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DEVELOPMENT OF NOVEL CERAMIC PROCESSING TECHNIQUES FOR MANUFACTURE OF HEART VALVES

Investigating the use of Powder Reaction Injection Moulding Engineering (PRIME) for the manufacture of novel, seam-free ceramic heart valves

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ABSTRACT

Past research at Nottingham Trent University led to the design of a new prosthetic heart valve, to be made from alumina (aluminium oxide) because of its excellent wear properties and unequalled bio-compatibility. This paper documents a project performed to meet the challenge of using powder reaction injection moulding and extrusion (PRIME) to manufacture the alumina valve to the necessary high accuracy and finish.

Butyl-cyanoacrylate and methyl methacrylate were investigated and compared as binders for the alumina powder. The cyanoacrylate binder was highly reactive, posing problems when mixing and handling feedstock, so inhibition levels were investigated. Catalysing mediums also were investigated, and steam and boiling water were found to be the best; these were subsequently used in moulding investigations.

The rheological properties of the mixture of cyanoacrylate and alumina were investigated and it was found that the viscosity was within acceptable limits for injection moulding. The feedstock behaved like a power law fluid at the investigated shear rates, and a model was developed and used to predict viscosity at the shear rates experienced within the moulding process.

The moulded feedstock was investigated to determine its suitability for machining so that, if necessary, the internal surface of the heart valve could be improved if necessary to achieve precise tolerances. Samples turned exceptionally well using a standard lathe, and the results suggested that green machining of PRIME feedstock would provide many benefits to a production process.

For the moulding process, an alloy mould and core were found to best withstand moulding pressures, and by melting them after moulding the heart valve could be released without any damage. A wax skeleton was used within the mould assembly to allow boiling water or steam to pass through it and so enhance polymerisation and venting of the mould. The process that was developed has been patented.

In order to understand exactly how the moulding process worked, a computational analysis (CFD) was used to determine the pressures inside the mould and highlight possible areas of increased pressure. The CFD model that was developed using PHOENICS 3.1 code was validated by analysing Newtonian fluid

flow through a perspex heart valve mould and comparing pressure results from the practical and computational investigation.

The processes developed in this project have been successfully applied to the manufacture of the alumina heart valve, and are equally suited to the manufacture of other low volume, high quality ceramic products.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to both Professor Barry Hull and Professor Richard Gentle for guiding me throughout this project.

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Finally, special thanks go to the support staff of the Nottingham Trent University, in particular Alan Tye and Melvyn Golds for their wit, wisdom, and commitment to my work.

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NOMENCLATURE AND ABBREVIATIONS

d_{50}	Median powder particle size	µm
T_g	Glass transition temperature	°C
vf	Volume fraction of powder to binder	n/a
a	Volume of powder	m^3
b	Volume of binder	m^3
v	Velocity	m/s
x	Fluid separation	m
τ	Shear stress	N/m^2
∇	Shear strain rate	s^{-1}
η	Dynamic viscosity	Pa.s
η_a	Apparent dynamic viscosity	Pa.s
K	Consistency index	n/a
n	Power law factor	n/a
η_b	Binder viscosity	Pa.s
η_o	Viscosity at a temperature T_0	Pa.s
Φ	Volume fraction of solid	n/a
Φ_m	Maximum solids loading	n/a
A	Constant that varies with particle size	n/a
D	Particle diameter	m
E	Activation energy	J
k	Boltzmanns constant	W/m^2K^4
T	Absolute temperature	°C
C	Pressure dependant enthalpy	KJ/Kg
P	Pressure	N/m^2
r	Cone radius	m
ϑ	Cone angle	°
ω	Angular velocity	Rad/s
h	Plate height	m

λ	Measured value from rheometer	n/a
C_c	Cone constant	n/a
η_z	Viscosity of fluid used for cone and plate calibration	cP
λ_z	Measured value (calibration)	n/a
τ_r	Shear stress calculated from cone and plate rheometer	Dyn/cm^2
η_r	Viscosity calculated from cone and plate rheometer	cP
T_m	Melting temperature	°C
R_a	Arithmetic average of peak to valley height	µm
N	Number of activated atoms	n/a
N_o	Number of total atoms	n/a
P_o	Reference pressure	N/m^2
J	Pressure coefficient	N/m^2
η_j	Reference viscosity	Pa.s
Q	Volumetric flow rate	m^3/s
h_c	Correction head	m
h_a	Actual head	m
h_m	Measured head	m
h_e	Mould exit height	m
h_h	Corrected pressure head	m
d_m	Hydraulic mean depth	m
p_1	Pressure at mould outlet	N/m^2
u_1	Velocity at mould outlet	m/s
a_1	Area of mould outlet	m^2
l	Outlet pipe length	m
z_1	Mould exit height to a datum	m
z_2	Datum point height	m
u_2	Velocity at pipe exit	m/s
p_2	Pressure at pipe exit	N/m^2
a_2	Area of pipe exit	m^2

h_l	Head loss	m
f	Fanning friction factor	n/a
d_p	Exit pipe diameter	m
g	Acceleration due to gravity	m/s^2
ρ	Density	kg/m^3
Re	Reynolds number	n/a
∇_a	Apparent shear strain rate	s^{-1}
r_2	Radius of flow area	m
$\eta_{kinematic}$	Kinematic viscosity	m^2/s
$\rho_{feedstock}$	Feedstock density	kg/m^3

PRIME	Powder Reaction Injection Moulding Engineering
PIM	Powder Injection Moulding
SEM	Scanning Electron Microscope
MMA	Methyl Methacrylate
PMMA	Poly Methyl Methacrylate
VHN	Vickers Hardness Number
EDM	Electro-discharge Machining
LBM	Laser Beam Machining
ECM	Electro Chemical Machining
USM	Ultrasound machining
AJM	Abrasive Jet Machining
EBM	Electron Beam Machining
DSC	Differential Scanning Calorimetry
TGA	Thermo-Gravimetric Analysis
CFD	Computational Fluid Dynamics
VR	Virtual Reality

Chapter 1 – Introduction

1.1 Aim

- To investigate the use of Powder Reaction Injection Moulding Engineering (PRIME) for the manufacture of novel, seam-free ceramic heart valves

1.2 Objectives

- To select an alumina powder that is acceptable for use with powder injection moulding
- To select a reactive binder that will combine successfully with alumina powder to form a feedstock
- To determine the optimum proportion of feedstock constituents that will successfully mould, debind, and sinter
- To review the reactivity of binders when mixed with alumina, with respect to inhibition and initiation characteristics
- To investigate the shear stress at various strain rates, and hence, determine the rheological characteristics of the feedstock at a range of powder volume fractions
- To design a moulding system that includes a removable insert for moulding the heart valve
- To determine moulding parameters such as, pressure, temperature, and mould insert melting temperature
- To investigate the possibility of machining moulded ceramic components when mixed with the reactive binder
- To determine the thermal degradation characteristics for the binder when mixed with alumina powder
- To investigate the parameters required to sinter the alumina powder to an acceptable porosity for the heart valve
- To review the pressure within the heart valve mould by computational fluid analysis.

1.3 Background

Artificial heart valve design has progressed greatly since the first experimental surgical implants in the early 1960s. Current heart valve prostheses, both mechanical and biological, can be considered one of the principal successes of biomechanical engineering. However, there is still significant scope for improvement, especially in the treatment of children, where the need for refined flow characteristics, extended wear life and complete biocompatibility is most acute (1,2).

Work done at Nottingham Trent University has resulted in the design of a new valve prosthesis mounted in a conduit. The conduit can be used outside the heart as part of a surgical procedure to correct gross congenital anomalies in a child's cardiovascular system - essentially, a replumbing operation (3). The success of this design is evidenced by the fact that an acrylic version has been adopted for the inlet and outlet valves of a novel ventricular assist device (4), which is under trials as a temporary mechanical heart to sustain heart failure victims until a transplant becomes available.

The most significant feature of the conduit valve, however, is the fact that it is to be made from alumina when intended for permanent implantation in children and adults. Early applications of ceramics in biomedical implants made use simply of their resistance to wear and chemical attack, but it has been documented that a fine covering of non-vascular tissue can grow on alumina when immersed in the blood stream (5). This covering is thought to be sufficient to camouflage the prosthesis from any further interaction with the blood, and fine enough (<0.1mm thick) not to interfere with the mechanical function of the valve. Accordingly, alumina valves should exhibit not just excellent wear properties but also unequalled biocompatibility that will obviate the need for continuing anticoagulation treatment. The challenge is to make the conduit in alumina to the necessary high accuracy and finish.

Conventional powder processing is well established as a cost-effective method of producing net or near net shaped products. In recent years, there has been increasing research activity in the USA, Japan and Europe into the efficient production of sintered components from green compacts manufactured by metal or ceramic injection moulding (6-8). Injection moulding of polymers filled with dispersed metallic or ceramic powders has become a recognised route for the production of a large series of complex shaped parts at low cost and with a high degree of accuracy.

Current technology for powder moulding is based on dispersion in non-reactive carriers or binders, followed by shaping, de-binding, and sintering. Many technical difficulties exist throughout the processing of powders by means of conventional polymer processing techniques, using polymers or waxes as binders/carriers. A major drawback is the long de-binding time, which can take hours or even days. Polymer or wax decomposition occurs relatively slowly, even at high temperatures, because of the fundamental chemical limitations of the rate of binder degradation and the diffusion rate of the inherently volatile fragments. Attempts have been made to improve the de-binding times. Hull, Birkenshaw, and Buggy use a reactive monomer, such as cyanoacrylate, which has a capability for rapid solidification through polymerisation (9). Subsequently, the binder can be removed in minutes from the powder compact, by thermal depolymerisation, and recovered for re-use.

The conduit heart valve has a complex geometry, making it difficult to machine using conventional ceramic machining techniques. However, the shaping flexibility of a powder processing method would be ideal for manufacturing the valve. Also, a powder system including a reactive binder would reduce processing time and increase the feasibility of green machining. Based on these suggestions, reactive monomers have been investigated as binders with alumina powder to create the conduit heart valve. The processing method selected for moulding the valve geometry is discussed in section 1.5 and 1.5.1.

1.4 Conduit Heart Valve Development

The first implantation of a prosthetic heart valve in a human was performed in 1952 by Hufnagel (10). This was deemed a success, although the valve was implanted in the descending aorta and not in the correct anatomical position. Following this achievement, Hufnagel and other surgeons continued researching operational procedures, resulting in the actual replacement of tissue valves.

In 1960, Harken (11) performed the first successful implantation of an aortic caged-ball prosthesis, and Starr (12) achieved the first mitral valve replacement in the same year, also using a caged-ball valve. It was reported that six out of the eight patients that received the mitral valve survived more than one year (13). This success rate was sufficient to create clinical acceptance of the caged-ball design, and 40,000 valves were implanted throughout the USA, between 1960 and 1967 (1). Since this early development, the design of cardiac prostheses has improved to include a larger product range; in 1979, Lefrak reported the clinical use of tilting disk, advanced caged-ball, and porcine tissue valves (12).

Prosthetic heart valves are generally used for the replacement of diseased aortic, mitral, tricuspid or pulmonary valves. However, further cardiac complications necessitate the use of a valved conduit for implantation *outside* the heart, as indicated in figures 1 and 2.

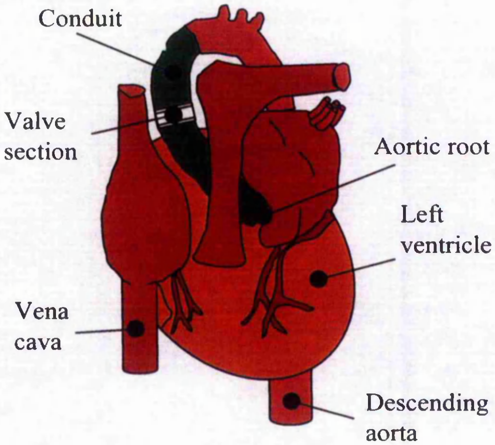


Figure 1. Valved conduit as a replacement aorta

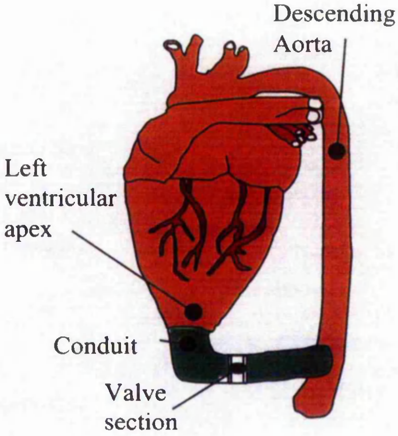


Figure 2. An apico-aortic shunt

Generally, there are three main uses for a conduit heart valve as detailed by Gentle (3); these include:

- *Apico-aortic shunt*

  This procedure involves connecting a valved conduit between the descending aorta and ventricular apex, creating an artificial outflow tract from the left ventricle, and bypassing the aortic valve. It provides relief from severe congenital aortic stenosis, but the placement of the conduit will not deal with retrograde flow through the aorta.

- *Replacement of the aortic valve and ascending aorta*
  When the existing aortic valve and the ascending aorta are both diseased, it is possible to replace them with a valved conduit.
- *Congenital malformations*
  An important application is in the repair of congenital cardiac abnormalities, by using a small valved conduit.

It is common for valved conduits to consist of a prosthetic valve intended for implantation at the normal anatomical position, and a length of tubing (normally made from Dacron). Although this approach is practical and economically viable, there is a significant problem, in that there is evidence that some existing conduit valves do not function correctly at certain operating conditions. Gentle cited that most valve prostheses rely on the formation of vortices or recirculating flow patterns behind the occluder or leaflets to assist their closure and it is difficult to achieve this in a straight tube which is not shaped to give ventricular flow (14).

Gentle & Tansley developed a conduit prosthesis to overcome the drawbacks identified with the limited range of existing conduit valves (15). The design philosophy was to use a rigid conduit body containing a ball occluder, similar to the original Starr-Edwards series of valves (16), so that the blood flow was guided around the occluder, maintaining a constant flow area and reducing areas of recirculation, blood shear, and pressure drops.

Harken (17) highlighted ten desirable characteristics for the design of a prosthetic heart valve:

- *It must not propagate emboli*
- *It must be chemically inert and not damage blood elements*
- *It must offer no resistance to physiological flows*
- *It must close promptly (less than 0.05 sec)*
- *It must remain closed during the appropriate phase of the cardiac cycle*
- *It must have lasting physical and geometric features*

- *It must be inserted in a physiological site, generally the normal anatomic site*
- *It must be capable of permanent fixation*
- *It must not annoy the patient*
- *It must be technically practical to insert*

Most of the above recommendations were included in the physical design of Gentle & Tansley's prosthetic valve. The selection of the material to be used was considered to be most significant, as this addressed the first, second, third and sixth of Harken's criteria.

Mechanical heart valves are normally manufactured with a material that provides a smooth surface, so that the blood flow is less volatile and fewer blood cells are destroyed (haemolysis). So, for example, because of its glassy, dense structure a specially modified form of carbon (Pyrolite) (18) is a popular choice for the manufacture of discs, or occluders for heart valves. But haemolysis still occurs with all existing designs of mechanical valves, and it is necessary for patients to have chronic anticoagulation (14). To help promote the patient's quality of life, there is a clear need to identify a material that will remove the need for anticoagulation treatment.

Gentle stated that Aluminium Oxide (alumina) is a promising material for the construction of heart valves because of its wear resistance, strength, and fracture toughness (19). This was followed up by Juden et al who demonstrated that porous alumina could grow a fine covering of tissue on its surface when submerged in a blood stream, thus enhancing flow properties and preventing haemolysis (5).

Figure 3. CAD model of Gentle & Tansley's conduit heart valve

Tansley's alumina heart valve (shown in figure 3) was focused on high performance and longevity, and hence the valve body was developed by computational flow analysis that considered the turbulent and Non-Newtonian blood flow characteristics (15). Initially, it was proposed that the valve should be manufactured in two sections joined by inorganic cementing, diffusion bonding, welding or mechanical interlocking. However, these methods of manufacture would introduce the possibility of operational fractures along the joining surface; and an internal weld line might interfere with flow characteristics and occluder movement.

A ceramic processing technique was required that would avoid these weaknesses and enable the heart valve to be manufactured in one piece, incorporating a porous internal structure and high geometric tolerance.

1.5 Ceramic Processing

High performance ceramics such as alumina are used for their hardness, resistance to wear and corrosion, high temperature strength, and capacity of heat insulation. However, these assets are marred by disadvantages, including low ductility and a tendency to crack, that reduce the processing options. Ceramics are not normally formed by machining methods, because these techniques require an inherent ductility (20), and dense ceramics are milled or chemically processed to produce a powder, that is either moulded or compressed into a shape by a subsequent process (21).

Ceramic powders are normally formed into a shape using a single processing method such as pressing, casting, extrusion, or injection moulding, the powders being usually transported by a liquid 'vehicle' commonly known as a binder. The forming technique to be used will depend upon the consistency of the material, which might be slurry, paste, or loose powder. However, each of these formats will eventually produce a similar unfired component, a "green body", which is normally dried or debound before firing to achieve a sintered, dense microstructure.

Pressing ceramic powders is a highly productive and robust process that involves simultaneously compacting and shaping the powder whilst it is confined to a die. The powder typically requires a low quantity of binder (2-13% by volume) to provide limited 'green strength' (22). A wide range of products is formed by this method, including magnetic ceramics, spark plugs, cutting tools, porcelain products, and grinding wheels. There are three pressing methods commercially available, each applying the compaction force in a different direction:

- *Dry pressing*
  Dry pressing uses a uniaxial compression force to produce components with a thickness greater than 0.5mm (23).
- *Isostatic pressing*
  Isostatic pressing involves suspending flexible rubber moulds within a compression chamber. This chamber is filled with a fluid that compresses the mould in either two or three dimensions, allowing complex components such as parts with elongated dimensions, to be formed (24).
- *Roll Pressing*
  Roll pressing involves the compaction of granulated powders between rollers, which produces large sheets with a thickness less than 1.5mm. This method is generally used for high volume production of components that have a simple geometry (24).

Casting is another common technique for forming ceramic powder. This method uses a low viscosity slurry (<2 Pa.s (24)) to fill a mould using no external forces except for gravity.

There are two casting methods used in industry, namely solid and drain. The first method is relatively simple, producing solid components by pouring ceramic slurry into an open mould where it is left to dry, or removed after a period when the material has formed sufficient strength. Drain casting is more complex, involving transfer of the slurry through a porous mould by capillary action, the thickness of the component being controlled by the casting period.

The casting slurry is commonly called a 'Slip', which normally contains between 45% and 60% water, mixed with either alumina or a clay/silica/feldspar composition (24). It is common for a slip to contain a reactive bonding agent that will accelerate the drying process when the agent cures.

Slurry is normally formed by using one of three common industrial casting techniques:

- *Slip casting*
  Slip is poured into a porous gypsum mould. The capillary suction of water into the mould coagulates the particles near the mould surface, leaving a solid casting (25).
- *Pressure casting*
  Polymer moulds are filled with slip under pressure. Draining then commences via built in filtration systems, which withdraw the aqueous part of the slip leaving a solid component. This technique can be readily automated and is used for casting relatively complex shapes. Advantages of this process include higher shape precision, green strength and density (26).
- *Centrifugal casting*
  This approach is used for forming advanced ceramics into a complex shape where the component requires a high density. The cast is formed when fluid is evacuated from a mould by the introduction of centrifugal forces. Particles with greater size or density settle first, and hence, the settling rate is controlled by adjusting the rotational velocity (27).

Extrusion is a processing method that forms cohesive plastic materials by forcing feedstock through the orifice of a die. The feedstock emerges from the die as a length of material (extrudate) with a controlled cross section, which is subsequently cut to a required length. The plastic consistency of the material is normally achieved by using a polymeric binder that is similar in composition to those used for injection moulding.

Extrusion feedstock can include a variety of materials such as oxide and non-oxide ceramics, metals, and plastics. The most common extruded components are normally polymeric and include symmetrical articles such as, rods, tubes, and channels, and there is a large market for extruded ceramics, such as furnace tubes and sewer pipe (28).

Although there is a resemblance between extrusion and injection moulding, in that both processes use single and twin screw pressurising devices and a similar powder/binder system, they are distinctly different: injection moulding is associated with forcing a single shot of feedstock into a closed mould; extrusion produces a continuous flow of material from a die, relying on the wet strength of the materials to prevent 'slumping' or collapse after moulding.

Each of the three ceramic processing methods described above - pressing, casting and extrusion - can be used to produce basic components from either powder or powder binder feedstock. But the manufacture of a component as complex as the conduit heart valve required a combination of three attributes - relatively low pressure, a viscous feedstock, and a mould incorporating an insert - that none of the processes could deliver individually without significant adaptation. However, a ceramic injection moulding process does provide the three attributes for moulding a conduit heart valve, because:

- Reactive binders could be used to aid debinding and also provide a high green strength (9)
- A mould could be used that incorporated an insert to create a conduit (29)
- Viscous feedstock such as that required for the heart valve can be forced into the mould under a relatively low pressure (29)
- The powder content can be adjusted by compensating with binder, which enables a greater control of the sintered porosity

1.5.1 Ceramic Injection Moulding

One of the earliest reported applications of ceramic injection moulding was the manufacture of spark plug insulators in 1937 (30). Since then, there has been considerable development and investigation towards a newer more efficient moulding

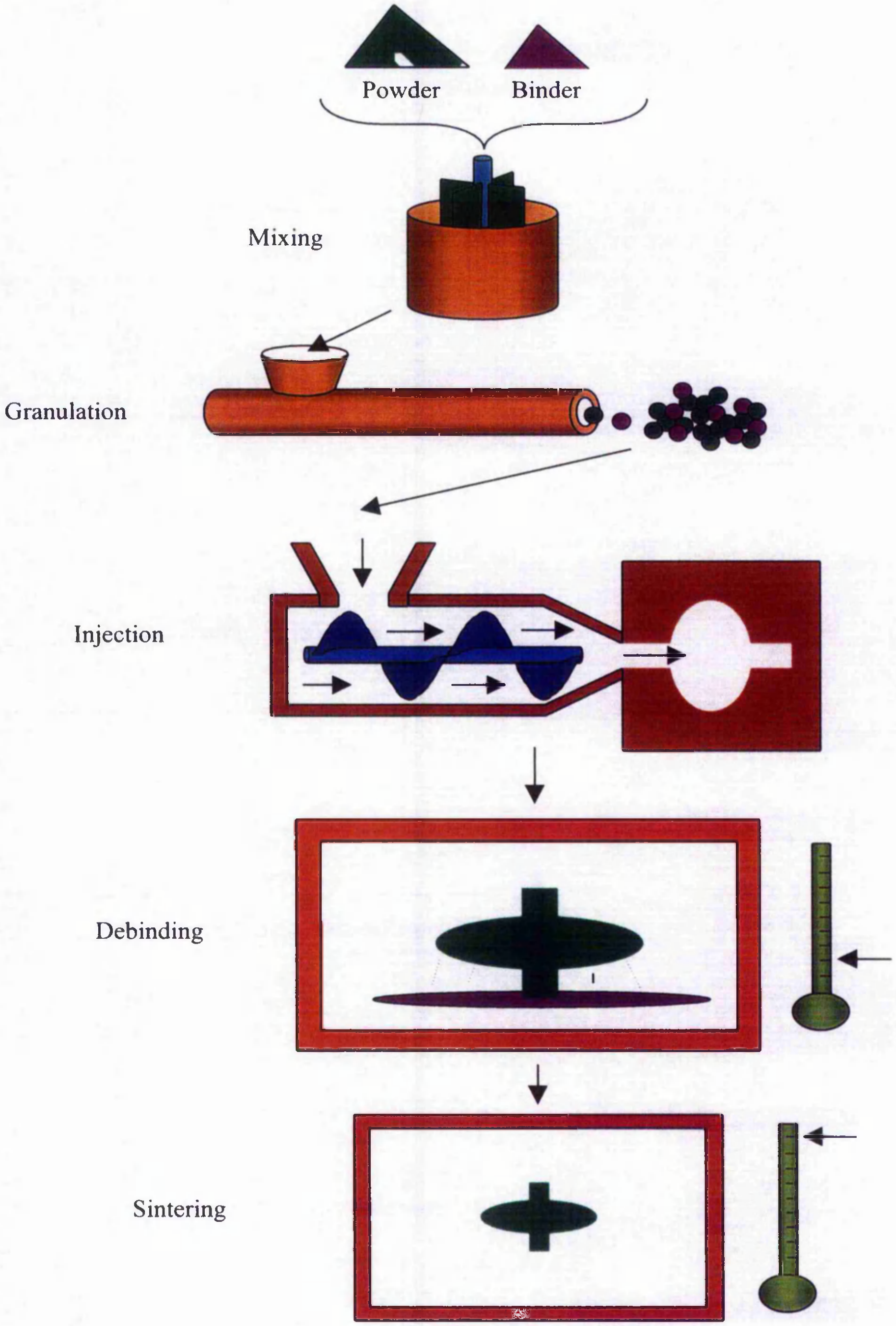


Figure 4. Injection moulding process

method for more demanding applications. The modern powder injection moulding (PIM) process is generally used for mass production of complex shapes and for relatively small ceramic parts such as thread guides, cutting tools, welding nozzles, and turbine blades. However, because injection moulding is an expensive and generally complex operation it is not usually the first choice for processing of ceramics, and if another process, such as casting or pressing, could be used then it should be considered. Nevertheless, PIM is sometimes the only viable option for moulding components with a complex geometry (22).

The process of injection moulding consists of five stages (31): preparation of materials; granulation; forming; binder removal (debinding); and sintering, as shown in figure 4. Preparation of the materials (or feedstock) consists of mixing a ceramic powder with an organic binder, which is usually based on wax or a polymeric material. This is normally achieved by using a high-torque mixer, or a twin-roll mill, which can produce ceramic pastes with very high solids loading (32). Mixing is performed whilst the binder is molten, and there is sufficient fluidity to enable a homogenous mixture with the ceramic powder. Typically, whilst molten, the feedstock has the consistency of toothpaste (22). However, on cooling the mixture becomes brittle, thus enabling granulation, and hence, the production of small pellets. Subsequently, these pellets are loaded into an injection moulding machine, which is sometimes under vacuum to eliminate air entrapment, and heated to enable flow whilst being forced under pressure into a cold mould. After cooling, the part is ejected from the mould and the process is repeated.

Debinding is the process of removing a binder from a moulded part, since the binder is only used as a temporary vehicle for conveying powder until it is formed into a shape. Techniques are used to carefully remove the binder content without damaging the appearance of the formed part; for example, it is common for polymeric binders to be thermally degraded or extracted by a solvent before firing the powder (33).

The final part of processing is sintering the ceramic powder to form a solid component with a relative density in the range of 50 to 98%. The first stage of firing removes approximately 5% of binder that remains in the component from the debinding stage, thus leaving only ceramic powder. Subsequently, this powder is sintered at a relatively high temperature, which contributes to mass transfer and, hence, an increased density. After firing, the component is checked for processing anomalies such as shrinkage or distortion, before being accepted as adequate.

1.5.2 Ceramic Injection Moulding: Current Limitations and PRIME

A major limitation to powder injection moulding arises from the current use of polymer or polymer/wax based binders and the process used to remove them.
The three main debinding processes are thermal degradation, wicking and solvent extraction. Of these, the simplest and most economical process is thermal degradation; its limitation being the lengthy binder removal time. Polymer/wax binders can take between one to five days to be thermally removed from moulded parts depending upon the cross-sectional thickness (34), although this time has been reduced down to four hours by combining removal methods with a mixture of polymeric binders (35). This approach greatly reduced debinding time but there was still room for improvement, and a novel approach to moulding technology was patented, titled "Powder Reaction Injection Moulding Engineering" (PRIME) (9).

The major difference between PRIME and conventional injection moulding was that the binder (or carrier) was a reactive monomer such as a cyanoacrylate. This was followed up by using ethyl-cyanoacrylate mixed with silicon nitride with encouraging results (36). However, since ethyl cyanoacrylate is fifty times more viscous than butyl-cyanoacrylate and, according to German (37), a high mixture viscosity usually correlates with a high binder viscosity resulting in a less homogenous mix; the indications were that butyl might be a better alternative.

It has been proven that cyanoacrylate will react instantaneously upon addition of metal or ceramic powders (38), and that dissolving measured quantities of para-toluene sulphonic acid into cyanoacrylate monomer will inhibit a polymerisation reaction. Furthermore, Cooke suggested that there is a link between acid inhibition and polymerisation, claiming that anionic polymerisation is inhibited at pH <5.5 (39). On the other hand, polymerisation of inhibited cyanoacrylate is important to promote a reaction, thus enabling the monomer to function as a binder. A weak electron donor (Lewis base) has been found to neutralise the dissolved acid in an inhibited monomer, enabling the binder to polymerise (39).

A selection of bases was mixed with 'as supplied' cyanoacrylate monomers to investigate the subsequent polymerisation time (39). N,N-dimethyl paratoluidine, piperidine and N,N-dimethyl piperazine were used, each one having different chemical characteristics. It was found that each of these chemicals caused a suitable polymerisation reaction, although N,N-dimethyl piperazine was too reactive. Other catalysts have been found useful as base initiators, including pyridine, butylamine, caffeine, and water (36 & 40), but the use of these initiators has been limited to laboratory investigations and their effect on the reaction in an actual moulding process was not known.

Conventional powder injection moulding and the PRIME method are both techniques that could produce a complex component such as the conduit heart valve. However, the PRIME method uses a reactive binder that can reduce debinding times and improve the moulding process compared to traditional PIM, which uses a polymeric binder. Therefore, the process of moulding would be simplified by using PRIME technology, avoiding the need for complex, expensive equipment

1.6 Research Programme

A research project has been undertaken within the Department of Mechanical and Manufacturing Engineering at the Nottingham Trent University to develop a novel conduit heart valve made from ceramic. Its aim was to investigate Powder Reaction Injection Moulding (PRIME), and determine whether this technology was suitable for manufacturing the prosthetic heart valve. The project was essentially split into three main themes:

- development of a moulding system using PRIME;
- applying this technology to the manufacture of the heart valve; and
- investigating the moulding characteristics by computational methods.

The work presented here details the design approach taken to formulating the moulding strategy using a reactive binder, the results of which were applied directly to manufacturing the conduit heart valve.

This first chapter of this thesis relates to the background and requirements of the research project, its aim and objectives. The background provides a brief explanation about the historical developments that have brought about the requirement of this investigation.

Chapters two to five detail the development of the feedstock, moulding methods, machining characteristics, and heating requirements that were required to create a probable manufacturing process for the conduit heart valve. Chapter six details a mould flow analysis to determine the unknown pressure distributions associated with moulding the heart valve. More particularly:

Chapter 2 - Materials Processing

- Review of alumina powder characteristics
- Selection of a suitable binder for PRIME
- Analysis of the powder/binder mixture

Chapter 3 - Design for Moulding

- Development of a rheological model for the powder binder mixture
- Review of moulding requirements
- Development and analysis of materials for the heart valve mould

Chapter 4 - Ceramic Machining

- Review of machining techniques available for ceramics
- Selection of a suitable method for machining the heart valve

Chapter 5 - Heat Treatment

- Review of debinding techniques
- Debinding of the heart valve
- Sintering and porosity investigation related to the heart valve

Chapter 6 - Flow Analysis of the Moulding Process

- Flow analysis of the feedstock composition used for moulding the heart valve
- Results and discussion related to the moulding pressure

The thesis is brought to a close with a discussion and the final chapter, which concludes the findings from each investigation followed by the recommendations for further work.

Chapter 2 – Materials Processing

2.1 Introduction

This chapter discusses the selection and properties of the chemicals to be used in preparing the feedstock for the powder reaction injection moulding process, and is in three sections: Powder, Binders, and Mixing.

The first section describes the characteristics and investigations of alumina powder that is suitable for injection moulding, because powders differ by particle size, shape and attainable packing density which will effect the moulding capability when mixed with a binder. The second section describes binder requirements, the investigation of two such chemicals that are suitable for reaction injection moulding, including the inhibition and initiation of the polymerisation reaction. The final section describes the mixing of alumina powder with both binders, and the selection of a binder for use in moulding investigations.

The key actions were to:

- establish the characteristics of alumina powder in relation to injection moulding, in particular, particle size, shape and packing density
- investigate the polymerisation initiation characteristics of each of the binders
- find the highest mixed volume fraction of binder to alumina powder
- select a suitable binder for developing a useful feedstock for PRIME
- develop a *consistent method* for mixing the feedstock, by using a suitable binder inhibition and initiation configuration

2.2 Powder

2.2.1 Heart Valve Requirements

The conduit heart valve had four basic requirements

(i) Wear resistant body
(ii) Resistance to chemical attack
(iii) Surface tissue covering (porous surface in contact with the blood stream)

(iv) Seam free structure

Each of these requirements can be satisfied by using a ceramic material. Generally, two types of ceramic powder (or metal oxide) are used in prosthetics, alumina, and zirconia. Either of these materials could be used to construct the heart valve as each satisfies the first two requirements, and can be processed to produce a seam free structure. However, it has been proven that alumina will grow a fine covering of non-vascular tissue when immersed in the blood stream making it a more suitable material for heart valve manufacture. This factor eliminated zirconia from this investigation, although it remained a viable alternative because it has been confirmed to work as a constituent ceramic powder for PRIME technology (41).

2.2.2 Alumina

The most commonly used engineering ceramic appears to be alumina (Al_2O_3), whose synonyms include aluminium oxide, sapphire and corundum. Generally, alumina is used for its superior mechanical properties such as high temperature resistance, corrosion resistance, and abrasion resistance, and it is used for a wide range of products including dinnerware, sanitary-ware, refractory insulation (furnace linings), and spark plugs. A small amount of high purity alumina is produced for special applications such as medical devices and prosthetics. In these cases (especially prosthetics) the alumina must have a purity of at least 99.80% (14 & 42).

Alumina used for this investigation had purity ranging from 99.80% to 99.99%, making it a suitable powder for manufacturing the conduit heart valve. Three batches of alumina were used for this investigation with different characteristics such as particle size, shape, purity, and tapped density, so that a comparison could be made after mixing with a binder. Details of the powders are tabulated in section 2.2.7. The impurities in some powders consist of useful chemicals such as magnesium oxide, which can be used as a sintering aid for alumina (43).

2.2.3 Characteristics of Powders for Injection Moulding

The success of powder injection moulding (PIM)) depends upon the correct choice of powder. Parameters such as particle size, shape, distribution, and the level of agglomeration can determine the optimal characteristics for moulding. These parameters are normally found by experimental investigation. Although there are many mathematical models available, they are generally based on monosized spheres (44-46). In practice, real powders do not have such geometric perfection, and there is a large distribution of size and shape, coupled with agglomerated powder particles, which cannot be modelled.

The powders normally used in PIM have fractional packing densities between 0.3 and 0.8 of theoretical, with a typical level near 0.6 (37). This is accomplished by using a wide size distribution of particles, which enables close packing of spherical or irregular shaped powders.

2.2.4 Particle Size

It has been suggested that powder particle size for injection moulding should be less than 20μm (6), and that an ideal mean particle size is between 2μm and 8μm (48). These values are relatively small in comparison to powders used with other powder moulding techniques. Small particles provide two advantages. Firstly, the fine size promotes a homogenous dispersion of the particles in a mixed feedstock, providing the correct combination of flow and viscosity conditions required for injection moulding. Secondly, a small particle size will sinter rapidly since the sintering rate is inversely proportional to the fourth power of the size (47).

Particle size is determined by measuring the dimensions of a particle, but differences can arise according to which method of measurement is employed and the chosen geometric parameters. There are many different procedures for measuring the size and distribution of particles, ranging from optical to streaming techniques, which use dispersed particles in a moving fluid (49). However, most particle size analysers use one geometric parameter and make the assumption of a spherical shape (37).

The simplest and most tedious method of analysis is the examination of particles with a scanning electron microscope (SEM). In this case, the observer would find it more difficult to analyse an irregular shaped particle because of the many different size parameters. It is also common to find disagreement between the SEM and alternative methods of measuring the particle size and distribution. Nevertheless, the SEM is considered to be an acceptable tool for measuring particle size when powders such as the ones used in this investigation do not have a wide geometric difference (50).

Particle sizes are often plotted as a histogram or a cumulative distribution. A histogram provides information about the spread of particle size over a sample, which can help determine whether the powder is useful for injection moulding. For example, a wide distribution typically defines a high packing density (37). However, a cumulative distribution provides a more convenient display of the data such as the mean particle size (d_{50}), and the percentage of powder at a certain size within a batch. Therefore, this type of analysis enables a direct comparison of powder batches.

2.2.5 Particle Shape

An ideal particle shape is difficult to identify, because desirable characteristics are often traded for other necessary attributes. For example, a spherical particle provides a high packing density that minimises the binder content, and reduces the sintering shrinkage. However, the resulting green part will have little strength and shape loss will occur during debinding and sintering because the particles are not mechanically inter-locked (50). On the other hand, an irregular shaped particle will result in a lower packing density and greater shrinkage when sintering, but irregularity promotes particle interlocking and thus a higher green strength and shape retention whilst sintering.

German identified an ideal particle shape with an aspect ratio ranging from 1.2 to 1.5 (y/x) (51). This ratio provides adequate particle interlocking, improving green strength whilst also offering a higher packing density than that experienced with a spherical particle.

Measurement of particle shape is usually accomplished using scanning electron or optical microscopy. Scanning electron microscopy is the preferred method for two reasons

(i) Resolutions are within the range of 5 and 15nm, which are two orders of magnitude smaller than the optical microscope.

(ii) SEMs have a greater depth of field than optical microscopes (providing enhanced 3-dimensional information)

2.2.6 Particle Packing Density

It is important to try and predict the loading capacity of a powder in order to achieve a green body that will de-bind and sinter without collapsing. A common technique for finding the loading capacity is the 'tapped density', which is based on the principle that all voids present between particles should be filled with a binder (52). Tap density is found by gently tapping 20g of powder in a graduated cylinder for 3000 cycles, according to BS EN 3953. Tapping of ceramic powder enables particles to

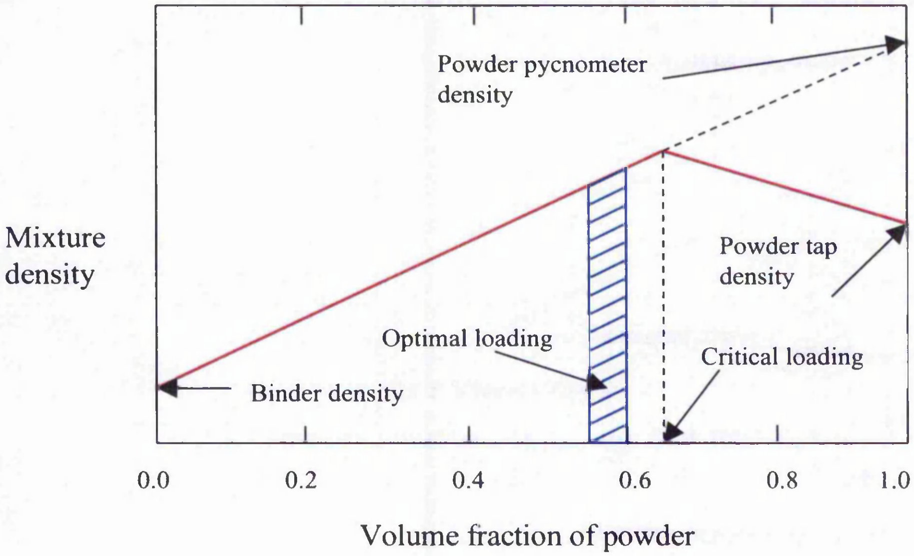


Figure 5. Relationship between powder density characteristics for a PIM feedstock

settle in a way that represents a comparison to the mixing process of powder to a binder.

