, for pure polymers, could be matched when blended with the required low molecular flow aids and lubricants because of the resultant reduction in structural order.
An alternative approach to formulating a matched thermal expansion plastisol would be to develop a polymer blend which has no overall cooling shrinkage because phase changes associated with cooling produce an expansion equal to the contraction. Such a technology has been developed in the "low profile" polyester moulding compounds, but the details are commercially secure and little information is in the public domain.

It was decided that formulation of a thermoplastic plastisol with a thermal shrinkage matched to that of steel was not practicable for the following reasons: (i) Many of the crystalline thermoplastics have too large thermal expansion coefficients for it to be possible to form a plastisol with a matched thermal expansion coefficient, (ii) the crystalline thermoplastics which have a thermal expansion coefficient low enough to form a matched plastisol according to the predictions of the LME are only just in range and formulations would have no lee way for downward adjustment, (iii) the crystalline shrinkage of the crystalline thermoplastic polymers is unavoidable if they are used, (iv) the essential use of low molecular weight material in the binder formulation would increase the thermal expansion coefficient above the values calculated with the LME; in view of the fact that the calculated values were only just low enough this was not considered favourable, and (v) the available amorphous thermoplastics were not considered desirable binder components.

With hindsight it was realised that polystyrene might have met the requirements for a plastisol with shrinkage matched to that of the steel. The polymers thermal expansion coefficient is low enough to form a matched thermal expansion coefficient and the polymer is free of crystallisation shrinkage. However the match would be operating at the limit of the thermal expansion range.
possible, with out scope for adjustment if reality did not meet the prediction of the LME. Further polystyrene is a rigid and brittle material and is not thought likely to be tolerant of interfacial stresses. It is possible that use of an impact modified polystyrene could form a less rigid plastisol. If it was found possible to raise the powder volume loading above 57 volume percent whilst maintaining flow properties this could slightly reduce plastisol shrinkage. Success for a polystyrene based plastisol as a coating feedstock is considered just possible but no great confidence in its successful development is held.

The intention to apply a thermoplastic plastisol directly to the steel was abandoned, because accommodation of the thermal shrinkage mismatch was considered inviable. In response to this conclusion, substrates were prepared with an inter layer coating of EVA elastomer. The inter layer was expected to provide good adhesion because: (i) the elastomer was very polar, (ii) it had high tack, (iii) it was "fluid" and conformable, and (iv) it was unimpeded in the adhesive function by powder filler. It was further expected that the interlayer could accommodate the differential shrinkage between steel and plastisol through creep and flow responses. The elastomer was used in an uncured state, permitting distortion without the boundary of an elastic limit, any distortions experienced by the interlayer would be permanent and free of residual stress. Adhesion to the coated substrates was excellent and stable, bonded steel-plastisol units were produced and stored at room temperature. The adhesion did not require the assistance of a heated substrate, and was specific to the substrate. This result met the process requirement for inmould adhesion.

However, on debinding the adhesion was lost, irrespective of the surface preparation underneath the EVA elastomer inter layer. During debinding the EVA elastomer layer was "burnt
out" removing the bridging phase between the steel and hardmetal. It is unlikely that good interfacial contact would be achieved in such circumstances because the plastisol would have replicated the surface of the interlayer not that of the substrate, this would not favour adhesion and is thought to be the cause of adhesion loss. It was realised that substrate coating with use of an EVA interlayer could not be extended to annular coatings because the absence of a free edge would make it impossible for the necessary shrinkage movements of the plastisol to take place.

6.3 Elastomeric plastisols

6.3.1 Introduction

The adhesive success of the EVA elastomer interlayer led to the idea of formulating an elastomeric binder to produce an elastomeric plastisol. It was expected that the thermal shrinkage of such a plastisol would be greatly reduced in comparison to the thermoplastic equivalent due to the absence of any crystallisation shrinkage. It was also expected that, because the elastomer was used in the uncured state and above the glass transition temperature, no defined stiffening temperature would be exhibited, but rather a gradual increase in viscosity with decreasing temperature. This behaviour would allow interfacial stresses arising from a shrinkage mismatch between substrate and plastisol to be accommodated throughout the plastisol bulk by flow and creep mechanisms, thus enabling successful adhesion. Under these conditions intimate plastisol-substrate contact would not be impeded by an interlayer, as was the case for the EVA elastomer interlayer discussed in Section 6.2. It was expected that use of an elastomeric plastisol would overcome the difficulties experienced with the thermoplastic
plastisol and enable the process requirement of substrate/plastisol adhesion to be met.

The choice of elastomer was guided by the criteria applied to thermoplastic polymers with the additional requirement that the possibility of spontaneous crosslinking should be avoided. Many elastomers have been developed for temperature and/or environmental resistance and include halogens in their structures, examples include chloroprene and fluoro carbon elastomers. This results in a hazardous and unfavourable prognoses for debinding due to production of hydrogen chloride and hydrogen fluoride gaseous fumes and so such materials were not considered as possible binder components. Silicone and nitrile elastomers were also rejected on the grounds of unattractive debinding properties; silicones are known to be detrimental to hardmetal properties and the nitrile structure contains pendant cyanide groups, a potential hazard when released during debinding. Some other elastomers were considered to have structures either resistant to breakdown and/or prone to form carbon residues, for example ring structures in acrylic elastomers. Polyurethanes were not considered for use as a binder because of the possible hazardous fumes generated during debinding and potential complications with respect to their hard-soft segment structure [251]. Other elastomers contain within their chain structure crosslinking sites which might be activated during processing for example natural, isoprene, butyl and styrene-butadiene rubbers (SBR). SBR has the further disadvantage that it is not compatible with the paraffinic materials typically used in PIM compositions. EVA elastomers were investigated as a binder material but no suitable processing aid was identified and the compositions were too viscous. An elastomer which seemed to have no disadvantages was ethylene propylene monomer (EPM). This elastomer contains no "built in" crosslinking sites, has a high molecular weight, a
reputation for readily incorporating large filler loadings, [252,253] and was expected to debind cleanly, and is compatible with polyolefins. Hence EPM was chosen as the favoured candidate elastomer, and used to produce plastisol. N.B. the elastomeric binder was not composed solely of elastomer as discussed previously in Section 2.2.5, but comprised a blend of elastomer with other polymeric materials.

6.3.2 Hardmetal elastomeric plastisols

The observed irregularity exhibited by the mixing torque of these plastisols may have corresponded to a transition point at which the process aid became integrated with the mix components and switched behaviour from that of a lubricant to that of a plasticiser. Such a transition would provide an explanation for the experienced dwell in mixing torque. An analogous mechanism is known to act during the gellation of PVC plastisols [254].

As reported, the Mk1 elastomeric plastisol was too soft, but could be stiffened by addition of EVA polymer to form the Mk2 elastomeric plastisol. The EVA was believed to act by increasing the binder—particle interactions as a result of the polar VA groups. A contribution to plastisol stiffening from the crystallinity of the EVA was expected but was not present. When mixed in the plastisol, the crystallinity was lost, as shown by the loss of a DSC endotherm on traces taken from the plastisol. This result and the reduction in polyethylene crystallinity experienced when it is mixed as part of a thermoplastic plastisol, as reported in Section 5.1.2, are possibly both caused by, (i) immobilisation of polymer chains on the particle surfaces, (ii) an increased subdivision of crystalline regions with a subsequent increase in the proportion of polymer in disordered domain.
boundaries and (iii) dissolution of crystallinity by low molecular weight binder components.

It was considered desirable to optimise the plastisol with respect to viscosity and powder loading level. This was achieved, as detailed in Section 5.3.3, when the Mk3 plastisol was produced. The discovery that dilatant flow was present below a minimum elastomer content led to the image of a minimum elastomer presence necessary to separate the particles, and hence prevent the particle-particle interactions that are causative of dilatant flow [255].