The tapped density method is a useful tool that can determine approximately how much powder a binder can hold. However, a typical moulding operation promotes turbulent mixing that results in a higher powder compaction than that found from the tapped density. This compaction is found experimentally using torque rheometry. Powder is added to a binder in a torque rheometer until the mixing torque significantly increases. This point is known as the 'critical solids loading' and is defined as 'the point where the binder cannot support any more powder' (37). When a feedstock is designed for powder injection moulding, the packing density is reduced to a value a few percent less than the critical loading, known as the 'optimal loading' (figure 5). This reduction of loading helps the powder mix with the binder because the feedstock viscosity reduces exponentially from the critical loading point (53). Generally, a high solids loading is preferred, because ultimately less binder needs to be removed, and a high sintered density is normally achieved. However, a conduit heart valve requires a porosity to promote tissue growth between the powder particles. This can be achieved by reducing the solids loading, thus increasing the amount of open pores between particles when the binder is removed.

2.2.7 Alumina Powder Investigation

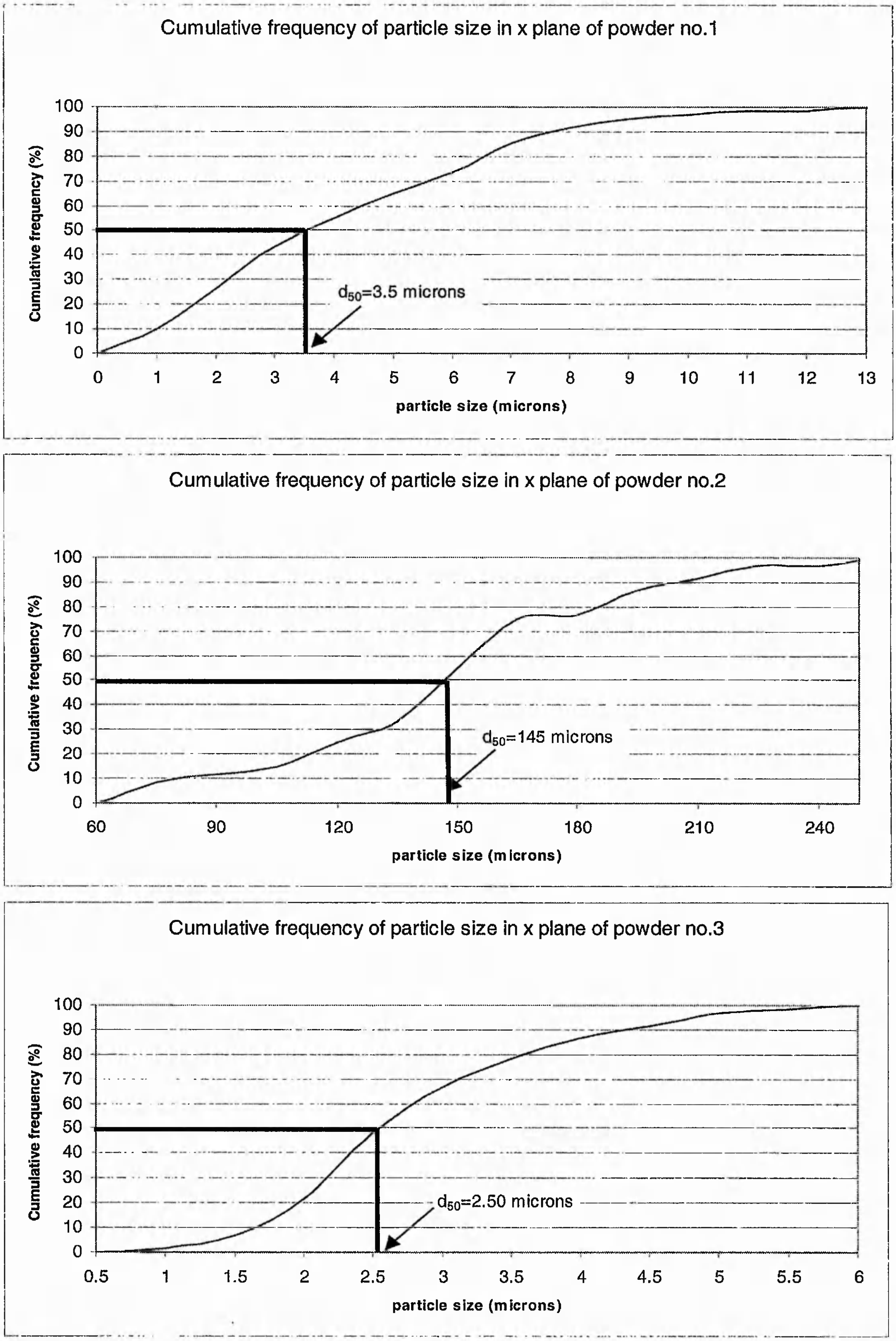
Three batches of alumina were selected with different geometric characteristics, and the size and shape of the powders were investigated using scanning electron microscopy. From the resulting plots, a number of particles (approximately 60) representing each batch were measured across the two most prominent geometric features, classed as x and y, which represented the shape of the particle. This data, tabled in appendix A, provided information about the size, distribution and shape of the three samples, as tabulated in table 1.

Table 1. Properties of alumina selected for study

No	*Purity (%)*	*Mean Particle Size x(µm)*	*Mean Particle Size y(µm)*	*y/x ratio*	*Solid Density (Kg/m^3)*	*Tap Density (of theoretical)*	*d_{50} x (µm)*	*Impurity*
1	99.80	4.6	6.5	1.74	3980	0.57	3.5	0.1% MgO
2	99.99	149	176	1.19	3980	0.59	145	N/a
3	99.80	3.0	4.2	1.48	3980	0.65	2.5	0.1% MgO

The y/x ratio, mean particle size, and median size (d_{50}) provided useful data for comparison between the three powders. Each powder had an acceptable purity (as discussed in section 2.2.2) but there were considerable differences between them in particle size and shape. Powder 3 appeared superior because its characteristics were between limits discussed in sections 2.2.4 and 2.2.5 and it could be expected to attain a higher packing density than the other powders. Powder 1 seemed to have an irregular, as opposed to rounded, shape that should provide a greater debound strength than the alternative powders.

The plots in figure 6 show the cumulative frequency distributions for the three powder types. From these graphs, the median particle size (d_{50}) was empirically determined. It was found that Powder 3 had a larger concentration of powder particles around the median value, whereas the other samples had more of a continuous distribution.



Cumulative frequency of particle size in x plane of powder no.1

Cumulative frequency of particle size in x plane of powder no.2

Cumulative frequency of particle size in x plane of powder no.3

Figure 6. Cumulative frequency distribution plots for powders 1, 2 and 3.

According to German (37), the packing density will improve when a powder has a wide, continuous distribution. However, powders that have this distribution *and* an irregular shape may not pack to a high density, unless they are compressed. Therefore, in theory, all three powders could mix to a low theoretical density, because of their characteristics including, size, shape and particle distribution. Nevertheless, this investigation required a powder that will sinter to a relatively low density, and hence, the tap density method was used to estimate the packing characteristics of the powder. The apparatus for measuring tap density is rather specialised and difficult to obtain, so a rig was developed, according to British Standard. Appendix B contains the technical drawings, and figure 7 shows the rig with alumina being investigated.

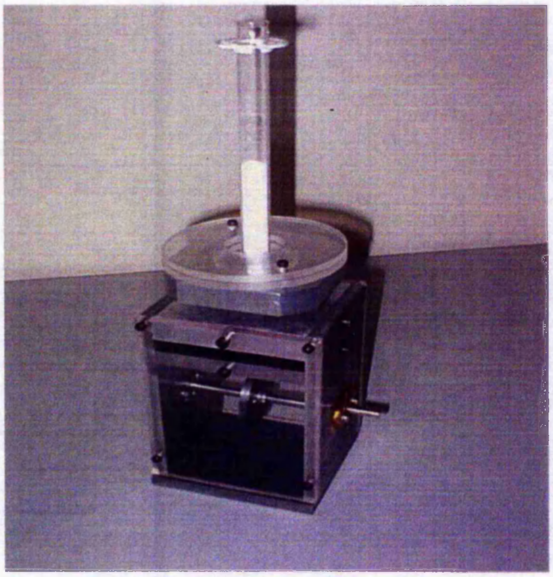


Figure 7. Tap density apparatus

The results were quite conclusive (table 1), showing that Powder 3 should pack to the highest density, and Powders 1 and 2 were quite similar. This type of investigation is acceptable, but much generalised, as it does not take account of factors such as powder agglomeration, and consistency of powder batches. However, the results were useful for deciding which powder may be the most desirable for the heart valve feedstock.

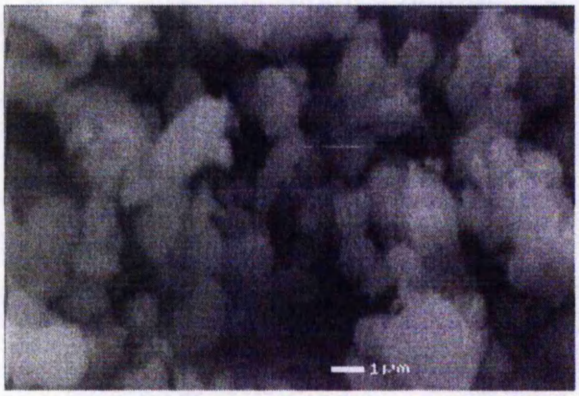


Figure 8. Scanning electron microscopy image of Powder 3

Figure 8 shows a SEM image of Powder 3, from which it can be seen how the particles tend to be more rounded and distributed between limits defined in table 1.

2.3 Binders

2.3.1 Background

The binder is described as a vehicle for packing ceramic or metallic powders into a desired shape and then holding the particles in that shape until the initialisation of sintering. Binders are mixed with ceramic powder to form a feedstock that is then moulded. Within this process, the binder influences particle packing, agglomeration, mixing, rheology, moulding, debinding, dimensional accuracy, and defects (37). Nevertheless, one binder alone may not satisfy all requirements (for example, a binder may provide perfect rheological properties for moulding, but debinding may take days because of the binder degradation process) and a combination of binders is normally used (54-65).

2.3.2 Binder Requirements

The choice of binder is influenced by parameters such as flow characteristics, powder interaction, debinding and manufacturing. Table 2, details these parameters and requirements of the binder to develop a successful moulding process (66-67).

Table 2. Binder attributes

Flow characteristics	Viscosity below 10 Pa.s at the moulding temperature
	Low viscosity change with temperature during moulding
	Strong and rigid after cooling (or curing)
	Small molecule to fit between particles
Powder interaction	Low contact angle and good adhesion with powder
	Chemically passive with respect to powder
Debinding	Noncorrosive, nontoxic decomposition product
	Decomposition temperature above moulding and mixing temperature
Manufacturing	Inexpensive and available
	Safe and environmentally acceptable
	Not degraded by cyclic heating (reusable)
	High strength and stiffness
	High thermal conductivity
	Low thermal expansion coefficient
	Soluble in common solvents
	Short chain length

A primary requirement is that the binder will allow flow and packing of powder into a die cavity. Therefore, it is mandatory that the binder ‘wets’ the surface of all the powder particles in a given feedstock. Various chemicals such as stearic acid are available to help complete this task, and also reduce the overall mixture viscosity (68-71). However, some binders such as those used in reactive moulding do not require processing aids, because the binder/powder mixtures are processed at a relatively low temperature, thus maintaining a consistently low viscosity.

The rheological characteristics of the binder have a large effect on the moulding temperature and solid content, hence there is a range of viscosity for binder systems, so that powders can remain dispersed whilst moulding. For a given solids content, a low mixture viscosity usually correlates with a low binder viscosity (37). Wax binders are typically used because of their low molecular weight, but because wax tends to promote agglomeration of particles at high solids content, other binder components are mixed with the wax to create a composite system.

Binder systems usually consist of two components: a low viscosity wax and a polymeric component for extra strength. This can lead to rheological problems, because polymeric binders are usually quite viscous and a compromise has to be made when the constituents are mixed. If the viscosity is too low, then the powder and binder could separate during moulding, leading to a deformed part due to density gradients. A reactive binder such as cyanoacrylate may avoid these problems for three reasons: firstly, the binder is a one component system, not compromised by another material's characteristics; secondly, the viscosity is relatively low; and finally, the binder has a high adhesive strength.

Powder injection moulding depends upon the binder viscosity increasing as the polymer melt cools when formed in a cold mould. This constitutes a large change in viscosity with temperature, which is detrimental to the control process of moulding. On the other hand, a reaction moulding process such as PRIME relies on a chemical reaction within the mould to increase the binder viscosity, and this method considerably simplifies process control whilst moulding.

The PIM binder must be designed to minimise debinding time. Typically, wax and a polymeric binder are used, the former having a lower melting temperature. When heated, the wax is removed to partially open pores at the surface of the moulding, whilst the polymeric binder holds the particles in place and maintains integrity of form. Eventually, the remaining binder vaporises through the open pores created by the wax as the debinding temperature is increased. This process is common, because it is quicker than a single component system but debinding time is still relatively lengthy and much work is being done to reduce it (72-75). On the other hand, the cyanoacrylate monomers used in PRIME technology enable rapid debinding in comparison to the typical polymeric systems used with powder injection moulding. This is because cyanoacrylate molecules are small enough to pass through the powder matrix to the surface without damaging the component structure (36). The debinding technique is discussed further in chapter 5.

2.3.3 Characteristics

There are generally five types of binder system, the most common being polymeric (37). These are categorised as:

- Water based
- Inorganic systems
- Gellation systems
- Thermosetting polymers
- Thermoplastics

Water based binders are normally used in freezing processes (76), where the organic vehicle is simply removed by heating the component. This method allows the feedstock to be formed at a low temperature, thus simplifying a typical moulding process, which normally requires heating to soften the binder. It is usual for the binder to include a small quantity of wax, to increase green strength and reduce slumping when the binder is thermally removed.

A typical organic binder system, commonly known as 'the rivers process' (77), involves mixing a ceramic or metallic powder with methyl-cellulose and water. These components are then *cold moulded* into a warm mould where the binder begins to gel, followed by a drying process to evaporate the water content of the binder and leave open porosity through which the gaseous decomposition products of the organic binder escape.

Thermosetting binders function by cross-linking polymer units at elevated temperatures. They have a high strength when cross-linked, thus providing a high green strength, which is helpful for maintaining shape during debinding. But although thermosets are useful for their strength properties, they are not practical: once linked, the reaction is irreversible and the polymer units cannot be separated; the process is quite slow; the catalyst used to instigate reaction causes problems at the mixing stage of production; and debinding periods are much greater than those of thermoplastic binders, because of the lengthy degradation process common with all thermosetting polymers. Accordingly, the use of thermosets is considered to be unsuccessful (37), and thermoplastics are generally used more frequently.

Thermoplastics are the most commonly used and best understood binders in powder injection moulding (PIM). Unlike thermosetting polymers, thermoplastics used in PIM do not cross link with increased temperature. Thermoplastic binders are heated before moulding, because the feedstock has to be fluid to transfer the ceramic powder through a die into the mould, and the binder must include additives, such as lubrication agents, viscosity controllers, wetting and debinding agents, to maintain the viscosity at a mouldable level. When heated, these binders experience a change in mechanical properties at the glass transition temperature (Tg), including the coefficient of thermal expansion, and an increase in volume. Further heating will melt the polymer at a temperature dependent on the molecular weight. These property changes can cause problems when debinding components. For example, the increase in volume effected by the glass transition and melting temperatures will crack components when the binder is removed, unless the heating rate is maintained at a low level. Debinding of thermoplastics is the lengthiest part of the PIM process, and many attempts have been made to improve it as detailed in section 2.3.2. Each binder has limitations, and methods have been developed to address some of the most common problems, such as debinding times, by using novel binders with a reactive moulding process (36,38).

Reactive binders are monomers that have a low enough viscosity to enable mixed powder to be transported through the moulding cycle, whilst the feedstock remains fluid. Before moulding, either a catalyst is added to the feedstock or initiation is influenced in the mould (if pre-mixed), so that a reaction occurs to polymerise the monomer. This is considered to be a revolutionary step in moulding technology, because it eradicates many problems associated with binders, such as moulding temperature dependency, and the use of complex techniques for debinding mechanisms. Feedstock designed for reaction moulding includes a single component binder that is fluid at room temperature within desired viscosity limits required for moulding. Other organic binder systems such as ones that are water based can also exhibit these properties, but they do not have the polymeric properties of strength, which are features of reactive binders.

2.3.4 Reactive Binders

2.3.4.1 Background

Reactive monomers have the potential to simplify a moulding process and increase production rates by eradicating the need for complex controls. It is the intention of this investigation to determine a reactive monomer that will suitably mix with aluminium oxide powder to a high enough volume to mould a ceramic heart valve.

Two common reactive monomers are methyl methacrylate (MMA) and cyanoacrylate, which both satisfy requirements for moulding as detailed in section 2.3.3. These chemicals were investigated to determine which would be the most effective for powder reaction moulding, and in particular as a binder for the conduit heart valve. The investigation was conducted empirically, and is detailed in section 2.4. However, the remainder of this section will discuss the theory of polymerisation, depolymerisation and the physical properties of these monomers.

2.3.4.2 Methyl Methacrylate

Generally, methyl methacrylate (MMA) is used by industry to cast large sheets of PMMA (or Perspex), which is used in many applications, most commonly for its superior optical qualities. MMA is also used in specialist applications as a fluid binder for casting dispersed poly-methyl methacrylate (PMMA) granules. This type of casting is principally applied in the medical sector, to form dental implants or acrylic bone cements for fixation prosthetics in orthopaedics. In the case of a total hip replacement, for example, the bone cement is inserted in a femoral axial cavity drilled by the surgeon and acts as a bonding agent between the prosthesis and the bone (78).

PMMA is also used in powder injection moulding as part of a multi-component binder system. Typically, 30% PMMA is dispersed in a formulation containing approximately 70% polyethyleneglycol (PEG), and moulded at 140°C (35). This binder combination has many advantages over other typical thermoplastic systems, mainly because PMMA can thermally degrade within two hours compared to a typical polymeric debinding time of twelve hours (35).

2.3.4.3 Polymerisation

Methyl methacrylate (MMA) is a common, relatively inexpensive monomer with ideal properties as an injection moulding binder, as detailed in table 3.

Table 3. Properties of methyl methacrylate

Physical property	***Typical Value***
Molecular weight	100.1
Boiling point	100.5°C
Freezing point	-48°C
Density	949 kg/m^3
Viscosity @ 25°C	0.66x10^{-6} m^2/sec (0.00063 Pa.s)
Specific heat	2.02 kJ/kg/°C
Thermal conductivity	0.1488 W/m^2/°C

The conversion of liquid acrylic monomers to solid polymers (polymerisation) can be initiated by the use of ultra-violet light, heat, high-energy radiation, or by the action of a catalyst. To prevent an unwanted reaction in commercial use, the monomer is supplied with an inhibitor, such as hydroquinone or topanol, at strengths up to 0.1% (79) by volume. The inhibitor must be depleted before polymerisation can commence, which is normally achieved by distillation or by washing the monomer with an alkaline solution (79).

There are three types of chemical species that can be used to polymerise methyl methacrylate (80):

- *Strongly acidic cations*

  As obtained from compounds such as boron triflouride
- *Strongly basic anions*

  As obtained from organometallic compounds such as butyl lithium
- *Free radicals*

  As obtained by decomposing a thermally unstable compound such as benzoyl peroxide

The most common method is free radical polymerisation, as the alternatives require a more carefully controlled technique. Polymerisation is initiated by free radicals that are produced from the decomposition of a catalyst such as benzoyl peroxide when it is heated. These radicals then react with monomer molecules, forming polymer chains, which are repeated until an event causes a chain end termination. The concentration of the catalyst and the rate of free radical production determine the polymerisation rate. The reaction is normally performed within a vacuum, because the presence of oxygen will influence the rate of reaction owing to the formation of methacrylate peroxides in a side reaction (80).

It has been observed that when MMA is heated in the presence of a catalyst, 'auto acceleration' affects the rate of reaction after about 20% of the monomer has been converted (79). This acceleration is commonly known as 'the gel effect' and is associated with a reduction in the rate of chain end termination reactions during conversion. A decrease in the termination rate will inevitably lead to an increase in both overall conversion rate and molecular weight, but as the mixture becomes more viscous there is less mobility of the chain end radicals, leading to a mutual termination reaction. However, smaller monomer molecules are not affected by diffusion at moderate conversions, and propagation reactions continue until the material becomes semi-solid. The gel effect could, therefore, be induced by addition of a powdered substance such as PMMA or alumina because this would also increase the viscosity of the system.

The gel effect and the associated characteristics of polymerisation are best shown by a reaction plot (81), as shown in figure 9.

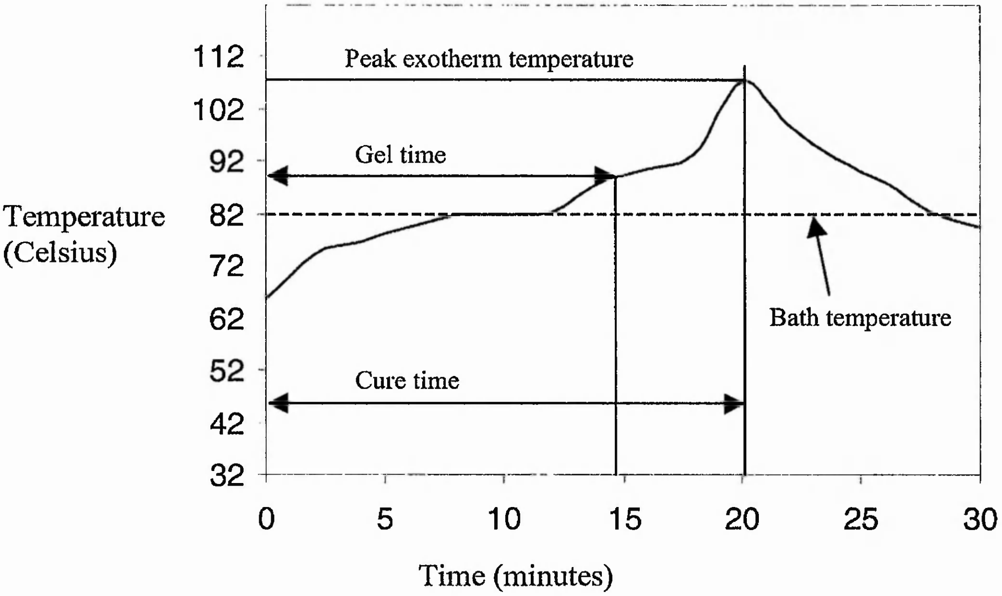


Figure 9. Typical characterisation curve for methyl methacrylate

Depolymerisation of MMA produces volatile molecular fragments that are all virtually monomeric (35), and potentially the monomer can be collected and re-cycled. However, a problem with using MMA as a binder is that when it is thermally degraded from a green body, the monomer is in its gaseous state at the burnout temperature, making it difficult to collect. Condensing the vapours could ease the collection of monomers, but this is considered impractical for small-scale production.

There are two further potential problems with MMA as a reactive binder. Firstly, the rate of shrinkage after conversion from monomer to polymer can be as high as 20%. Secondly, the curing process is exothermic which adds an extra, but controllable, variable to the processing. If this monomer were to be selected as the most efficient in comparison to cyanoacrylate, these two problems could be minimised by adjusting the processing procedure.

2.3.5.2 Methyl Methacrylate Polymerisation Investigation

The aims of this investigation were to:

- Observe the different reaction characteristics using two types of inhibited methyl methacrylate
- Observe the effects of a catalytic initiator
- Find polymerisation times of methyl methacrylate with varying initiator concentrations
- Find the most efficient ratio of initiator to monomer
- Produce plots of reaction profiles to enable a comparison between the data

The polymerisation characteristics of methyl methacrylate were investigated using benzoyl peroxide as a free radical initiator. Two types of stabilised MMA were studied, the first being a topanol (0.05% by volume) and the second a hydroquinone (0.1% by volume). Both types of monomer were initiated by bulk polymerisation, using a range of initiator concentrations by volume; these were, 0.1%, 0.3%, 0.5%, 0.7%, 1%, 2% & 3%.

The first stage involved dissolving benzoyl peroxide into the monomer. 6cm^3 of MMA was placed in a test tube and suspended in a water bath at 90°C, whilst a measure of benzoyl peroxide (initiator concentration) was dissolved whilst stirring. This operation was stopped after one minute as otherwise too many free radicals would be produced, causing an uncontrollable polymerisation. Finally, the mixture was poured in to a polymeric mould and placed in an oven at 80°C. The sample and ambient oven temperatures were measured by thermocouples and transmitted to a workstation through an analogue to digital converter. The experimental setup is shown in figure 10.

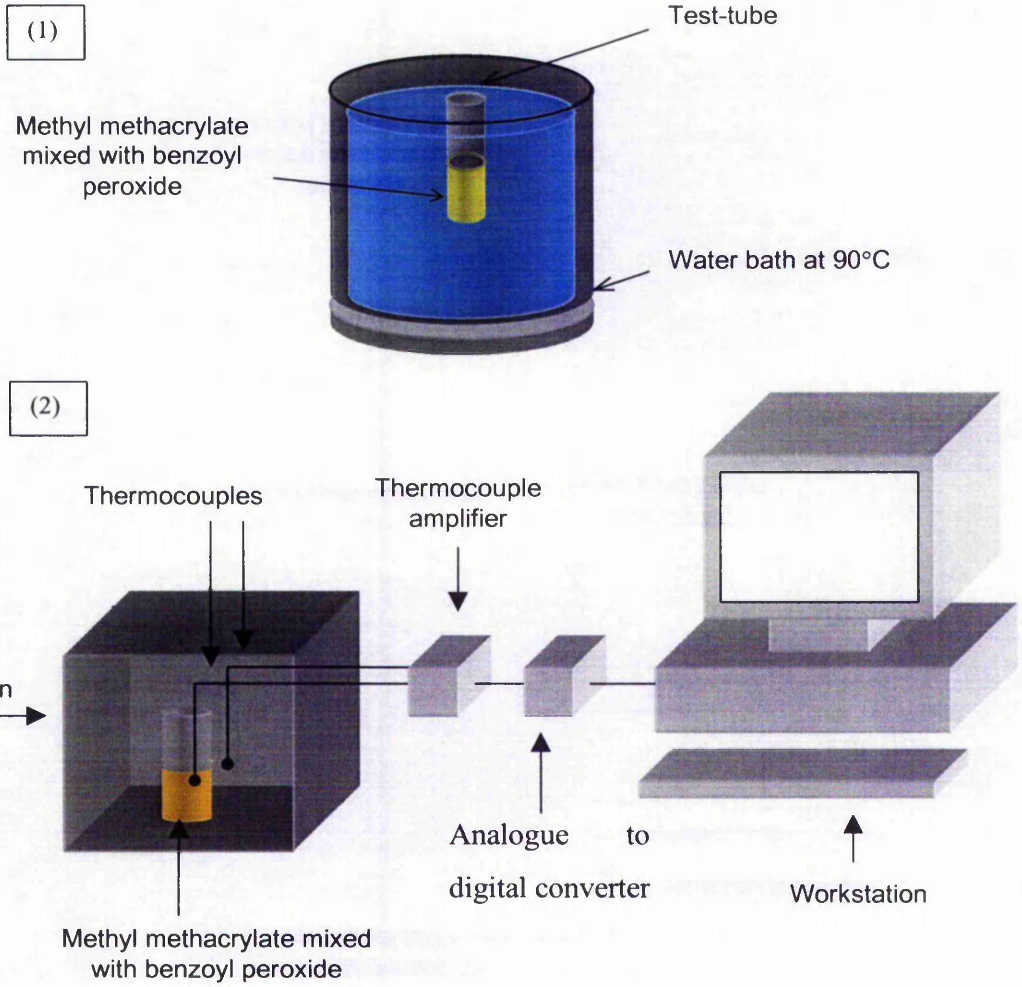


Figure 10. (1) Method for dissolving benzoyl peroxide and (2) Apparatus for monitoring temperature against time for polymerisation

The reaction time (which was defined as the time to reach the peak exothermal rise) was plotted against catalyst concentration for both types of inhibitor, as shown in figure 11.

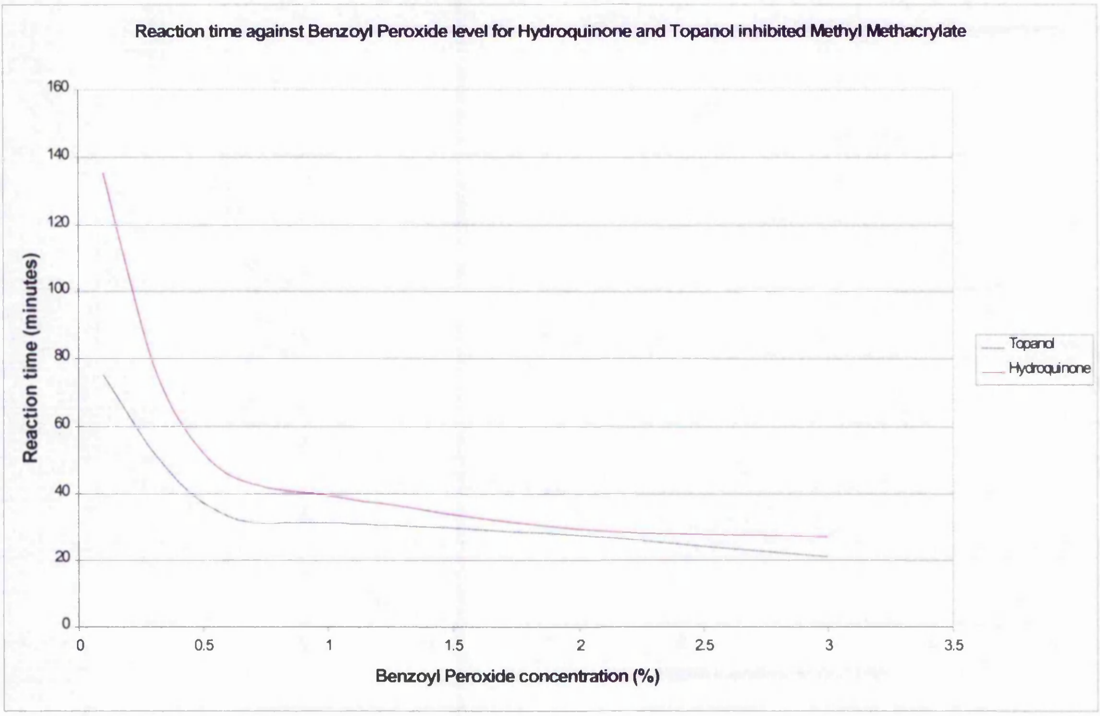


Figure 11. Reaction times for two types of inhibited methyl methacrylate

It can be seen that the topanol inhibited MMA reacted faster at lower concentrations of catalyst, whilst at concentrations greater than 1.5% there was a similarity in the trend. This phenomenon was probably related to the fact that there was less of a concentration of topanol than hydroquinone in the MMA, hence the topanol inhibitor was depleted faster. On the other hand, at inhibitor concentrations exceeding 1.5%, there was possibly a saturation of catalyst, which would tend not to affect the reaction period.

Figure 12 shows the reaction temperature against time for the hydroquinone inhibited MMA at concentrations of catalyst ranging from 0.1% to 3% by volume of binder. It can be seen that each reaction profile was similar to the standard reaction profile of (MMA) as shown in figure 9. Each reaction followed the same trend when the monomer heated up to the oven temperature, which followed a period (gel period) during which the temperature of the monomer remained largely constant. It was believed that within this period, the inhibitor (or stabilizer) was being depleted and a small conversion of monomer to polymer was taking place. A peak exothermic temperature followed this gel period, which determined complete conversion from monomer to polymer. The topanol inhibited samples experienced a second exothermic peak at catalyst concentrations greater than 0.3%, which is shown in figure 13. It was thought that this observation could be associated with the auto-acceleration effect.

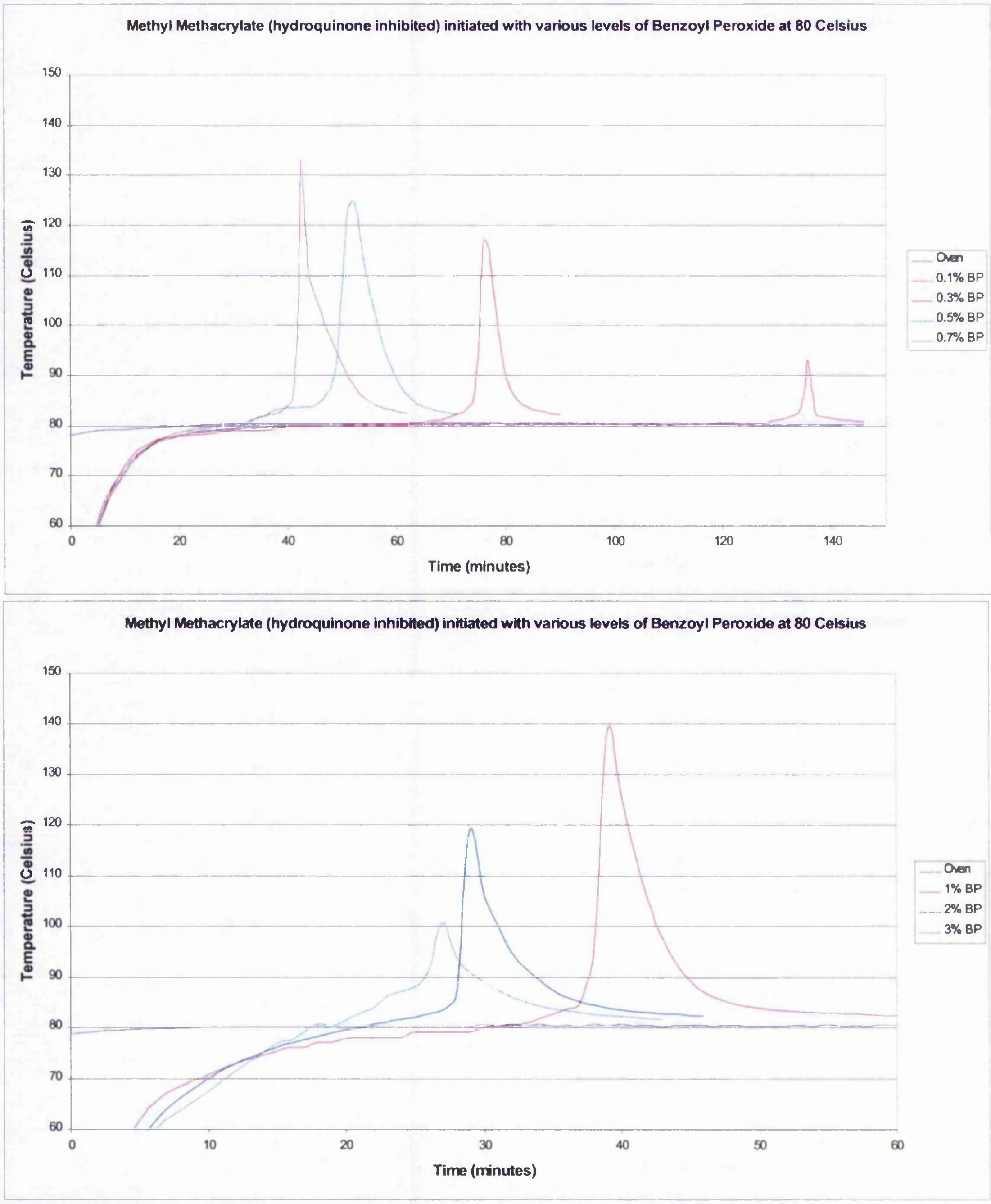
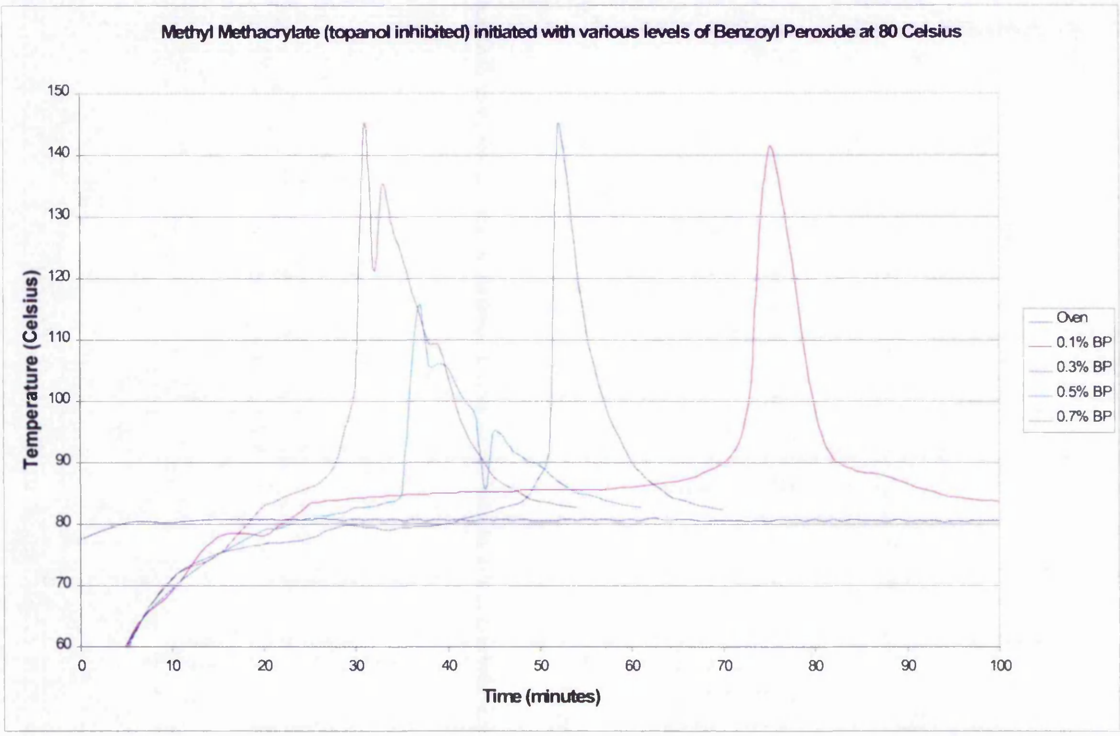


Figure 12. Reaction plots for hydroquinone inhibited methyl methacrylate initiated with benzoyl peroxide



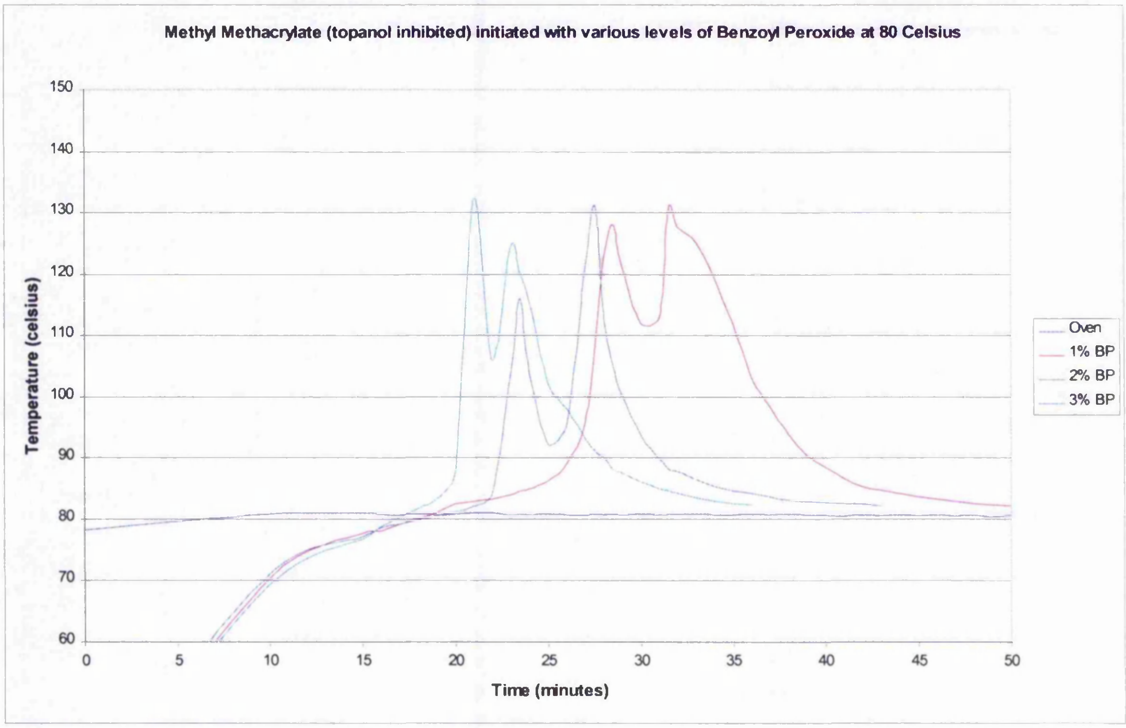


Figure 13. Reaction plots for topanol inhibited methyl methacrylate initiated with benzoyl peroxide

This investigation confirmed the previous suggestion that extra catalyst reduced polymerisation time by the production of extra free radicals. This is evidenced in figures 12 &13, which show that the greater the concentration of catalyst the shorter the polymerisation time became.