Of the many plastisol characteristics investigated the tensile behaviour was of particular interest. Particle reinforcement was not expected in this system because, in reinforcement terms, the hardmetal powder was very large [256]. The partial stress relaxation could not be explained in terms of physical crosslinks generated by particle reinforcement because the behaviour was exhibited by both filled and unfilled binder. Hence it may be concluded that the binder contained an inherent limitation to stress relaxation, which was unexpected. There was no evidence that chemical crosslinks were present in the material and no crystallinity was detected in DSC traces. This raises the question, what other factor(s) might be responsible for the limitation of stress relaxation? It is possible that under stress elastomer chain orientation was generating extended chain crystallinity, which acted as a source of crosslinks. The 740 Keltan elastomer used has a relatively high ethylene content and it is possible that this promoted microcrystallinity. The limit to stress relaxation put a limit on the potential of the plastisol to relieve residual stresses and hence placed a potential limit on plastisol coating operations.
Mixing the Mk3 binder with the 110μm sized BO1 powder was not a success, the plastisol produced lacked strength and was inadequate for moulding purposes. This behaviour was in great contrast to the behaviour of the hardmetal plastisol. The large particle size of the BO1 steel precluded the possibility of particle reinforcement; this effect could not be investigated because the plastisol was too weak and soft to be successfully gripped during tensile testing. It was possible that the elastomer was generating a polymer-particle interaction with the hardmetal powder, which did not occur when mixed with BO1 steel, though this is considered unlikely in view of the reputation for inertness possessed by the polyolefins. In the absence of polymer-particle interactions and particle reinforcement the mechanisms available to provide plastisol cohesion are limited. An uncured elastomer owes much of its cohesion to chain entanglements, as depicted with the commonly used spaghetti analogy for polymer structure. Spaghetti style polymer strands were seen on plastisol fracture surfaces as shown in Figure 5.3.3.3. It is possible that the presence of large particles disrupted the entanglement process, and it was of interest to calculate what particle size would cause a breakdown of the entanglement process by requiring the full elastomer chain length to wrap round a single particle. Such a calculation was performed, as detailed in Appendix 4. Elastomer chain length was found to be greater than the particle size of the hardmetal, but less than the particle size of the BO1 powder. In consequence reduction of particle size was considered a likely route to improved plastisol strength.

As reported, in Section 5.6, reduction of particle size increased plastisol strength, at 47μm the strength gain was large, a factor of $10^3$, and plastisol properties approach
those of the hardmetal plastisol. Increasing the proportion of elastomer in the binder or utilising a higher molecular weight, greater chain length, elastomer, both improved plastisol strength.

The results discussed above support an entanglement model of elastomeric plastisol cohesion, when the potential for entanglements was increased so did the plastisol strength.

Unfortunately the supply of 47\(\mu\)m sized BO1 powder was insufficient for extended moulding trials and the 85\(\mu\)m sized powder was used. This powder was mixed with a binder containing 50 weight percent elastomer and yielded a plastisol with adequate properties for investigation of the MLIM process.

The use of high molecular weight elastomer to improve plastisol properties was limited by the oil compounded with such polymer. The oil provided internal lubrication and reduced the attainable mechanical properties.

In an attempt to improve plastisol strength the use of a coupling agent was explored with a fatty acid, as described in Section 5.6. The disastrous consequences highlighted the need for very careful selection of such agents if compatibility is to be achieved. Besides reducing plastisol mechanical properties the fatty acid bloomed on the plastisol surface forming a layer very unfavourable to adhesion. A wider search for a coupling agent was not undertaken because firstly, a BO1 plastisol adequate for the experimental investigation had been developed and secondly, most of the available coupling agents contained either metal ions whose effect on the metallurgy of the graded structure was unknown, or halogens or cyanide groups, both unwelcome when debinding, as discussed in Section 6.3.1. A suitable
agent was not found in the range of commercial materials surveyed.

A possible route to promote an elastomer-particle interaction could be to use ethylene-propylene-diene-monomer (EPDM) elastomer with selection of a tacky, polar termonomer.

The loss of properties exhibited by the BO1 tool steel plastisol during processing indicated the occurrence of polymer chain breakdown during processing. This was noted with interest but no explanation other than the possibility of catalytic action by the powder can be proposed without further investigation.

6.3.4 A thermoplastic elastomeric plastisol?

A possible route to improved elastomeric plastisol properties could be to use a thermoplastic elastomer [257,258]. These materials have thermolabile crosslinks, which can be made and broken repeatedly in the same manner that thermoplastics can be remelted. Such a material could gain stiffness from the crosslinks but not experience the large degrees of shrinkage or hardening associated with macro crystalisation. Thermoplastic elastomers are available as synthesised polymer, for example SBS block copolymers, [259] but they can also be prepared by blending polyethylene or polypropylene with EP(D)M elastomer [260,261,262].

6.4 Powder metallurgy substrate fabrication

It was realised that a powder metallurgy substrate was essential for the graded structure fabrication process. To obtain full benefits of the structure, complete densification was necessary. Use of a fully dense substrate would generate a situation were, after debinding, about a 40
volume percent difference between substrate and graded layer densities would be present. To expect that this mismatch could be absorbed during consolidation was considered unrealistic. Hence there was a need to fabricate substrates with a density more closely matched to that of the PIM layers, and powder metallurgy was the only perceived route to produce such a porous part. The ideal substrate would have a density of about 60 volume percent, matching the density of the debound PIM layers.

A compact density of 60 volume percent is lower than that usually produced by powder compaction. To achieve this density level only a small amount of compaction work is required, this can limit the development of compact strength. It was considered possible that the graded structure consolidation process could accommodate up to a 10 volume percent difference between substrate and PIM layer densities [246], permitting a substrate density of up to 70 volume percent to be utilised. At this density no difficulties achieving compact strength were expected.

Unfortunately it was found that compacted substrates, for the MLIM tooling, were too weak when pressed to a density of 70 volume percent. At this density the compacts could just survive an injection moulding cycle but crumbled and spalled, depositing loose powder in the tool cavity. Such powder can cause damage to the ejector mechanism and many other machine parts and this behaviour was not acceptable. Compacts pressed to 70 volume percent density were strengthened by a low temperature sinter to provide substrates for the investigation of other steps in the total process. It was recognised that the introduction of an additional sintering process step was undesirable in that it represented an increase in the total process time and cost. It was considered that the cause of poor compact green strength was the high hardness, Hv 325, of the AISI 4815
powder used to fabricate the substrates. A typical powder hardness for iron powders is 100 Hv [263]. It was noted that the laboratory standard sponge iron powder exhibited much greater compressibility than the 4815 powder. It was thought that a powder annealing operation or selection of a softer powder could resolve the problem of poor compact strength.

The substrate surface produced, by compaction and presintering, as described above, was favourable for adhesion. The surface was rough, particularly at the lower compaction densities. However, it is possible that some of this roughness might be lost if a softer powder was used. The sintering operation performed to strengthen the substrates had the advantage that a clean surface, free of any pressing lubricant or oxides, was produced and this could also play an important role in the adhesion process. It was not possible to investigate if good adhesion was possible in the presence of the pressing lubricants because they were burnt out during the essential presintering operation.

6.5 Elastomeric Plastisol Layer Lamination

6.5.1 Coating substrates with elastomeric plastisol

The success experienced in coating the wrought steel substrates with elastomeric plastisol validated the use of an elastomeric plastisol. The adhesive failure associated with the shrinkage of the thermoplastic plastisol was absent.

It was noted with interest that the plastisol adhesion to nickel electroplate was better than that to shot blast steel; the surfaces had comparable roughness average values and an explanation of their different behaviour was sought. It is possible that the different chemical nature of the metals
caused the difference in adhesion, but there was also a reasonable physical explanation as explained below. Surface electron micrographs, as shown in Figure 5.2.2, revealed that the plastisol surface had a pimply texture - the surface was particle rich. The shot blast steel had a jagged, flaky surface and the nickel electroplate had a dimpled, rounded texture. It was reasonable to assume that the adhesion difference was due to the better matching of the surfaces present at the nickel electroplate/plastisol interface compared to the shot blast steel/plastisol interface. A surface with a texture in which the plastisol particles could "nestle" was seen as beneficial to adhesion, as discussed in section 2.4.1.

The very good adhesion developed between the P/M substrate and the elastomeric plastisol was attributed to surface texture matching because both surfaces were particle dominated. The adhesion would be further enhanced if the substrate subsurface was explored by plastisol or binder. There was no clear evidence for this but the residual material left on a substrate surface after forced debonding was most heavily present near the mould gate where the pressure during moulding was the highest and most likely to cause penetration of the substrate porosity. A thermodynamic driving force for exploration of the porosity by the plastisol in response to wetting thermodynamics should be present but was unlikely to be dominant because the particle surface area available for wetting within the plastisol was larger than the area present inside the substrate, hence providing a driving force to retain binder within the plastisol. As discussed for the case of adhesives in section 2.4.1. In view of this it is likely that any penetration of substrate porosity would be pressure driven.
6.5.2 Elastomeric plastisol laminates

The next process step investigated was the lamination of plastisol layers. During the initial overmoulding operation used to produce a plastisol/plastisol laminate, the substrate layer of premoulded plastisol was unable to resist the stresses applied to it. Calculations of the expected temperature rise of the overmoulded plastisol, utilising the heat transfer equations given in Section 3.1.3 indicated that the heat transfer was small and the depth of penetration limited. In consequence the distortion of the plastisol layer was thought to result from a lack of inherent mechanical strength rather than the effect of temperature softening. The observed distortions indicated a need for additional plastisol stiffness. In the absence of crystallisation or crosslinking, stiffening of an elastomer depends on the temperature coefficient of viscosity. The higher this coefficient the greater the viscosity gain and hence stiffness gain of the material for each unit temperature decrease below the "melt" or "softening" temperature necessary for injection moulding. The coefficient is an inherent property of the elastomer and little can be done to increase it. It was however possible to gain an increase in plastisol stiffness by cooling it from room temperature, (25°C) to 15°C, by use of mould cooling. This improvement in stiffness was adequate to prevent the distortion effects. For a Mk2 elastomeric plastisol this temperature decrease corresponded to a plastisol shear modulus increase from about 25 MPa to 35 MPa. This indicates that the success of the inmould lamination was strongly influenced by mould temperature because small temperature changes were capable of causing proportionally large changes in plastisol stiffness and hence distortion resistance.
Other possible routes to stiffen a plastisol could act by affecting the binder formulation to reduce the inherent softness of the material. However, this process can only be taken so far before impeding the ability of the plastisol to accommodate shrinkage mismatches by flow and creep. A tight balancing act would be required to achieve an increase of inherent plastisol stiffness whilst retaining the ability to relieve shrinkage stresses. Possible methods to stiffen the plastisol to a level intermediate to thermoplastic and elastomeric behaviour include manipulation of the glass transition temperature (Tg) and development of thermoplastic elastomer properties. If an elastomer with a Tg just above ambient could be found or synthesised, the shrinkage mismatch could be accommodated by the mechanisms mentioned above and then with the last stage of cooling stiffness gained. In a similar manner if a thermoplastic elastomeric composition was utilised physical crosslinking could be brought in to play, as discussed in Section 6.3.4.

The cracking experienced in sintered laminates was probably due to an additional effect of plastisol shrinkage. Besides disrupting adhesion to substrates the shrinkage could deform and crack the mouldings. After initial mould filling the plastisol cooled and consequently shrunk. This reduction in part volume could be offset by maintaining the injection pressure to pack in additional material. If this hold on pressure was not applied severely cracked and internally voided mouldings were produced, as illustrated in Figure 5.1.4.3. In principle if a hold on pressure was maintained until the moulding reached mould temperature, then all the shrinkage should be compensated for; in practice however this was not often possible, though Martyn and James have experienced problems due to over packing [117]. The viscosity of a cooling plastisol will rise and it is possible for a point to be reached at which the available pressure is insufficient to cause further flow. Also the
narrow gate and/or mould runners may solidify before the moulding because of their greater surface area available for heat loss. This would isolate the moulding from the material and pressure in the injection moulder. Further to perform a complete part cooling in the mould is a time consuming process which is not economically desirable, it is normal practice to eject a moulding as soon as it has gained sufficient strength to be self supporting.

Excessive shrinkage will lead to the formation of voids within the centre of a moulding and this was experienced with the hardmetal laminates and was expressed as intra laminate cracks in the sintered material. The use of increased pressure hold on time and a lower viscosity feedstock eliminated this problem. However an hourglass type distortion was still present. This effect is a normal feature of plastics moulding, especially with the large thickness (6mm) in use. During the proposed moulding of the graded structure 1mm thick layers were to be placed, at this low thickness the shrinkage level approximated to a distortion of 0.02-0.04 mm, which was considered acceptable.

The intra laminate cracking and hourglass distortion may also have contained a contribution from plastisol dilatancy. During cooling an injection moulding will develop a temperature gradient with "frozen" material near the cavity walls and mobile material in a central pipe [264]. Formation of a central void was prevented by packing extra material into this volume during the pressure hold on time. The plastisol dilatancy experienced with increased pressure hold on times, reported in Section 5.3.2, can be interpreted as the result of the cooling material in the narrow central pipe becoming increasingly restricted, and hence experiencing higher effective shear rates whilst losing temperature, and hence increasing in viscosity. These factors would favour the onset of dilatant flow. If the
packing of the pipe volume of a moulding takes place under dilatant conditions the volume will be occupied but the material there will have a lower density than the rest of the moulding. This could generate voids during sintering. Dilatancy induced density variations may have accounted for the finding that laminates made with a Mk2 plastisol formulation exhibited intra lamina cracks whilst the corresponding monoliths were crack free. The laminate moulding shots were forced into a cavity with half the height of that for moulding monoliths and, inconsequence, were exposed to conditions of higher shear and hence would be more prone to dilatant flow behaviour.

The elimination of interlaminate cracking by increased pressure hold on time indicates that its cause was large scale shrinkage. However a possible second reason for the presence of the inter lamina cracks is that of air entrapment during the moulding operation. Such defects have been reported by Gaspervich [145], and were generated by jetting or poor mould venting. The latter case may apply to this work because the ejector pins, the main air vent from the injection mould, were covered by the lower plastisol layer.

6.5.3 Individual adhesion steps

After the basic process steps of coating substrates and laminating plastisol had been established, it was possible to perform an evaluation of each adhesion step, as reported in Section 5.7. The success achieved paved the way to attempt the MLIM procedure.

The P/M substrate prevented curling of the 4815/BO1 tool steel plastisol laminate in response to plastisol cooling shrinkages by providing the necessary shape stability. The other laminate pairs exhibited curling, which was more
pronounced than that exhibited by the 6% cobalt balance tungsten carbide plastisol used during the initial lamination trials. This former plastisol was mixed in the Brabender plastograph before correction for Haftolat losses was applied to the mix formulations. The higher resultant powder loading is believed to have stiffened this plastisol sufficiently to resist curling.

The adhesion achieved is believed to have been promoted by the good matching of the powder surfaces. The 4815 and BO1 steel powders had very similar morphologies and good interfacial contact was expected. Similarly, the hardmetal powders were expected to readily intermesh. At the BO1 / hardmetal powder interface the particle size difference was such that the hardmetal could "nestle" in the BO1 powder surface and good interlocking was expected.

The graded structure plastisols exhibited an average debinding expansion of 1.4%. The 6% cobalt balance tungsten carbide powder did not exhibit such a large expansion. It is possible that the larger particle sizes, hardmetal (3μm) BO1 tool steel (85μm) of the graded structure powders compared with 1μm particle size of the 6% cobalt balance tungsten carbide powder may have had an influence, resulting in fewer particle-particle contacts per unit volume, reducing the potential for particle interlocking.

6.6 Multi layer injection moulding

6.6.1 Test moulding

The first step of the MLIM procedure was established when BO1 tool steel plastisol was moulded over a P/M substrate to investigate the adhesion at individual interfaces. Moulding of the first hardmetal layer to produce a three layer composite of substrate plus two plastisol layers was
likewise achieved with the standard process conditions. The over moulding of two layers appeared to be insensitive to process conditions and could be performed without complications.

Attempts to over mould a third plastisol layer using the standard moulding conditions was not successful, as predicted by the modelling approach of Section 3.1.3. A large increase in transient strain energy was predicted to be associated with placement of a third moulded layer. The successful placement of the third layer after increasing the plastisol melt temperature to reduce viscosity, lent confidence to the reasoning that a route to defect free layer moulding would be to reduce the forces involved with moulding the higher layers. Further confidence was lent to the modelling results by the fact that, to achieve placement of the third layer, the plastisol viscosity needed to be halved. This matched the projection of the modelling results, that plastisol viscosity would be required to be halved in order to halve the shear stress transmitted to the coated layers. In response to this support for the process analysis, utilisation of the derived graded processing parameters was undertaken. However, further reductions of plastisol viscosity by increasing the temperature was impractical.