The temperature rise associated with the gel effect was observed to have no connection with the quantity of catalyst. Furthermore, the boiling point of MMA was 100.5°C and whenever an exothermic reaction temperature increased over this value the sample boiled whilst it polymerised, producing a sample full of air pockets. The method was modified to control this effect, by decreasing the polymerisation temperature.

The oven temperature was reduced to 70°C to help reduce the boiling effect observed with samples polymerised at 80°C. Two samples were mixed, the first with a high concentration of catalyst, the second with a low, to investigate the reaction time. The sample with a high level of catalyst reached a peak temperature greater than 100.5°C, and hence boiled as shown in figure 14, but the peak reaction temperature was found to be independent of the catalyst concentration, suggesting that the polymerisation temperature should be reduced further to prevent this effect.

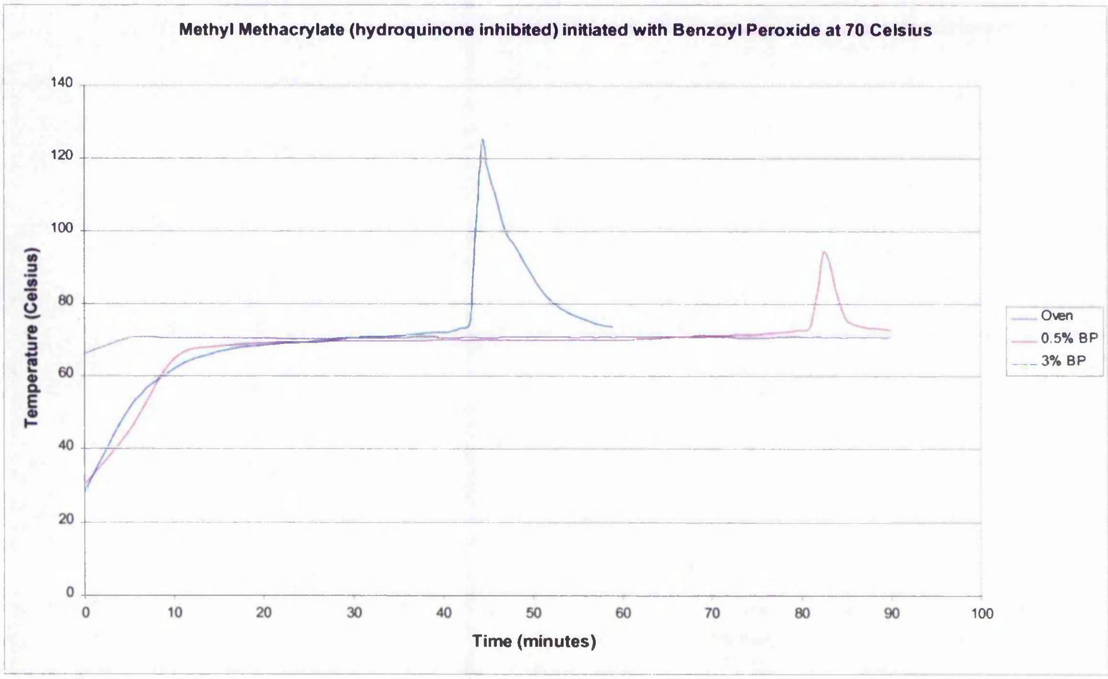


Figure 14. Reaction of hydroquinone inhibited methyl methacrylate initiated by benzoyl peroxide at 70°C

The reaction time was increased significantly when the polymerisation temperature was reduced, suggesting that MMA may be impractical as a binder. This suggestion was not sufficient to dismiss MMA from this study, however, because the reaction kinetics may change substantially when a powder, such as alumina, is mixed with the monomer.

2.3.4.5 Cyanoacrylate

The development of cyanoacrylates can be traced back to wartime research at Eastman Kodak (38). Their use as adhesives only became of commercial importance in the 1970s, when they were marketed as 'Super Glue'. In the 1990s, cyanoacrylate adhesives are used in a wide range of industries, ranging from the assembly of complex electronic components to 'cottage industries' where products such as lampshades are made.

The success of cyanoacrylate has derived from the variety of substrates it can adhere to, including most of the industrial plastics, rubbers, wood, metal, fabric, and leather, and many different formulations have been developed by adjusting the viscosity.

Advantages of cyanoacrylate adhesives include (39):

- Versatility in the wide range of adherents with which they can be used
- Extreme rapidity of cure under very light pressure
- Very high tensile and shear strength of the bonds
- Low fire and toxic hazards because no solvents are involved
- Ease of application, because the adhesive is a one component system requiring no mixing

On the other hand, cyanoacrylate adhesives have some commercial disadvantages:

- Poor heat resistance
- Poor moisture resistance

- Poor peel and impact resistance
- Susceptible to acidic or very dry substrate surface conditions
- Relatively short shelf life

In the context of reaction moulding technology, however, some of these commercial disadvantages become positive benefits. For example, poor heat resistance enables the debinding process to initiate more rapidly than a conventional binder does, and acidic surfaces can prevent the propagation of polymerisation.

Three types of cyanoacrylate are commercially available: butyl-, ethyl-, and methyl-. Each type exhibits different mechanical properties and there is a large range of viscosity between them, methyl being the most viscous, and butyl the least. Butyl-Cyanoacrylate was selected based on its lowered viscosity, so that it would conform to Germans standards for a binder (section 2.3.2). The monomers' physical properties are listed in table 4 (the amount of information from the supplier is limited).

Table 4. Properties of cyanoacrylate monomers

Physical property	*Value*
Viscosity	
Butyl	20 cps (0.02 Pa.s)
Ethyl	1100 cps (1.1 Pa.s)
Methyl	2000 cps (2.0 Pa.s)
Density (All)	1050 Kg/m^3

2.3.4.6 Cyanoacrylate Polymerisation

Cyanoacrylates are a highly reactive species that can readily polymerise through anionic addition across the carbon-carbon double bond, as illustrated in figure 15.

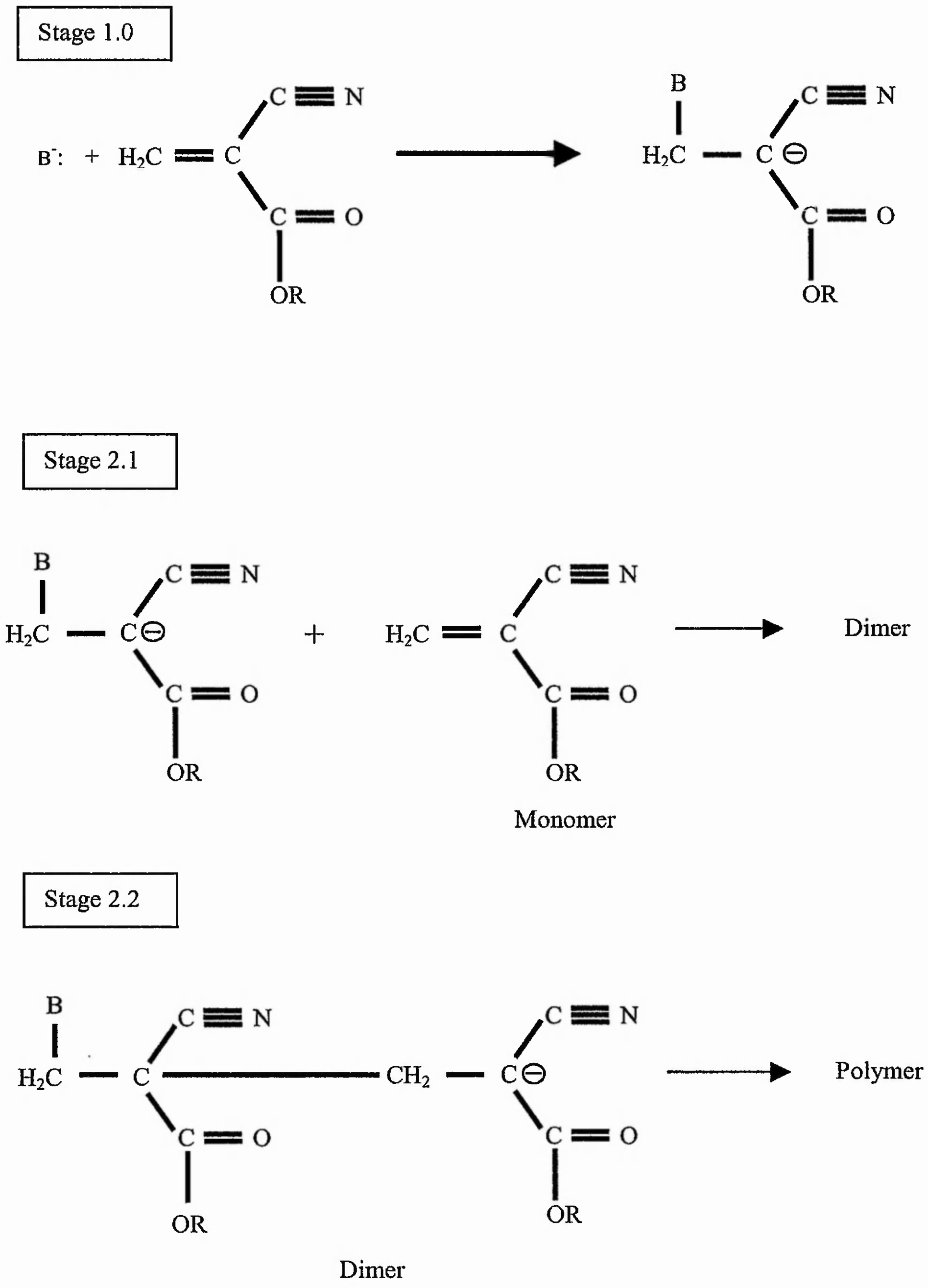


Figure 15. Stages of polymerisation for cyanoacrylate

A weak electron donor molecule (Lewis base) is capable of forming an anionic species by nucleophilic addition (as shown in stage 1). The product of this addition then reacts with a monomer (stage 2.1) to produce a dimer unit (stage 2.2). Finally, the dimer reacts with additional monomers to form a long polymer chain, which can have a molecular weight within the range of 10^5 to 10^7 (39). Cyanoacrylate will readily polymerise with only a relatively weak electron donor, such as water, and a film of moisture that is usually present on surfaces is sufficient to initiate a reaction.

Cooke demonstrated that the ionic species of a cyanoacrylate monomer is blocked by a hydrogen ion from an acid, and suggested that an acid would prevent polymerisation at a pH less than 5.5 (39). Hence, weak acids such as carboxylic are used to inhibit the monomer throughout storage. Initiation of polymerisation therefore requires a base to neutralise this acid, with free surface moisture being a suitable catalyst. Birkinshaw has found potentially suitable surface catalysts that include caffeine, pyridine, and t-butylamine (36).

If the cyanoacrylate were to be used as a binder then the polymerisation reaction would need to be delayed until the feedstock had been moulded. A strong acid used in quantities starting at 0.1% by volume dissolved into the monomer solution delayed a reaction, even if a base such as surface moisture was introduced. P-toluene sulphonic acid was found to be capable of preventing reactions, and, provided that a strong base initiator was not introduced to the monomer, delayed inhibition for hours when used in strengths greater than 0.1% (36).

Investigations have been carried out into the thermal degradation effects of butyl-cyanoacrylate monomer (82). The mechanism of depolymerisation (unzipping) was considered as ‘chain end activated’, with a zip length greater than that for polymerisation. Unzipping was rapid at temperatures greater than 180°C, and the rate was determined by the initiating species. A thermogravimetric analyser and differential scanning calorimeter device have been used to determine the kinetics of debinding the feedstock used within this investigation, which is discussed in Chapter 5.

When cyanoacrylate breaks down throughout the debinding process, the monomer could be recaptured and recycled by exhausting the vapour through water to polymerise the monomer. A different process could ‘degrade’ the polymer in a controlled environment to be recovered as monomer. This is discussed in chapter 5.

2.4 Mixing

2.4.1 Background

Mixing is the initial stage of creating a feedstock for moulding, and it is essential that the quality of the feedstock is established at this stage, since deficiencies cannot be corrected by subsequent processing adjustments.

The homogeneity of the feedstock is a prime concern when mixing, since uniform quantities of the binder and powder are required throughout the mixture. This could be difficult to achieve if the powder particles are very small, and intensive mixing is therefore required to cover every particulate surface with binder.

Three generalised rules of mixing feedstock for the powder injection process are to:

(1) Coat the particles of powder with binder
(2) Break up agglomerates
(3) Attain uniform distributions of binder and powder throughout the feedstock

Rules (1) and (3) are quite self-explanatory and were followed. In respect of rule (2), however, it was considered to be unnecessary to break up agglomerates to produce a successful feedstock for the heart valve, since voids caused by agglomeration may help to provide the desired porosity. Normally, agglomerates are caused by weak attraction of small particles (Van der Vaals forces), and can prevent dense packing of particles whilst mixing (83). This attractive force between particles can contribute to voids within the part, and it was thought that these voids would reduce the final sintered density, but enhance the apparent porosity level within the process. For this same reason, dispersants such as stearates were not used in the feedstock.

Commercial mixers are designed with two or more mixing elements to cope with the high and low shear rates required to homogeneously mix a powder into a binder. When mixing a system that has a high viscosity, considerable amounts of energy and torque are required to disperse agglomerates and induce bulk flow. The type of mixer used is dependent upon the rheological properties of the feedstock, whereas the apparent viscosity decides which mixing method should be used, as shown in figure 16 (24). In order to avoid the introduction of air into the mixture, which can cause defects when moulded, a mechanical type of mixer is usually operated within a vacuum. An MMA binder would appear to be suited to this type of mixing since its physical properties compare to other polymeric binders, but as cyanoacrylate is technically an adhesive, a standard commercial mixer could not be used.

Mixing was therefore performed manually, because of the chemical limitation of the cyanoacrylate binder, and without a vacuum. This introduced an advantage, in that the air entrapped by the feedstock when mixed could contribute to an inherent porosity.

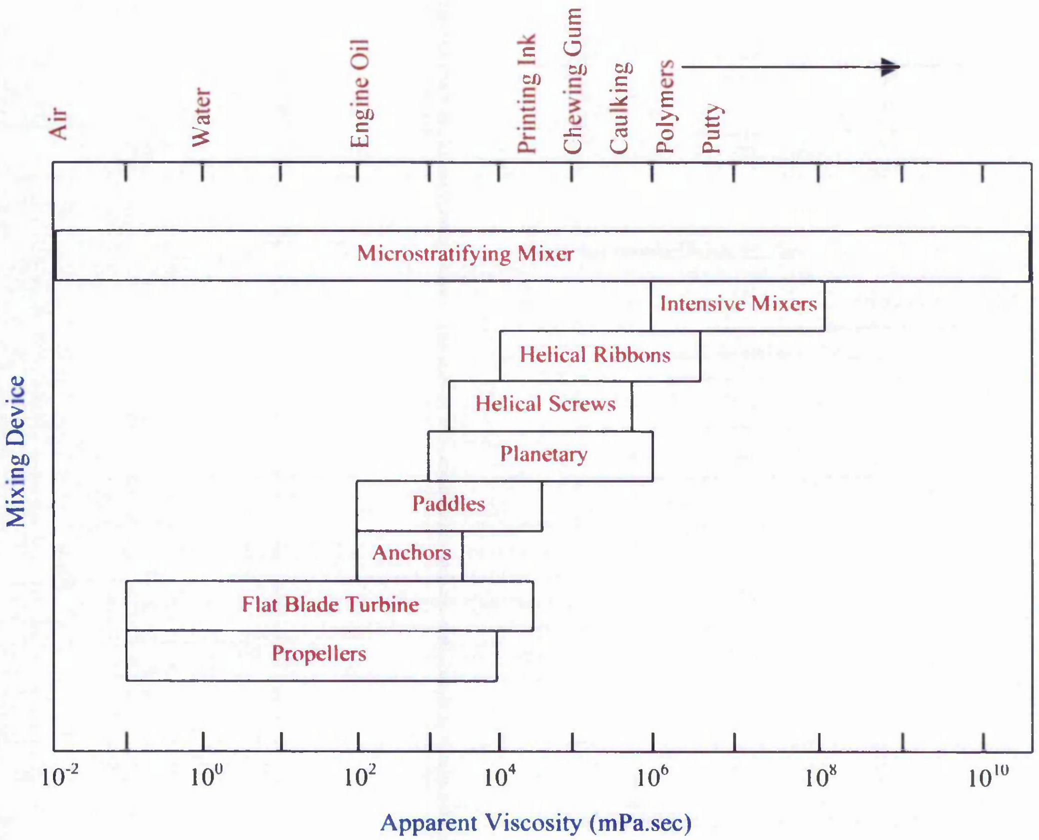


Figure 16. Working ranges of mixes used for PIM

$$vf = \frac{b}{b+a} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (1)$$

Where,

Vf = *Volume fraction of powder to binder (n/a)*

a = *Volume of binder (m^3)*

b = *Volume of powder (m^3)*

It was convenient to use a standard measure of quantities when discussing mixed feedstock, and the simplest method of expressing units was to use the volume fraction of powder to binder. An equation for finding this relationship is shown as equation (1).

The volume fraction of powder was required to be sufficiently high so that components could be successfully sintered. German (37) had suggested that the range of *vf* should be between 0.45 and 0.85 (approximately). If this level was not achievable then a change of powder or binder was necessary.

The next section describes the mixed properties of each binder with alumina, and a binder selection was made based mainly on the highest attainable volume fraction. In order to reduce the amount of experimental variables, the mixing investigations with both MMA and cyanoacrylate binders used Powder No 1 (table 1).

2.4.2 Methyl Methacrylate and Alumina

Two types of stabilised methyl methacrylate have been investigated, as described in section 2.3.4.4. It would be beneficial to choose the inhibited monomer that promoted the fastest reaction, since this would reduce processing times, but there was little difference between them, as shown in figure 11. In practice, the topanol stabilised MMA was selected for use in this investigation.

The aims of the mixing investigation were to:

- observe the behaviour of the reactive monomer when mixed with alumina powder
- observe the effects of temperature on processing
- find the maximum volume fraction of alumina powder that can be added to methyl methacrylate
- see how reaction times are affected when a powder is added
- discover whether MMA is suitable as a PRIME binder with alumina

Table 5. Samples created with MMA and alumina

Powder No	*vf*	*Curing Temperature (°C)*	*Benzoyl peroxide (%)*	*Peak Temperature (°C)**	*Curing Time (m)*	*Observations*
1	0.20	80	0.5	91.4	80	No problems
1	0.20	80	0.7	87.2	55	No problems
1	0.20	80	3.0	95.9	45	No problems
1	0.33	80	0.5	80.2	<100	No peak noticed but polymerised within 100 minutes. Powder not fully bound by monomer, difficult to mix, probably at critical loading
1	0.40	80	0.5	N/A	N/A	Vf too high, not enough binder to contain powder, crumbly mixture
1	0.40	80	3	N/A	N/A	Vf too high, not enough binder to contain powder, crumbly mixture
1	0.50	80	0.5	N/A	N/A	Could not mix, vf too high
1	0.50	80	3.0	N/A	N/A	Could not mix, vf too high
1	0.25	90	1.0	114.6	18	Sample contained voids, as peak temperature is greater than boiling point
1	0.30	90	3.0	97.3	12	Fast reaction, peak temperature very close to boiling point of monomer

**Peak exothermic temperature rise*

The method of preparing a mixture was similar to the experimental procedure in section 2.3.5.2, except that powder was introduced to the mixture prior to casting. Quantities varying up to 3% by volume of benzoyl peroxide were dissolved for 60 seconds into 6cm^3 of topanol inhibited monomer solution at 90°C, to instigate a reaction. Dissolving time was limited to 60 seconds to prevent the reaction7 becoming autocatalytic whilst mixing. Alumina powder was manually mixed into the monomer solution at various volume fractions, starting at 0.2vf, until the critical loading level was reached. The reaction was investigated whilst monitoring the ambient and sample temperatures by thermocouple, after placing the samples into an oven at 80°C.

The effects of changing the curing temperature to 90°C were also investigated. If a higher curing temperature could successfully cure the mixture without an exothermic rise above 100°C, then processing time will be improved, because the curing time is related to the curing temperature, as discussed in section 2.3.4.4.

Table 5 details the curing time and exothermic rise associated with a selection of samples with various volume fractions. In all cases at 0.2vf, samples exhibited an exothermic reaction temperature, fortunately below the boiling temperature of MMA. This could be because the combined mass and sample size was greater when the alumina was included, affecting the thermal conductivity so that heat may not have been transmitted as effectively throughout the compact.

The volume fraction of 0.2 was below the limit for moulding acceptable green parts, as the component would collapse if the binder were thermally degraded. Therefore increasing the volume fraction of alumina powder was vital to guarantee the structural properties required for a green part.

The maximum volume fraction that could be achieved by manual mixing samples was 0.3. Either the mixture level was close to the critical loading volume or there was an incompatibility between the powder and binder. Mixture concentrations greater than this could not be mixed with current techniques because the solution became too viscous to realistically continue. There were two possible explanations for this rise in viscosity. Firstly, polymerisation could be occurring when the catalyst was dissolved into the solution; secondly, MMA may be chemically incompatible with the investigated samples of alumina.

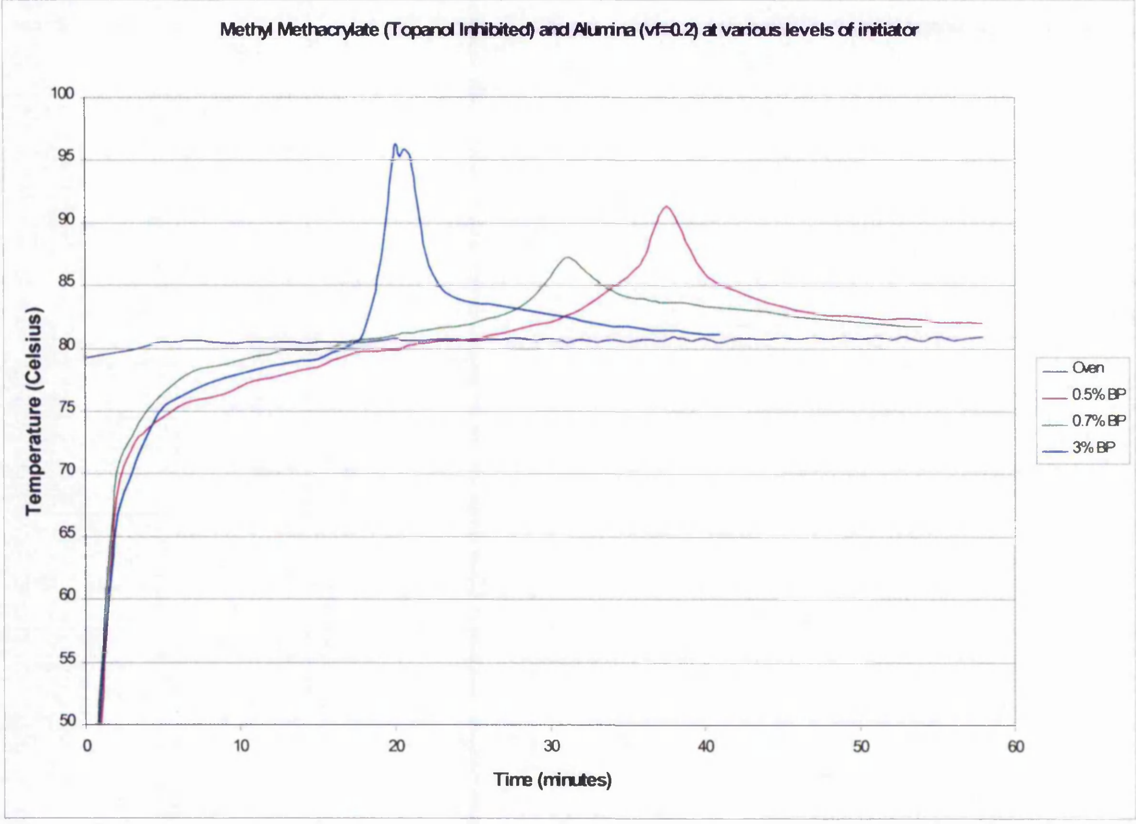


Figure 17. Methyl methacrylate (topanol inhibited) mixed with alumina at a volume fraction of 0.2.

In an attempt to prevent the viscosity rise, the volume of initiator was decreased from 3% to 0.5% at the higher volume fraction of 0.4 and 0.5. However, there was no change to the mixture viscosity and polymerisation still seemed to occur before mixing was complete. Therefore, the concentration of initiator did not seem to affect the mixing problem at a higher volume fraction, probably because the critical loading point had been reached, and the powder loading was then independent of the binder. Figure 17 shows the reaction profile for the samples at a volume fraction of 0.2.

This trend was similar to that noted in figure 13, when only the binder was initiated. Only the sample with a 3% benzoyl peroxide concentration reacted with a double peak, which was typical of topanol inhibited methyl methacrylate, but reaction times were very similar to an unloaded binder, possibly suggesting that alumina powder did not contribute to provoking an auto acceleration by increasing the viscosity as discussed in section 2.3.4.3. The exothermic peak temperature was noted to be less than 100°C and independent of the initiator concentration. Therefore, the reaction was investigated at a curing temperature of 90°C, at two levels of powder loading.

The samples exposed to 90°C reacted within 20 minutes, which was very fast compared to the samples cured at 80°C, but the peak temperature rose above the boiling point of MMA, causing voids within the moulded structure whilst the monomer polymerised.

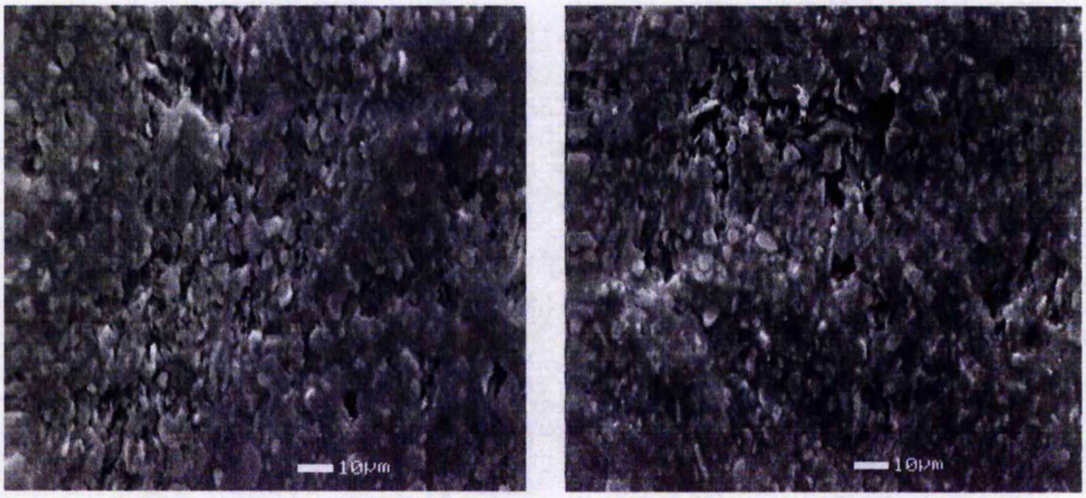


Figure 18. SEM images of a 0.2vf MMA and alumina

Samples cast at a volume fraction of 0.2vf were investigated by scanning electron microscopy (SEM) to determine how the binder accommodated the alumina particles. It was observed that the MMA completely engulfed the alumina as shown in figure 18 and the high concentration of binder was obvious at this level of solid loading, because of the regions of pure binder without powder.

2.4.3 Cyanoacrylate and Alumina

2.4.3.1 Reactivity and Inhibition

Cyanoacrylates are highly reactive monomers that can react almost instantaneously with the addition of a simple *basic* catalyst like pyridine or water, as discussed in section 2.3.4.6. In consideration of the fact that alumina is an alkaline powder, its reactivity with cyanoacrylates was investigated. A small quantity of alumina was dispensed into 3cm^3 of butyl cyanoacrylate monomer at room temperature and the resulting temperature rise was monitored by a thermocouple linked to a workstation via an analogue to digital converter.

Figure 19 shows that a surface contact with the powder instigated rapid polymerisation of the monomer, associated with an exothermic temperature rise. It was thought that the surface moisture and alkalinity of the alumina powder had caused a *basic* reaction with the cyanoacrylate monomer, thus promoting anionic polymerisation. This rate of reaction posed a problem in relation to mixing feedstock; although it could be reduced by using a strong acid, the acid in turn would neutralise the catalysing alkalinity.

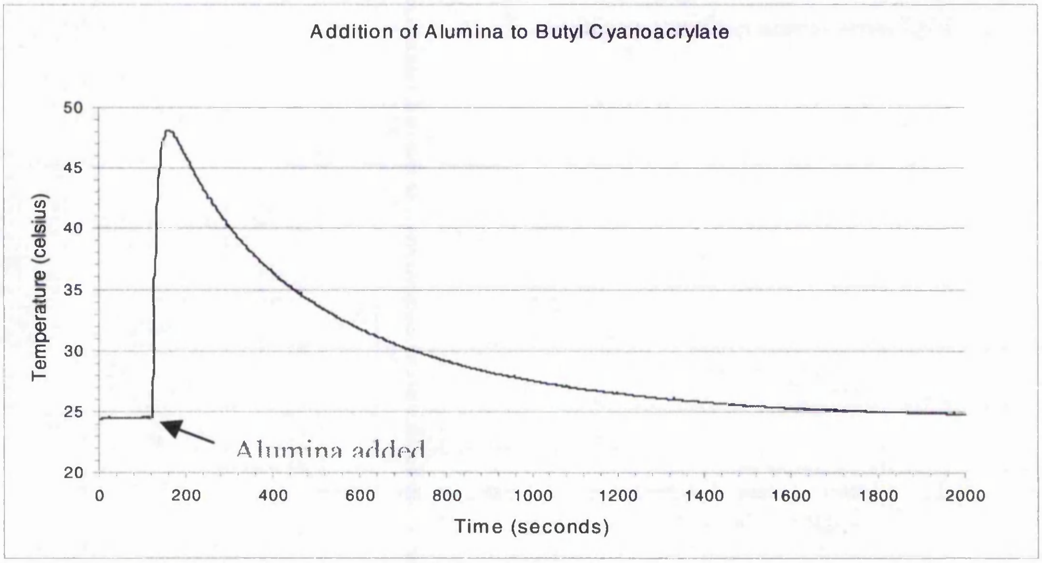


Figure 19. Reaction time and temperature from the addition of aluminium oxide to butyl cyanoacrylate

p-toluene sulphonic acid had previously been used successfully to inhibit cyanoacrylate monomers, and on this basis was selected as an inhibitor. Attempts have been made to try and reduce the alkalinity of alumina powder by washing the surface with nitric acid prior to mixing (38), but this approach failed. The only other available option was to dry the powder in an effort to reduce surface moisture content, and therefore the alumina used in this investigation was dried for at least 24 hours prior to mixing with the binder.

The inhibition of cyanoacrylate monomers was the most important part of the mixing process, because errors would lead to premature polymerisation within seconds.

Accordingly, this stage of the investigation was considered the most important, with most attention being paid to preventing a reaction rather than provoking it.
The inhibition and mixing process was achieved by the following steps:

- A measured quantity of para-toluene-sulphonic acid was dispensed in to a glass beaker
- A measured volume of butyl cyanoacrylate was dispensed on to the acid, using a polypropylene syringe
- The solution was heated at 50°C in a water bath for 15 minutes, whilst the acid dissolved into the cyanoacrylate monomer. It was noted that the solution changed colour in stages, from transparent to a dark red, as the pH level decreased.
- The solution was removed from the heat, and alumina was added (by small quantities) into the binder, whilst continuously mixing
- It was considered important to maintain the same dissolving time for samples when comparing mixtures; otherwise, one sample could be more inhibited than another.

Cyanoacrylate was investigated by mixing with powder one (the same powder as used with MMA in section 2.4.2) so that a direct comparison could be made between the binders. The aims of this analysis were to:

- find the highest mixable volume fraction of alumina to cyanoacrylate
- eliminate a binder based on the mixable volume fraction
- find the cure time for cyanoacrylate binders
- find a relationship between inhibition level, reaction time and mixed volume fraction

The level of inhibition was varied from 1% to 10% inhibitor, to distinguish between a fast reaction and a period that would be safe for moulding. These quantities of acid were individually placed into a glass beaker, followed by a small level of butyl cyanoacrylate. The solution was heated at 50°C for exactly 15 minutes whilst the acid dissolved; this maintained consistency when batches were compared, because they were inhibited to the same level of acidity. Alumina was mixed into inhibited solutions at increasing quantities starting at a volume fraction of 0.2, until the maximum volume fraction (limited by the critical loading) was reached. The final volume of fluid mixed was approximately 5cm^3, as detailed in table 6.

One of the factors controlling the polymerisation rate was the inhibition period (or time to cure), so cyanoacrylate was inhibited with varying concentrations of acid at two of the largest mixed volume fractions of powder. After mixing, the samples were loaded in to a 5cm^3 syringe; this form of containment is comparable to that of the barrel of an extruding machine. Periodically a small quantity of the mix was extruded from the syringe, and the extent of polymerisation was estimated by means of the resistance to extrusion. The results are shown in figure 20.

Table 6. Samples (5cm^3) created with butyl cyanoacrylate and alumina

Powder No	*Vf*	*Acid level (%)*	*Observations*
1	0.20	1.0	Polymerised whilst mixing
1	0.20	4.0	No problems mixing
1	0.30	1.0	Polymerised whilst mixing
1	0.30	4.0	No problems mixing
1	0.40	1.0	Polymerised whilst mixing, large temperature rise
1	0.40	4.0	No problems mixing
1	0.40	4.5	No problems mixing
1	0.40	5.0	No problems mixing
1	0.40	8.0	No problems mixing
1	0.45	4.0	Polymerised whilst mixing, large temperature rise
1	0.45	4.5	Polymerised whilst mixing, large temperature rise
1	0.45	5.0	No problems mixing
1	0.45	5.5	No problems mixing
1	0.45	6.0	No problems mixing
1	0.50	6.0	Could not mix, vf too high
1	0.50	8.0	Could not mix, vf too high

The samples that had acid quantities less than 4% polymerised whilst mixing. This could be because the acid had not fully dissolved, a condition that could be avoided by increasing the dissolving time. It was noted that samples mixed with ease up to a volume fraction of 0.45, falling within the limits set by German (section 2.4.1) for powder injection moulding. The aim of this exercise was to eliminate a binder, based on mixable volume fractions. Methyl methacrylate was excluded, because the largest volume fraction mixed was 0.33, compared to 0.45 with the same powder used with cyanoacrylate.

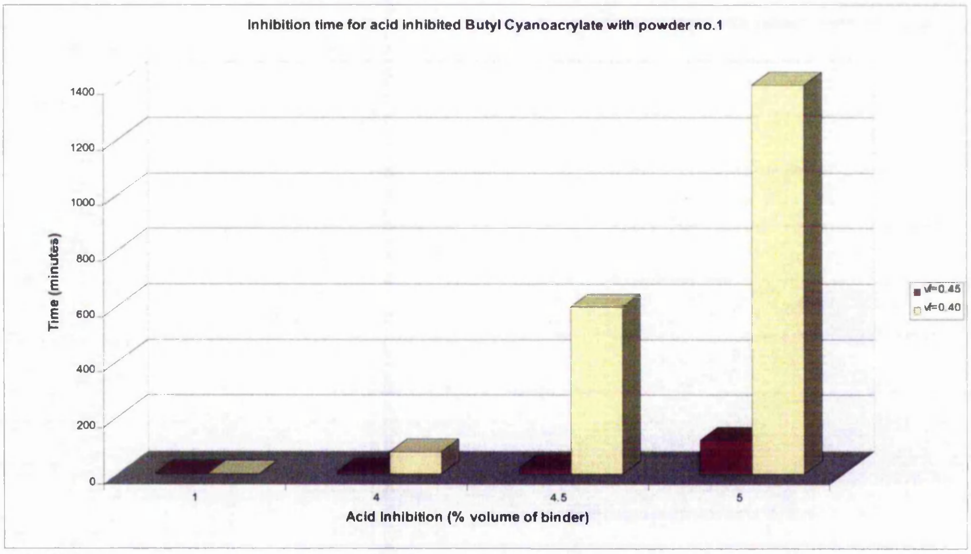


Figure 20. Inhibition characteristics for cyanoacrylate mixed with alumina Powder No.1 at two volume fractions

Figure 20 shows the inhibition characteristics for 0.4vf and 0.45vf. As shown, the greater amount of inhibition required for the higher volume fraction of powder was probably caused by the increased level of alkalinity that is typical to alumina powder. This data was useful to help ensure polymerisation will not occur prematurely during moulding. However, to obtain the same characteristics there were many variables that had to be consistent, such as powder type, volume fraction, acid level, dissolving time, dissolving temperature, polymerisation atmosphere, and the area exposed to a catalyst. It was extremely difficult to maintain consistency with all these parameters, and therefore larger quantities of acid were normally used to ensure a safe inhibition period.

Cyanoacrylate tended to bind alumina particles by polymeric strands whereas MMA, tended to submerge alumina in a sheet of polymer. Figure 21, shows a sample mixed to a volume fraction of 0.2, bound together with cyanoacrylate. It can be seen on the low magnification that the alumina was bound together by strands of polymer, and on the high magnification that each particle had adhered to the polymer.

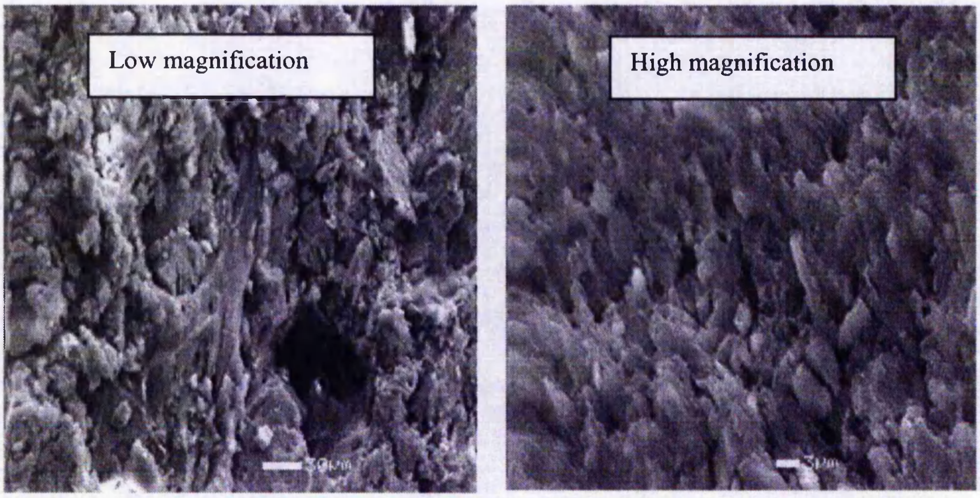


Figure 21. SEM images of powder one mixed with butyl cyanoacrylate (0.2vf)

2.4.3.2 Alumina Powder Characteristics when Mixed with Cyanoacrylate

As planned, the other two grades of alumina were tried with the most effective binder. Cyanoacrylate had proved to have significant advantages over methyl methacrylate, especially with respect to loaded volume, and therefore the work was performed with this monomer.

Because there was not a common inhibition level for each batch of alumina powder when mixed with cyanoacrylate, a powder had to be singled out for moulding. Favourable characteristics at this stage included availability and ease of mixing, and also the ability of the powder to sinter and debind without slumping. These matters are discussed in chapter 5, where a comparison is made between each successful powder.

Compact samples were created with a volume of 6cm^3 and a large diameter/width ratio, by forcing mixed feedstock into cylinders and sectioning them with a diamond saw after polymerisation had occurred. Each batch of sample had a different volume fraction and inhibition level, using the three grades of alumina, which are listed in table 1.

Table 7 shows the results for the three powders.

Table 7. Mixed compositions of Alumina and Cyanoacrylate

Sample No	*Powder No*	*vf*	*Acid Level (%)*	*Dissolving Time (minutes)*	*Notes*
1	1	0.40	4	15	No agglomeration, no exotherm
2	1	0.40	3	15	No agglomeration, exotherm
3	1	0.45	4	15	No agglomeration, exotherm
4	1	0.45	5	15	No agglomeration, no exotherm
5	1	0.48	6	15	Polymerised whilst mixing. Volume fraction too high for moulding
6	1	0.48	6	20	Polymerised but mixing was easier with the longer dissolving period. Volume fraction too high for moulding
7	2	0.40	4	15	No agglomeration, no exotherm
8	2	0.45	4	15	Polymerised whilst mixing
9	2	0.45	4	20	No agglomeration, no exotherm
10	2	0.48	4	20	Polymerised whilst mixing
11	2	0.48	5	20	Polymerised whilst mixing
12	2	0.50	6	20	No agglomeration, no exotherm, however, volume fraction too high for moulding
13	3	0.40	5	15	Agglomeration, no exotherm
14	3	0.45	6	15	Agglomeration, slight exotherm
15	3	0.45	6	25	Agglomeration, no exotherm
16	3	0.48	6	15	Polymerised whilst mixing
17	3	0.48	7	25	Agglomeration, no exotherm
18	3	0.50	7	15	Polymerised whilst mixing
19	3	0.50	7	25	Agglomeration, no exotherm

All of the powders investigated caused binder polymerisation whilst mixing, because the acid inhibitor had not fully dissolved within the investigated periods. Extending the acid dissolving time would overcome this problem and also lengthen the inhibition period, although, the most effective solution would be to increase the inhibitor concentration. This observation was more appropriate with higher volume fractions of powder. For example, when the volume fraction was high, such as Powder 3, then raising the acid inhibition level alone was not an adequate solution, because eventually the monomer became saturated. Therefore, increasing the level of acidity, in conjunction with a longer dissolving time was a preferred method to prevent saturating the binder.

It was observed that Powder 3 mixed to the highest ratio of binder without causing polymerisation (volume fraction of 0.5), and it was therefore selected for moulding investigations. The other two powders would not mix with the binder to a higher volume fraction at the investigated processing conditions, even though the acidity level was increased to prevent polymerisation. The limiting factor causing this was considered to be the powder reaching its critical loading condition, therefore relating to physical properties, such as particle characteristics, rather than chemical limitations associated with inhibition.

The agglomeration witnessed with Powder 3 was a useful characteristic, which may even contribute to the level of porosity prerequisite for moulding a conduit heart valve (section 2.2.1).

Finally, the aim of mixing was to achieve a workable volume fraction of powder to binder. A desirable level for conventional moulding would be between 0.45vf and 0.8vf as this yields theoretical sintered densities approaching unity. Nevertheless, high densities were not required for a porous medium, hence feedstock were mixed to a maximum of 0.5vf. At this ratio, the mixture viscosity had dramatically increased compared to a 0.4vf, since the powder was reaching its critical loading level. It was concluded that Powders 1 and 2 could not mix to the desired volume fraction of 0.5 without additional processing aids such as surfactants.

2.4.3.3 Working Window for Cyanoacrylate Inhibition

Inhibition levels for cyanoacrylate monomer change with different powders, as observed in table 7. It was thought that this might be caused by two reasons: firstly, the powders could have a different level of alkalinity; and secondly, powders with a greater surface area are exposing the monomer to a higher dosage of alkalinity. Inhibition level was very important when the feedstock was moulded; premature polymerisation would severely damage a moulding machine, which could take days to repair. Therefore, parameters such as inhibition level and mixing time had to be carefully selected, to reduce any risks. These observations helped the development of a working window for mixing cyanoacrylate feedstock (figure 22).

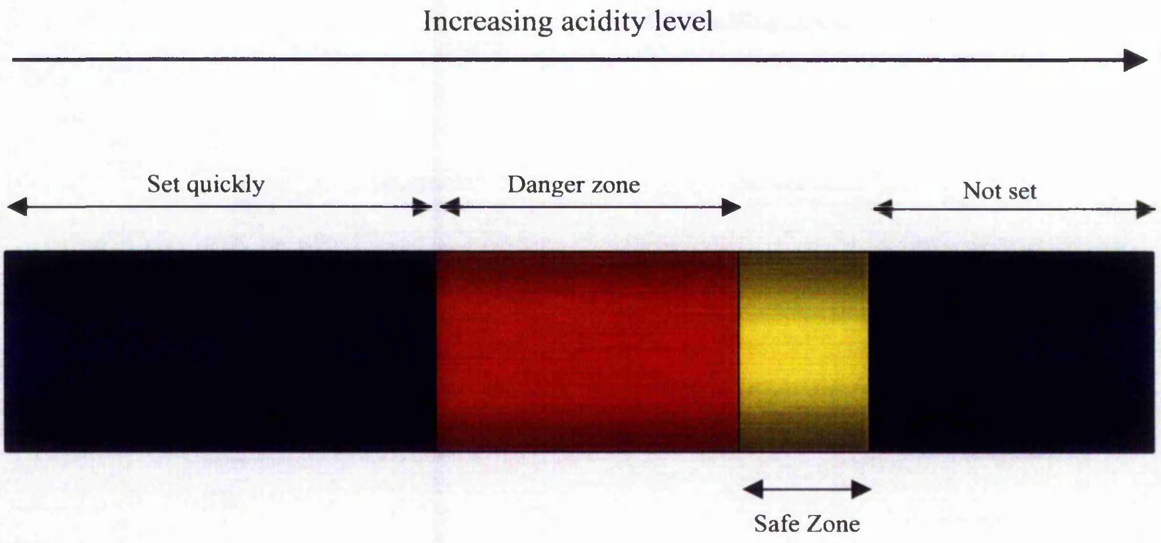


Figure 22. Working window for acidity levels of inhibited monomer

Figure 22 details the effects that a change in acidity of the monomer will have on a feedstock. The four zones and the acidity levels are detailed below,

(1) ***Set quickly***	this corresponds to an acid level that is too low. Feedstock will polymerise whilst mixing.
(2) ***Danger zone***	this area is associated with chance polymerisation whilst mixing. Sometimes the monomer will react and other times it will not. Avoid this zone at all costs.

(3) ***Safe zone***	the acid level is just right in this portion. The feedstock will not set whilst mixing and it will remain fluid for a short period until moulding is complete.
(4) ***Not set***	If too much acid is dissolved into the monomer the feedstock can take a very long time to polymerise. For example, feedstock could remain in a fluid state within a moulding barrel for weeks without any signs of polymerisation.

2.4.3.4 Cyanoacrylate Initiation Investigation

Much attention is given to the inhibition of cyanoacrylate when considering using it as a binder, mainly because of its reactivity, but little attention is normally paid to the initiation. This is, however, a significant concern after feedstock has been moulded. Accordingly, initiation investigations were carried out, to determine an efficient method of polymerising a cyanoacrylate/alumina composite contained in a cylindrical vessel.

Because of the difficulty of ascertaining if and when the binder had polymerised, a method of measuring relative polymerisation was devised using a Vickers hardness machine, and polymerisation was determined by the hardness of one sample compared to the hardness of another.

The aims of this investigation were to:

- determine a safe and simple medium that can polymerise cyanoacrylate;
- determine how holes in a mould will affect surface polymerisation;
- obtain a value of hardness for polymerised feedstock;
- determine how a change in inhibition level affects the polymerisation in different mediums.

Table 8. Sample data for polymerisation investigation

Sample	Volume Fraction (vf)	Acid Level (%)	Syringe status	Powder dried
1	0.46	8.0	No holes	Dried
2	0.46	8.0	Holes	Dried
3	0.46	8.5	Holes	Dried
4	0.46	8.5	No holes	Dried
5	0.46	8.5	No holes	Not dried

The investigation began by preparing five syringes (with a volume of 5cm^3), and two of these were drilled throughout their entire length with 1mm holes. All syringes were then filled with feedstock, as detailed in table 8. Both ends of the syringe body were removed so that the catalyst could have an access point to the surface of the cyanoacrylate proportion of the feedstock. Finally, each batch was placed in the medium, for polymerisation to commence.

The mediums were water based, because this was a safe and abundant fluid that was well documented as a cyanoacrylate catalyst (36,38) and could be easily integrated into a processing method. The following mediums were used:

- Water at 100°C
- Water at room temperature
- Steam at 100°C
- Oven at 100°C

The samples were held in the listed atmospheres for 5 hours, then they were removed and cut into six sections with a diamond saw. Each cut section provided access to the surface of the feedstock throughout the entire length of the sample, so that the hardness could be determined as shown in figure 23.

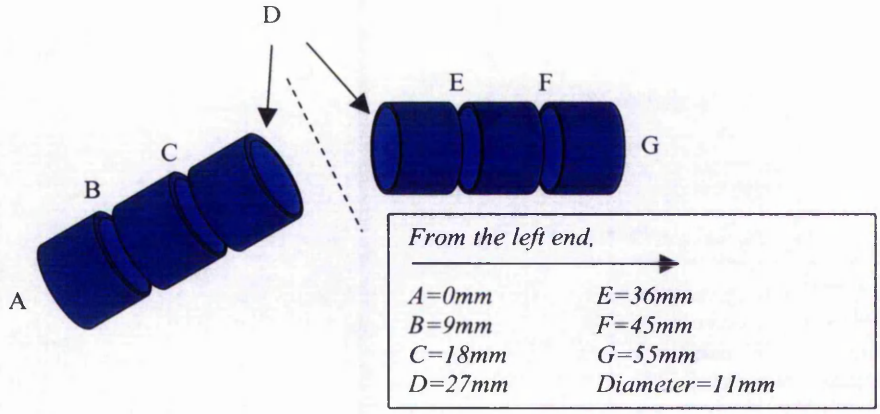


Figure 23. Sectioned sample showing faces for hardness measurement

The hardness was measured using a 5kg load on a Vickers diamond indentation hardness machine, and averaged over four measurements on each sectioned surface. It was noticed that some of the measurements taken were below the range of the Vickers machine, which is <10 VHN. Therefore, these samples were considered fluid, which indicated that they had not polymerised within the investigation period of 5 hours. These values have been plotted as zero on the graphs, even though technically they actually have a hardness value less than 10VHN.

The samples that were positioned in water at room temperature did not polymerise within the 5 hour period, even at the lowest inhibition level. However, the other samples had polymerised. It was noticed that steam and heated water methods were very similar at causing the feedstock to polymerise as shown in figures 24 to 27, and either method was suitable for use in moulding investigations. The samples placed within a heated oven were not as successful; in some cases, the binder had only cured at each end.

The holes in the two drilled syringes helped cause polymerisation throughout the length of the sample, because the catalyst could access all areas of the feedstock. However, samples contained in syringes without holes only polymerised in the regions at either end of the cylinder, leaving soft uncured regions towards the centre (18 to 36mm from the left (figure 24)). This indicates that the anionic reaction cannot propagate far into the 11mm diameter samples, probably because there is not a continuous distribution of monomer throughout the feedstock.

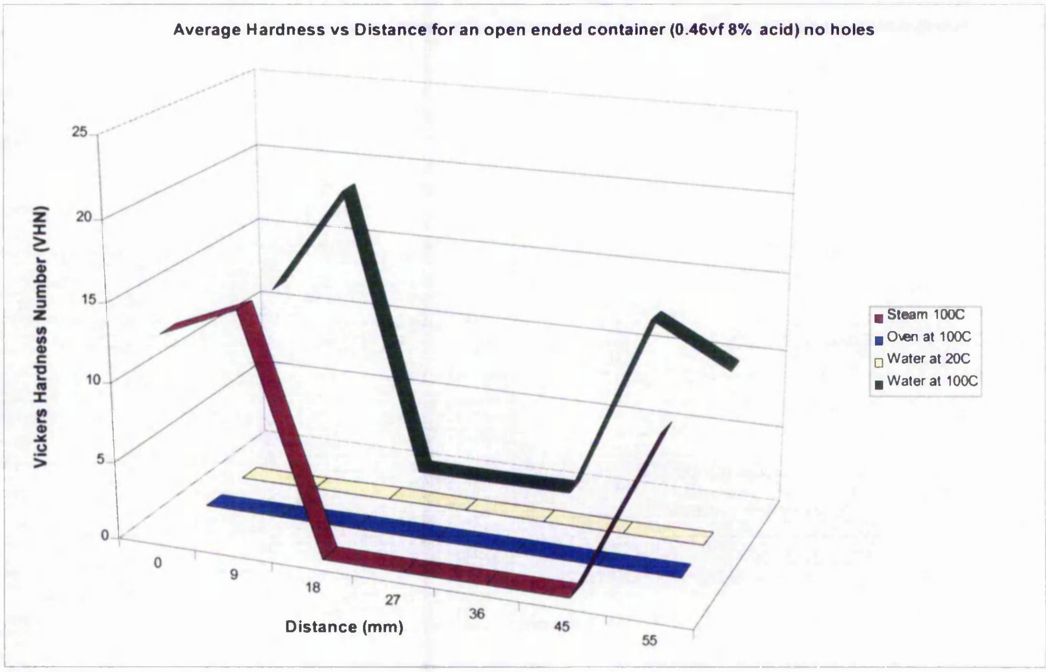


Figure 24. Vickers hardness for polymerised samples at 8% acid in a container without holes

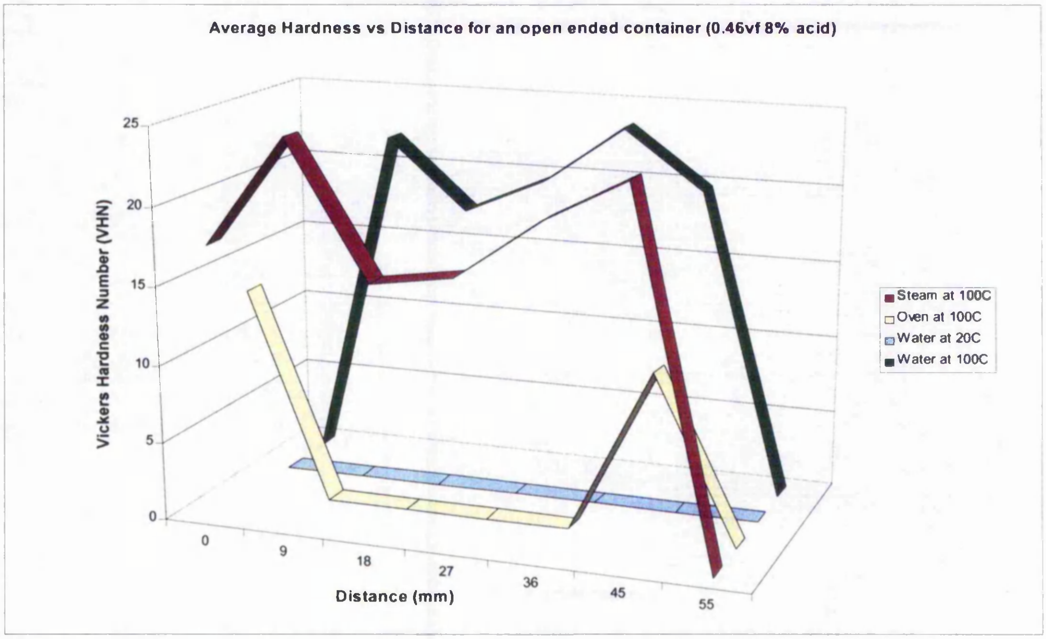


Figure 25. Vickers hardness for polymerised samples at 8% acid in a container with holes

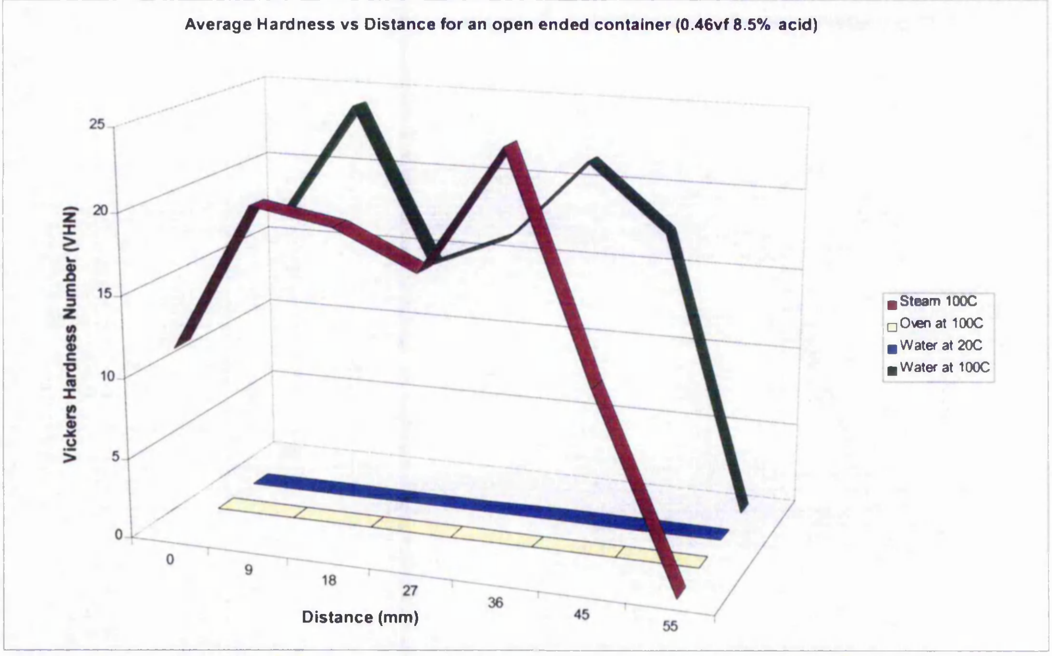


Figure 26. Vickers hardness for polymerised samples at 8.5% acid in a container with holes

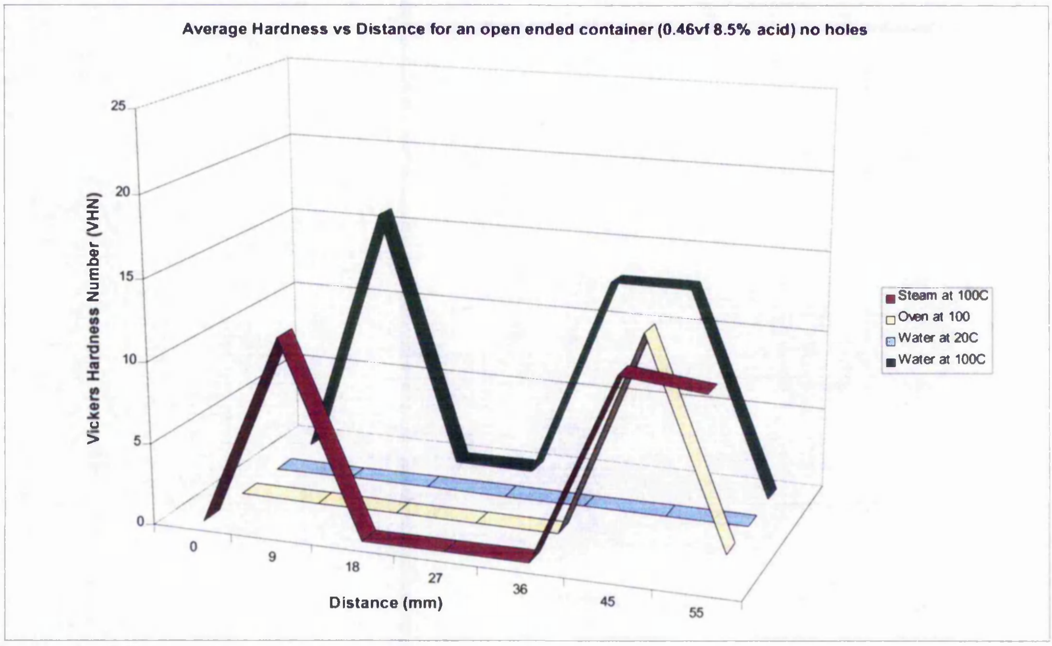


Figure 27. Vickers hardness for polymerised samples at 8.5% acid in a container without holes

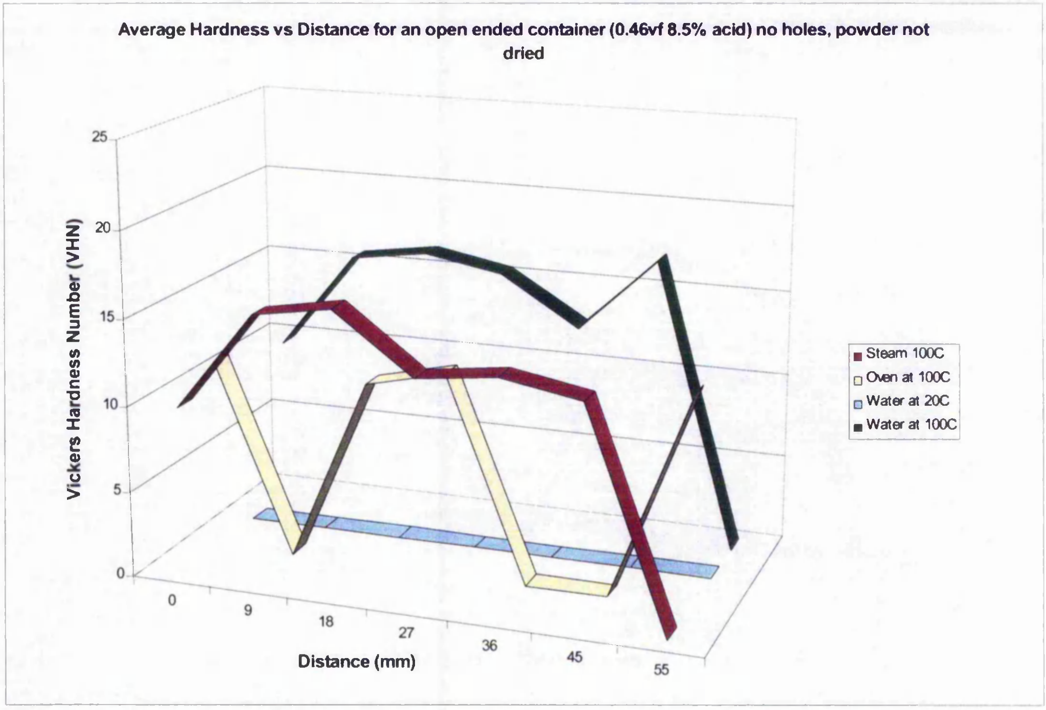


Figure 28. Vickers hardness for polymerised samples at 8.5% acid in a container without holes. The powder has not been dried

The inhibition level did not seem to make any difference to the reactions. For example, each sample polymerised to more or less the same hardness number, regardless of the amount of acid present. The acid had probably neutralised within the experimental period, and if the investigation was performed over a shorter period then a change may be noticed, especially if there is a larger variance in the acidity level of the inhibited monomers.

The samples in figures 24 to 27 were prepared with a powder that had been dried for 24 hours before mixing, to reduce the moisture content. However, figure 28 shows a sample mixed with alumina powder that had not been dried before this investigation. It can be seen that the sample had polymerised throughout to a greater extent than the corresponding sample shown in figure 27. This proves that drying powders does affect the inhibition time and is therefore important when designing feedstock for moulding. Accordingly, ceramic powders used for this investigation were dried before mixing, because inhibition was considered to be more important than initiation in the control of a moulding process.

2.4.3.4.1 Initiation summary

The favoured method for the initiation of a moulded part using a cyanoacrylate binder inhibited with para-toluene-sulphonic acid was to:

(1) submerge the component in boiling water after moulding' or

(2) place the component in an oven that had a humid atmosphere similar to steam.

Chapter 3 – Design for Moulding

3.1 Introduction

It was clear from the work described in Chapter 2 that the feedstock contains a high loading level of alumina powder, increasing its viscosity. Since a high viscosity could effect its mouldability, rheological investigations were required to ensure that an acceptable level would not be exceeded. This chapter describes first the investigation of the rheological behaviour of the feedstock, using a cone and plate rheometer, and the development of a model to predict shear stress and strain. It then goes on to consider moulding methods, and finally describes the development of a novel moulding process for forming the feedstock using a wax skeleton and metallic core.

Key actions were:

- rheometer calibration
- feedstock investigation with a cone and plate rheometer
- development of a model describing the mixture rheology
- moulding machine design
- design of moulds for reactive binders
- design of the heart valve mould including the use of various materials
- production of a prototype heart valve using the PRIME process

3.2 Feedstock Rheology

3.2.1 Rheology Basics

In order to fill the mould, the binder/powder feedstock mixture used in the PIM process must be *viscoelastic*; that is to say, it must be both viscous and elastic. Viscosity is the product of a relationship between the shear rate and shear stress, and elasticity is determined by the ability of a material to regain its shape when stress is removed below a certain yield point.

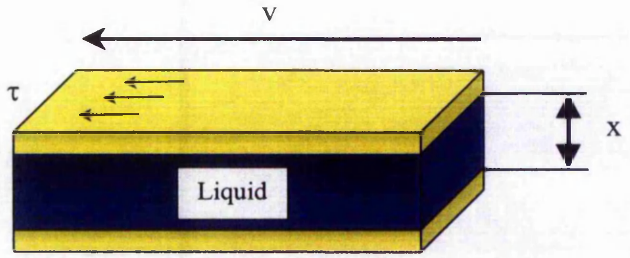


Figure 29. Two plates, with an applied shear stress on the top whilst the bottom is constrained.

Viscosity is defined by considering two parallel plates, separated by a liquid at a distance (x) as shown in figure 29. If the lower plate is stationary, and the upper one is moving with a velocity (v), then a shear stress (τ) is applied to the fluid. Whilst the plates are sheared, the shear strain rate (∇) is equivalent to the change in strain divided by time, as expressed in equation 2.

$$\nabla = \frac{v}{x} \quad (s^{-1}) \qquad \text{————————} \qquad (2)$$

Where,

∇ = *Shear strain rate* (s^{-1})
v = *Velocity(m/s)*
x = *Fluid seperation (m)*

Assuming that the velocity remains constant, the viscosity (η) is defined as '*the resistance of the fluid to shearing*'. The viscosity will change when influenced by external factors such as temperature, pressure, and polymerisation. Equation 3 shows the general relationship between shear stress and viscosity for a Newtonian fluid.

$$\tau = \eta.\nabla \quad (\mathrm{Nm}^{-2}) \qquad \text{———} \qquad (3)$$

Where,

τ = *Shear stress* (N/m^2)

η = *Dynamic viscosity (Pa.s)*

∇ = *Shear strain rate* (s^{-1})

A Newtonian fluid is one where the viscosity is constant throughout a range of shear rates; if the viscosity is affected by the shear rate, the fluid is termed as Non-Newtonian.

In solutions such as PIM feedstock that contain anisotropic particles, laminar flow may orient the molecules, which tends to reduce the resistance to shear. Therefore, the stress required to increase the shear rate by an increment will diminish with increasing shear rate (24). This phenomenon is typical to PIM and has been aptly named *'shear thinning'*, which is often described by the empirical Power Law Equation, where (η_a) is the apparent viscosity and K is the consistency index.

$$\eta_a = K\nabla^{(n-1)} \quad (\mathrm{Pa.s}) \qquad \text{———} \qquad (4)$$

Where,

η_a = *Apparent dynamic viscosity (pa.s)*

K = *Consistency index (n/a)*

∇ = *Shear strain rate* (s^{-1})

n = *Power law factor (n/a)*

The (n) factor within the power law equation 4 determines the flow behaviour as listed below and detailed in figure 30.

- $n < 1$ Pseudoplastic flow, with shear thinning behaviour.
- $n > 1$ Shear thickening behaviour caused by large agglomerates and particle

interference.

- n = 1 Newtonian behaviour

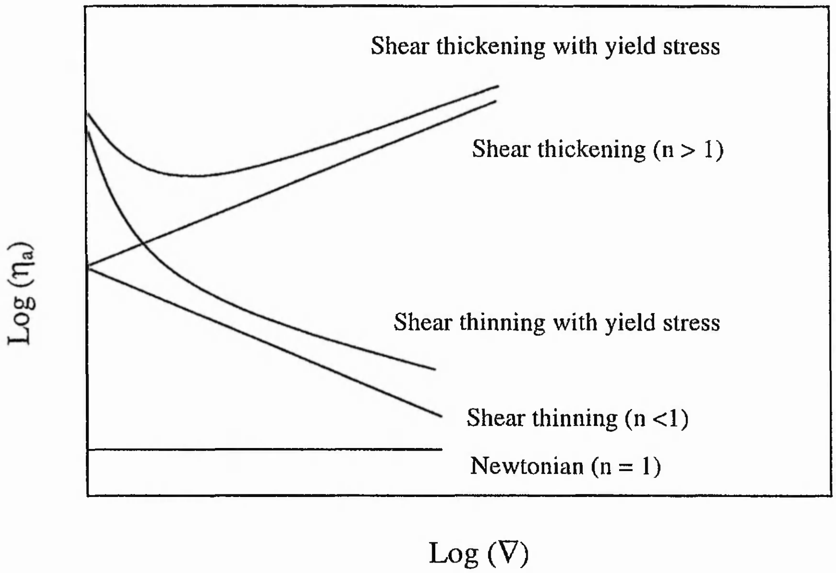


Figure 30. Relationship between models of flow behaviour

3.2.2 Suspension Behaviour

PIM feedstock can be very complex and, because the power law does not generally fit a powder system with multiple constituents, sophisticated modelling is normally used to determine the rheological behaviour. Many such models have been devised (84-90).

A master model for predicting rheological behaviour (equations 5-7) has been developed by German (37), although a substantial amount of further information is required, in order to use this particular equation:

- Shear stress needs correcting for the yield strength
- Viscosity needs correcting for any thixotropic behaviour
- Viscosity of the pure binder is required
- Particle size distribution

- Solids loading
- Shear rate
- Temperature
- Pressure
- Yield strength

$$\eta = \eta_b A\left(1 - \frac{\Phi}{\Phi_m}\right)^{-n} \text{ ———— } (5)$$

$$A = \left[\frac{A_0 + A_1}{(D + A_2).D^2}\right]\nabla^{n-1} \text{ ———— } (6)$$

$$\eta_b = \eta_0 \exp^{\left[\frac{E}{K}.\frac{1}{(T-1)T_0}\right]} \exp^{[C(P-P_0]} \text{ ——— } (7)$$

Where,

η = *Dynamic viscosity (Pa.s)*

η_b = *Binder viscosity (Pa.s)*

A = *Constant (n/a)*

ϕ = *Volume fraction of solid (n/a)*

ϕ_m = *Maximum solids loading (n/a)*

n = *Power law factor (n/a)*

A_0 = *Constant (n/a)*

A_1 = *Constant (n/a)*

D = *Particle diameter (m)*

A_2 = *Constant (n/a)*

∇ = *Shear strain rate* (s^{-1})

η_0 = *Viscosity at a temperature* T_0 *(Pa.s)*

E = *Activation energy (J)*

k = *Boltzmanns constant* (W/m^2K^4)

T = *Absolute temperature (°C)*

T_0 = *Temperature (°C)*

C = *Pressure dependent enthalpy (kJ/kg)*

P = *Pressure* (N/m^2)

P_0 = *Initial pressure*(N/m^2)

An empirical investigation to find a rheological relationship for a feedstock can be time consuming and expensive. The use of a model is an inexpensive and well-documented alternative, but it is inappropriate to rely too heavily on these equations to predict rheological behaviour, since 50% relative errors are common due to inaccuracies in many of the terms (37).

Empirical studies have determined ideal rheological behaviour for powder injection moulding feedstock in relation to moulding and viscosity (91). Shear rates during moulding can range between 10^2 and 10^5 s^{-1}, with the largest being at the gate. Generally, the largest viscosity experienced with PIM feedstock at these shear rates is 10^3 Pa.s at the binder moulding temperature. These are maximum values based on a typical powder injection moulding cycle, and the viscosity must be lower than this by a factor of 10, to less than 100 Pa.s, for successful moulding (37,91). There are many options available to reduce the mixed viscosity, the most common being the use of processing aids such as stearic acid.

3.2.3 Measuring Equipment

A range of techniques is available for measuring the viscosity of powder/binder mixtures. Generally, PIM feedstock is Non-Newtonian and the measuring equipment reflects this. Testing techniques for Non-Newtonian materials include the use of rotating coaxial cylinders, rotating parallel plates, mixing rheometers, and cone and plate rheometers. The latter can be used for measuring the rheological properties of PIM systems, but is limited to a relatively small range of shear rates, and a capillary rheometer is usually used, since it accommodates the range of viscosities and shear rates encountered in practice (66,92).

The cyanoacrylate adhesive binder used in the PRIME process would, however, cause excessive damage to a capillary rheometer, since it cannot easily be removed. A cone and plate rheometer could be used instead, as the required measurements fall within its range, and the cyanoacrylate binder could be simply removed.

The cone and plate rheometer measures the torque experienced when shearing a fluid that is held between a flat stationary cylinder and a rotating cone. There is normally a range of cones available for use with the rheometer, each with a different radius (r) and angle (φ). This difference in geometry allows a variety of shear stresses (hence viscosity) to be measured at a selection of shear rates. Figure 31 illustrates the cone and plate, and table 9 details the capabilities of the cone and plate rheometer that was used for this investigation.

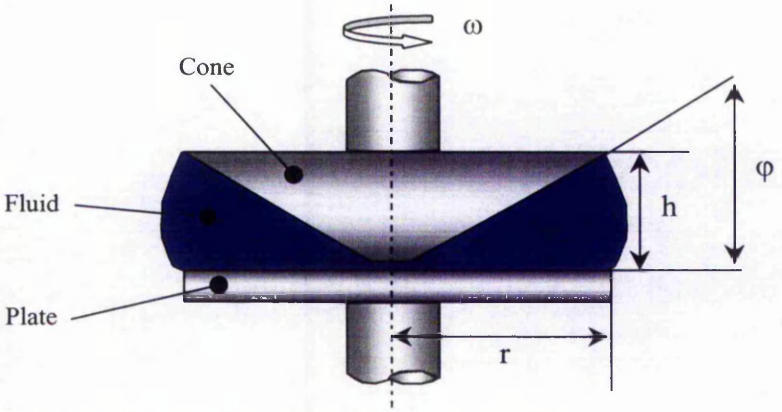


Figure 31. Schematic of a cone and plate rheometer

Table 9. Cone properties for a Rheotest 2 series rheometer.

Cone	Geometry	Torque level	Shear stress Pa	Shear rate s^{-1}	Viscosity Pa.s
K1	φ=0.3°	I	40-800	5 to 4860	0.008-140
	r=18mm	II	400-8000		0.08-1400
K2	φ=0.3°	I	135-2700		0.03-500
	r=12mm	II	1350-27000		0.3-5000
K3	φ=0.3°	I	11100-22000		0.22-4000
	r=6mm	II	111000-220000		2.2-40000

The type of cone used was determined empirically, with the limiting factor being the measured shear stress which was represented by a value (λ) ranging between

1 and 100. This value represented the torque required to shear the fluid at the given shear rate and was dimensionless.

The Rheotest 2 required calibration before use, and this was always done before each new batch of material was tested. Calibration involved using a (Newtonian) fluid of known viscosity at a temperature range coinciding with the heating ability of the rheometer. A reading (λ) was then taken and averaged at a range of shear rates for each cone at a torque level, to provide a unique cone constant (C_c). Equations 8 to 10 show how the viscosity and shear stresses were calculated from the measured value.

$$C_c = \frac{\eta_z . \nabla}{100.\lambda_z} \qquad (\mathrm{Dyn/cm^2}.\lambda) \qquad \text{————————} \qquad (8)$$

$$\tau_r = C_c . \lambda \qquad (\mathrm{Dyn/cm^2}) \qquad \text{————————} \qquad (9)$$

$$\eta_r = \frac{\tau_r .100}{\nabla} \qquad (\mathrm{cP}) \qquad \text{————————} \qquad (10)$$

Where,

C_c = *Cone constant (n/a)*

η_z = *Viscosity of fluid used for cone and plate calibration (cP)*

∇ = *Shear strain rate (s^{-1})*

λ_z = *Measured value (calibration) (n/a)*

τ_r = *Shear stress calculated from cone and plate rheometer (Dyn/cm^2)*

λ = *Measured value from the rheometer(n/a)*

η_r = *Viscosity calculated from the cone and plate rheometer (cP)*

The readings taken from the rheometer were affected by temperature fluctuations, and adjustment of the plate height (h). Hence, the distance between the cone and plate was calibrated before every investigation, and the plate was maintained at a constant temperature. Other parameters that can affect the measured value are:

- Zero adjustment on the measuring equipment

- Temperature variation of the fluid, due to shear heating effects
- Temperature variation between the calibrated value (C), and experiments using this value as a constant
- Wear of the drive, affecting the shear rate
- Consistency of material
- Quantity of material under investigation (too little would not fill the gap between the cone and plate, on the other hand, too much promotes edge effects on the cone)
- Accuracy with the micrometer, when adjusting the plate height

3.2.4 Rheological Investigation

The rheological characteristics of the cyanoacrylate/alumina powder were required to determine whether it was suitable for an injection moulding feedstock. Analytical methods such as mathematical prediction are available to produce the data, but in order to fully understand the rheological properties of the feedstock a thorough investigation at a range of solid loading and shear rate was required, using a rheometer.

The viscosity of the feedstock must be within a range suitable for moulding. Therefore, the range of solid loadings investigated represented an acceptable injection mouldable feedstock composition, starting with a volume fraction of 0.4, increasing to 0.48. The aims of this investigation were to:

- Determine whether the feedstock was mouldable
- Determine the rheological characteristics at a range of solids loading
- Find the rheological relationship (Newtonian or Non-Newtonian)
- Determine an equation for the characteristics
- Predict what the viscosity will be at higher shear rates
- Determine the shear stress and viscosity at shear rates between 5 and 4860s^{-1}

The equipment used for this investigation was a Rheotest 2 series cone and plate rheometer, with a useful range indicated in table 9 (section 3.2.3). Sample temperature was maintained on this rheometer by pumping water at 22.5°C around the plate section, which was monitored by a thermocouple within the plate.

The output from the Rheotest 2 was a dimensionless value, which was displayed on an analogue meter with a range between 1 and 100. This value was a representation of the torque and was converted to shear stress by using the simple equations listed in section 3.2.3. The values were represented by a voltage range (0-100mV), and relayed into a workstation through an analogue to digital converter. The data were analysed over a period long enough to allow the shear stress measurements to settle to a constant value before readings were taken. The data collected also indicated whether the feedstock was polymerising; if the torque continuously rose whilst tests were running, then the binder had started to cure and the investigation was restarted. The software written to perform this task is listed in appendix C. Figure 32 shows the rheometer equipment.

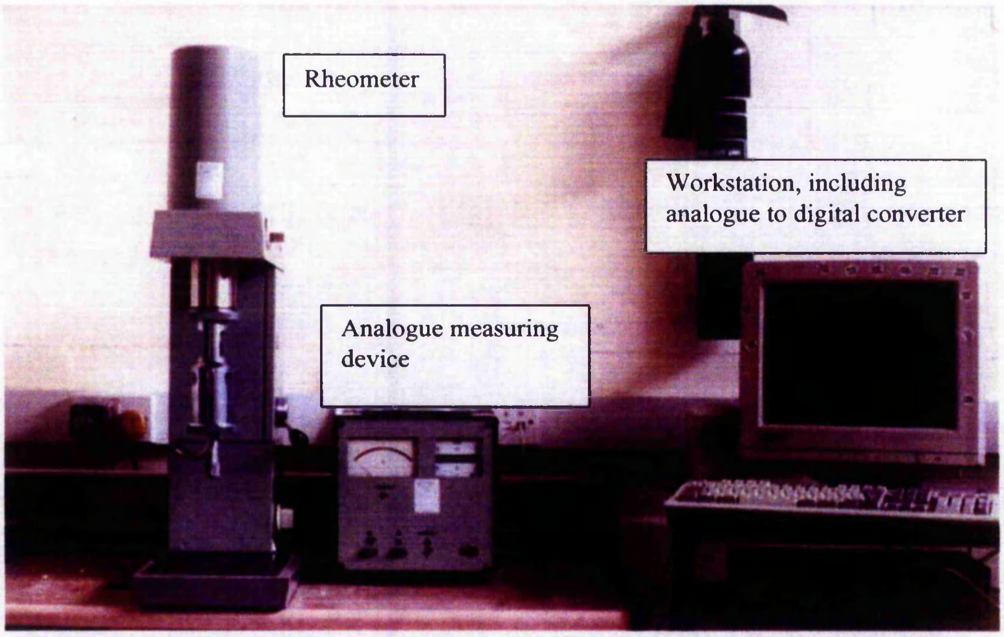


Figure 32. Rheotest 2 rheometer with measuring devices

3.2.4.1 Calibration

The rheometer required calibration with a liquid that had known rheological properties, before any investigation was performed. Glycerol was selected, a liquid with known viscosity at a range of temperatures.