Controlling plastisol viscosity by altering the proportion of elastomer in the plastisol formulation was a more precise method than use of temperature variation and permitted a greater viscosity range to be developed. For these reasons variable elastomer content plastisols were mixed in the viscosity ratios specified by the modelling results for successful moulding of the multi layers. Use of these feedstocks with the parallel gradation of injection pressure was successful and led to confidence in the basis of the modelling approach. It was noted that lamination with the
graded processing parameters would occasionally fail and that this could be overcome by a slight increase in melt temperature. This effect may have been caused by the reduction in plastisol strength caused by the decrease in elastomer content. The higher layers of the composite had reduced elastomer content and hence reduced strength and were less able to resist deformation when over moulded, when compared to the lower layers. This may have created a need to reduce plastisol viscosities in ratios slightly larger than the ratios derived from the modelling because this did not take into account the presence of strength differences between layers.

The oozage of the BOI tool steel plastisol out of position in response to the over moulding of the hardmetal plastisol layers, was believed to be caused by transmission of the moulding pressure to the substrate-plastisol interface. The oozage indicated that an improvement in the strength of the BOI tool steel plastisol was needed.

The maintenance of adhesion after debinding was expected because firstly, all the adhesion steps had been proved as individual cases and secondly, it was known that the dimensional changes associated with debinding were small and hence unlikely to disrupt the structure.

The successful consolidation of the units confirmed that B.P.'s developed graded structure technology can be successful when fabricated by PIM.

The poor adhesion achieved when moulding plastisol over debound hardmetal was believed to be caused by the presence of loose powder rubbed off the surface by the incoming melt. It would be impossible to remove such a weak boundary layer because it is regenerating. To coat debound hardmetal surfaces some stabilisation method such as resin
impregnation would be required. This would not be an attractive addition to the MLIM process because an additional process step would add to the process cost.

The occasional delamination and arching exhibited by the top two layers of the debound MLIM test geometry units may have been caused by the debinding expansion experienced by the plastisols, coupled with the low pressures used during placement of the top layers. Because the low pressures may have reduced the bonding with the underlying layers allowing the debinding expansion to be expressed.

6.6.2 Multi layer injection moulding: A process overview

Some key features of the MLIM process can be summarised.

A porous substrate was essential in view of the low powder density that could be achieved in plastisol feedstocks. After debinding the injection moulded material contained about 40 volume percent porosity. If the substrate does not contain some porosity the volume shrinkage mismatch during consolidation will be gross.

Plastisol adhesion to a steel substrate was not successful with thermoplastic based plastisols but could be obtained with elastomeric plastisols.

Plastisol adhesion to the substrate but not the injection mould wall was achieved by ensuring that the substrate surface roughness was greater than that of the mould wall, and then formulating a plastisol with adhesive tack at a level which adhered to the rough substrate but not the smooth mould wall. The range of plastisol composition was bounded by the upper extreme of adhesion to both smooth and rough surfaces and the lower extreme of adhesion only just
being attained to the rough surface; plastisol behaviour must fall between the two.
The plastisol surface was particle rich and in consequence interfacial adhesion could be attributed to particle-particle interactions as well as the action of the polymeric binder. When selecting powders this aspect of their performance must be considered.

Use of a P/M substrate provided the required substrate porosity and allowed the porosity level to be manipulated. The substrate surface was particulate which provided roughness and the potential for particle-particle interactions. There was no need to shot blast the surface. But the thermal expansion of the substrate was less than that of solid material, increasing the mismatch with the plastisol.

The placement of the multilayers was successful if the graded processing parameters were used. This gave confidence to the modelling approach of Section 3.1.3, and the graded processing parameters were considered an essential part of the MLIM process.

6.7 Rock bit manufacture

6.7.1 Substrate compaction

The jamming of the substrate tip in the punch cavity was unexpected, the cavity was not reentrant. It was possible to derive a criterion for spontaneous ejection, after external pressure release, from a wedge shaped cavity, as detailed in Appendix 5. The form of the criterion is given below and the fields of spontaneous and nonspontaneous ejection are diagrammatically shown in the Appendix 5.
The criterion is: \[ 90 - 2\theta > \mu \theta \]

where: \( \theta = \) half the wedge angle
\( \mu = \) coefficient of static friction

For the case in question, \( \theta \) is 27°, and so a value of \( \mu \) in excess of 1.4 would be required to prevent spontaneous ejection; such a value is high. Mallender [365] and Zaamount [366] report compact - die wall coefficients of friction in the range 0.03-0.46 for similar materials and equipment. This implies that spontaneous ejection from the punch cavity should in fact occur. No clear cut explanation of the mismatch between the prediction of spontaneous ejection and the observed jamming was developed. The poor densification may be a contributive factor to tip jamming because, at lower densities, the compact surface had a higher roughness which could promote tip jamming. It was noted that the jamming problem decreased after the pressing of many compacts led to a reduction of cavity roughness due to wear. It was also noted that ejection was achieved with feedstocks containing an increased lubricant content.

N.B. When a substrate tip was jammed in the tip cavity it was often found to break away from the shank. When a substrate was ejected from the compaction die the pressure was released from the shank allowing it to expand, whilst the tip was still constrained. This behaviour would create a stress discontinuity at the shank - tip join and may have caused the observed fractures.

A second difficulty was associated with substrate compaction, in that the tip did not develop the strength level attained in the shank and, as a result, was too weak. The development of strength in the substrate shank, but not the tip, indicates that the pressurisation was not effective within the tip cavity. Compaction resulted in a reduction of
powder volume, this reduction could be readily taken up in the case of the shank volume by punch movements and direct application of pressure maintained. However, the reduction of volume generated by compaction inside the tip cavity cannot be compensated for by tooling movements. There is a requirement for powder to flow from the larger shank volume into the tip cavity as densification progresses. It was noted that the wear around the cavity entrance was severe indicating that some flow was taking place, but pressurised powders do not exhibit pronounced flow, as discussed in Section 2.1.6. It is considered likely that a large pressure drop was present at the entrance to the tip cavity. The use of increased pressing pressure enabled complete substrates of handleable strength to be produced. These substrates were not ideal, with shanks denser than desired, but they were the best that could be produced with the tooling and were hence accepted for use to investigate further process steps.

6.7.2 Moulding of graded structure layers

The adhesion exhibited by the BO1 tool steel plastisol to the epoxy cavity insert rather than to the substrate, illustrated the effect of surface roughness on inmould adhesion. The combination of a smooth substrate, and a rough cavity wall, led to preferential adhesion to the cavity, the opposite of the desired outcome. The position was reversed by reducing the cavity roughness. This result affirms the approach of achieving preferential adhesion to substrate surfaces by differentiating the surface roughnesses.

The rock bit injection mould was vertically gated, this necessitated the use of a nozzle extension because of the geometry of the Fox and Offord injection moulder. Also, a runner length several times longer than that used with the MLIM injection mould was required to reach the mould cavity. The combination of these factors resulted in a long flow
path for the plastisol to traverse before entering the cavity. This flow path was unheated and plastisol cooling could occur along the length. The cavity shape was more complicated than that of the MLIM tool, involving two corners to be negotiated by incoming plastisol. All these factors were believed to have, resulted in the poor mould filling capability found with the rock bit injection mould. Too much pressure could be lost negotiating the difficult and cool flow path. It is possible that use of a heater around the nozzle extension may have gone some way to alleviating this problem.

The substrates appeared to be self centring within the mould cavity. It was unnecessary to use the positional lock built into the mould body. Substrates were positioned in the mould with sufficient accuracy to avoid contacting the cavity wall during mould closure, but were left free to rotate. It is possible that the substrates were well aligned after the positioning operation and that further substrate rotation did not occur. This scenario would have produced the equiaxed mouldings found. An alternative scenario can be proposed in which a freely rotating substrate was subjected to a couple generated by plastisol pressure differentials. If the substrate - cavity gap was large the expanding plastisol could lose pressure, allowing the pressure of confined plastisol acting on the opposite face to rotate the substrate into the central position, equalising the pressures.

Plastisol moulded over the substrate took the shape of a "witch's hat" sitting over the substrate tip. With this annular geometry there were no free edges at which plastisol shrinkage could be accommodated, as was the case for the MLIM geometry. Hence there was concern that plastisol shrinkage might cause the "witch's hat" to rise up the tip, so becoming detached from the "brim" like base. Fortunately
this behaviour was not observed, perhaps because the plastisol absorbed any shrinkage strains within itself as its elastomeric nature was intended to. Alternatively the soft B01 tool steel plastisol over which the other plastisol layers were moulded may have deformed to accommodate the plastisol cooling shrinkages. Oozage of the B01 tool steel plastisol out of position was observed and this would be consistent with the latter suggestion. N.B. The oozage was present for the MLIM geometry graded structure units and was, in that case, interpreted as arising from the action of injection pressures. It may be that in the rock bit geometry the B01 tool steel layer was strained by both plastisol cooling shrinkages and injection pressure.

The successful moulding of four layer rock bits was welcome and demonstrated the potential of the MLIM process to form three dimensional shapes.

6.7.3 Proposed Tooling Modifications

Compaction Die

It was thought possible that the jamming problem experienced inside the tip cavity could be avoided if a core rod was used within the punch to push the tip out during ejection. This would however, complicate the tooling specification. Redesigning the tip shape could have many benefits. If the slope angle of the tip was reduced to form a squatter shape the tip would be less prone to jam in a pressing cavity and the powder flow requirement during compaction would be reduced, potentially improving tip strength. Powder flow would also be aided if the entrance to the tip cavity was radially more extensively. However, it is believed that many of the compaction difficulties would be alleviated by use of a softer powder because greater powder flow under pressure and increased green strength would be present.
Rock bit injection mould

Improved moulding performance would be achieved by use of more direct gating of the cavity, the reduction of the flow path from moulder barrel to cavity is necessary to fully utilise the limited flow properties of plastisols. Utilisation of an improved cavity finish is also necessary. Placement of the runner on the mould split line would prevent the problems which arose from the lack of any positive means to eject the runner. If the moulding remained gated via the top edge of the tip, then placing the runner on the split line would necessitate use of a split cavity, increasing the mould cost. However the advantages would be great. An alternative method to cure the difficulty of ejecting the runner would be to use a hot runner system where the runner channel is heated and not allowed to "freeze" off. Separating a moulding from such a soft runner would be an easy operation and the runner material would not need to be removed from the tool after each moulding shot. It might be possible to fabricate substrates with a stepped bottom face which could locate with a corresponding step in the injection mould tool. This modification would ensure correct substrate alignment. The tooling required would have increased complexity and it is not known if rock bits with a stepped bottom face would be acceptable to rock drill manufactures. It can be envisaged that in commercial operation the MLIM process could be run using a carousel of moulds, one for each cavity size.

6.7.4 Debinding and Consolidation

This part of the fabrication was performed in an identical manner to that used with the MLIM geometry units, with the same successful results. There was some doubt as to the outcome because of the large difference about 25 volume percent between the starting densities of the substrate and moulded
layers. With hind sight, however, it was realised that the density of the substrate tip was bound to be substantially less than the substrate shank because of the poor pressure transmission into the tip cavity during compaction. Hence the shrinkage mismatch during consolidation was reduced in the region of the substrate tip which was the part of the substrate most closely joined to the moulded materials.
7.0 CONCLUSIONS

The use of plastisols incorporating a thermoplastic binder, for the injection moulding of coatings on steel substrates, was not successful. The cooling shrinkage of the plastisol destroyed any interfacial adhesion developed during moulding.

It was possible to use elastomeric material as a plastisol binder, to create an elastomeric plastisol. This type of plastisol was successfully used for the injection moulding of coatings on steel substrates, the interfacial adhesion developed was stable.

When a plastisol coating was injection moulded it was possible to selectively achieve adhesion to a steel substrate surface but not to the steel mould wall, if the two surfaces were differentiated by texturising to produce a smooth mould wall and a rough substrate. For this differentiation to be effective the plastisol had to exhibit adhesive tack sufficient for adhesion to the rough surface but insufficient to adhere to the smooth surface; plastisol and surface properties had to be paired to exploit this process window.

The AISI 4815 steel powder used in this work was considered too hard to enable fabrication by die compaction of substrates with significant green strength at the low densities desired.

Elastomeric plastisols formulated with B01 tool steel powders were mechanically weak, improvement in strength was possible with use of fine powders, increased elastomer content and increased elastomer molecular weight.
Adhesion between the individual layers of the graded structure was validated for the conditions of multi layer injection moulding, and subsequent debinding / consolidation operations.

The multi layer injection moulding process could be successfully applied if graded processing parameters were utilised. A prototype graded structure rockbit was fabricated to demonstrate in principle the applicability of the multi layer injection moulding process to three dimensional shapes.

Experience in the design and practicalities of injection moulding tools for multi layer injection moulding has been gained.
8.0 Recommendations for further work

A) It could be valuable to extend the investigation of elastomeric plastisol properties to increase the amount of data available. In particular, the assessment of EPDM grades and possible alternative elastomers would be of interest.

B) The use of a thermoplastic elastomer (TPE) composition may provide a route to stiffening moulded plastisol layers to better resist the stresses of over moulding. A TPE could form physical crosslinks during cooling, hence limiting subsequent deformations of the plastisol. A large crystallisation shrinkage would not be associated with this process. Such a TPE composition might be formed by blending polymer components.

C) Improvements in the properties of the B01 tool steel plastisol are expected if a finer, sub 10μm powder is used. It may be of value to investigate the poor resistance to processing temperatures exhibited by the B01 plastisol.

D) Use of a softer AISI 4815 powder is expected to reduce the difficulties experienced when pressing substrates. If the powder production process cannot yield such powder directly it may be worth annealing the material.

E) There is much scope for improvement of the injection mould tooling as discussed in section 6.7.3 and this is considered essential to development of the multi layer injection moulding process.

F) More refined modelling of the multi layer injection moulding process, capable of specific and quantitative predictions of the required plastisol properties, would promote development of the process.


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steels and specifications, 6th Ed, June (1984)
<table>
<thead>
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<th>Table Number</th>
<th>Description</th>
</tr>
</thead>
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<td>3.1.1</td>
<td>Adhesion processes</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Polymers</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Sintering procedures</td>
</tr>
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<td>4.3.3</td>
<td>Plastisol mixing conditions</td>
</tr>
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<td>5.1.2</td>
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<td>5.2.1</td>
<td>Surface replication data from thermoplastic plastisol coatings</td>
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<td>5.3.1</td>
<td>Elastomeric plastisol formulations</td>
</tr>
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<td>5.3.3</td>
<td>Effect of binder elastomer molecular weight on viscosity</td>
</tr>
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<td>Trial BO1 tool steel plastisols</td>
</tr>
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<td>5.6.2</td>
<td>Dynamic Mechanical Analysis of BO1 tool steel trial plastisols</td>
</tr>
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<td>5.8.1</td>
<td>Graded viscosity plastisol formulations</td>
</tr>
<tr>
<td>5.8.2</td>
<td>Graded injection pressure values</td>
</tr>
</tbody>
</table>
**Table 3.1.1 Adhesion Processes**

**Interfaces:**

<table>
<thead>
<tr>
<th>AISI 4815 / BOI tool steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOI steel / hardmetal 30.28%</td>
</tr>
<tr>
<td>hardmetal 30.28% / hardmetal 20%</td>
</tr>
<tr>
<td>hardmetal 20% / hardmetal 15.16%</td>
</tr>
<tr>
<td>hardmetal 15.16% / hardmetal 12.14%</td>
</tr>
</tbody>
</table>

The percentage figures given indicate the amount of cobalt in the hardmetal, the balance was tungsten carbide.

**Adhesion requirements:**

- Plastisol to steel substrate.
- Plastisol to plastisol.
- Debound BOI tool steel powders to steel substrate.
- Debound hardmetal powders to BOI tool steel powders.
- Debound hardmetal powders to themselves.
- BOI steel – hardmetal weld.
- Hardmetal – hardmetal welds.

**Adhesion transfers:**

- From green plastisol to "brown" plastisol.
- From "brown" debound powders to metallurgical welds.

During these process steps there would be a need to transfer the adhesion to a new mechanism, transfers from polymer binder to powders and particle contacts to bulk contact.
### Table 4.1.2 Polymers

#### A) Thermoplastics:

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Trade Name</th>
<th>Grade</th>
<th>MFI (g/10 min)</th>
<th>% VA</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>Novex</td>
<td>LM2150</td>
<td>5</td>
<td></td>
<td>B.P.</td>
</tr>
<tr>
<td>&quot;</td>
<td>Escorene</td>
<td>LD655</td>
<td>150</td>
<td></td>
<td>Exxon</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>LD657</td>
<td>250</td>
<td></td>
<td>&quot;</td>
</tr>
<tr>
<td>EVA</td>
<td>extrusion</td>
<td></td>
<td></td>
<td></td>
<td>ATO</td>
</tr>
<tr>
<td>&quot;</td>
<td>Escorene</td>
<td>UL40028</td>
<td>400</td>
<td>28</td>
<td>Exxon</td>
</tr>
<tr>
<td>&quot;</td>
<td>Ultra</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>UL15019</td>
<td>150</td>
<td>19</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

MFI = melt flow index, as detailed in BS3412:1976.