Rheometer calibration involved finding both the plate height and cone constants using the calibration fluid. The plate height was found first by adjusting the level using an in-built micrometer, until there was minimum friction between the cone and plate. Cone calibration was then determined by the following procedure:

- Clean the cone and plate surfaces using an alcohol solution
- Remove the plate
- Set the shear rate and torque level
- Start the motor and reset the measuring device
- Zero the analogue scale
- Switch off the motor
- Replace the plate with 0.1cm^3 of Glycerol
- Set the plate height (as calibrated previously)
- Start the motor and log data using the workstation
- Using figure 34, find the viscosity of Glycerol at the test temperature
- Find the average data value from the workstation
- Use equation 8 to find the cone constant (C)

This procedure was undertaken to find the cone constants at 22.5°C, and table 10 lists the values at two levels of torque.

Table 10. Calibrated data for cones

Cone	Torque Level	Actual Temperature (°C)	Calibrated cone constant	Plate height (h) (mm) (relative to gauge)
K1	I	22.3	178.5	9.30
	II	22.5	1476	9.30
K2	I	22.6	920	9.29
	II	22.4	5043	9.29
K3	I	22.5	4195	9.30
	II	N/A	N/A	N/A

The determined cone constants were investigated at the full range of shear rates, with the same glycerol that was used for the calibration. Hence, the constants could be justified by matching data with known viscosity values for glycerol. The data was very accurate, showing Newtonian behaviour between shear rates of $5s^{-1}$ and $4860s^{-1}$ (figure 33). However, the measured viscosity according to figure 33 was 975 cP (0.975 Pa.s) by taking a gradient at any point. This value differed to the plot in figure 34, which showed a higher viscosity of 1050 cP (1.05 Pa.s), at the investigated temperature of 22.5°C. This discrepancy was probably because the temperature measurement was taken not from the fluid itself, but from an area within the plate that was close to the fluid. Also, because of the shearing action of the cone, localised heating effects would have occurred within the fluid.

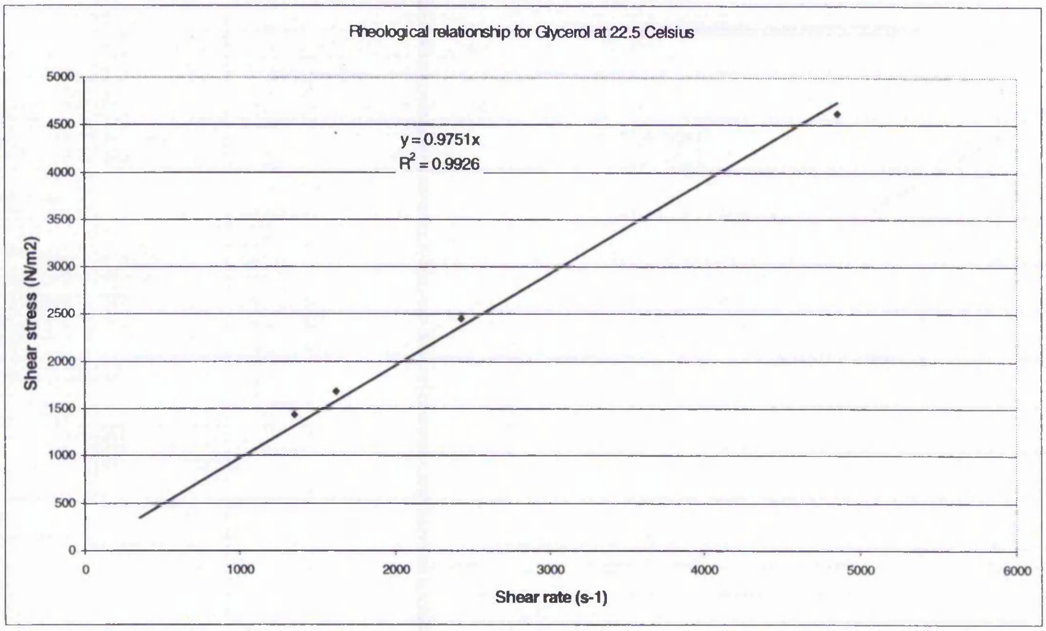


Figure 33. Measured stress/strain relationship for glycerol at 22.5°C

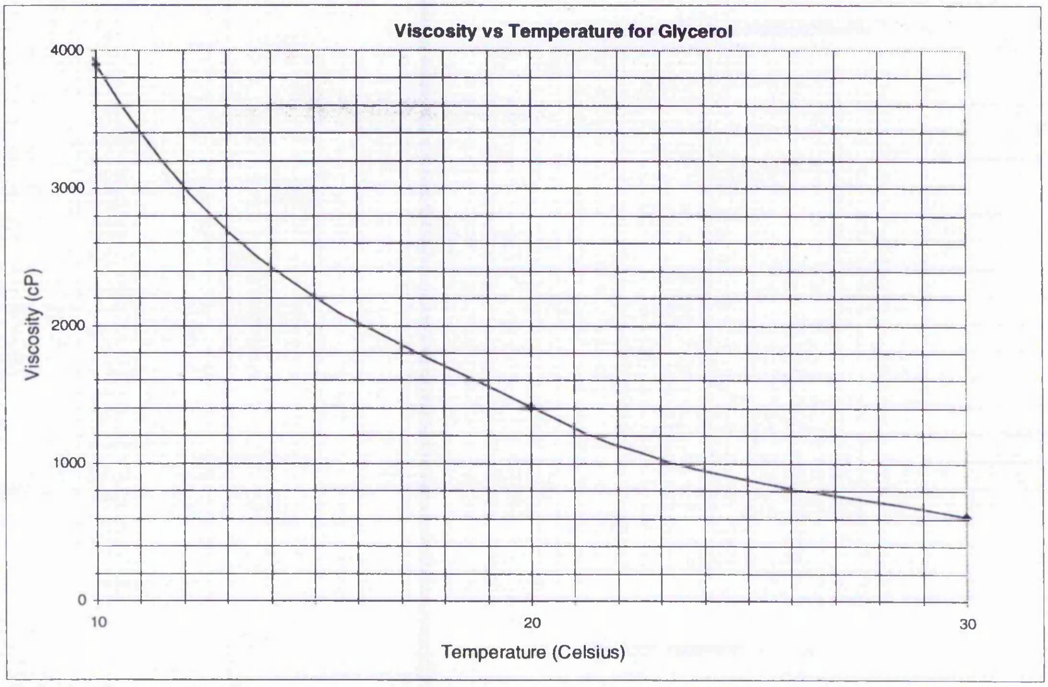


Figure 34. Viscosity/Temperature relationship for glycerol. (source: Fisher Scientific UK)

3.2.4.2 Results and Discussion

An investigation was carried out using Powder 3 with butyl cyanoacrylate on the Rheotest 2 rheometer. Table 11 details the mixture concentrations, the cone type and the temperature.

Table 11. Samples investigated for rheological properties

Sample	*Cone*	*Shear range (s^{-1})*	*Volume Fraction (vf)*	*Acid (%)*	*Cone Height (mm)*	*Temperature (°C)*
1	K1	810-4860	0.00	8.5	9.31	22.2
2	K1	900-4860	0.00	8.5	9.29	22.1
3	K1	810-4860	0.00	8.5	9.30	22.2
4	K1	30-180	0.40	9.0	9.32	22.7
5	K1	10-270	0.40	9.0	9.32	22.5
6	K1	10-270	0.40	9.0	9.31	22.3
7	K1	6-270	0.40	9.0	9.32	22.3
8	K1	6-270	0.40	9.0	9.30	22.2
9	K1	6-270	0.40	9.0	9.31	22.4
10	K2	6-180	0.45	9.0	9.30	22.2
11	K2	6-180	0.45	9.0	9.31	22.5
12	K2	6-270	0.45	9.0	9.31	22.6
13	K2	6-270	0.45	9.0	9.32	22.5
14	K2	6-270	0.45	9.0	9.31	22.4
15	K2	6-150	0.45	9.0	9.31	22.4
16	K2	6-50	0.48	9.0	9.32	22.5
17	K2	6-90	0.48	9.0	9.32	22.4
18	K2	6-90	0.48	9.0	9.32	22.5
19	K2	6-90	0.48	9.0	9.31	22.7

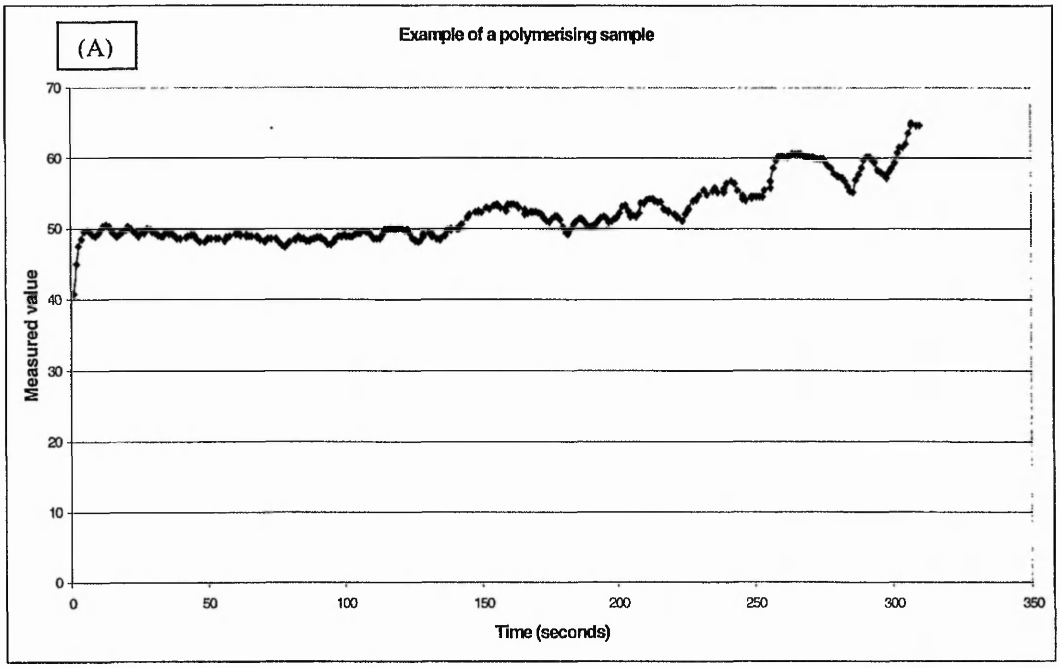


Figure 35. Example of a polymerising sample whilst being measured on the cone and plate rheometer

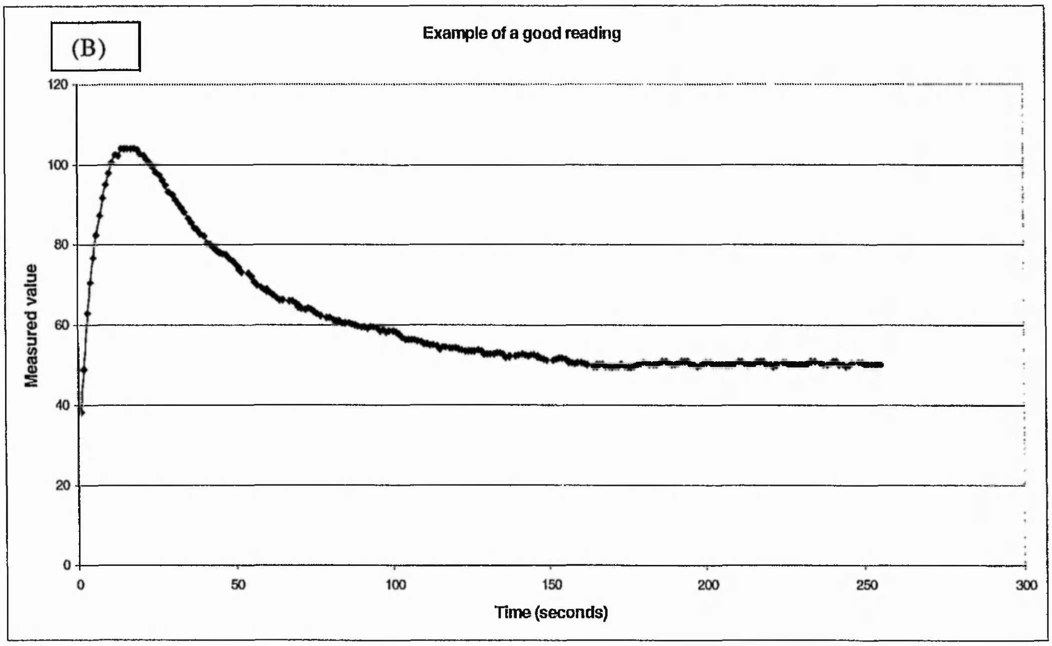


Figure 36. Example of a normal sample whilst being measured on the cone and plate rheometer

Whilst the data was being collected from the rheometer, each sample batch was monitored by examining the torque output from the rheometer against time. If a sample showed signs of polymerisation, the torque would gradually increase until the binder cured; in these instances, the experiment was repeated with a new batch of feedstock. On the other hand, when the torque remained constant over the experimental period, the binder was known to be sufficiently inhibited. Figures 35 & 36 detail an example of the plots taken from the data analysis software (appendix C), showing (a) a sample that is polymerising and (b) sufficiently inhibited sample.

It can be seen from figure 36 that the sample was being mixed whilst torque was measured from the cone and plate rheometer. The initial peak represented the high torque encountered from an inhomogeneous, unmixed sample. As time increased, the particles were aligned and, hence, reduced the required torque. It was at this stage that data was recorded for calculating the shear stress.

On the other hand, figure 35 shows a polymerising sample with a characteristic rise in measured value as time increased, because of the increase in torque required to shear the mixture.

The three volume fractions of powder investigated did not show an individual

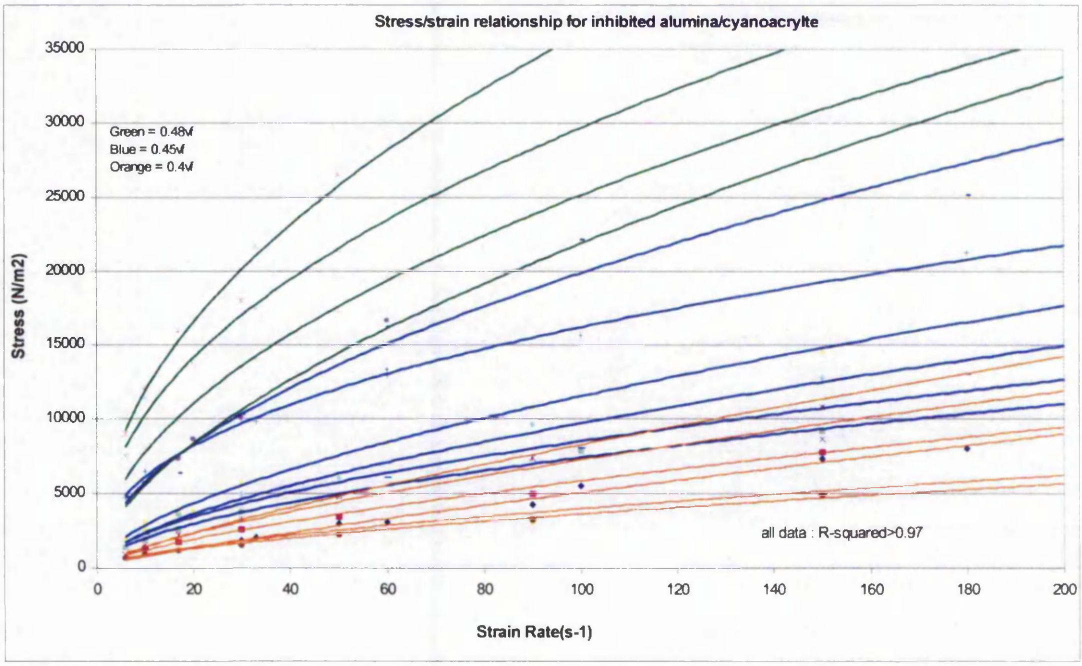


Figure 37. Rheological data from solids loading of 0.4, 0.45 and 0.48

trend that defined the rheological characteristics of that particular system. As shown in figure 37, there was a range of results for each powder loading, because of a batch variation between samples. This was probably typical of PIM feedstock, especially when binders are loaded to a high powder level. External factors such as mixture inhomogeneity, chance polymerisation, temperature, and density could all affect the results.

To reduce the risk of polymerisation, large quantities of acid were dissolved into the binder before these investigations, because it is known that this will inhibit cyanoacrylate.

The solid loading for mixed feedstock was limited to 0.48, because a higher loading tended to increase the viscosity towards an infinite value and was impractical for injection moulding. Unfortunately, a high solids loading was difficult to measure at higher shear rates, especially with the cyanoacrylate binder. Samples mixed at a volume fraction of 0.48 caused extreme shear stresses when investigated, and so the maximum shear rate was limited to $90s^{-1}$. On the other hand, mixtures with a low solid loading were measured at shear rates up to $270s^{-1}$.The viscosity of all the investigated samples was within limits for an injection moulding feedstock, except for the samples with a high solid loading at low shear rates below $10s^{-1}$, shown by the steep gradients in figure 37.

A possible method to widen these observations would be to use the high shear stress cone, K3, but when it was used with the feedstock the monomer seemed to polymerise rapidly (probably because the sample size was too small with this cone). This promoted a reaction, especially if the binder was not homogeneously inhibited throughout the feedstock.

Nevertheless, the shear thinning behaviour experienced with all samples closely resembled a power law with a great level of accuracy. In fact, all data fitted the equations with an R^2 value greater than 0.97, which is considered strong statistical evidence in favour of the feedstock being a power law fluid.

The variation in data experienced with inhomogeneous mixing and other factors such as solids loading and density should not affect the data collected for unloaded cyanoacrylate. However, the quantity of acid dissolved into the monomer solution caused the fluid to become saturated, and the variation in data was still encountered. The inhibited cyanoacrylate without powder best matched a power law equation as opposed to a linear relationship (Newtonian) as shown in figure 38. It was unknown if this result is attributable to the fact that the binder was inhibited with acid, or if this was normal for uninhibited cyanoacrylate, because an uninhibited solution could not be tested. Figure 38 shows the variation in data and the apparent viscosity for the three samples at a solid loading of zero. Each data set had an apparent viscosity similar to the manufacturer's supplied value of 0.02 Pa.s at a shear rate of $4860s^{-1}$, and these values could be expected to converge further at higher shear rates.

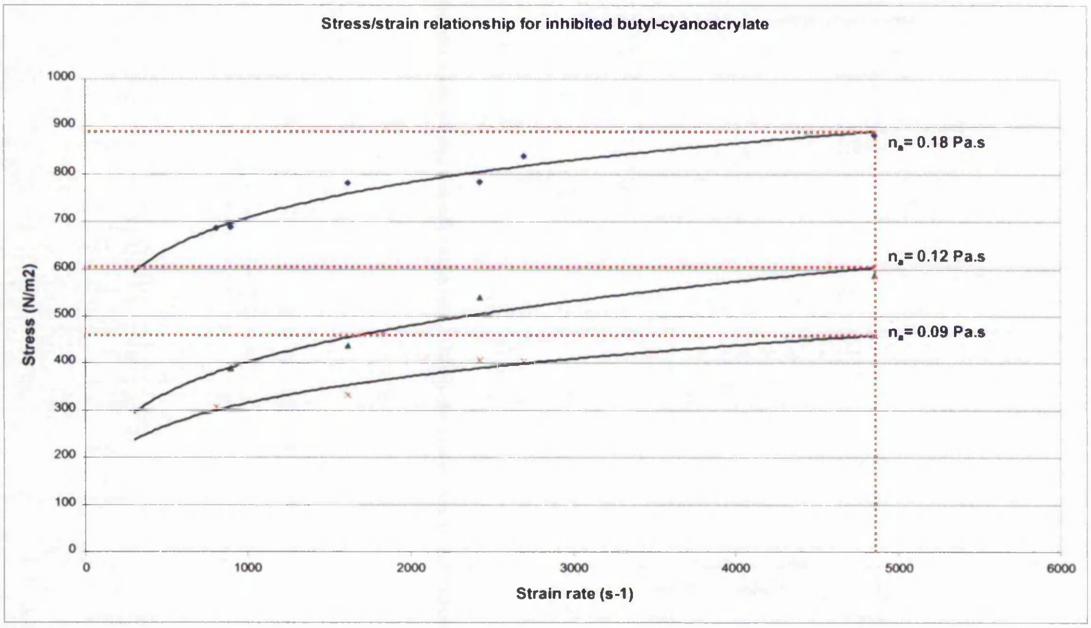


Figure 38. Rheological properties of butyl cyanoacrylate inhibited with acid, and the apparent viscosity at a shear rate of $4860s^{-1}$

Feedstock typically experiences different flow fronts whilst being forced through a mould, such as corners, expansions and contractions. These changes obviously affected the rate of shear, which can be as high as 10^5s^{-1} when passing through a gate. Therefore, a prediction was made to find what the viscosity would be at a higher shear rate, as shown in figure 39. It was found by interpolation that if the power law were maintained at a high rate of shear, the viscosity would reduce to a level below 100 Pa.s. This value was very low in comparison to a highly loaded feedstock at low shear rates.

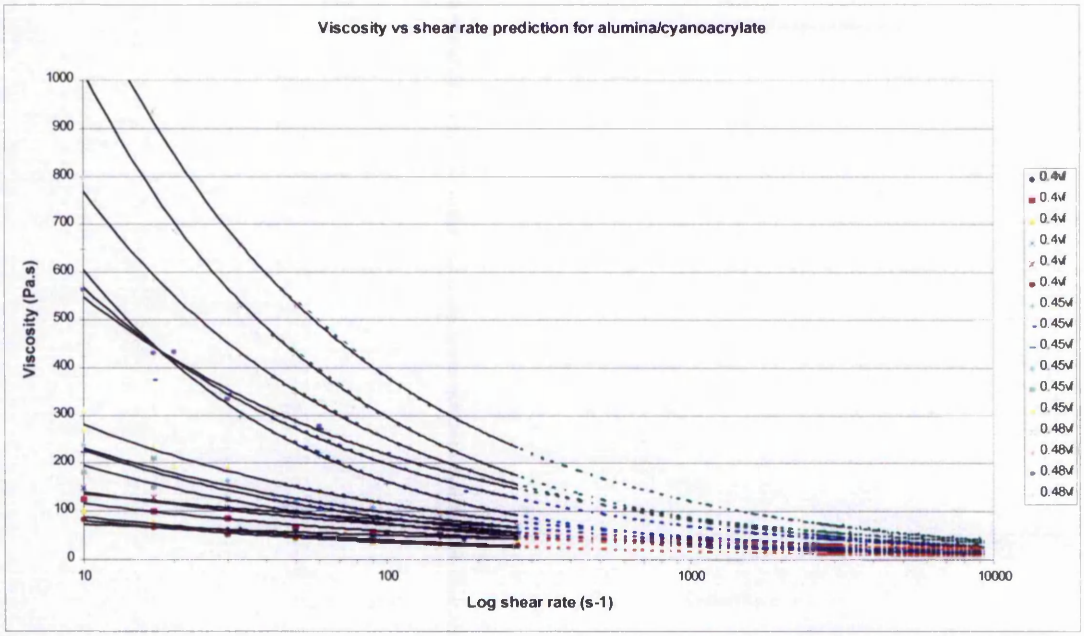


Figure 39. Prediction of viscosity at high shear rates, based on the power law equation

The rheological information that was gathered through this investigation was additionally useful for fluid behaviour predictions and computation fluid dynamics (CFD); a model of the rheological characteristics was required for the CFD investigation detailed in chapter 6, which was based on an injection mouldable feedstock.

A high solid loading was best suited to the moulding process, such as the sample that was mixed to a volume fraction of 0.48, because this represented the feedstock composition that was to be used for creating the ceramic heart valve (section 3.4.7). Therefore, a rheological model was determined based on the results that experienced the *highest* viscosity at this level. This was because when the feedstock was sheared between the cone and plate, agglomerates could have dispersed and particles re-orientated themselves in the direction of flow, with the effect of reducing the viscosity. The equations empirically determined (from figure 37) for shear stress and apparent viscosity are shown in equations 11 and 12 respectively.

$$\tau = 3856.\nabla^{0.48} \quad (\mathrm{N/m^2}) \quad \text{————————} \quad (11)$$

$$\eta_a = 3856.\nabla^{(0.48-1)} \quad (\mathrm{Pa.s}) \quad \text{————————} \quad (12)$$

Where,

τ = Shear stress (N/m^2)

∇ = Shear strain rate (s^{-1})

η_a = Apparent dynamic viscosity (Pa.s)

3.3 Basic Moulding Techniques

3.3.1 Introduction

In a traditional powder injection moulding (PIM) cycle, temperature, and pressure are varied to deliver feedstock to the die. This involves heating the feedstock inside a moulding barrel whilst mixing and pressurising it with a reciprocating screw. The mould cavity is then filled by a forward thrusting of the screw in the barrel to inject a shot of molten feedstock. Normally, the feedstock is at a higher temperature than the mould tooling, and as the feedstock cools the viscosity rises, thus requiring extra pressure to fill the cavity.

Whilst the concept of injection moulding appears simple, the actual process is complex with many variables potentially leading to errors. For example, a high solid loading in the feedstock means a high viscosity, and requires high pressure to fill the mould; this pressure also has to vary, however, to maintain flow rate, since the viscosity varies through temperature influences when the polymeric binder melts or cools. This indicates the type of control parameters that must be identified and applied for a successful moulding cycle. The adequacy of control will be evidenced in the quality of the moulded component, where, for example, the formation of density gradients, will cause warping when subsequently sintered.

The parameters that are required for a quality component are highly dependent on particle characteristics, binder formulation, feedstock viscosity, tool design, and machine operating conditions (93). For example, a typical cycle for powder injection moulding is associated with approximate flow rates of 1.5cm^3/s, which in turn requires pressures as high as 60MPa (600 Bar) (37). Hence, these volatile processing conditions contribute to high shear rates, even at 200°C, because of the high mixture viscosity at such a flow rate. However, powder reaction moulding (PRIME) differs somewhat to these conventional PIM conditions, and in certain cases has many advantages. The use of a cyanoacrylate allows processing at low temperatures (typically around 20°C), a relatively low flow rate and a low pressure cycle. Little or no process control is required when moulding, because the binder is fluid at room temperature, and the feedstock flows with relatively low force. One key controllable variable in PRIME is the onset of polymerisation, which can be controlled by inhibition with a suitable acid. Moreover, moulding at a constant temperature reduces the complexity of any moulding process. No viscosity/temperature relationships need to be considered and the machine and tooling can be quite simple, since thermal transfer coefficients can be neglected.

3.3.2 Moulding Problems

Problems can arise when moulding the feedstock, especially when forming complex parts. A fast injection speed can cause a phenomenon known as *jetting* which has undesirable effects on the quality of the part (94). This is where the combination of high pressures and low viscosity associated with moulding cause air entrapment and weld lines. These defects can cause cracking and a low surface quality when de-binding as the air expands and escapes. The problems are managed by filling the mould slowly and controlling the amount of pressure applied, a process called 'progressive filling' (see figure (40)). It is not expected that PRIME, which inherently moulds at a low pressure and flow rate, will encounter any issues associated with jetting.

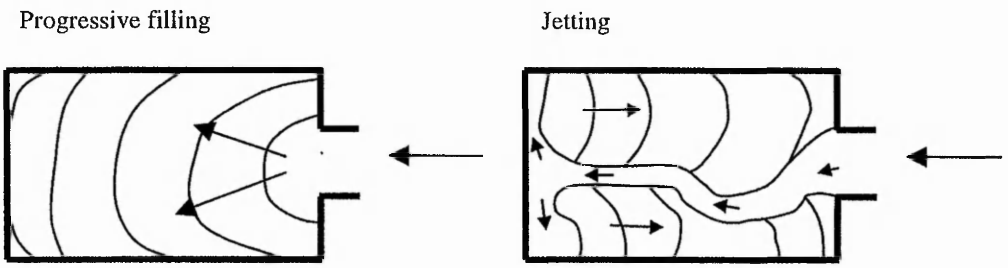


Figure 40. Progressive filling and jetting

Moulding defects can be caused by something as simple as unwanted air in the mould cavity. This is generally avoided by providing a continuous, smooth flow of feedstock into the mould, with an adequate vent to exhaust the air, but the problem can be exacerbated if there are inserts or cores within a mould, which tend to split the flow front causing multiple air pockets. The only method for solving such problems is to manually inspect the component to find the defect positions, and then re-design the location of vents to aid air dispersal.

A problem that arises with traditional moulding processes is *fountain flow* of the feedstock along the die wall. This flow phenomenon is typical to thermoplastic binders moulded whilst molten. When the molten binder flows through a cavity, it will tend to freeze at the cooler contact surface of a die, thus resembling a flow similar to the spray from a fountain. Ceramic powder/ thermoplastic binder mixtures tend to freeze quicker than an undiluted thermoplastic feedstock, which allows more opportunity for the development of large thermal stresses and, hence, high rates of component failure due to cracking. Fountain flow undoubtedly increases the pressure requirements in a moulding process, because increasing pressure is needed to force the fluid through a flow area that is constantly reducing.

The phenomenon of fountain flow will not be experienced in PRIME reactive moulding as the binder only polymerises significantly when the mould fill is complete. Hence, the pressure requirements are significantly reduced, which aids the moulding process.

Differences in thermal expansion associated with temperature gradients within components may lead to component failure, such as cracking, and warpage. Fortunately, this syndrome is not applicable to PRIME, where the temperature remains constant up to the point of polymerisation, and the exothermic rise associated with cyanoacrylate polymerisation is relatively low in comparison to the melting temperature of thermoplastics.

Although reactive moulding with a cyanoacrylate binder seems to have desirable advantages over a traditional powder injection moulding process, it does have detrimental effects when being used with a standard piece of moulding equipment. Historically, cyanoacrylate was created as an adhesive, bonding a wide range of materials from metals to rubbers in seconds. When being used as a binder it presents processing problems. Conventional PIM machines cannot be used to mould it as the binder will adhere to the barrel or screw surface. Consequently, a re-design of the traditional process was required, to develop a simple, low pressure, low temperature moulding system for manufacturing low volume parts (typically 30cm^3) for the heart valve.

3.3.3 Machine Requirements and Design

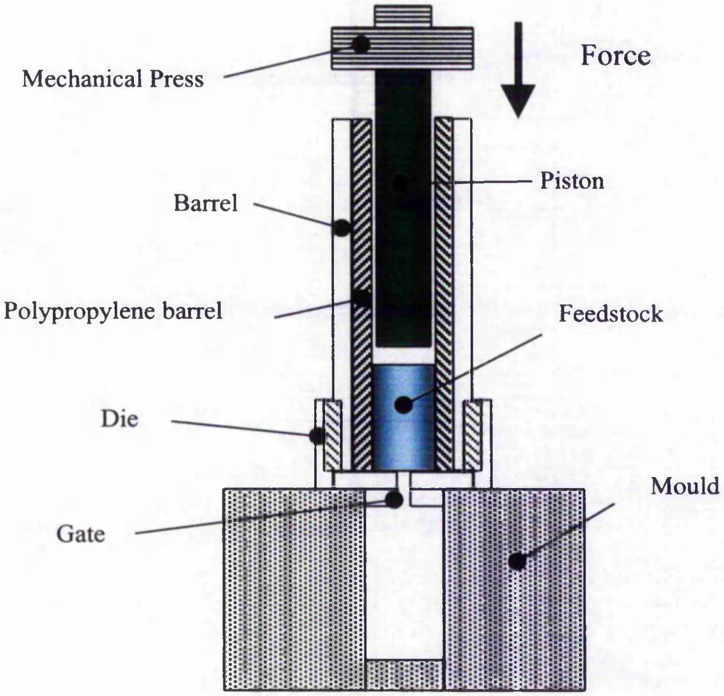


Figure 41. Moulding system

There are three types of injection moulding machine commercially available: the reciprocating screw; the hydraulic plunger; and the pneumatic (37). The hydraulic plunger literally forces feedstock from a cylinder into a die using a piston, hence the mould is filled by the forcing action. A pneumatic machine uses compressed air to apply a force to the feedstock, in a similar arrangement to the hydraulic setup, however, the pneumatic system has no surface contact (ie by piston) with the feedstock. The weakness of these two systems is in the controlling mechanism, as the only control that they have is the amount of pressure that can be applied to the feedstock. Accordingly, a typical PIM moulding operation is performed with a reciprocating screw machine in a heated barrel, because of the superior control attributes it allows, including temperature/viscosity variation and pressure control.

When using a thermal dependent binder such as a thermoplastic, the reciprocating screw injection machine is ideal, and a pre-requisite, for the manufacture of quality components through metal or ceramic injection moulding. With a cyanoacrylate binder, however, a simple arrangement such as a hydraulic plunger is appropriate, simply based upon the temperature dependency. On this basis, a moulding system using the same principles as the hydraulic ram machine was developed as shown in figure 41. The geometric data for this equipment is detailed in appendix B.

The force applied to the piston was provided by a mechanical press, which in essence was relatively simple, and *uncontrollable*, mainly because of the limitations invoked by manual operation. However, when the moulding operation was only dependent upon the polymerisation of the feedstock, this arrangement was more than adequate if the binder was sufficiently inhibited.

A major difference between a traditional hydraulic plunger machine and this arrangement was the method of feedstock containment within the barrel (or cylinder). The barrel as shown in figure 41, contained an insert that was manufactured from a material that cyanoacrylate would not adhere to, such as polypropylene or polyethylene. Without such an insert, the acid inhibitor would tend to neutralise when placed in contact with a machined surface, probably because of entrapped moisture, even if the barrel were to be dried before moulding. Equally, the barrel would need cleaning down after mouding, and since cyanoacrylate cannot be simply removed from a surface as it tends to adhere even if inhibited, removal would imply machining the barrel after every operation, which would be impractical. The solution was to use a polymeric disposable barrel insert. Polypropylene tubing was relatively inexpensive and suited to the application, and hence, a method for moulding was developed as detailed below:

(1) A polypropylene insert was fitted inside the barrel
(2) Feedstock was loaded in to the polypropylene insert
(3) The die attached to the end of the barrel
(4) The barrel fitted into the surface of a mould
(5) The piston was forced inside the barrel with a manual press, extruding the feedstock through the die and into a mould
(6) The cyanoacrylate was initiated using a suitable method and catalyst

There were some problems with this system for moulding cyanoacrylate binders, principally in the removal of the piston from the insert after moulding. This problem arose through differences in batch size of the polypropylene tubing either causing the piston to distort the tubing as it moved, because of being oversize, or the feedstock to become trapped within the annular gap along the edge of the piston. This second situation was more serious, because polymerisation could initiate when the binder was spread to a film, causing a severe increase in required pressure to overcome the raised friction. A possible solution would be to use a sealing ring on the piston, similar to the arrangement within an internal combustion engine, although cyanoacrylate would probably adhere to the surface of the ring. Therefore, investigations were made using the simple arrangement as shown in figure 41.

3.3.4 Testing of Moulding Arrangement

The designed system for moulding cyanoacrylate/alumina feedstock was used to determine the following parameters:

- Mouldability of the feedstock
- Moulding pressure (which was determined by flow from the outlet vent of the mould; inadequate pressure would result in no flow)

- Quality of components
- Moulding characteristics of the three ceramic powders

It was intended to injection mould simple cylindrical shapes, and the feedstock was mixed using the same combination of materials used in previous investigations, shown in table 7. After mixing, the materials were individually loaded into a polypropylene tube, and formed to create 11mm diameter compacts, using the developed moulding process. The mould used to create this shape is shown schematically in figure 42.

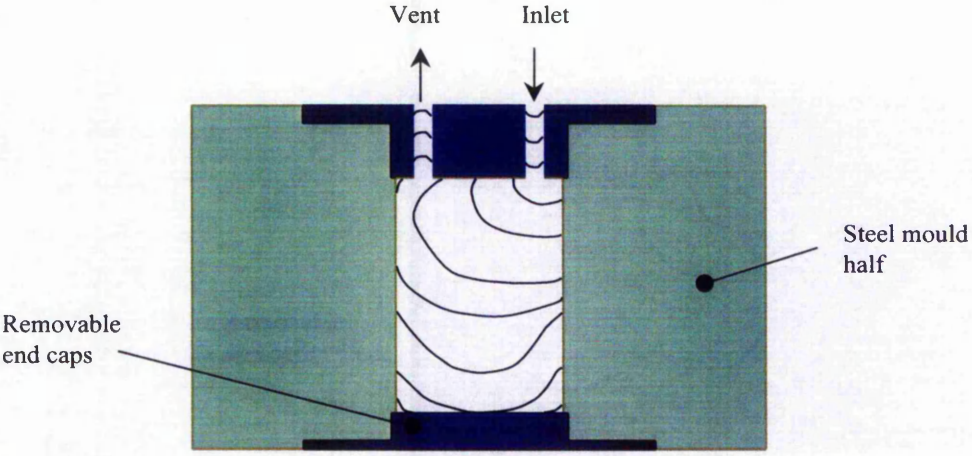


Figure 42. Steel mould half for creating cylindrical components, which shows the suggested flow front of the feedstock

Powder two was discarded at this stage of the investigation, because the mixture viscosity was too high to allow the feedstock to be forced into the mould, and any reduction of the powder-loading ratio would have undesirable effects on the sintering ability of the powder. Powders 1 and 3 each had desirable moulding characteristics, however, even at a high solid loading level.

The removable end cap (as shown in figure 42) was withdrawn and the vent removed, before the feedstock could be removed from the mould, because the binder had to polymerise. This could be achieved by two methods; leaving the feedstock to polymerise by moisture, or accelerating the polymerisation by using one of the mediums detailed in section 2.4.3.4. The latter was more time effective, but polymerisation could still take up to five hours even when the feedstock was exposed to hot steam. This *polymerisation time* was thought to be dependent on three factors: firstly the volume loading of ceramic; secondly, inhibition as defined by the operational window (section 2.4.3); and finally the shape of the moulded section. The last factor was important since the shape can make it very difficult to allow passage of a catalyst to the surface to polymerise the binder. With a cylinder contained in a mould it was only possible to polymerise two surfaces, and therefore propagation of the catalyst into the section was time consuming. However, suspending the mould in a steam atmosphere for five hours cured all the samples.

The moulded compacts had adhered to the surface of the steel mould, and some surface damage was inevitable as they were removed. Once removed, each cylinder was sectioned into three millimetre portions using a diamond saw, enabling further debinding and sintering tests to be carried out.

Inspection of the sectioned disks revealed defects that had been caused in moulding. The defects, in the form of small air pockets, were scattered randomly across the sectioned surface of each compact. This problem could be associated with jetting, which would mean that the mould was filled too rapidly, but, since the feed rate was relatively slow compared to traditional processing, this theory was abandoned. It was more probable that the mixing of feedstock introduced air, because it was not performed in a vacuum. As listed in section 2.2.1, this was not a serious problem because a limited amount of porosity is required for the heart valve. Nevertheless, any defect was undesirable and required further investigation to reduce any greater risk.

Although Powder 1 had promising characteristics in terms of mouldability, the powder did not sinter to an acceptable density and collapsed after further study, as detailed in section 5.2.4. Accordingly, based on the results of these tests, Powder 3 was selected as the powder to be used to manufacture the conduit heart valve.