#### B) Waxes

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Trade Name</th>
<th>Grade</th>
<th>Molecular Weight</th>
<th>% VA</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Escomer</td>
<td>H101</td>
<td>700-2000</td>
<td></td>
<td>Exxon</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td>AC6</td>
<td>≈1100</td>
<td></td>
<td>Allied</td>
</tr>
<tr>
<td>EVA</td>
<td></td>
<td>AC400</td>
<td>≈2000</td>
<td>13</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
C) Elastomers

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Trade Name</th>
<th>Grade</th>
<th>Molecular Weight</th>
<th>Viscosity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>Levapren</td>
<td>500</td>
<td>50% VA</td>
<td></td>
<td>Bayer</td>
</tr>
<tr>
<td>EPM</td>
<td>Keltan</td>
<td>740</td>
<td>Medium</td>
<td>63</td>
<td>DSM</td>
</tr>
<tr>
<td>EPDM</td>
<td>&quot; &quot;</td>
<td>712</td>
<td>&quot; &quot;</td>
<td>63</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>778</td>
<td>&quot; &quot;</td>
<td>63</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>578</td>
<td>Low</td>
<td>46</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>Royalene</td>
<td>521</td>
<td>&quot; &quot;</td>
<td>45 ##</td>
<td>Uniroyal</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>539</td>
<td>High</td>
<td>73</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>&quot; &quot;</td>
<td>400</td>
<td>very high</td>
<td>39</td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>

filled with 100phr oil

" "          | " "        | 622   | High             | 55 ##     | " "     |

filled with 40phr oil

# Mooney viscosity ML 1+4 125°C

## Mooney viscosity ML 1+4 100°C

All EPDM termonomers ethylideneborbornene except Royalene 400 with dicyclopentadiene.

Ethylene contents Keltan 740 60%, 712 55%, 778 65%, 578 65%, Royalene 521 52%, 539 74%, 400 68%, 622 75%.
Table 4.3.2 Sintering Procedures

A) Hardmetal, 6% cobalt balance tungsten carbide:

Furnace flooded with an atmosphere of 6% H₂ balance N₂ during heating up to 800°C and then evacuated to a vacuum of 1mm Hg prior to sintering. Temperature 1450°C, time 30 minutes, parts packed in a powder blend of 7% carbon, balance alumina.

B) All other materials

The other materials were constituents of the graded structure and were required to be sintered together. A sintering temperature of 1300°C was adopted, this temperature was considered acceptable for all the different materials. The conditions of a) were used with the reduced temperature and without the packing media.
Table 4.3.3 Plastisol mixing conditions

A) For Brabender: After initial incremental filling over 10 minutes at 25 rev/min, mixing for a further 20 minutes at 50 rev/min.

B) For Baker Perkins: After initial incremental filling mixing for 50 minutes at 20 rev/min.

Mixing temperatures: 180°C for thermoplastic plastisols, and 150°C for elastomeric plastisols.
Table 5.1.2 Trial binder blends

<table>
<thead>
<tr>
<th>No.</th>
<th>Component 1</th>
<th>Proportion 1</th>
<th>Component 2</th>
<th>Proportion 2</th>
<th>Component 3</th>
<th>Proportion 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>ACS 40</td>
<td>7) ACS 40</td>
<td>UL15019 30</td>
<td>100</td>
<td>LD657 50</td>
<td>100</td>
</tr>
<tr>
<td>2)</td>
<td>LM2150 50</td>
<td>8) LM2150 30</td>
<td>LD655 30</td>
<td>100</td>
<td>H101 2</td>
<td>100</td>
</tr>
<tr>
<td>3)</td>
<td>ACS 15</td>
<td>9) ACS 15</td>
<td>UL15019 30</td>
<td>100</td>
<td>LM2150 5</td>
<td>100</td>
</tr>
<tr>
<td>4)</td>
<td>LM2150 40</td>
<td>10) ACS 16</td>
<td>UL15019 31</td>
<td>100</td>
<td>LM2150 6</td>
<td>100</td>
</tr>
<tr>
<td>5)</td>
<td>LM2150 45</td>
<td>11) LM2150 40</td>
<td>LD657 20</td>
<td>100</td>
<td>UL40028 40</td>
<td>100</td>
</tr>
<tr>
<td>6)</td>
<td>ACS 30</td>
<td>12) LD657 100</td>
<td>LD657 30</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Component proportions in parts per hundred by weight.
Table 5.2.1 Surface replication data from thermoplastic plastisol coatings

During the attempts to coat wrought steel substrates with thermoplastic plastisol, the failure of adhesion produced many pairs of substrate plus detached plastisol layer. The surface texture parameters of some debonded surfaces were measured. N.B. It was not valid to average data from different substrate - coating pairs because the shot blast surface preparation was performed on an individual basis.

Ra = surface roughness average
Va = slope angle
λa = surface wavelength

For unheated substrates:

<table>
<thead>
<tr>
<th></th>
<th>Ra (μm)</th>
<th>Va</th>
<th>λa (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel surface</td>
<td>0.90</td>
<td>5.0°</td>
<td>0.08</td>
</tr>
<tr>
<td>Plastisol surface</td>
<td>0.88</td>
<td>4.8°</td>
<td>0.07</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>0.82</td>
<td>4.3°</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>4.0°</td>
<td>0.07</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>0.98</td>
<td>5.0°</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>5.0°</td>
<td>0.07</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>0.90</td>
<td>5.8°</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>4.0°</td>
<td>0.08</td>
</tr>
</tbody>
</table>

For heated substrates:

<table>
<thead>
<tr>
<th></th>
<th>Ra (μm)</th>
<th>Va</th>
<th>λa (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel surface</td>
<td>0.90</td>
<td>5.2°</td>
<td>0.07</td>
</tr>
<tr>
<td>Plastisol surface</td>
<td>0.99</td>
<td>4.9°</td>
<td>0.08</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>1.00</td>
<td>4.5°</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>4.3°</td>
<td>0.08</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>1.40</td>
<td>8.0°</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>6.5°</td>
<td>0.08</td>
</tr>
<tr>
<td>&quot;ditto&quot;</td>
<td>0.85</td>
<td>4.5°</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>4.0°</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Table 5.3.1 Elastomeric plastisol formulations

<table>
<thead>
<tr>
<th></th>
<th>Component 1</th>
<th>Component 2</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA:</td>
<td>Leavapren 500</td>
<td>Escorene UL40028</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>EPM:</td>
<td>Keltan 740</td>
<td>Haftolat</td>
<td>50</td>
</tr>
<tr>
<td>Mk1</td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Mk2</td>
<td>Keltan 740</td>
<td>Escorene UL40028</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Haftolat</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Mk3</td>
<td>Keltan 740</td>
<td>Escorene UL40028</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Haftolat</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Component proportions in parts per hundred by weight.

Table 5.3.3 Effect of binder elastomer molecular weight on plastisol properties

Mk3 plastisols mixed with Keltan 778 & 578, medium and low molecular weight respectively. Properties measured by DMA at 25°C.

For 778 elastomer:
Shear Modulus = 0.54 GPa, Viscosity = 18 Pa Sec

For 578 elastomer:
Shear Modulus = 0.23 GPa, Viscosity = 8 Pa Sec
Table 5.6.1 Trial BOI tool steel plastisols

Plastisols were mixed at 58 volume percent powder loading with the particle sizes and binder formulations detailed below. Binder component proportions in parts per hundred by weight.

Keltan 740  25
UL40028   25
Haftolat  50
100

Mixed with coarse (110μm) powder = mix A
Mixed with medium (85μm) powder = mix B
Mixed with fine (47μm) powder = mix C

Keltan 740  50
UL40028   25
Haftolat  25
100

Mixed with medium (85μm) powder = mix D

Royalene  521, or 539, or 400 25
UL40028  25
Haftolat  50
100

Mixed with medium (85μm) powder,
and Royalene 521 = mix E
and Royalene 539 = mix F
and Royalene 400 = mix G
Table 5.6.2 Dynamical Mechanical Analysis of BQI tool steel trial plastisols

<table>
<thead>
<tr>
<th>Mix</th>
<th>Limit of hot strength</th>
<th>Shear stiffness, MPa @ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>79°C</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>89°C</td>
<td>23</td>
</tr>
<tr>
<td>C</td>
<td>96°C</td>
<td>436</td>
</tr>
<tr>
<td>D</td>
<td>100°C +</td>
<td>28300</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>49</td>
</tr>
</tbody>
</table>

N.B. corresponding values for hardmetal mixed with the binder formulation of mixes A, B & C were 100°C + and 600 MPa.
Table 5.8.1 Graded viscosity plastisol formulations

<table>
<thead>
<tr>
<th>BO1 tool</th>
<th>Hardmetal</th>
<th>Hardmetal</th>
<th>Hardmetal</th>
<th>Hardmetal</th>
</tr>
</thead>
<tbody>
<tr>
<td>steel</td>
<td>28% Co</td>
<td>20% Co</td>
<td>15% Co</td>
<td>12% Co</td>
</tr>
<tr>
<td>Kelten</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740</td>
<td>40</td>
<td>35</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>Escorene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UL40028</td>
<td>40</td>
<td>32.5</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>Haftolat</td>
<td>20</td>
<td>32.5</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>viscosity</td>
<td>300</td>
<td>200</td>
<td>100</td>
<td>70</td>
</tr>
</tbody>
</table>

Viscosities measured at 150°C, shear rate 500 Sec⁻¹.

Balance of hardmetal compositions was tungsten carbide.

Table 5.8.2 Graded injection pressure values

<table>
<thead>
<tr>
<th>BO1 steel</th>
<th>Hardmetal 28% Co</th>
<th>Hardmetal 20% Co</th>
<th>Hardmetal 15% Co</th>
<th>Hardmetal 12% Co</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000 psi</td>
<td>2000 psi</td>
<td>1000 psi</td>
<td>600 psi</td>
</tr>
</tbody>
</table>

Balance of hardmetal compositions was tungsten carbide.
FIGURES

2.1.6 Schematic diagram of a die compaction tool
2.2.4 Schematic diagram of an injection moulder
2.4.1 The Young Equation
2.6.3 The Graded Structure
3.1.3.1 Shear deformation of over moulded plastisol
3.1.3.2 Pressure transient - step generation
4.1.1.1 Particle size distribution of AISI 4815 powder
4.1.1.2 Micrograph of AISI 4815 powder
4.1.1.3 Particle size distribution of BO1 tool steel powders
4.1.1.4 Micrograph of BO1 tool steel powder
4.1.1.5 Micrographs of hardmetal powders
4.3.2.1 Powder compaction - tooling operation
4.3.2.2 Furnace ancillaries
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5.1.3 Jetting behaviour
5.1.4.1 TGA profile of EVA polymer
5.1.4.2 Micrograph of sintered hardmetal, 6% cobalt balance tungsten carbide
5.1.4.3 Cracked hardmetal specimen
5.2.1 Plastisol coating layer
5.2.2 Micrographs of interface surfaces
5.2.3 Coating failure modes
5.2.4 Plastisol coating layer shrinkage differential
5.3.2.1 "Short" shot coating layer
5.3.2.2 Mixing torque of elastomeric plastisol
5.3.2.3 Moulding parameters of elastomeric plastisol
5.3.2.4 TGA trace of elastomeric plastisol
5.3.3.1 Plot of plastisol viscosity versus percentage of elastomer in the binder
5.3.3.2 Plot of elastomeric plastisol viscosity as a function of temperature
5.3.3.3 Fracture surface of elastomeric plastisol
DMA trace of elastomeric plastisol
Lamination distortions
Cooling distortion of plastisol laminates
Inter and Intra lamina cracks
Compressibility curve of AISI 4815 powder and sponge iron powder
P/M substrate surface
Plot of P/M substrate surface roughness versus density
Curling of laminates
Three layer graded structure unit
Moulding distortions of graded structure units
Six layer graded structure unit
Sintering distortion of graded structure unit
Rock bit substrate
Rock bit mouldings
Plot of thermoplastic plastisol thermal expansion coefficient as a function of powder loading
Figure 2.1.6 Schematic diagram of a die compaction tool

--- Upper punch

--- Die

--- Lower punch

Figure 2.2.4 Injection Moulder

1 Feed hopper
2 Drive unit
3 Barrel heaters
4 Screw
5 Mould bolster
6 Clamping unit
Figure 2.4.1 The Young Equation

\[ \gamma_{se} = \gamma_{sl} + \gamma_{la} \cos \theta + \pi \]
Figure 2.6.3 The Graded Structure

1-14% of the thickness

5-14% of the thickness

0.5-3% of the thickness

Surface layer WC + Co binder

Interface layer WC + Co binder, binder content increasing stepwise from surface.

Layer of high carbon steel, tool steels such as BO1

Substrate Bainitic transforming steel, Ni rich such as 4815
Figure 3.1.3.1 Shear deformation of over moulded plastisol

Figure 3.1.3.2 Pressure transient - step generation
Figure 4.1.1.1 Particle size distribution of AISI 4815 steel powder
Figure 4.1.1.2 Micrograph of AISI 4815 steel powder

Scanning electron micrograph, magnification X 90.
Figure 4.1.1.3 Particle size distribution of BO1 steel powder. Batch (a)
Figure 4.1.1.3 Particle size distribution of BO1 steel powder, Batch (b)
Figure 4.1.1.3 Particle size distribution of BO1 steel powder. Batch (c)
Figure 4.1.1.4 Micrograph of BO1 tool steel powder

Scanning electron micrograph, magnification X 90.
Figure 4.1.1.5 Micrographs of hardmetal powders

A) 6% cobalt balance tungsten carbide

Transmission electron micrograph, magnification X 10K.

B) 12% cobalt balance tungsten carbide

Scanning electron micrograph, magnification X 4.5K.
Figure 4.3.2.1 Powder compaction - tooling operation

A) Die filling

B) Prepressurisation

C) Compaction

D) Ejection
A) Gas ancillaries

cylinder

column of silica gel

catalytic deoxidation column

column of silica gel

column of molecular sieve

furnace

one way bubbler

atmospheric vent

B) Vacuum ancillaries

two stage rotary pump

oil trap

furnace tube

needle valve for gas bleed
Figure 5.1.2 Plot of thermoplastic plastisol thermal expansion coefficient as a function of powder loading.
Figure 5.1.3 Jetting behaviour

Magnification, X 2.
Figure 5.1.4.1 TGA profile of EVA polymer
Figure 5.1.4.2 Micrograph of sintered hardmetal, 6% cobalt balance tungsten carbide

Fabricated from thermoplastic plastisol, optical micrograph, magnification 1K.

Figure 5.1.4.3 Cracked hardmetal specimen

Fabricated from a 6% cobalt balance tungsten carbide thermoplastic plastisol, optical micrograph X 10.
Figure 5.2.1 Plastisol coating layer

```
Plastisol
Substrate
```
Figure 5.2.2 Micrographs of interface surfaces

A) Surface of shot blast wrought steel

Scanning electron micrograph, magnification X 12K.

B) Surface of nickel electroplate

Scanning electron micrograph, magnification X 12K.
C) Surface of thermoplastic plastisol

Scanning electron micrograph, magnification X 12K.
Figure 5.2.3 Coating failure modes

A) Delamination

Specimen, thermoplastic plastisol moulded over shot blast wrought steel substrate, magnification X 2.
B) Cracking

Specimen, thermoplastic plastisol moulded over shot blast wrought steel substrate, magnification X 2.
Specimen, thermoplastic plastisol moulded over a wrought steel substrate, magnification X 4.
Specimens, EVA elastomer based plastisol moulded over wrought steel substrates, magnification X 2.
Figure 5.3.2.2 Mixing Torque of elastomeric plastisol
Figures 5.3.2.3
Moulding parameters of elastomeric plastisol.
Figure 5.3.2.4 TGA trace of elastomeric plastisol
Figure 5.3.3.1 Plot of plastisol viscosity versus percentage of elastomer in the binder.
Figure 5.3.3.3 Fracture surface of elastomeric plastisol

Specimen elastomeric plastisol, scanning electron micrograph, magnification, X 5K.
Figure 5.3.3.2  Plot of elastomeric plastisol viscosity as a function of temperature

apparent viscosity
Ns/mm$^2$

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- shear rate 610 s$^{-1}$
- temperature (°C)
Figure 5.3.3.4 DMA trace of an elastomeric plastisol
Figure 5.4.1 Lamination distortions

Two layer units schematically shown inside the mould cavity.