3.4 Mould Design

3.4.1 Introduction

The initial design recommendation for the conduit heart valve suggested that it be made seamless, using powder reaction injection moulding technology, to help increase the in-service reliability. This ruled out the simple approach of casting the heart valve in two halves and bonding them together, and another process was developed.

A common method used in investment casting is to mould the feedstock around a core, which is later removed. This type of processing is not employed with traditional powder injection moulding, because high temperatures and pressures combined with full automation make it impractical. PRIME, however, is a low temperature, low-pressure process that can utilise investment casting technology (using waxes or metallic alloys as sacrificial cores) to create a complex geometry such as the heart valve (appendix B).

The moulds used for such operations have to be compatible with the materials that are formed within them. For example, cyanoacrylate would not be cast or formed in a mould with a substrate that it adheres to, hence moulding materials had to be carefully chosen.

Part of the PRIME process involves polymerising formed feedstock within the mould. It was thought that this could be achieved by one of three methods: surface initiation; a method of entering the catalyst into the mould; or, finally, air within the mould might be sufficient to cause a reaction. Each of these methods was investigated to find the most effective.

3.4.2 Requirements

Powder 3 proved to be the best suited to the PRIME process (section 3.3.4), and was used for creating the conduit heart valve. It was the most viscous, a volume fraction of 0.5 being the maximum mixture level attained previously with this powder; although a reduced volume fraction of 0.48 was used for moulding, because it could be moulded with less pressure. The force required for injecting the feedstock was provided by the method shown in section 3.3.3.

The basic requirements for the mould design were as follows:

- The material had to be one to which cyanoacrylate would not adhere. Two materials were investigated, teflon and nylon-66
- Sufficient mechanical strength to withstand moulding pressures
- Room temperature moulding
- Fixture of the moulding barrel to the mould inlet
- Releasing agent
- Inlet
- Vent(s)

3.4.3 Design Implementation

Based on the requirements outlined in section 3.4.2, a polytetraflouroethylene (PTFE or teflon) mould representing a solid conduit heart valve was designed and manufactured. This design was used to test the mouldability of feedstock and provide useful information about curing. Figure 43 is a diagram of the design.

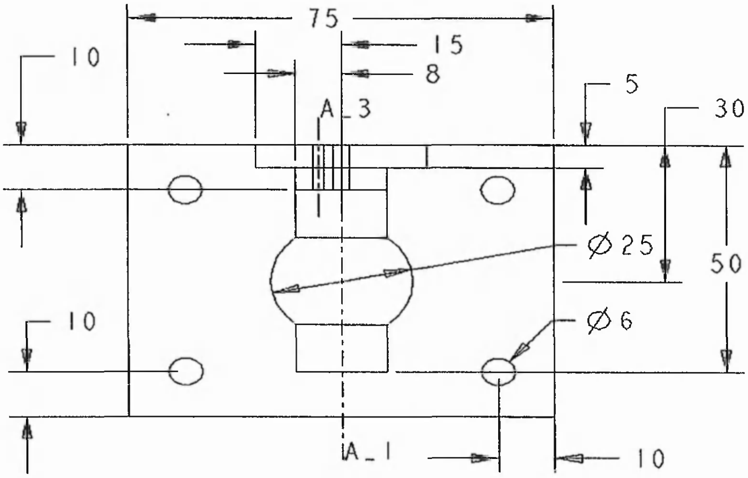


Figure 43. PTFE mould for solid conduit valve (all dimensions are in mm)

In an attempt to prevent the feedstock from adhering to the mould, the inner surfaces of the teflon mould were treated with a silicon oil surfactant. A feedstock inhibited with 7% acid (by volume of binder) was injected into the mould cavity, and was left in a flow of steam for five hours whilst the feedstock cured.

On opening, the formed surface in contact with the mould displayed a close replication and satisfactory curing, but inspection of the centre of the part revealed that the cyanoacrylate had not fully polymerised. This problem of incomplete curing was probably associated with the large diameter of the part: it was thought that propagation of the polymer chains would cease at a certain depth within a component, because of a large amount of chain end terminations.

Further investigation of the mould highlighted a problem with machining. The teflon had warped whilst the mould was being manufactured (probably caused by high temperatures produced when cutting) and the inner surfaces of the mould did not seal correctly during moulding, producing a part with excess flash. This could be eradicated by either changing the mould material or bracing the mould during the machining process. On this basis, an alternate material was investigated (nylon-66) to determine whether the mould would seal better after machining. However, the broken seal probably allowed the steam to contact the surface of the component, which would accelerate the curing process.

Three methods of eliminating the binder initiation problems encountered with moulding a solid part within the teflon mould were to:

- Provide a passage for a catalyst to enter the mould
- Control levels of acid inhibition using the working window method (section 2.4.3.3)
- Limit parts to a small thickness (less than 11mm, since this thickness polymerised in previous investigations (section 3.3.4))

The development of a *conduit* part, such as the heart valve, would automatically meet two of the above recommendations. Firstly, the conduit heart valve has a small thickness in its cross section and secondly, a sacrificial core associated with the 'lost wax' process will create a passage for a catalysing agent.

To test the process, an aluminium mould was designed to create wax inserts with a diameter of 8mm. This insert fitted inside a nylon-66 mould with an internal diameter of 19mm, so that a hollow cylinder with a thickness of 5.5mm would be created. Figure 44 is a CAD model of an aluminium mould for the wax inserts, and figure 45 details the arrangement of the insert inside a Nylon-66 mould.

Inserts were created by casting molten paraffin wax into the aluminium mould, which was pre-heated to eradicate distortion caused by rapid cooling on contact. An insert and the surface of the nylon 66 mould were then treated with a silicone oil surfactant as a releasing agent, and clamped together. After the mould was positioned under the injection apparatus, a feedstock inhibited with 7% acid was injected and left to cure in air for seven days. The standard polymerisation method using steam could not be used to cure the feedstock within five hours, because the paraffin wax had a melting temperature lower than that of steam.

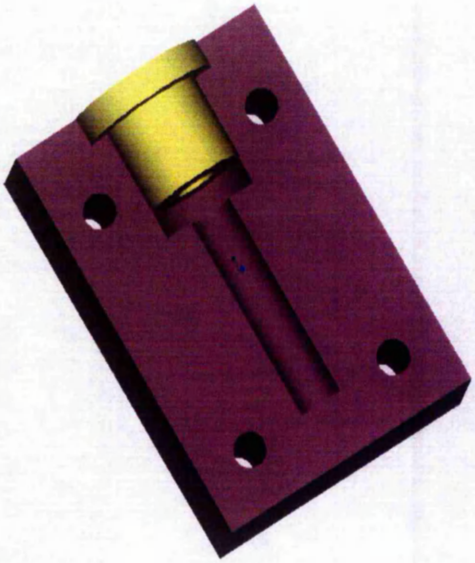


Figure 44. Aluminium mould half for wax inserts

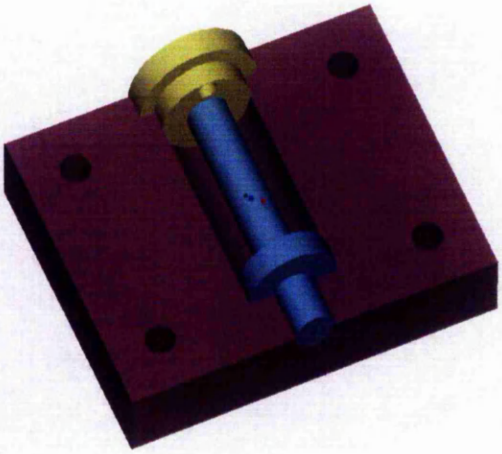


Figure 45. Nylon-66 mould half with wax insert

After seven days the nylon mould was suspended in a water bath at 90ºC for two hours, so that the wax melted. On opening, the part had adhered to the inner mould surface but no flash was noticed at the joining seam, and vigorous tapping on a steel block released the part for further inspection.

Pitting was noticeable on the part surface due to the difficult release from the mould. Polymerisation appeared complete on the internal surface, because of the contact with warm water when the insert was melted. On the other hand, the external surface still showed signs of fluidity and defects caused by lack of polymerisation, although the mould had been left undisturbed for seven days before the insert was melted.

The sample was dimensionally accurate when compared to the mould, showing no signs of shrinkage through polymerisation. Figure 46 shows a photograph of the finished part.

A different approach to moulding was needed to ensure complete polymerisation over the whole surface of the component and avoid surface defects.

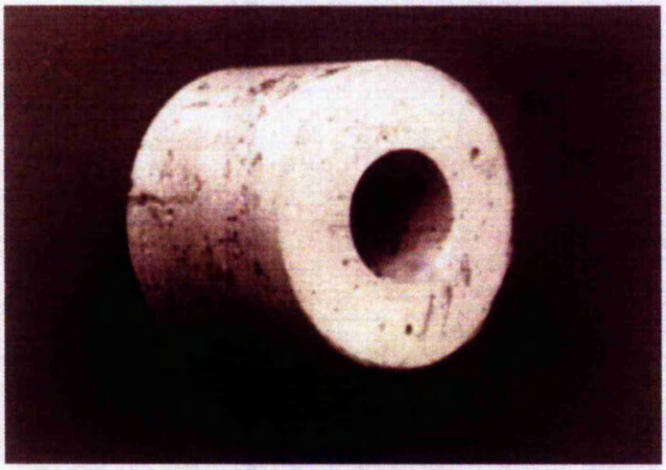


Figure 46. Photograph of a conduit part shaped in a Nylon mould

3.4.4 Novel Mould Design

So far, this investigation had used a simple injection moulding process for the creation of conduit parts formed in teflon and nylon moulds as detailed in section 3.4.3. A sacrificial core made from wax was placed within the mould and parts were formed around it, and after processing the core was leached out. The following observations were noted from these investigations:

(1) When the nylon mould was used, the outer surface of the part lacked quality and the process time was too long. The contact interface between the formed part and the nylon mould did not allow a free passage for the flow of a catalyst, therefore this region of the part did not polymerise within seven days.

(2) Cyanoacrylate adhered to the surface of the nylon mould causing pitting and slight damage to formed parts upon removal, even when a silicon oil release spray was used.

(3) The inner surface of moulded parts were of a high standard, especially where the wax core had been in contact.

(4) The process of leeching out wax cores allowed passage of water into the mould cavity. This caused fast polymerisation at the contact point of the cyanoacrylate binder.

Based on these observations it was decided to use an 'alloy mould' within a clamp to surround the part, along with a sacrificial wax or alloy core. This arrangement provided the following improvements:

(1) Any mould material could be used with a melting temperature lower than the de-binding point of cyanoacrylate, such as a low melting alloy.

(2) Removal of the core allowed the part to polymerise very quickly on the inner surface, and possibly the outer (through catalytic propagation through a thin section, which is only 3mm for the conduit heart valve), reducing processing time from seven days to a matter of hours.

(3) The part was easily removed after processing, since there was no surface contact with the mould, because the mould had been melted away.

(4) An alloy has sufficient mechanical strength to withstand the injection pressures associated with the injection moulding process.

(5) The use of a mould material such as an alloy eliminated the warping problem encountered with machining nylon, thus providing a good seal between the mould halves.

(6) No release pins were required to eject the formed part, because the mould had been thermally removed.

(7) No mould release agents or surfactants were required.

(8) The mould and core were re-cycled after processing, by simply re-casting them to form new components.

(9) A newer, inexpensive material was welcomed, because nylon was expensive, it had to be machined, and it was prone to wear.

Design of the moulds was relatively simple, mainly because the heart valve was symmetrical. The mould halves could have been aligned so that the seam was either vertical or horizontal, but a vertical seam alignment was preferred, to help the material 'fall' away from the valve when it was thermally removed.

The mould consisted of only six components:

a) 2 x outer mould halves
b) 2 x outer clamps
c) 1 x die/gate
d) 1 x central insert (or core)

The mould halves and the central insert were cast, and recyclable. The die/gate was machined from solid steel, which included the inlet and vent, and was positioned to support the top of the central insert.

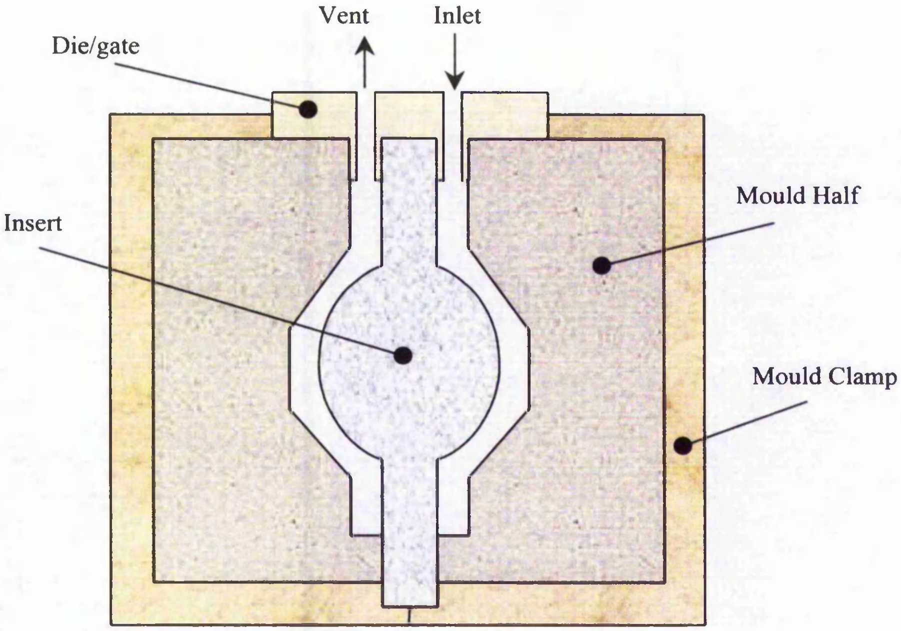


Figure 47. Moulding arrangement

Figure 47 diagrammatically represents the moulding arrangement, and figure 48 is a photograph of the clamped mould. The mould design is also included as CAD drawings in appendix B.

Figure 48. Photograph of a clamped mould

3.4.5 Material Selection and Casting

3.4.5.1 Mould and Insert Materials

Poly-cyanoacrylate thermally degrades at temperatures greater than 170°C. The mould material must melt at a temperature lower than this, otherwise the feedstock would degrade when the moulds were heated to remove them. On this basis, an alloy of tin and bismuth was selected as the material for the mould halves, because it melts at approximately 140°C.

The material for the central insert had to have a lower melting temperature than the mould halves, otherwise the mould would collapse around the uncured feedstock before polymerisation had occurred. Two options, wax or alloy, were investigated. Wax generally has a low melting temperature and would allow the insert to be removed in either a hot water bath or steam flow. The alloy would have to have a melting temperature that was considerably lower than the mould alloy, to reduce the risk of both alloys melting at the same time, and an alloy of tin, bismuth and lead was selected.

3.4.5.2 Wax

Wax had two advantages as the material for the mould insert: the melting temperature is generally lower than an alloy; and it can be removed from the mould using hot water or steam. There are many types of wax available, ranging from natural to polymeric/paraffin blends, and a selection was investigated by casting heart valve mould inserts. The wax types were:

- Candelilla - Hard natural wax, very brittle
- Carnauba (refined) - Hard natural wax not as brittle as candelilla
- Paraffin - Soft wax
- Investment Casting - Mixture of polystyrene and paraffin wax, which is used for commercial investment casting

The moulding characteristics were different for each wax, mainly because of the various melting temperatures. Therefore, the waxes were cast in an aluminium mould to empirically determine the required melting, casting and mould temperatures.

The melting temperature was simply found by placing a thermocouple within the wax whilst it was heated. However, the casting and mould temperatures were found after much iteration, until the insert castings were considered acceptable.

The drawings that detail the insert mould configuration are shown in appendix B, and table 12 details the casting observations and data for the wax types.

Table 12. Wax casting information for inserts

Wax type	*Melting Temp (°C)*	*Casting Temp (°C)*	*Mould Temp (°C)*	*Observations*
Carnauba	≈85	100	110	Little shrinkage, but cracks when cooling
Candelilla	≈85	100	110	Low shrinkage, very brittle and cracks when cooling
Paraffin 1	52-65	80	90	Low amount of cracking but high shrinkage, very soft
Paraffin 2	75-82	90	100	Low amount of cracking but high shrinkage and extremely soft
Investment Casting	63-70	90	65	Casts easier than natural waxes but cracks easily, extreme care required on cooling rates, very tough wax and malleable, noticeable shrinkage

The large surface area and thickness of the inserts caused cooling problems for the waxes. Hence, cracks were commonly found throughout the cast inserts, because of thermal gradients causing differential expansion rates. The moulds were lagged with aluminium silicate in an attempt to reduce the cooling rate, but this had little or no effect on the waxes. Nevertheless, a small proportion of waxes were cast without defects, and used for comparison.

The investment casting wax cracked less frequently than the other waxes whilst cooling, and the polymeric/wax blend provided a composition that was not too soft, with an appreciable strength. It tended to shrink more than carnauba and candelilla, but these natural waxes were too brittle for use in the heart valve mould. Therefore, investment casting wax was preferred as the material for casting inserts.

3.4.5.3 Alloys

Alloys were the preferred material for casting inserts and mould halves, because their mechanical strength was considerably higher than wax. Two alloys were selected for casting the insert and mould halves, as mentioned in section 3.4.5.1.

These alloys were investigated to find the melting temperature, casting temperature and mould temperature by filling aluminium moulds. The method was similar to that used with the wax casting investigation detailed in section 3.4.5.2, and the temperatures were determined empirically using an iterative approach. Table 13 summarises the data obtained from casting these alloys.

Table 13. Metallic alloys casting information

Alloy	*Component*	*Temperature (°C)*			*Notes*
		Alloy Melting (T_m)	*Casting*	*Mould*	
Tin/Lead/ Bismuth	Insert	104	120	85-90	Cast easily
Tin/Bismuth	Mould half	138	150	150	Cast easily

The mould cast perfectly with the tin/bismuth alloy, and there were no defects such as cracks, shrinkage, inclusions, or warping. However, the casting characteristics of the tin/lead/bismuth alloy were more difficult to determine. The insert regularly contained surface pitting and suffered from a low strength. It was suspected that the casting and moulding temperatures were incorrect, hence each parameter was individually adjusted until eventually the attributes were finalised as shown in table 13.

It was found that the tin/lead/bismuth alloy had to be cast at the tabulated temperatures, otherwise the component was brittle, and hence, failed. Nevertheless, when the parameters were correctly applied, the insert casting was of the same high quality as the outer mould and was ideal for use within the heart valve mould.

Both alloys had exceptional casting qualities with zero shrinkage; this was an important point, because the mould halves relied on close tolerances for clamping the insert. Wax, on the other hand, had appreciable shrinkage and casting limitations. Additionally, the use of alloy materials reduced the amount of reject components, thus improving the processing time.

Another observation indicating these alloys were a better choice than waxes for casting was associated with the cooling rate. The waxes were very sensitive to cooling rates, as noted by thermal gradients causing differential shrinkage, and crack formation. However, after casting, both alloys could be cooled rapidly using forced convection.

The moulds were placed under a fan until the mould temperature had fallen to an appreciable amount lower than the melting temperature, and then opened. There was no difference in cast quality between castings that were lagged whilst cooling, and those that were cooled by forced convection. The alloy materials were therefore cooled using the convection method to reduce processing time.

3.4.6 Moulding Investigation

The major aim of this investigation was to determine how to create the heart valve using PRIME, with a cyanoacrylate binder. However, to achieve this goal, many parameters had to be determined and optimised, and the following aims were set:

- Create a seam-free heart valve using a single mould
- Determine moulding pressures
- Determine (if any) temperature requirements
- Find the most useful material for an insert (wax or alloy)
- Determine whether alloy is a satisfactory material for the outer mould
- To find out if the materials can be re-cycled after processing
- Determine an ideal processing route for melting away the moulds and insert
- Find problems with the process
- Investigate the surface quality of the heart valve, inside and out
- Suggest methods of improving quality

- Investigate mould surface initiation of the binder
- Determine any shrinkage or distortion of the component after moulding

The heart valve mould was assembled using the parts cast as detailed in section 3.4.5, using both wax and alloy inserts. When being assembled, some moulds were treated with a cyanoacrylate acceleration agent (trichloroethane), which was supposed to promote a reaction with the binder. This type of initiation would improve processing time and assist with polymerising the binder before the insert was removed.

Before moulding, polypropylene tubes were loaded with the feedstock, which had been adequately inhibited to last through the mould filling stage. The valves were then moulded using the equipment designated in section 3.3.3, with a manual hydraulic press to supply the force. Whilst moulds were filled, the inlet pressure and feed rates were determined, and documented for a mould pressure analysis (the results of which are discussed in chapter 6). Finally, when the moulds were full (evidenced by feedstock leaving the vent), the remainder of the feedstock was injected through to ensure that any entrapped air was ejected.

The mould was left for two hours, to promote the initiation of polymerisation by the binder, before the insert was removed. The insert was of either wax or alloy, therefore two alternative processing steps were used to thermally remove the material from the mould, because the materials had different melting temperatures.

(1) *Wax insert removal procedure after moulding*

- Mould was inverted
- Wax insert melted out in a water bath at ~90°C for 2 hours
- Whilst inverted, the mould was agitated to ensure complete removal of the wax
- Mould was drained of water
- The remainder of the mould assembly was placed in an oven at ~150°C, with a humid atmosphere
- The oven, mould and heart valve temperatures were monitored by thermocouple

- The alloy outer mould was recovered as it melted
- Mould clamp was removed from the oven
- Heart valve was simply removed from the mould clamp (it was not attached to anything since the outer mould had been removed)
- Alloy was recovered and re-cast to form new mould halves

(2) *Alloy insert removal procedure after moulding*

- Mould was *not* inverted
- Mould was placed in an oven at ~110°C, with a humid atmosphere
- Alloy insert melted out
- Alloy was recovered for recycling
- The oven temperature was raised to ~150°C, with a humid atmosphere
- The oven, mould and heart valve temperatures were monitored by thermocouple
- The outer mould was melted and recovered
- Mould clamp was removed from the oven
- Heart valve was simply removed from the mould clamp (it was not attached to anything since the outer mould had been removed)
- Alloy was recovered and re-cast to form new mould halves

Table 14 details some of the results and observations made when creating the heart valves. An index was developed ranging from 1 to 10, providing a comparison of observed features of the moulded components, including cracks and surface quality.

Table 14. Moulding results

Acid level (%)	*Insert Type*	*Melting Temperature (°C)*		*Observations*		
		Insert	*Mould*	*Cracks 1-bad 10-good*	*Surface Quality 1-bad 10-good*	*General*
7	Paraffin Wax 2	95	155	8	6	Surface pitting related to internal collapse
6	Investment Wax	80	155	9	9	Internal collapse near injection point
6	Sn/Bi/Pb	110	150	3	6	Major internal collapse
6.2	Sn/Bi/Pb	110	155	8	5	Internal collapse, exotherm noted whilst moulding
8	Sn/Bi/Pb	110	150	N/a	2	Inverted mould whilst melted out core which caused serious collapse
7.5	Sn/Bi	N/a	110	N/a	N/a	Tried to melt outer mould first, by reversing the insert and mould alloys. Feedstock had not polymerised causing a termination

The moulding process was successful; each part was effectively removed from the mould without any major external defects. However, the feedstock collapsed in all cases when the insert was melted out. Further investigation of the damaged heart valves indicated that the collapse was probably caused by lack of support when the insert was removed. Therefore, a method of accelerating the polymerisation reaction was required, and hence, two samples were inhibited with 6% and 6.2% acid and moulded around alloy inserts that were coated with a surface initiator. However, the catalyst had no noticeable effect on binder initiation and other methods were required to polymerise the feedstock.

An aim of this investigation was to identify the centre insert material that produced better quality components. Contrary to the expectation that the wax would collapse because of moulding pressure, the sample containing the investment wax insert produced a high quality surface finish without cracking, although the internal surface had collapsed. Overall, the results indicated that heart valves had similar surface characteristics using either type of insert material; and subsequent investigations were performed using them both because there was no reason to eliminate either.

The mould half alloy (tin/bismuth) proved wholly successful, and was used as the material for mould halves throughout subsequent investigations.

The amount of shrinkage or distortion could not be determined from the moulded heart valves, because the internal collapse had caused the external surface to warp in compensation. Figure 49 shows a moulded heart valve with an internal collapse. It can be seen that the internal surface was reasonable at one end of the valve (left hand side of the photograph) even though the other end had collapsed, and this phenomenon occurred in most of the moulded components.

The external surface of the valve was slightly, but noticeably, coloured. It was thought that this colouration was attributable to the outer mould removal temperature, which may have caused a reaction with the binder. This effect was not considered a problem, because the valve could be machined using a subsequent process to remove this layer.

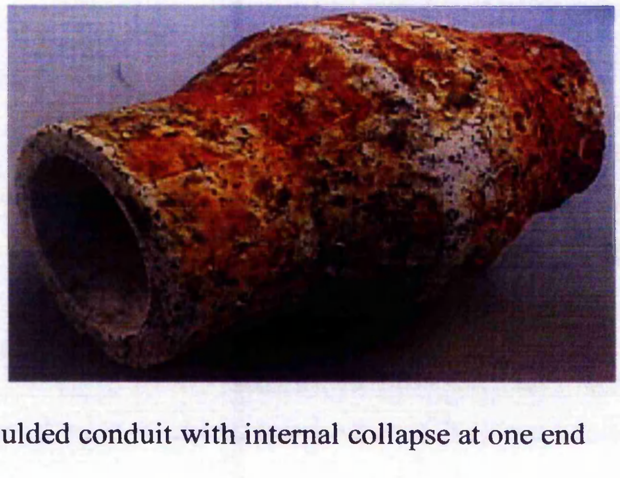


Figure 49. Moulded conduit with internal collapse at one end

3.4.7 Further Design

The results from section 3.4.6 showed that the feedstock was not polymerising properly during processing, and the moulded heart valves were suffering from collapse when the alloy core was melted. A method of addressing this would be the introduction of a catalyst to the surface of the uncured feedstock, and this was attempted by coating the surfaces of the mould with an initiator. It did not prove to be successful and collapse was still apparent because, it was thought, there was insufficient catalyst present to promote a complete polymerisation of the binder. Therefore, a solution was developed by introducing a continuous flow of catalyst to the surface of the heart valve, thus polymerising the feedstock, *before* the insert was removed.

A novel design was implemented that used a wax skeleton to surround and support the feedstock whilst in the mould. Subsequent thermal removal of this skeleton enabled the passage of a catalyst direct to the external surface of the heart valve, causing binder polymerisation soon after contact. The feedstock then had extra support from the polymerised section, allowing the insert to be melted from the mould without 'dragging' any materials with it. This process is the subject of a patent that was developed throughout this investigation, and is detailed in appendix D.

The mould design that included this new feature is provided in appendix B. Figure 50 shows a photograph of the wax skeleton that was inserted into a mould half, The mould halves with and without the wax skeleton are shown for comparison in figure 51.

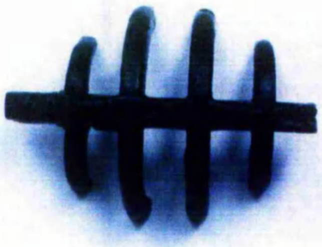


Figure 50. Wax skeleton (investment casting wax)

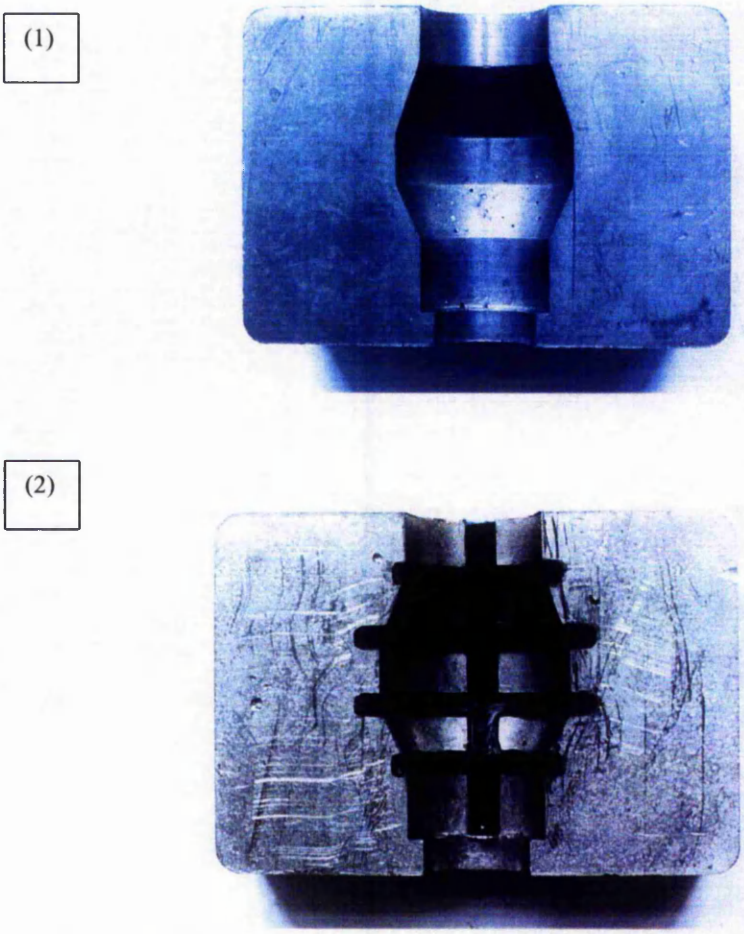


Figure 51. Alloy mould half without a wax skeleton (1) and with a wax skeleton inserted (2)

The processing steps for polymerising the feedstock and removing the heart valve after moulding were different to the procedure without a wax skeleton:

- Wax skeletons were cast using a wax that melted below the melting temperature of the mould half and insert.
- The wax skeleton was inserted into the mould halves before the mould assembly was clamped
- The feedstock was injected into the mould cavity and subsequently left for 2 hours
- The two extra vents that provided an exit for the wax were cleared if they were blocked by feedstock
- The mould was *not* inverted
- The mould was placed in a water bath at 90°C
- The wax skeleton proceeded to melt out
- When the wax had melted, the mould was agitated until all the wax was removed ensuring that no air was left within the cavity
- Water entered the cavity and polymerised the binder constituent of the feedstock
- The mould was drained (although the water could be left inside the cavity for the remainder of processing)
- The mould was placed in an oven at ~110°C with a humid atmosphere
- Alloy inserts melted out
- The alloy was recovered for recycling
- The oven temperature was raised to ~150°C with a humid atmosphere
- The oven, mould and heart valve temperatures were monitored by thermocouples
- The outer mould melted and was recovered
- Mould clamp was removed from the oven
- Heart valve was removed from the clamp
- Alloy was recovered and re-cast to form new mould halves

The feedstock used to investigate the wax skeleton method consisted of a volume fraction of 0.48 and binder inhibition level of 8% acid. This combination was similar to the investigations detailed in section 3.4.6, and hence, a comparison was made between the results. In addition, the feedstock was injected using the same procedure as that indicated in section 3.4.6 with a hydraulic press providing the force.

The wax skeleton had to be melted out before the centre insert was. Therefore, the insert was manufactured from tin/bismuth lead alloy instead of wax, otherwise the melting temperature of the skeleton and insert would be too similar. Combinations of wax types were used for skeletons, to enable a comparison of results. Table 15 tabulates the observed results from this investigation.

Table 15. Result from moulding using a wax skeleton within the mould halves

Insert material	*Skeleton material*	*Melt temperature (°C)*			*Observations*		
		Skeleton	*Insert*	*Mould*	*Cracks 1-bad 10-good*	*Surface Quality 1-bad 10-good*	*General*
Sn/Bi/Pb	Paraffin 2	85	120	155	10	8	Slight internal imperfections, paraffin wax compressed with moulding pressures indicated by raised lumps on the internal surface of the heart valve
Sn/Bi/Pb	Investment Wax	80	120	155	8	9	Slight internal imperfections, investment casting wax caused little external surface imperfections
Sn/Bi/Pb	Investment Wax	80	120	155	10	9	Virtually no internal imperfections, although external pitting. Noticed that a large amount of feedstock appeared through wax injection points whilst moulding

N.B. Surface quality represents pitting and smoothness

Although wax centre inserts could not be tested within this moulding arrangement, use of the alloy insert was observed to improve the quality of moulded heart valves, as shown in table 15. Thereafter, alloy inserts were the favoured alternative to wax, because of the increased mechanical strength and superior casting ability without shrinking.

For the skeleton, both paraffin and investment casting wax were tested. Each gave good results in comparison to the moulding observations made in table 14, but the sample that used paraffin wax had some imperfections because of the soft nature of this material. Because of this, and because the results indicated that the moulding pressure did not affect the skeleton, investment casting wax was used to create the heart valve.

The moulded conduits were compared to a mould half to determine whether there was any noticeable shrinkage. The components were found to fit inside the mould without interference, indicating that shrinkage was either non-existent or very low. However, this method did not compare the internal surface, which was assumed to have retained its shape, like the external surface.

When the mould was being filled, it was observed that feedstock was exiting the mould via the vents provided for melting the wax skeleton. This had no adverse affect on the moulding process, and probably aided the process by providing additional venting. Hence, there were two possible reasons for the success of the improved moulding:

(a) The wax skeleton provided a passage to the surface of the part, so that the catalyst promoted polymerisation of the binder within the mould. This extra support from the polymerised 'skeleton region' thus prevented the remaining semi-cured feedstock from collapsing when the insert was subsequently melted out. (N.B. this suggestion was the intention of the design)

(b) When the heart valve mould was being filled with feedstock, the pressure burst the wax within the vents that were intended for removal of the wax skeleton, providing two extra (albeit unintended) mould venting positions. These new vents provided a pressure relief from the mould whilst it was being filled, and aided the dispersal of trapped air from the mould cavity. Finally, when the insert was removed, the feedstock had been relieved from a pressure build-up that could have otherwise caused feedstock to collapse from pressure relief.

It was thought that suggestion (a) was the principal reason for the success of the skeletal cage. Whilst slight pressure relief may also have occurred, this was only a suggestion, because the pressure within the mould was unknown. In order to clarify these observations, an investigation into the mould pressure was the subject of a computational analysis which is detailed in chapter 6.

Chapter 4 – Ceramic Machining

4.1 Introduction

Ceramics are being used more frequently for the production of engineering components and biomedical prosthetics. This increased use is directly related to the superior properties of the material, such as resistance to wear, high temperature strength, and resistance to corrosion. Applications that take advantage of these attributes are many and varied, including valves and valve seats, turbine blades and liners, cutting tools, artificial hip joints, dental prosthetics and artificial heart valves.

However, the properties of ceramics also have drawbacks with respect to engineering fabrication. High hardness and low toughness present difficulties when machining monolithic ceramics and bulk material removal is normally by the traditional approach of diamond grinding. Nevertheless, although diamond grinding is used for more than 80% of all machining performed on advanced ceramics (95), it is limited in the complexity of shapes that can be produced and new physical and chemical (P&C) machining techniques have been introduced to try and overcome this. P&C removes small, solid particles by methods that include ultrasonic machining, electrical discharge machining (EDM), laser beam machining (LBM) and electro chemical machining (ECM). Practical limitations to their use are high initial investment costs and restrictions on the types of material that can be machined.

Diamond grinding and P&C are best suited to machining dense, sintered ceramics. Conversely, the design of sophisticated ceramic components is often constrained by the limits of these techniques. An alternative approach to the forming of ceramics is to mould the component and then machine it to a high tolerance, using a simple traditional technique such as turning with a lathe, before sintering. This is known as 'green machining', which occurs by particle attrition, and is typically used for the production of spark plug insulators. However, usually because of a low fracture strength, ceramic binders cannot normally withstand the forces associated with traditional machining (24).

Powder Reaction Injection Moulding and Extrusion (PRIME) is a technique that involves mixing a reactive binder with a particulate material, moulding, debinding and finally sintering to near net density (9). This process has proved to be successful for developing conduit articles out of ceramic as detailed in chapter 3. Components produced by this method appeared to have good mechanical properties in the 'green' unfired state. It seemed that the binder could provide adequate strength for green machining, which would provide the possibility of making parts to a high tolerance before being sintered. For articles where surface finish is a prime concern, such as the heart valve, this method is of significant benefit.

This chapter demonstrates the ceramic machining options that were available, and the selection of a suitable process that could further enhance the geometry of the as-moulded, unfired heart valve. The machining characteristics, or machinability, of the moulded feedstock were investigated to determine feasibility, and to compare them against machined steel.

4.2 Ceramic Machining Techniques

4.2.1 Background

Some ceramic products are initially moulded to an approximate geometry and then further processed by machining to a final shape. The product is in one of three states before it is machined; green, partially sintered, or densely sintered. "Green machining" is the machining of unsintered or very porous sintered material, and is a method used to produce contoured surfaces on spark plug insulators, shape bioceramic implants, manufacture wear resistant inserts and threaded structural components (24). Green machining can be performed using a traditional or non-traditional machining method, depending on the type of material and complexity of the geometry.

Densely sintered parts are machined to a final shape by hard machining techniques, which relies on non-traditional methods or grinding with diamond inserts. Table 16 details the difference between these traditional and non-traditional machining techniques.

Table 16. Traditional and non-traditional machining operations, and a comparison of how well they machine common materials

	Machining Process	Material				
		Aluminium	Steel	Titanium	Fired Ceramic	Plastic
Non-traditional	Ultrasonic	Poor	Fair	Fair	Good	Fair
	Abrasive Jet	Fair	Fair	Fair	Good	Fair
	Electrochemical	Fair	Good	Fair	N/a	N/a
	Chemical Milling	Good	Good	Fair	Poor	Poor
	Electrical Discharge	Fair	Good	Good	N/a*	N/a
	Electron Beam	Fair	Fair	Fair	Good	Fair
	Laser	Fair	Fair	Fair	Good	Fair
	Plasma Arc	Good	Good	Fair	N/a	Poor
Traditional	Turning	Good	Good	Fair	N/a	Good
	Milling	Good	Good	Fair	N/a	Good
	Diamond Grinding	Good	Good	Fair	Good	Good
	Grinding	Good	Good	Fair	N/a	Good
	Drilling	Good	Good	Fair	N/a	Good

*Only special conductive ceramic composites can be machined by EDM

Source: data taken from non-traditional machining book

There are many non-traditional machining techniques: some are used extensively for commercial operations; some used only on a limited basis; and others are still experimental, used only for research purposes because of the associated expense.

Non-traditional processes are distinguished from traditional techniques, by their higher power consumption and lower material removal rates. Throughput is typically low when using non-traditional methods, and therefore they tend to be used for more specialised operations, such as producing extremely complex parts and machining exotic materials (96).

Sections 4.2.2 To 4.2.5 detail the traditional and non-traditional machining processes used for ceramic machining, which could be used for increasing the tolerance of the conduit heart valve.

4.2.2 Traditional Machining

Traditional machining can be split into five categories, sawing, grinding, milling, turning, and drilling. Essentially, these processes shape materials by particle attrition, shearing material from the surface of a workpiece. The techniques have been developed and used successfully since the 18th century, for products made from a variety of materials from natural wood to steel. Although the advent of tougher, harder new materials (such as ceramic composites in the second half of the 20th century) and specialist operations requiring very fine tolerances have demanded new methods of working, traditional machining continues to be relatively inexpensive, more productive and more widely accepted than non-traditional techniques.

4.2.3 Ultrasonic Machining

Ultrasonic machining (USM) was developed primarily for the effective machining of hard brittle materials. Typical materials that are commercially machined by this method are carbides, stainless steels, ceramics, and glass.

The process works by means of a cutting tool, which oscillates at a range of frequencies, typically between 20 and 40kHz, in abrasive slurry (97). Hence, the shape of the machined workpiece represents the geometry of the vibrating tool. Machining takes place as the high speed oscillations of the tool cause the abrasive slurry to impact the workpiece, providing the energy for material removal. This is because the gap between the tool and workpiece is minute, typically around 1×10^{-5} m (96). Figure 52 details a schematic representation of the cutting process.