A) Rucking

B) Push off

C) Inclining
Figure 5.4.2 Cooling distortion of two layer plastisol laminates

A) Curling

B) End step
Figure 5.4.3 Inter and Intra lamina cracks

A) Inter lamina crack

B) Intra lamina crack

Both specimens fabricated from Mk2 elastomeric plastisol, optical micrographs, magnification, X 6.
Figure 5.5.1 Compressibility curves of AISI 4815 powder and sponge iron powder.
Figure 5.5.2 P/M substrate surface

Scanning electron micrograph, magnification X 90.
Figure 5.5.3 Plot of P/M substrate surface roughness versus density
Fabricated from elastomeric plastisol, magnification X 2.
Fabricated from elastomeric plastisols moulded over a P/M substrate, magnification X 2.5.
Figure 5.8.2 Moulding distortions of graded structure units

Specimens elastomeric plastisols moulded over P/M substrates, magnification X 2.5.
Specimen fabricated from graded viscosity elastomeric plastisols moulded over a P/M substrate, specimen in debound state, magnification X 3.
Figure 5.8.4 Sintering distortion of a graded structure unit

Specimen showing peeling of hardmetal layers away from the P/M substrate, magnification X 2.5.
5.9.2 Rock bit substrate

A front view

Specimen compacted at 700 MPa and presintered, magnification X 2.5.
Specimen compacted at 700 MPa and presintered, magnification X 2.5.
Figure 5.9.4 Rock bit mouldings

A) Substrate plus first plastisol layer of B01 tool steel
B) Substrate plus two plastisol layers
Four layer graded structure rock bit
To match the plastisol and steel, the plots would need to be moved into the shaded area.

Figure 6.2.1 Plot of thermoplastic plastisol thermal expansion coefficient as a function of powder loading
APPENDICES

1. Process tooling
2. Electrical conductivity of plastisol mixes
3. Plastisol debinding profiles
4. Elastomer molecular weight for particle entanglement
5. Spontaneous ejection criterion for the rock bit tip
Appendix 1. Process tooling

1) Impact test bar mould
2) Compaction die set for MLIM test geometry substrates
3) MLIM test mould
4) MLIM test mould: ejector assembly and shims
5) Rock bit tooling
   RBT1 General view
   RBT2 Substrate
   RBT3 Compaction die
   RBT4 Compaction die: punch cavity
   RBT5 Injection mould base
   RBT6 Mould clamp unit
   RBT7 Injection mould top
   RBT8 Epoxy moulding tool
   RBT9 Epoxy moulding blanks

All dimensions in mm

Material: mild steel except No2 and RBT3,5 & 7.

Tolerances

0 +/- 0.5mm
0.0 +/- 0.1mm
CAVITY SHOWN WITH BLANKING
INSERT AND SUBSTRATE, LENGTH 28
SECTION AA
TO TAKE 8 M ALLEN BOLTS

DIE BODY - TWO HALVES

UPPER 65
LOWER 130

TO BE CUT IN
HALF AS SECTIONED

SPACER

DRAWN PETER LANE
TITLE COMPACT
DIE SET
NOTES:
1. DIMENSIONS SHOWN
2. LAYER THICKNESS 1.1 x 2.2 mm
3. INTERNAL GEOMETRY TRUNCATED CIRCULAR BASED CONES, WITH TWO ESCARPMENT FACES.
NOTES:

1. CYLINDER PUSH FIT ON BASE
2. TO BE SUPPLIED WITH A MG GRUB SCREW, LENGTH 15 mm

DRAWN  PETER LANE  6.12.89
TITLE  EPOXY MOULDING TOOL
SCALE  2:1
DRG NO  RBT9
NOTE: DIMENSIONS SHOWN AS CALCULATED, THE DECIMAL PLACES MAY BE ROUNDED UP AS REQUIRED FOR FABRICATION.

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Appendix 2. Electrical resistivity of plastisol mixes

Thermoplastic plastisols mixed with hardmetal powder, 6% cobalt balance tungsten carbide, were investigated. Samples were taken from capillary rheometer extrusions, test length 40mm, diameters 2-5mm. Electrical contact was made by crocodile clips forced into the surface; results were very sensitive to surface pressure, i.e. the quality of contact and the values given below are only of an indicative nature. N.B. The resistivity was measured along the extrusion direction.

<table>
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<tr>
<th>Plastisol formulation</th>
<th>Resistivity (Ω m 10^-8)</th>
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<tr>
<td>50 v/o powder mixed in LDPE LD657.</td>
<td>190</td>
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<tr>
<td>60 v/o powder mixed in LDPE LD657.</td>
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<tr>
<td>60 v/o powder mixed in blend 7#, containing EVA.</td>
<td>60</td>
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<tr>
<td>55 v/o powder mixed in LDPE LM2150.</td>
<td>310</td>
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v/o = volume percent
LDPE grade designations detailed in Table 4.1.2
# detailed in Table 5.1.2

Note: [267] Resistivity of; (i) mild steel = 15*10^-8
(ii) aluminium = 2.7*10^-8 and (iii) polymers = 10*10^10
Appendix 3. Plastisol debinding profiles

The profiles were imposed by an Eurotherm 818P programmable logic controller using the configurable element sequence of: ramp rate (Pr, °C/Hr), plateau level (Pl, °C) and dwell time (Pd, Hrs.). The program elements are listed below and the profile for debinding elastomeric plastisol is shown diagrammatically to illustrate the form of the profiles.

A) 36 hour cycle:

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<td>Pl3</td>
<td>400</td>
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### E) 87 Hour Cycle for Elastomeric Plastisol

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Plot of the 87 hour debinding cycle for elastomeric plastisol
Appendix 4. Elastomer molecular weight and particle entanglement

How long is an elastomer chain? This can be calculated as below:

Data: C-C bond length 0.154 nm [95]
Bond angle 109° (tetrahedral)
Elastomer molecular weight 1-5*10^6 [268]

Assuming a linear zig zag chain conformation

then the length of a two atom repeat unit is thus:

\[\sqrt{(0.154)^2 + (0.154)^2 - 2(0.154)(0.154) \cos 109°} = 0.251 \text{ nm}\]

and the number of repeat units for a paraffinic structure is

\[1-5.10^6/28 = 36000-214000\]

Hence chain length lies in the range 9040-32960 nm

i.e. 9-33 µm

This length is greater than the particle size of the hardmetal but is less than that of the BO1 tool steel powder.
Appendix 5. Spontaneous ejection criterion for the rockbit substrate tip

Consider the cavity shown below:

A compacted powder fills the cavity volume and is held there by a compaction pressure (P). On release of the external compaction force will the compact spontaneously eject from the wedge shaped cavity?

The two dimensional geometry is equivalent to the three dimensional situation if radial symmetry is present.

The problem is a two body problem, i.e. spontaneous ejection is only possible through the action of forces at the cavity wall.

For an infinite cavity with isostatic pressure conditions all forces on the compact except the normal reaction are matched by an opposite.

So what is the effect of the normal forces; assuming an inelastic cavity:
If \( F = \text{normal force} \)
\( Q = \text{friction force} \)
\( \mu = \text{static coefficient of friction} \)
\( N = \text{effective pressure at point } a \)
\( Q = \mu N \)
\( S = \text{wall shear force} \)

If \( \theta > 45^\circ \) then \( F \) will act outside of the cavity and no jamming action is possible, hence spontaneous ejection will occur.

If \( \theta < 45^\circ \) then at point "a" \( S = F \cos (90-\theta) \)

For spontaneous ejection \( S > Q \)

\[ \Rightarrow F \cos (90-\theta) > \mu N \]

now \( F = P \) (isostatic)
and \( N = P + F \cos \theta \)

near the cavity exit \( P \) tends to zero

thus \( P \cos (90-\theta) > \mu F \cos \theta \)

\[ \Rightarrow 90-\theta > \mu \theta \]

This condition for spontaneous ejection can be plotted out as overleaf.
Plot of friction coefficient ($\mu$) versus cavity slope angle ($\theta$)

- No spontaneous ejection
- Spontaneous ejection