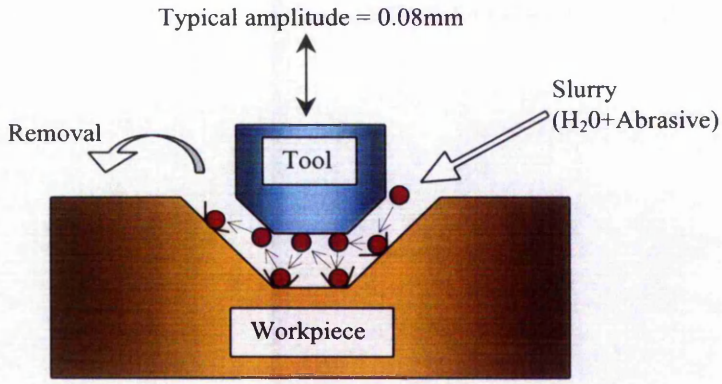


Figure 52. Schematic of an ultrasonic machining device

The USM process is particularly suited to $^{(96)}$:

(1) Holes with a curved axis; non-round holes; holes of any shape for which a tool can be made. The range of shapes obtainable can be increased by moving the workpiece whilst cutting.
(2) Threading by rotating and translating the workpiece as the tool penetrates.

USM is useful for creating complex shapes based upon the profile of the tooling, and the wide range of brittle/hard materials that it is capable of cutting. Generally, non-metals that cannot be machined by other non-traditional machining methods, such as electrical discharge machining, are suitable for the ultrasonic process. However, USM cannot compete with traditional machining operations because of its slow material removal rates, and it can be cost-effectively used only in specialist applications.

4.2.3 Abrasive Jet Machining

Abrasive jet machining (AJM) is a process that removes material by impinging fine abrasive particles carried by a high velocity gas stream on to a workpiece. The method is used for cutting, cleaning or deburring hard/brittle materials, such as glass and ceramics. Coolant is not required for such machining operations, because the gas tends to cool the workpiece whilst it is being cut, and there is no inherent chatter or unwanted vibration in the system, because the tool is not in contact with the workpiece. Figure 53 details the layout of the apparatus for machining.

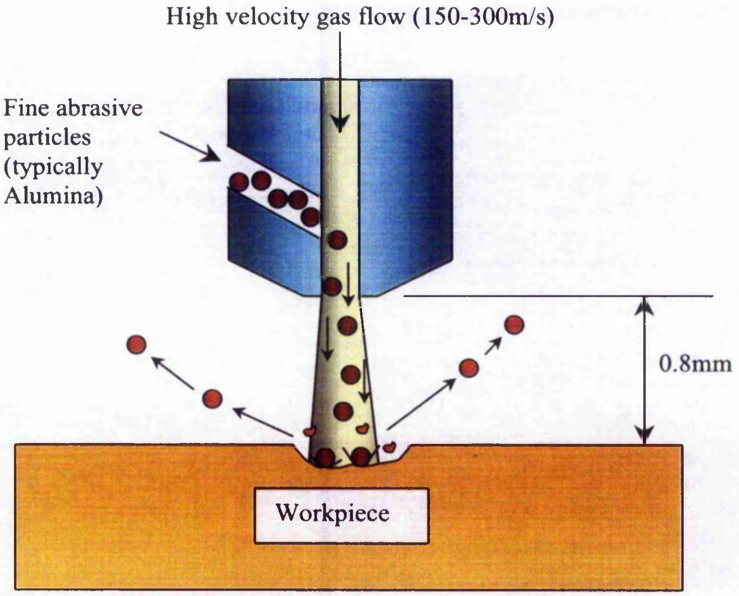


Figure 53. Abrasive flow machining

There are many uses for abrasive jet machining, because of the non-invasive action of the gas flow (96):

(1) Frosting: AJM can frost glass quicker than other available methods, such as etching or grinding. Varying the abrasive powder particle sizes affects the type of finish attainable, thus broadening the scope of this process.

(2) Cleaning: AJM is particularly useful for cleaning surfaces (such as metallic smears on ceramics, oxides on metals and resistive coatings) and is mainly used on materials that are too delicate to withstand the forces involved with grinding or scraping.

(3) Semiconductors: Fast and accurate drilling, cutting, cleaning or dicing can be performed on semiconductor materials such as silicon and gallium.

(4) Metalworking Applications: AJM can be used to cut or drill thin sections of hardened metals.

AJM is similar to other non-traditional techniques since it cannot be used for mass material removal. The process is particularly useful for surface cutting or cleaning of materials, as opposed to other techniques used in traditional machining that use particle attrition and shear forces to shape components. It is a very flexible process, because different abrasive powders can be inserted into the jet stream, increasing the range of materials that can be machined. For example diamond particles could be used to cut hard brittle materials, whereas a less abrasive particle could be used for surface treatment of softer materials.

4.2.4 Electron Beam Machining

Electron beam machining (EBM) is a common method used in many types of industrial processes. An electron beam is accelerated in an electric field to produce a narrow beam that can be simply manipulated by use of electrostatic or electromagnetic fields onto a workpiece.

The operating principle is relatively complex, there are numerous components that need fine-tuning; and the process is expensive in comparison to other non-traditional techniques. The main components, and workpiece, are contained in a vacuum chamber, evacuated to approximately 10^{-4} torr. Electrons are produced from an electron gun, which basically consists of a cathode, cathode cup and anode that is at ground potential. The cathode is usually constructed from tungsten and takes the form of a filament heated to temperatures between 2500-3000°C in order to emit the electrons. The electrons are accelerated towards the anode by introducing a high potential (usually 150kV) between the cathode and anode. After the initial acceleration, the electrons are diverted through a small hole in the anode by the cathode cup. Finally, the beam is focused onto the workpiece by a magnetic or electrostatic lens system. When the beam hits the workpiece, the kinetic energy of the electrons is rapidly converted into heat, which causes the

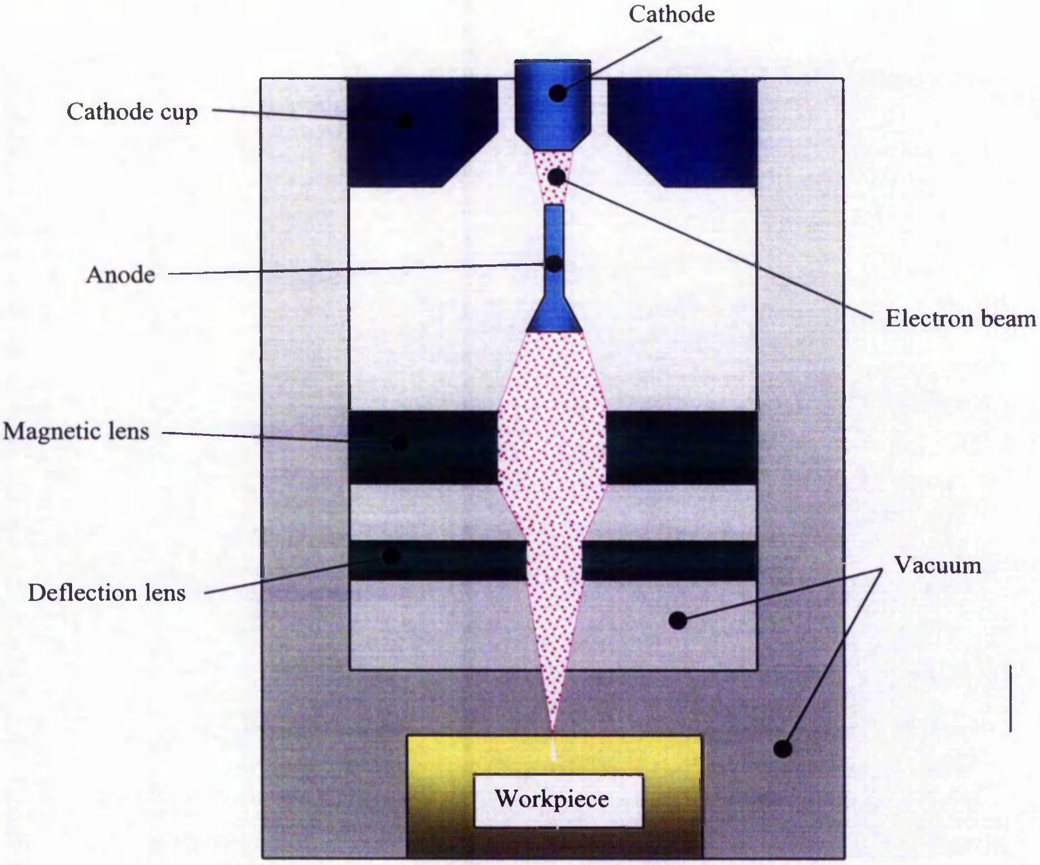


Figure 54. Schematic of an electron beam machine

workpiece to rapidly increase in temperature. This exchange of energy causes an extreme temperature rise that is sufficient to boil any material that it is focused on, so there are no limitations on the materials to which EBM may be applied. Figure 54 details the arrangement of the components used in a typical electron beam machine.

Electron beam machining is used for a variety of applications including, heat treatment, welding, cutting, and drilling. An advantage of this system is that the beam power can be adjusted to suit different applications, and hence, the range of uses for this type of equipment is vast.

In similarity to abrasive jet machining, EBM is a process that works on the surface of a material, which limits the machining ability of complex geometries. For example, it would be difficult to work on a conduit or underneath the surface of a workpiece. Nevertheless, EBM is a process that can machine *any* known material provided only that the workpiece can sustain a shape within a vacuum.

If there is a need to cut a difficult material or drill a very fine hole, then the advantages of EBM can outweigh its limitations. The principal constraints on the use of the process are its cost and the size restriction on machinable workpieces caused by the need to work in a vacuum.

4.2.5 Laser Beam Machining

Laser (light amplification by stimulated emission of radiation) beam machining (LBM) is similar to electron beam machining, in that it is a process that focuses energy onto a workpiece. However, laser beams use light energy (photons) whereas electron beam machining uses electrons. The machining process is physically simple, yet the energy production in theory is complex. The workpiece is cut using monochromatic (single wavelength), coherent (in phase) light at a sufficient power to vaporise any known material, including diamond. Unlike EBM, however, not all the material is removed by evaporation. Laser machining is an ablation process, where the material is heated by light radiation to the point where the material melts and evaporates. This occurs at such a high speed that an impulse is transmitted to the liquid, which causes non-evaporated liquid to leave the surface at a relatively high velocity. The workpiece heating process is described diagrammatically in figure 55.

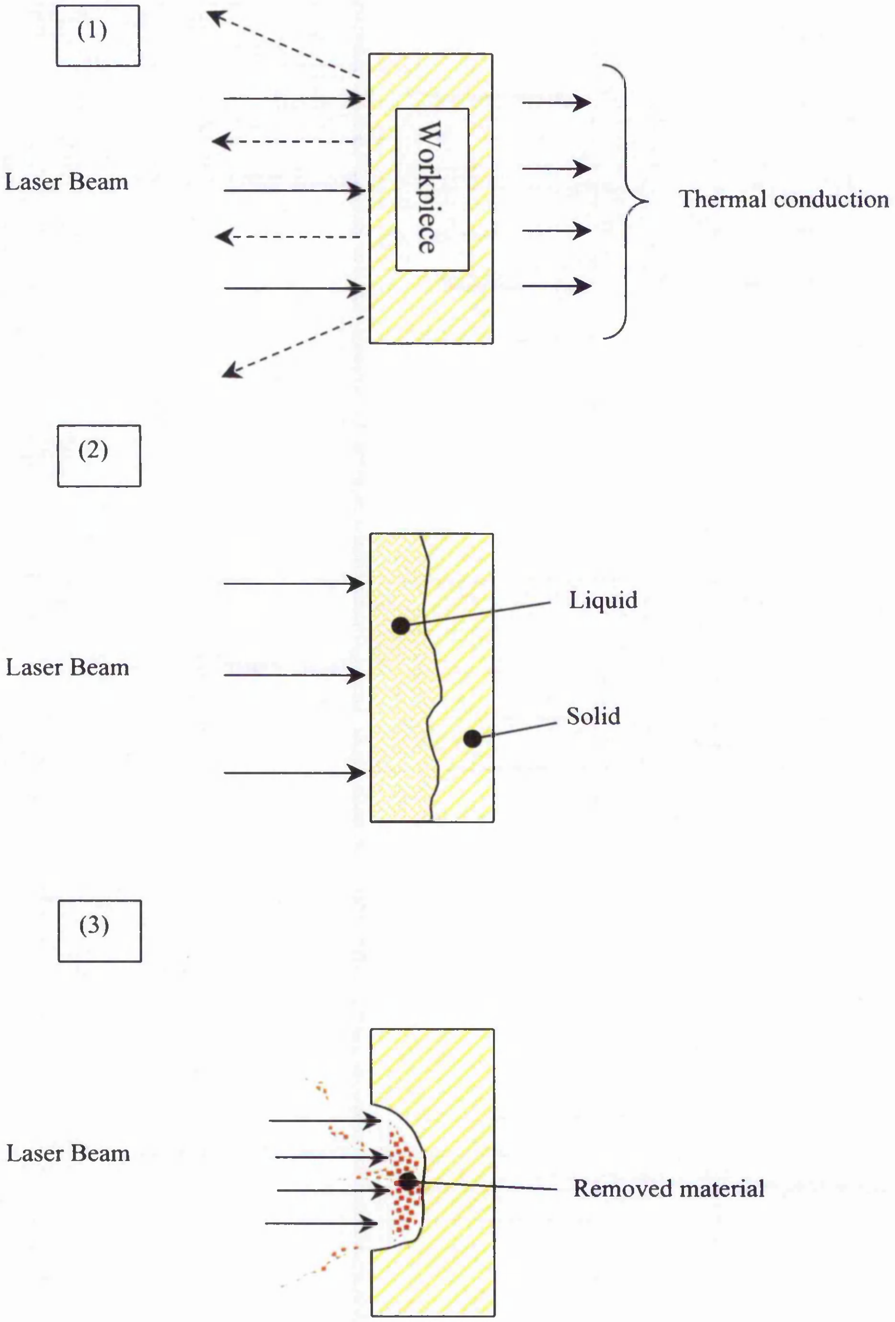


Figure 55. Laser Beam Machining, effecting a workpiece. (1) Initial contact, (2) Molten surface of the workpiece, (3) Material evaporation and impulse removal

Many machining operations can be performed by laser on ceramics and other materials, including drilling, cutting, scribing, controlled fracturing, and trimming. As with EBM, however, these applications require the beam to be focused at an exact point on the workpiece, and would require complex control to machine conduit components. Some geometries cannot be machined, but lasers can produce extremely complex geometries by the addition of materials, though this is beyond the scope of this investigation.

4.3 Green Machining of PRIME Feedstock

Non-traditional machining methods are generally used for hard, brittle materials, and, at first sight, could be thought ideal for improving the geometry of a fully sintered heart valve. However, because of the geometrical restrictions, the internal surface geometry of the heart valve would be difficult to machine using any of the non-traditional methods mentioned in section 4.2.

The alternative method of improving the tolerance of the valve is to "green machine" the internal surface, by turning it on a lathe. Green machining is a method that can only be applied to materials that have sufficient mechanical strength to withstand the shearing action produced by a machine tool (24). Normally feedstock designed for powder injection moulding consists of a binder that contains a wax/polymer mixture, which has low mechanical strength and probably cannot be easily machined.

The most important characteristic of the part being machined is its fracture strength. The workpiece must be able to resist the induced stresses involved with machining and clamping without fracturing. The strength of a green material has to be greater than 2MPa (24) to withstand machining forces, although catastrophic component failure can occur if the strength is too high.

The strength of injection moulded components is dependent upon the volume fraction of solid to binder. Higher loading equates to lower fracture strength, because of the reduced amount of binder adhesion between particles. Successful green machining will also depend upon the particle size of powders and the thermo-mechanical properties of the binder. For example, some polymeric binders have a glass transition temperature that could coincide with temperatures produced by friction when machining, and wax binders have melting temperatures as low as 50°C. If this was the case, then components would fail when machining, because of the friction induced temperature rise.

The novel feedstock developed for creating the conduit heart valve seemed to have a remarkable level of strength after moulding. It had, for example, once polymerised, been clamped in a vice and sawed into sections without any obvious sign of fracture or failure. These observations prompted an investigation to determine the machinability of the alumina/cyanoacrylate feedstock, using a traditional machining operation.

4.3.1 Machinability of Alumina/Cyanoacrylate Feedstock

Machinability has no definition, and therefore any process that can compare one material to another is acceptable. This investigation compared the surface finishes obtained from turning an alumina/cyanoacrylate feedstock and mild steel. The basic intention behind surface profiling was to form an understanding of the quality of surface that was obtained by machining the feedstock, thus providing a visual awareness of the materials machining ability. The aims of the investigation were to:

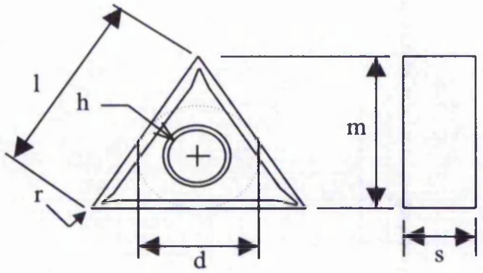
- Determine the effect of cutting speed on surface finish
- Determine the effect of feed rate on surface finish
- Provide a comparison between the surface finish of mild steel machined samples to alumina/cyanoacrylate samples
- Investigate how machining effects chip formation for a green sample
- Determine the effects of machining temperatures on the cyanoacrylate binder
- Assess the strength of green compacts for machining
- Assess the effectiveness of green machining with respect to the surface quality

Cylindrical compacts were needed for machining trials, and this required a simple mould that would allow release of the part without damage. This ruled out a metallic mould, because cyanoacrylate would adhere quickly to the surface, especially if there were any pits or imperfections resulting from fabrication. However, cyanoacrylate would not adhere to some polymeric materials such as polyethylene and polypropylene, and therefore a polymeric (polypropylene) mould was selected for a moulding vessel, with a number of 1mm holes drilled throughout its entire length. This provided two advantages related to processing,

(1) The part did not need to be removed from the polypropylene mould whilst machining. The mould was simply turned off, exposing the part for machining.
(2) The 1mm holes in the mould allowed the ingress of a catalyst to the surface of the part, which would polymerise the binder.

After mixing, the feedstock was compressed into the polypropylene moulds, by using a piston attached to a hydraulic press. The moulds were then suspended in a flow of steam for 10 hours, whilst the feedstock polymerised. From the work described in section (2.4.3.4), it was already known that this method would polymerise the feedstock to a level sufficient for machining investigations.

The test pieces were machined using a Colchester Student 1800 series lathe. The measured parameters included tool type, tool material, tool geometry, cutting speed and feed rate. A range of feed rates at three cutting speeds were selected for turning, using a coated carbide tool with geometry as shown in figure 56. This tool was selected because of its suitability to small cuts below 2.5mm and feed rates up to 0.5mm/revolution. A nose radius of 0.4mm was selected for good chip control between the chosen feed rates of 28mm/min to 576mm/min.



l=16.5
d=9.52
s=4.76
r=0.4
h=3.81
m=13.89

All dimensions are in millimetres

Figure 56. Tool geometry

The green bodies, and mild steel samples, were clamped into the Colchester lathe, and turned down to a diameter of 13mm (x), with a 0.5mm cut, and faced off at 20mm(y) intervals for surface roughness inspection. Figure 57 shows a schematic representation of the machining process, with a drilled polypropylene tube containing the polymerised feedstock.

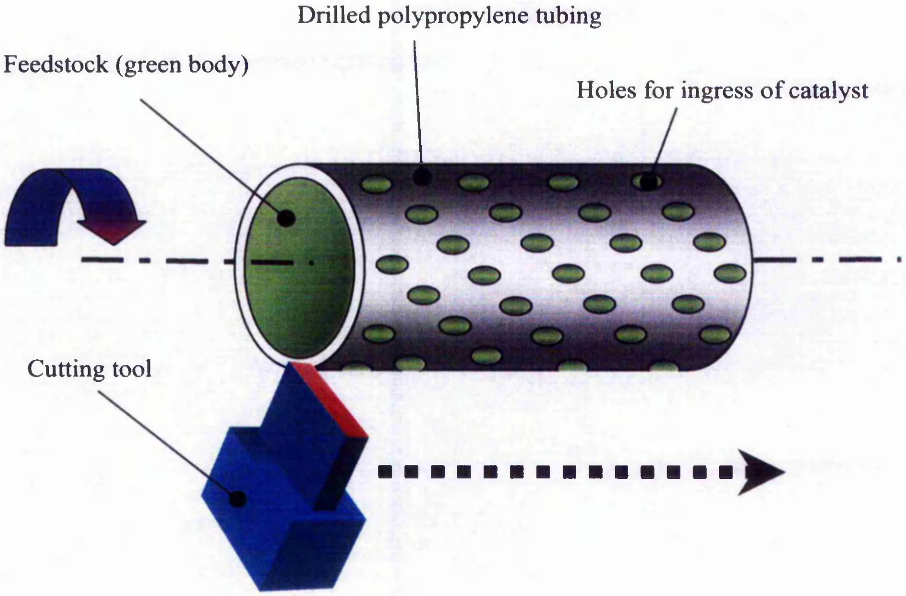


Figure 57. Schematic of the machining operation on a drilled polypropylene tube

The feedstock (green body) machined with ease, indicating that the fracture strength of the composite was within acceptable limits. The fracture strength would significantly decrease, however, if the volume fraction of powder were increased, because the binder concentration contributed to the mechanical strength. Therefore, these results would vary if parameters such as the powder characteristics were adjusted.

The chips that were produced when machining provided a basic indication of the machinability. Specimens were collected and examined under a scanning electron microscope for characteristics such as size and colour. Figure 58, shows the chip formation from a machined green sample.

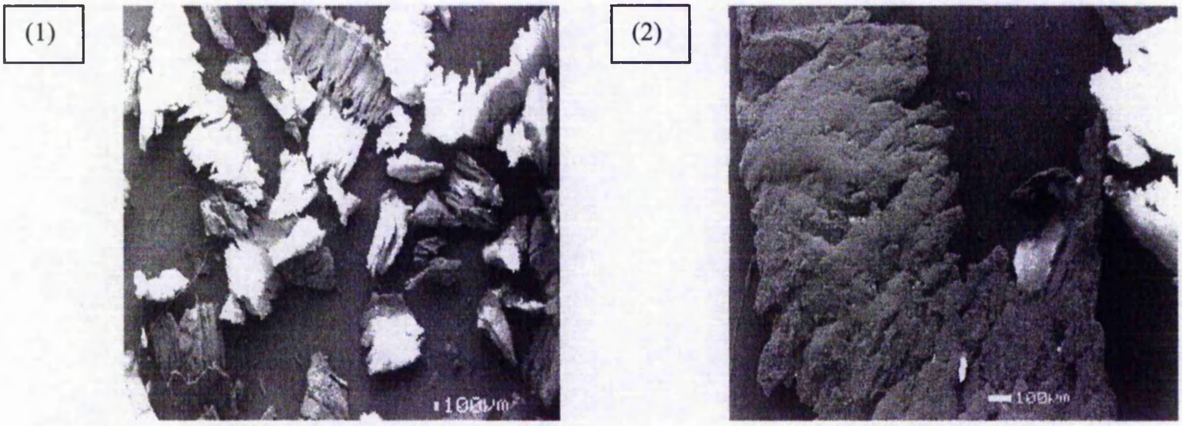


Figure 58. (1) Chips Produced from sample 4 (green), (2) magnified image of a chip

The chips produced from the green samples were discontinuous, unlike those formed from the mild steel, indicating that the feedstock material was not as ductile as steel, probably because of the particulate composition (98). The chips were not discoloured, indicating that there was little friction induced by the process, and the sample temperature was below the debinding point of cyanoacrylate. Because the feedstock was not showing any signs of thermal degradation, coolant was not required when turning the samples.

Another method of characterising the samples involved measuring the surface roughness by finding the arithmetic average (or R_a) of the peak to valley height of the surface. Hence, the R_a value was determined for all samples, using a Taylor Hobson Tallysurf series profileometer. The profile of each sample was averaged over four measurements and the high and low values of R_a were recorded as shown in table 17.

Table 17. Machining data

Sample	*Feed Rate (mm/min)*	*Cutting Speed (rpm)*	*Feedstock (green body)*		*Mild Steel*	
			R_a High (μm)	*R_a Low (μm)*	*R_a High (μm)*	*R_a Low (μm)*
1	28	555	3.6	2.1	2.4	2.4
2	56	555	5.3	3.7	3.3	2.7
3	111	555	5.2	4.2	4.6	4.3
4	50	1000	3.4	1.9	0.9	0.9
5	100	1000	4.9	3.6	1.0	0.9
6	200	1000	5.6	3.2	2.5	1.9
7	108	1800	3.6	2.7	0.9	0.9
8	234	1800	7.0	4.6	1.8	1.7
9	576	1800	9.4	8.8	4.6	3.8

Generally, the surface quality of the green compacts was acceptable, because the roughness did not exceed 10μm. At 1000rpm, the average R_a value approached 2μm, which was considered to be a good surface, because it was similar to the mild steel. The quality of the green compacts was not as good as the steel at the higher cutting speeds, particularly at higher feed rates.

The large deviation of R_a values for the green compacts was characteristic of particulate composites because, at the higher speed and feed rates, particles of powder tended to 'pull out' of the surface, leaving pits. It can be seen that the green compact (figure 59) had a coarse surface, with large peaks and troughs, arising from the 'pull outs' whilst machining. In comparison, the mild steel sample (figure 60) had a much smoother profile which was characteristic of the good turned surface typically achieved with mild steel.

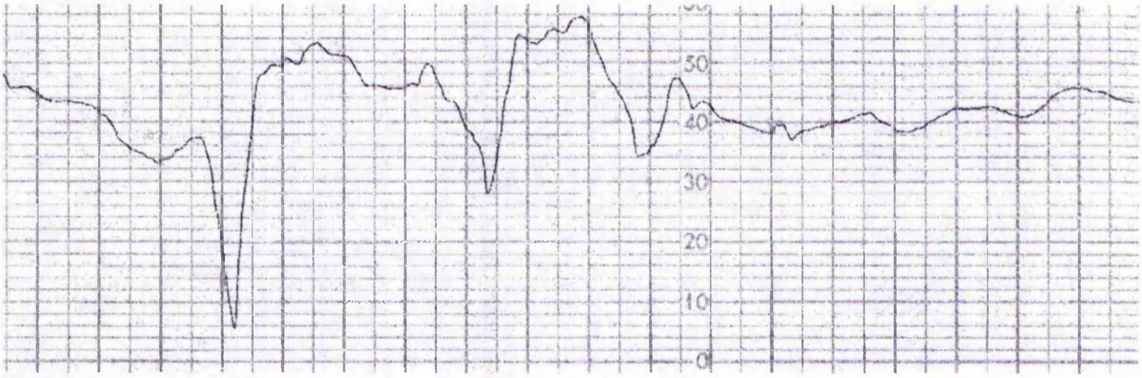


Figure 59. Surface profile of sample 8 (green body)

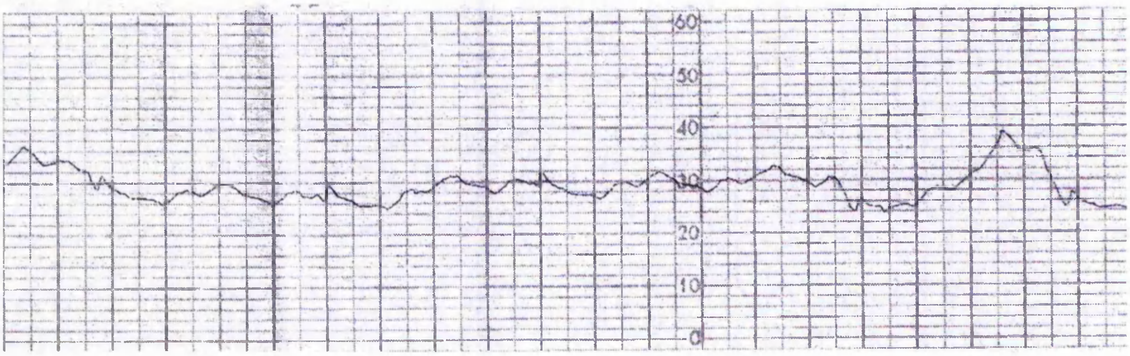


Figure 60. Surface profile of sample 6 (mild steel)

A method to overcome this observed problem might be to use a ceramic with a smaller particle size. The, 'pull outs' would be limited to the size of the particles, and the surface quality may be better. However, smaller particles tend to agglomerate whilst preparing compacts, which lowers the attainable volume fraction of powder to binder, hence reducing the ability of the compact to sinter.

Figure 61 is a plot of the roughness against cutting speeds at a feed rate of 100mm/min. It can be seen that the R_a value of the green compacts decreased when the cutting speed increased. As with steel, an increase in cutting speed and a low feed rate, were required to attain finer finishes.

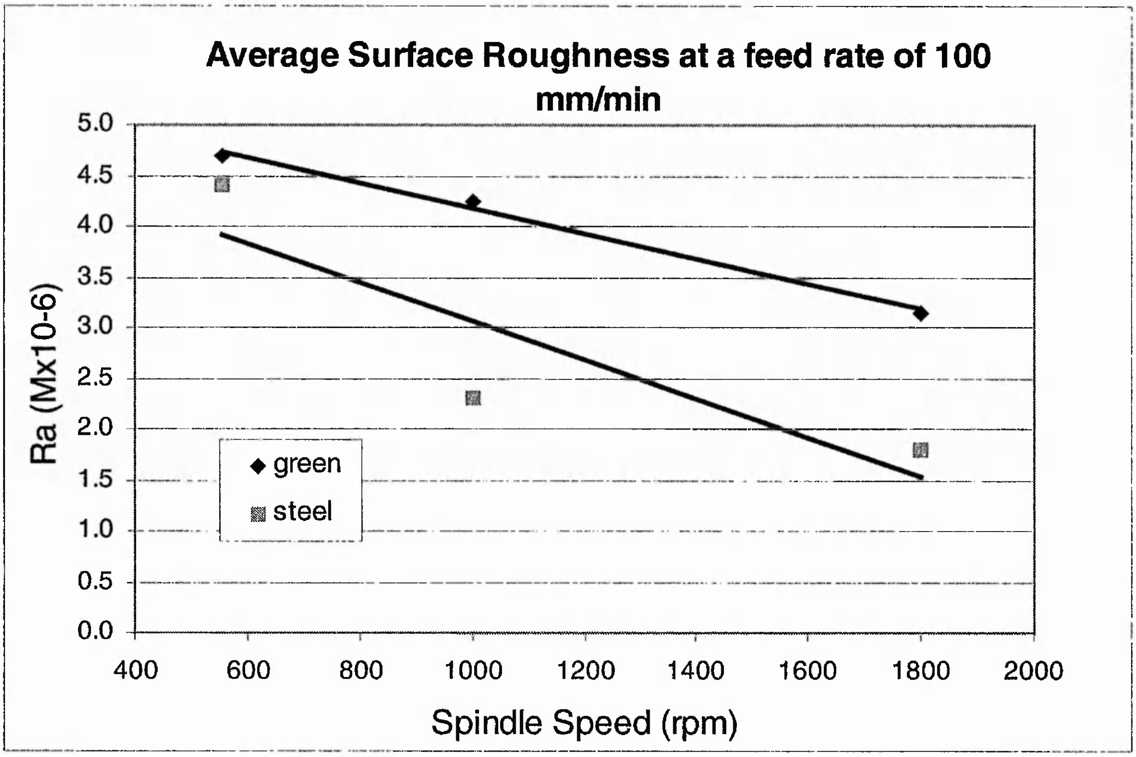


Figure 61. Average surface roughness at a feed rate of 100mm/min

4.4 Summary

Grinding techniques are typically employed to machine ceramics because of the material hardness and equipment availability.

After moulding, the feedstock was observed to have a high strength that could probably withstand traditional machining operations, and allow the heart valve to be machined to improve tolerance and surface finish.

Complex equipment such as that involved with non-traditional machining was not required for the Alumina/Cyanoacrylate feedstock. Instead, a simple traditional machining arrangement was used, which increased the flexibility of the process because of the equipment availability and cost.

Non-traditional techniques would probably not machine a complex geometry, such as that associated with the conduit heart valve, unless specialised tooling was developed. Nevertheless, ultrasonic machining would probably be the most realistic alternative for cutting the heart valve geometry, because a tool with a complex profile could be developed to machine the internal surface.

Polypropylene was a useful material for the moulding of the PRIME green compacts, because the moulds were readily drilled to allow the ingress of steam to polymerise the binder. Furthermore, the mould provided a support for the feedstock whilst it was turned down to the required diameter of the investigated compacts.

Samples turned with ease, suggesting that the binder material had sufficiently high fracture toughness for green machining. Chip formation whilst machining suggested that the compacts had a brittle nature. Inspection of the chips and the compact surface showed no sign of debinding or thermal degradation, and no coolant was required whilst turning at the investigated cutting speeds and feeds rates. The compacts turned with similar characteristics to mild steel, and when the cutting speed was increased at a low feed rate the surface finish improved.

The surface of the green compacts had a roughness (R_a) less than 10μm, with some samples approaching 2μm. These are acceptable limits for turning operations, indicating a good surface finish. Although large deviations were found between the R_a values for the green compacts, caused by 'pull outs' from the material, adjusting the powder parameters such as volume fraction, particle size and shape would reduce this.

This investigation proved the suitability of the PRIME alumina/cyanoacrylate composite for green machining, and that it will allow the manufacture of complex shaped articles with a good surface finish without a need for investment in expensive physical or chemical machining equipment.

Chapter 5 – Heat treatment

5.1 Debinding

5.1.1 Introduction

'Debinding' is a term used for removal of the binder from a component after moulding or machining. If the binder were not removed before sintering, then the component would probably crack and fail, because of thermal expansion and vapour pressures attributable to the polymer rapidly decomposing. In order to preserve the geometric integrity of the moulded part, the binder must be removed without disturbing the powder particles. This is a delicate operation, especially when the particles are bound together by more than one component.

The process of debinding begins by gradually heating the moulded component to a temperature where the binder will soften, and hence, is unable to withstand shear stresses caused by gravity, internal vapour pressure or thermal gradients. The shape of the component is maintained by particular friction; if this is insufficient, it will collapse.

The binder must be removed from the powder particles as a fluid, either liquid or vapour. Six methods have been devised to promote and assist this process as shown in figure 62.

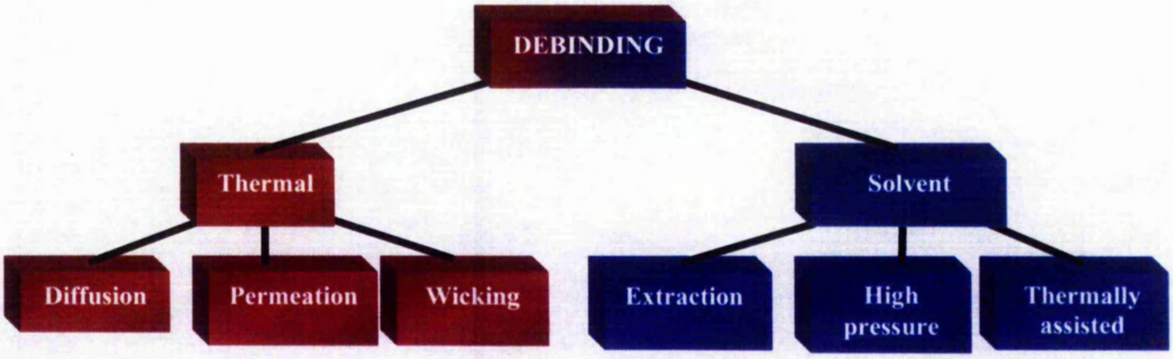


Figure 62. Debinding techniques

Solvent debinding involves submerging a component in a fluid that will dissolve some of the binder, leaving an open pore structure between the remaining particles of powder. Hence, a path is created for subsequent removal of the remaining binder by thermal evaporation at an elevated temperature. There are three methods for dissolving the binder in a solvent: simple immersion, high solvent pressure, and a process that involves heating the component in the presence of a reactive vapour. The choice of method depends upon the type of binder and solvent used, and the geometry of the component.

The alternative approach to debinding is to remove the binder without chemicals, by thermal methods alone. As with the solvent techniques, there are three methods that are commercially used for binder removal: wicking, diffusion, and permeation. Wicking (also known as the liquid extraction method) is based upon heating the compact until the binder viscosity is sufficiently low, thus inducing flow into the pores of a wicking substrate. The other two methods (permeation and diffusion) are based on gaseous flow of a binder following depolymerisation, thermal degradation, or molecular chain scission. The difference between diffusive and permeation flow is associated with the gas pressure. At low pressures, diffusive flow occurs in a component; however, if there are large pores and high pressures then gas permeation tends to dominate binder removal.

In practice, injection moulded components are constructed with a matrix of multiple binders that must be removed in a number of consecutive operations. Therefore, these six debinding techniques are normally combined in order to remove binders in controlled stages and to reduce overall de-binding time.

Originally, binders that were used for injection moulding comprised a single polymeric or wax component. Debinding was therefore a straightforward operation based upon thermal evaporation, typically requiring up to 300 hours for complete binder removal (37). Such a long debinding period was uneconomical, however, and modern binder systems (containing multiple components such as waxes and polymers) were developed to accelerate the removal process. A combination of debinding techniques is normally used commercially, and complete removal of multiple binder components has been achieved in two hours (35). However, these techniques are sometimes regarded as being too complex, since fine control of processing is required to attain such rapid binder removal. A binder and removal method that enables rapid debinding with simplicity would be a welcome development for the economical production of injection moulded components.

A binder that meets these parameters is cyanoacrylate, which depolymerises almost instantaneously when thermally degraded at elevated temperatures. This chapter therefore details the debinding behaviour of this binder when used within simple compacts, and ultimately the conduit heart valve.

5.1.2 The Debinding Process

When a binder is removed from a component, the pore structure will exhibit two forms of structure, funicular and pendular (37). The funicular state is formed first, and is composed of liquid monomer with interlaced vapour capillaries caused by binder evaporation. The transition from this state occurs at binder volume concentrations between 6% and 24% by volume (99), leaving pendular bonds remaining. Since the bulk of the binder has been removed, the bonds exist between ceramic particles, thus maintaining the shape of the component. Any remaining binder, including the bonds, is finally removed by evaporation when the powder is sintered at a high temperature.

Evaporation begins when the funicular state occurs, and continues until the final stage of debinding, where sufficient material remains for the component to maintain a shape before sintering. During the evaporation stage, binder removal is controlled by a combination of two mechanisms, liquid flow, and evaporation. Initially, binder flows to the external surface of the component and evaporates, whilst the capillary induced flow continues to supply liquid from in-between the pores. Eventually, the concentration of binder at the surface cannot maintain the funicular state and pendular bonds are left remaining. At this stage, evaporation continues by flow from the funicular state at a greater depth within the component, by vapour flow through open pore channels. Finally, the pendular bonds at the surface are evaporated, leaving only a small fraction within the component. Hence, particles at the surface rely on Van-Der-Vaals forces to maintain a bond; otherwise, the component would crumble and lose its shape. The evaporation process is illustrated in figure 63.

Problems that occur when debinding are associated with compact shape loss through slumping, distortion, warping, discolouration, cracking and surface pitting.

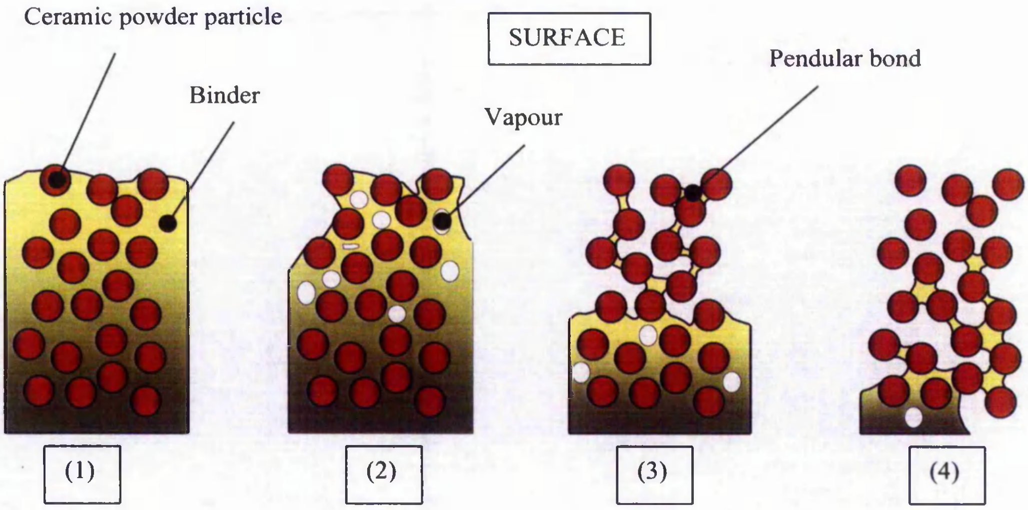


Figure 63. Stages of binder removal by liquid flow and evaporation. (1) Solid binder, (2) Funicular stage at the surface, (3) Pendular bonds at the surface and funicular state at a depth within the binder and (4) Final stage of evaporation with complete evaporation at the surface, and pendular bonds retaining particles within the component.

Some of the defects are due to inhomogeneous mixing and the entrapment of air, which causes internal pressure build-up and crack formation.

When a compact is heated, the polymeric binder softens and loses its yield strength. The compact can then distort by viscous flow induced by gravity and the shape of the component (37). This can be controlled by changing three parameters: firstly, by using a short molecular chain length polymer; secondly, by using a multi-component binder system; and finally, by using powders with greater inter-particular friction. Hence, the use of a binder such as cyanoacrylate will reduce the risk of distortion, because poly-cyanoacrylate has a short molecular chain length, since chain propagation is difficult through a lattice of ceramic particles. In addition, poly-cyanoacrylate will debind at a much faster rate than a multi-component system, because the process relies upon an unzipping mechanism rather than softening due to melting.

Cracking and distortion problems experienced in de-binding can be the result of a low feedstock packing density, allowing the powder particles to rearrange when the binder softens. Regions of high packing density are created at the expense of these low density regions thus causing cracks (100). Another condition that can cause cracking and distortion is a fast heating rate. As a result of rapid heating, the hottest surface will lose binder first and thus have a lower thermal expansion coefficient. This will cause the component to distort and eventually crack, since the surfaces will expand at different rates. Therefore, it is essential that the temperature effects of a binder are understood, before successful debinding can be achieved.

5.1.3 Cyanoacrylate Debinding

Cyanoacrylates debind by a chain end initiated unzipping reaction. The product of degradation is a monomer with a relatively small molecule, which will easily diffuse through a porous matrix, and could be collected for re-use (36). The degradation is dependent upon factors such as the binder chemistry, temperature, initiating species and chain length. Nevertheless, the only variable parameters that affected this investigation were the debinding temperature and heating rate, because the initiator was fixed and the chain length uncontrollable.

It has been shown that butyl-cyanoacrylate will thermally degrade between 150°C and 320°C to give volatile products, the greater part of which is the monomer (82). The liquid monomer then flows through the open pore structure of a component to the surface, where the heat transfer is primarily convective, causing evaporation. Therefore, two states exist whilst debinding, liquid and gas. (Better approximations of the degradation effects of the feedstock used in this study were found by using a Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyser (TGA). This is discussed in section 5.1.4.

When heated gradually, poly-cyanoacrylate will melt and crack as the unzipping reaction commences. Monomer is then produced, which tends to evaporate at the debinding temperature, sometimes releasing products such as CO_2, NO_2 and H_2O. However, these common gasses are not essentially hazardous in comparison to the cyanoacrylate vapour that is also released. Therefore, all these investigations were performed in a sealed oven (BINDER FED-50) with a custom designed extractor fan, which ensured that the monomeric vapours were dispersed in to a safe atmosphere. The apparatus used for this operation is shown in figure 64.

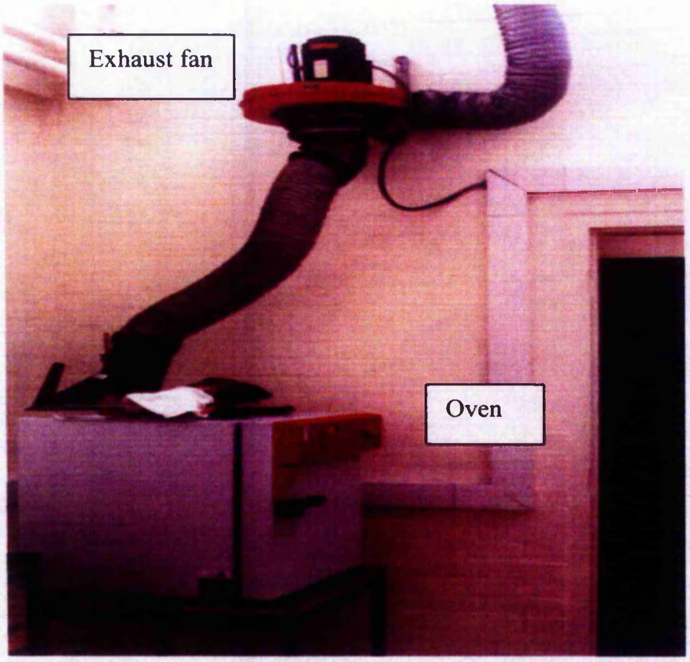


Figure 64. Debinding oven (BINDER FED-50) and extractor fan for safe monomer vapour release

The oven and extractor set-up was acceptable for the safe debinding of components. However, a greater risk existed when sintering.

After debinding, powder particles within the component were held together by weak attractive forces and pendular bonds of cyanoacrylate. When heated at rates associated with a sintering furnace, the component was subjected to a rapid change in temperature that provoked 'flash debinding'. This term relates to the rapid heating effect on the component, which causes an instant release of gas when the monomer evaporates. This monomeric gas is a hazard that can cause serious harm when it condenses; thus, areas and equipment were adequately ventilated.

During the debinding phase, the evaporated monomer could either be condensed for re-collection or polymerised for disposal. This would require adjustment of the oven exhaust flue to include a condensing unit for collection, or a water spray to polymerise the vapours. In reality, these methods would only need to be employed if large volumes of monomer were being evaporated, such as debinding on an industrial scale. For research purposes, it was economical and practical to release the small volume of gas produced into the atmosphere.

5.1.4 Thermogravimetric and Differential Scanning Calorimetry Analysis

The thermal effects of debinding butyl-cyanoacrylate when mixed with alumina were assessed using a Du Pont 990 system. Two types of analysis were used, Thermogravimetric and Differential Scanning Calorimetry. Each of these methods produced results that were used for subsequent debinding investigations using small compacts.

Two small samples were mixed to volume fractions of 0.48 and 0.50, using alumina and inhibited cyanoacrylate respectively. After the samples were polymerised in steam, they were analysed in air by heating from 25°C until a temperature where the mass loss reduced to zero at a rate of 20°C/minute. The aims of the thermogravimetric analysis were to:

- Determine the temperature where complete binder degradation had occurred
- Determine the rate of mass loss
- Determine the differing effects of debinding two different volume fractions of powder to binder

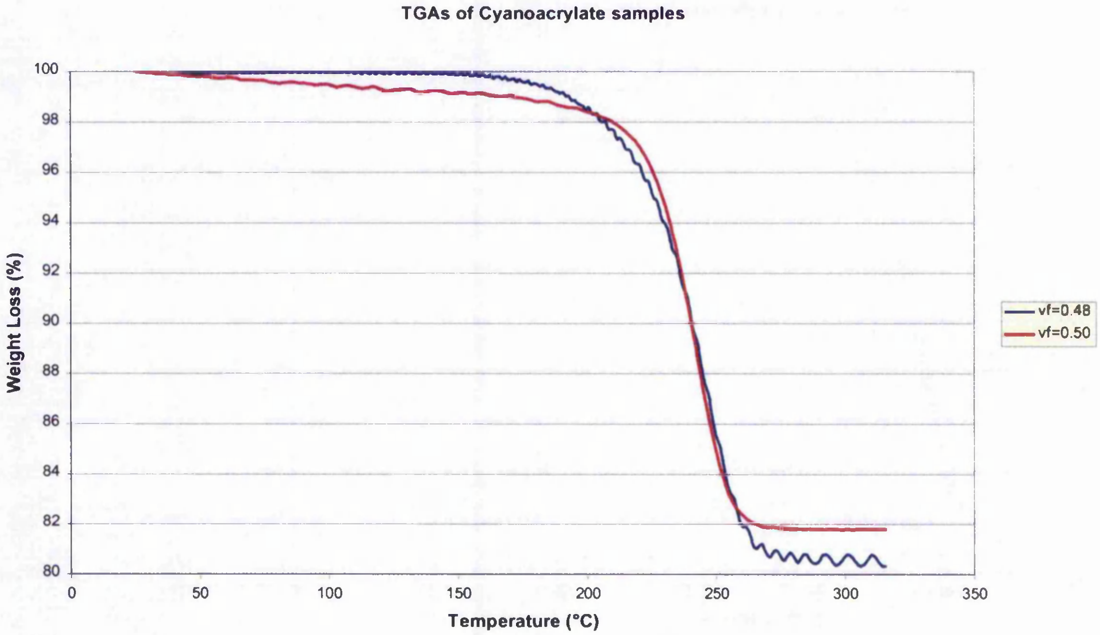


Figure 65. Thermogravimetric analysis of degradation of cyanoacrylate mixed with alumina

There did not seem to be a major difference between the degradation characteristics of the 0.5 volume fraction compact and the 0.48. The only noticeable observation was that the sample with a volume fraction of 0.48 had a larger weight reduction than the other sample, probably because there was a greater volume of binder that had degraded. Moreover, it has been reported that a change in sample size will affect the degradation time (82). This is mainly because of a thermal lag due to the extra mass or a hindrance caused by the diffusion of produced monomer.

It was evident that both samples had debound by 300°C, which equated to 15 minutes. This confirmed that the monomer will unzip rapidly. However, if the unzipping temperature was reduced then the debinding period would be extended. A method of thoroughly analysing the effects of temperature on the degradation reaction was to use a DSC.

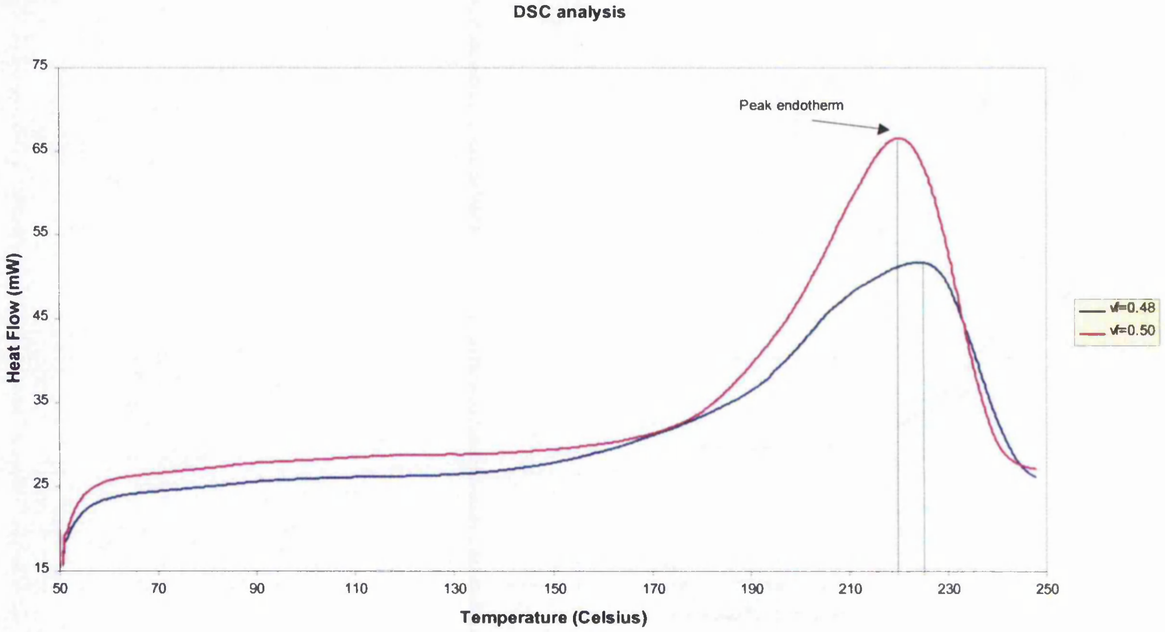


Figure 66. DSC analysis on the degradation of alumina/cyanoacrylate feedstock

The same mixture concentration for the samples analysed with the TGA was used to investigate the degradation properties by a DSC analysis. The samples were analysed in air at a heating rate of 20°C/minute starting with a temperature of 50°C until after a point where the peak endothermic temperature had occurred. The aim of the differential scanning calorimetry analysis was to determine a range of temperatures at which the feedstock would debind, and in particular, a temperature that provided the most efficient heat flow.

The results provided useful information regarding the range of temperature that effects cyanoacrylate degradation. The peak endothermic heat flow occurred between 220°C and 225°C for the investigated samples, as shown in figure 66. It was found that an unzipping reaction started to occur at approximately 170°C, with the major effect being at the peak endothermic heat flow. Hence, further debinding investigations were performed at temperatures within this range, to ensure that thermally instigated depolymerisation would take place.

There did not seem to be a difference between the two mixed volume fractions, both samples debound at the same range of temperature, although the peak heat flow was different. The peak endothermic temperature could be affected by the sample size of the investigated feedstock, because the smallest would debind faster.

5.1.5 Debinding of Moulded Components

The main aim of this investigation was to determine the most effective method to debind moulded samples. The data obtained from TGA and DSC analysis in section 5.1.4 was therefore used for the debinding temperature range. The other aims that were resolved from this investigation were:

- Determine whether the moulded component will retain its shape after debinding
- Determine if debound components crack at the mixed volume fractions with certain heating rates
- Determine the amount of shrinkage that occurs
- Determine whether the binder was recoverable when depolymerised
- Calculate the true volume fraction of mixed components
- Determine whether there were any differences between the three powder batches

Cylinders were moulded for debinding trials, and they were all mixed to a high concentration of alumina, using the two successful powder types. However, because the thickness of the cylinders would affect debinding parameters (such as time, heating rate) they were sectioned into three millimetre discs using a diamond saw. This size represented the thickness of the conduit heart valve.

The samples were heated to 220°C for two hours using a BINDER FED-50 oven (section 5.1.3), at a heating rate shown in table 18. This debinding temperature was found most suitable for this feedstock from the results measured with the Differential Scanning Calorimeter, detailed in section 5.1.4.

The samples were removed from the oven after a period where the mass loss had reduced to zero, because this period ensured that all the binder had evaporated. After debinding, the sample diameter was measured with a micrometer to determine whether there was any dimensional change. Table 18 details the debinding temperatures and observations.

Table 18. Debinding temperature profiles and observations

Sample	*Heating time (hours)*	*Temperature (°C)*		*Heating rate (°C/min)*	*Comments*
		Start	*Set point*		
1	2	19	220	5	Large amounts of warping, crumbled when touched
6	2	19	220	5	Negligible shrinkage, no warping
6	2	19	220	5	Negligible shrinkage, no warping
15	2	21	220	5	Negligible shrinkage, no warping
17	2	20	220	5	Negligible shrinkage, no warping
17	2	20	220	5	Negligible shrinkage, no warping
19	2	20	220	5	Negligible shrinkage, no warping
19	2	20	220	5	Negligible shrinkage, no warping
19	2	21	220	10	Negligible shrinkage, cracks noticed on surface
19	2	170	220	10	Negligible shrinkage, large cracks

The diameter of all measured samples had reduced to within a small percentage of their original dimension, which was acceptable for successful debinding. However, the sample that had a volume fraction of 0.4 collapsed, and its diameter could not be measured. The reason for this collapse was associated with the low solid loading when the binder was removed; hence, there was not enough support for the particles, which moved under the influence of gravity. The other samples had powder volume fractions greater than 0.48 and they retained shape without any noticeable distortion. Therefore, it was acceptable to maintain this powder loading as the base level for moulding successful components.

The heating rate of 10°C/minute was too high for the components. Thermal gradients between the sample and oven temperature caused uneven expansion, and hence, unacceptable cracks appeared on the surface at this heating rate. This phenomenon was noticed particularly with sample 19, which was placed in the oven at 170°C. The sample probably expanded unevenly, causing major cracks that rendered the component unsuitable for sintering. Minor cracks and slight surface pitting were noticed on all parts, but at an acceptable level indicating that the selected heating rate was reasonable.

The surface pitting could be associated with vapour blowholes, which are produced when the pressure gradient of the liquid binder is too high between the internal and external surfaces of the component. It was thought that this phenomenon could be eradicated by adjusting the heating rate along with the set-point temperature. However, reducing the heating rate would lengthen the de-binding time, so a compromise would have to be made. Furthermore, the heating rate should be sufficient to produce equal heating throughout the part at the most efficient debinding temperature. This would normally be determined empirically.

The volume fraction had to be assumed from the measured quantity of ingredients when a feedstock was mixed. Therefore, the consistency of mixed batches was unknown when mixing, and the mixing process required validating to ensure that the process was consistent. Hence, the powder volume fraction was determined by debinding a sample and measuring the remaining mass of powder.

The initial mass and the mass of the remaining powder were found after debinding, by measuring the weight of the discs with digital scales. It was assumed that all the binder had been removed from the compact after debinding (except for the pendular bonds, but the mass of these was negligible). The actual volume fraction of powder to binder was therefore determined from this data, using equation 1. Table 19 details the mass change and the final volume fraction of the samples.

Table 19. The mass of debound samples and the calculated volume fraction

Sample (related to table 18)	*Powder No (related to table 18)*	*Volume fraction*	*Start mass (g)*	*End Mass (g)*	*Calculated volume fraction*
1	1	0.40	7.126	5.162	0.41
6	1	0.48	6.970	5.483	0.48
6	1	0.48	4.431	3.476	0.49
15	3	0.45	5.809	4.436	0.46
17	3	0.48	5.403	4.299	0.50
17	3	0.48	5.293	4.171	0.49
19	3	0.50	5.360	4.256	0.50
19	3	0.50	6.805	5.482	0.52
19	3	0.50	5.145	4.156	0.52
19	3	0.50	5.637	4.557	0.51

All debound samples had a volume fraction within two percent of the value suggested from mixing concentrations. Therefore, the mixing method was considered consistent and the feedstock was being homogeneously mixed.

It was the intention of this investigation to recover the binder after removal from the component. However, the binder either evaporated at the debinding temperature, or 'glued' components to the oven where the component contacted the surface. Therefore, the binder was irrecoverable, since it was highly contaminated with alumina powder. Powders within the component tended to displace at the contact point with the oven, thus causing distortion. This would be avoided if components were suspended within the oven.

It was noticed that the mass of all samples remained constant when observed after 90 minutes, indicating that removal was complete within this period. In comparison to a typical polymeric binder used for traditional injection moulding, cyanoacrylate debinds at a much faster rate with a simple thermal process, since PRIME is a single binder system.

5.1.6 Debinding of Moulded Conduits

The resulting heating requirements observed from debinding circular samples in section 5.1.5, were applied to the larger moulded heart valves created in section 3.4.7. The two conduit valves created with a wax skeleton were debound using a heating rate of 5°C/minute up to 220°C, where they remained for two hours.

The conduit valves had a more complex geometry and a much larger surface area than the circular samples; therefore, it was expected that some shape distortion would occur when the binder was removed. However, both valves were measured with a micrometer gauge after debinding, and no shrinking or distortion was discovered. Moreover, the component had not cracked when using the heating rate that was used with the circular sections.

Finally, the success of debinding the heart valves could only be realised if the density increased to a significant level by sintering the remaining powder.

5.2 Sintering

5.2.1 Introduction

After debinding, components are heated to a temperature that is sufficient to bond powder particles together by a process called ‘sintering’. Normally, this is combined with a debinding cycle, so that the components are heated in the same furnace that is used for binder removal. However, it is also common to use a two-stage process of debinding in a low temperature oven, and then transferring components to a furnace for sintering.

In practice, ceramic powders are normally sintered by applying a large pressure to a compact whilst heating. This combination of high temperature and pressure, called ‘hot pressing’, is a common approach used for creating and shaping components to a high density. However, PIM components are formed from a moulding process where pressure is not required to create the shape. Therefore, these products are sintered in a furnace without pressure; densification takes place by controlling parameters such as sintering atmosphere, temperature, and the rate of heating.

The two powders that had proved to mould and debind successfully were investigated by heating in an induction furnace to determine their sinterability. Sinterability describes a method that determines the characteristics of a sintered component, which normally involves measuring and analysing the sintered density. Therefore, the density and porosity of the samples debound in previous experiments (table 19) were investigated to critically assess how effectively the powders had sintered. Based on the results, a powder was then selected for further use with the conduit heart valve.

The furnace that was used for sintering the compacts and heart valve was developed specifically for hot pressing small circular components. However, the furnace had a graphite core that matched the geometric requirement of the conduit heart valve. Moreover, the core was surrounded by an induction coil, capable of heating the graphite to approximately 2000°C, which was sufficient for sintering alumina (43). This arrangement was used to heat components inside the core by emitted radiation. Heat transfer was also affected by the argon gas that was used to provide an inert atmosphere, and contributed to convecting the heat energy around the furnace.

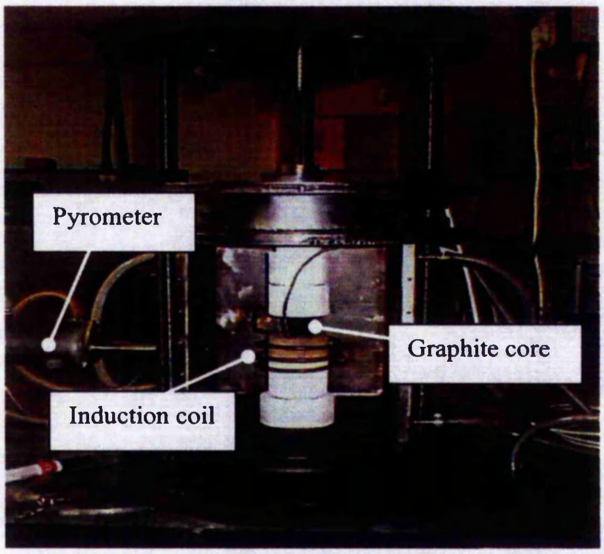


Figure 67. Induction furnace used for sintering

A programmable logic controller was used to control the heating rate and temperature, by using direct feedback from a pyrometer attached to the furnace wall.

Figure 67 shows the furnace used, with the front cover removed, revealing the core and coil.

The overall aim of this investigation was to determine a ceramic powder which sintered to a suitable strength whilst maintaining a porous structure. After selection, this powder was then used for forming the conduit heart valve, with the knowledge that the internal surface should support tissue growth.

5.2.2 Theory

Sintering is the process used for bonding powder particles whilst they are heated at a high temperature. Bonding occurs when necks grow at the point of contact between the particles. Events leading to neck growth depend on several possible transport mechanisms, which are mainly based on diffusion processes. Diffusion is thermally activated, meaning that there is a minimum energy necessary for atomic movement. This depends on the atoms attaining energy equal to or greater than the activation energy (37).

The number of such atoms is determined from the Arrhenius equation, which relates atomic movement with temperature (equation 13). Therefore, sintering is faster at a higher temperature, because of increased atomic movement.

$$\frac{N}{N_o} = \exp^{(\frac{-E}{kT})} \qquad (13)$$

Where,

N = *Number of activated atoms (n/a)*

N_0 = *Number of total atoms (n/a)*

E = *Activation energy (J)*

k = *Boltzmanns constant (W/m^2K^4)*

T = *Absolute temperature (°C)*

There are three stages to sintering, each determined by the growth of bonds between particles and the internal pore structure. Each contact point is termed a grain boundary, which develops throughout the stages, as shown in figure 68.

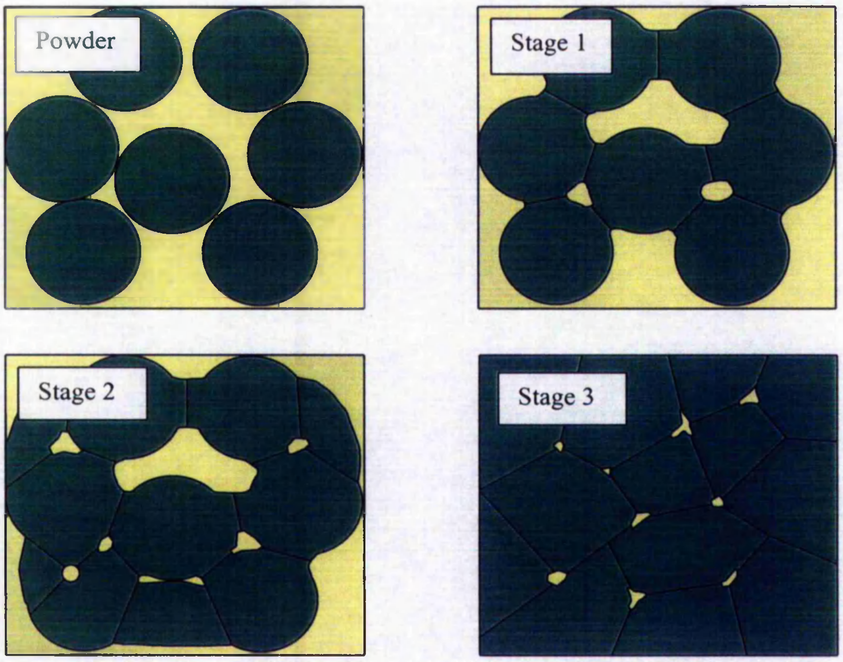


Figure 68. Changes in structure during sintering

The sintering process is said to occur when the ratio of the neck length to the particle diameter is less than 0.3 (37). At this initial stage, the pores are fully inter-connected, with small necks formed between the particles.

The pore structure at stage 2 is also interconnected, but the connection is much smoother than the initial stage, with pores formed as cylindrical shapes. However, pores tend to become isolated at the latter part of stage 2, because of grain growth. Grain growth at boundaries is generally unfavourable for PIM products, because a small grain size is required to maintain a high sintering rate.

A fine grain size will sinter at a faster rate, because the surface energy per unit volume depends on the inverse of the particle diameter (37). Hence, a small quantity of sintering aid is normally mixed with alumina to retard grain growth during densification. Magnesium oxide (MgO) is a typical sintering aid that is included with powders at an approximate volume concentration of 0.1 percent (table 1).

The final stage of sintering begins when the pore structure has reduced to 8% of the total volume. This is accompanied by a collapse of the pores, leading to isolation. Therefore, the final density of components is dependent upon the amount of gas entrapment within these pores.

5.2.3 Sintering Practice

The variables that determine successful sintering are particle size, component size and shape, time, temperature, atmosphere, heating rate and packing homogeneity. After debinding, components are normally 60% dense with the final density approaching 100%. Therefore, components must be shrinking whilst sintering, to account for this change in density.

However, the feedstock used for creating the heart valve started with a lower debound density near 48%, and was sintered to a level approximately 10% greater. Hence, the heart valve has a porous structure. Another advantage of only partially sintering the feedstock should be that the shrinkage would be relatively low, thus reducing distortion.

On the other hand, whilst low shrinkage and low relative density contribute to a low sintered strength, this would probably not affect the heart valve, because in-situ the material will not be used for a structural purpose.

Sintering cannot be used to correct defects introduced in previous processes such as mixing, moulding, or debinding. For example, if the size of the component required adjusting because of shrinkage or distortion after being sintered, then parameters needed to be changed beforehand. These problems mainly exist from poor mixture homogeneity or a low level of interparticle friction through using an erroneous combination of feedstock materials. Table 20 lists the factors that affect the sintering process, including their advantages and disadvantages (37).

Table 20. Advantages and disadvantages of sintering process parameters

Factor	*Effect*
Decrease in particle size	Faster sintering
	Greater expense
	Higher level of impurities
Increase in time	Greater expense
	Grain growth
Increase in temperature	Greater shrinkage
	Grain growth
	Greater expense
Increase in packing density	Less shrinkage
	Less binder
Use of sintering aids	Distortion
	Grain growth

It can be seen from table 20 that adjusting the sintering factors can have a positive or negative effect on processing. Therefore, an iterative approach had to be taken when sintering components, by adjusting more than one factor to achieve the desired results.

5.2.4 Investigations Using the Induction Furnace

5.2.4.1 Sintering of Compacts

The sinterability of the powders shaped into cylindrical compacts (section 5.1.5) provided information that was directly related to the conduit heart valve feedstock, because they were created with the same material combination and dimensional thickness. Therefore, it was decided to investigate these samples instead of debound heart valves, because shrinkage and porosity measurements were easier to obtain with a simple geometry.

The sintering of alumina with a magnesia aid was possible at 1750°C (101). Therefore, a time/temperature profile was developed and used for all the sintering investigations, as shown in figure 69. The furnace was set to full gain whilst heating, arriving at an operating temperature of 1750°C within 20 minutes. This rate of heating was not typical, but it provided an accelerated test of the powder sinterability. Figure 69 shows a hold time of 100 minutes, although this was adjusted to 60 minutes for some samples to determine if there was any noticeable difference with the sintered porosity.

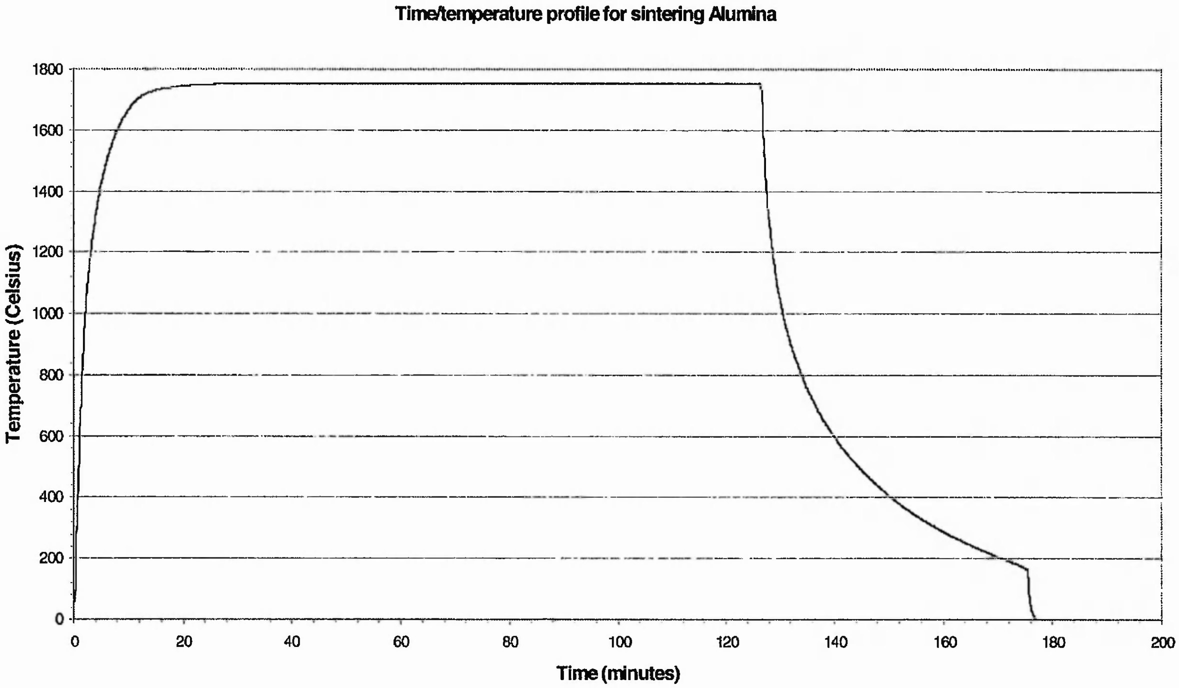


Figure 69. Heating profile for Alumina samples

The aims of sintering the small compacts were:

- To determine whether the powders will bond when heated
- To determine if the volume fraction affected the bonding capability of the powder
- To determine whether the sintering period was long enough to provide sintered strength

The compacts were heated in the induction furnace using an argon atmosphere. The period was 60 and 100 minutes at 1750°C for each sample using the profile that is shown in figure 69.

After sintering, the hardness and shrinkage were investigated, to select a powder with the characteristics most suited to manufacturing the heart valve. The hardness test was only very basic and involved scratching a glass surface with the sintered compacts, because the indentation of a hardness machine was difficult to notice on the porous surface. If the compact did not crumble or show any sign of stress induced fracture, then it was considered to have sintered. Shrinkage of the samples was measured by comparing the change in diameter between the unfired and fired compacts, using a micrometer. Table 21 provides a list of the processing parameters and sintered observations.

Table 21. Sintering results for selected samples

Sample No.	*Volume Fraction*	*Sintering Temperature (°C)*	*Hold Time (minutes)*	*Comments*
6	0.48	1750	60	Sintered, very fragile, easily damaged
6	0.48	1750	100	Sintered, very fragile, easily damaged
15	0.45	1750	60	Sintered, rigid and strong
15	0.45	1750	100	Sintered, rigid and strong
17	0.48	1750	60	Sintered, rigid and strong
17	0.48	1750	100	Sintered, rigid and strong
19	0.50	1750	60	Sintered, rigid and strong
19	0.50	1750	100	Sintered, rigid and strong

The processing temperature and time was sufficient to sinter Powder 3, noted by samples 15-19. However, sample 6 collapsed when removed from the furnace. This observation provided adequate evidence to eliminate Powder 1 from this study, although, parameters could be adjusted to initiate particular bonding. Furthermore, Powder 3 was selected because it sintered without difficulty, and it proved to be successful when moulding the heart valve (section 3.4.6).

Both investigated powders contained 0.1% MgO as a sintering aid. However, Powder 3 maintained a sintered strength down to a volume fraction of 0.45. It was thought that the homogenous packing obtained by a rounded particle shape was one of the factors that contributed to this observation. In addition, Powder 1 had an irregular particle shape that would require greater energy to sinter.

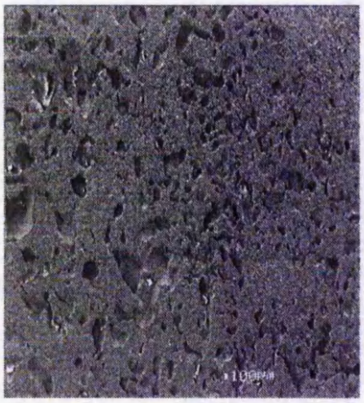


Figure 70. Image of surface from sample 17

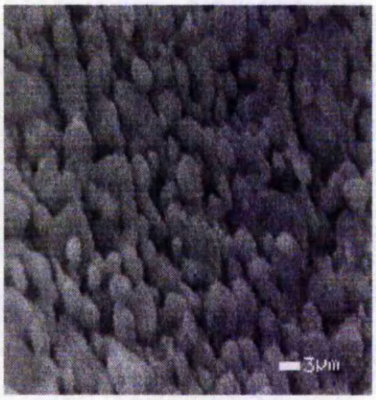


Figure 71. Magnified image of surface from sample 17

The porosity of sample 17 was evident from observing the SEM images shown in figures 70 and 71. It was thought that this sample had sintered to the early part of the intermediate stage, because small necks had formed between particles. Increased sintering would densify the component further, sacrificing the porosity that was required for the heart valve. Moreover, the pore structure had to be inter-connected to support tissue growth, and further sintering would diminish this, by increasing the relative density.

The final observation was related to the geometric changes that occurred through sintering. The diameter was noted to reduce by five to ten percent, which indicated an increase in density. Therefore, it was evident that the samples required further investigation to determine the level of porosity.

5.2.4.2 Density measurements

Two methods of identifying the quality of sintered components are by mechanical testing or evaluating the sintered density. Mechanical testing can be a time consuming exercise, because special test pieces are required for bending analysis and fracture toughness that conform to a strict British Standard. Therefore, a realistic alternative was to measure the density using a well-practised method.

The Archimedian principle has long been established as a technique for determining the density and thus the porosity of sample components. This method involves placing samples in boiling distilled water until the point where the samples become completely saturated. The suspended, dry and wet mass for each sintered sample is then measured, and the corresponding density and porosity calculated.

The main aim of this investigation was to find the relative density, and hence, the level of porosity, which would enable the samples to be characterised. Therefore, the three samples sintered with Powder 3 (table 21) were investigated using the Archimedian method. The cylindrical samples were prepared by grinding down the open surfaces, hence removing any unwanted powder deposits that were considered as 'flash' from the sintering stage (which is why the dry mass of these samples differed from those listed in table 19). After preparation, each component was boiled in distilled water for two hours, which was thought to produce complete saturation. The process was completed three times providing an average value for the mass, which was then used in calculations for the parameters tabulated in table 22.

Table 22. Average Density measurements for sintered samples

SAMPLE	*Sinter Time (m)*	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
15	60	2.785	2.052	3.621	1.569	0.837	0.732	53	3.80	1.77	44.59
15	100	1.591	1.185	2.045	0.861	0.455	0.406	52	3.91	1.84	46.44
17	60	3.292	2.418	4.155	1.738	0.864	0.874	49	3.77	1.89	47.60
17	100	2.904	2.138	3.626	1.488	0.723	0.766	48	3.79	1.95	49.01
19	60	3.677	2.702	4.511	1.809	0.834	0.975	46	3.77	2.03	51.08
19	100	4.090	2.979	4.967	1.988	0.877	1.111	44	3.68	2.05	51.69

A - Dry mass (g)
B - Suspended mass (g)
C - Saturated mass (g)
D - Exterior volume (cm^3)

E - Volume of open pores (cm^3)
F - Volume of impervious parts (cm^3)
G - Apparent porosity (%)
H - Apparent specific gravity (%)
I - Bulk density (g/cm^3)
J - Relative density

Table 22 details the apparent porosity, relative density, and associated data for the sintered parts. The apparent porosity varied from 44% to 53%, which should be sufficient for a porous heart valve. Tissue growth on the surface of a porous alumina mitral valve had already been investigated. It was discovered that ≅150μm pores encouraged tissue to develop an adhesion to the valve surface, but this was a basic investigation, and an acceptable pore size was generally unknown (5). It was assumed that the porosity levels attained from sintering alumina with a cyanoacrylate binder were acceptable.

Two of the compacts had a relative density that was lower than the mixed volume fraction. Although these samples had sintered, noted by the resistance to breaking when using the basic hardness test, it was thought that the mixed volume fraction could be incorrect, and a proportion of the feedstock probably must have had a lower solid loading. For most of the compacts, however, the relative density increased, indicating that sintering was occurring. If the porosity was too high then further sintering would increase the relative density by adjusting parameters such as time and temperature.

The relative density increased with samples that had a higher powder loading. This was because the starting density was larger for samples that had a greater initial density, such as powders with a volume fraction of 0.50. However, the apparent density was considerably lower than conventional powder injection moulded components. It was unknown what effect this would have on the sintered strength.

Porosity is a parameter that is required to be consistent if the heart valve is to be a success. Many processing parameters will vary the pore size and distribution, such as mixing homogeneity, moulding pressure, packing density, particle size and shape. Some of these variables are linked directly to processes such as mixing, moulding and sintering, and therefore porosity is a complicated attribute to control.

Sintering is the final process in PIM therefore control must be targeted at the mixing and moulding stage, starting with a homogenous feedstock.

5.2.4.3 Sintering Debound Heart Valves

After debinding, the two heart valves created using the wax skeleton method were sintered using the same heating profile as the small compacts; this is shown in figure 69. The sintering temperature was 1750°C and the hold time 90 minutes. The aims of the investigation are listed below:

- To determine whether the furnace is suitable for sintering the heart valve
- To determine whether the heart valve will collapse through slumping
- Provide a basic knowledge of component shrinkage
- To determine whether the mixed powder volume fraction of 0.48 is sufficiently high to create a heart valve
- To investigate processing problems and suggest solutions

After sintering, the valves were measured with a micrometer gauge to determine any shrinkage or slumping. The valves appeared to have reduced in diameter by 3%, indicating that sintering had occurred. Moreover, there did not appear to be any slumping or distortion, noted by the internal diameter not being oval when it was measured. This suggested that the feedstock had mixed homogeneously and the interparticle friction was sufficiently high to retard any collapse.

The internal surface of the valve seemed to be porous, with many pores being observable by optical investigation. An investigation by SEM would provide further information, but this would be useful only if information was available about the types of pore structure that would support tissue adherence.

The valve did not fully sinter in some areas. Figure 72, details these areas diagrammatically.

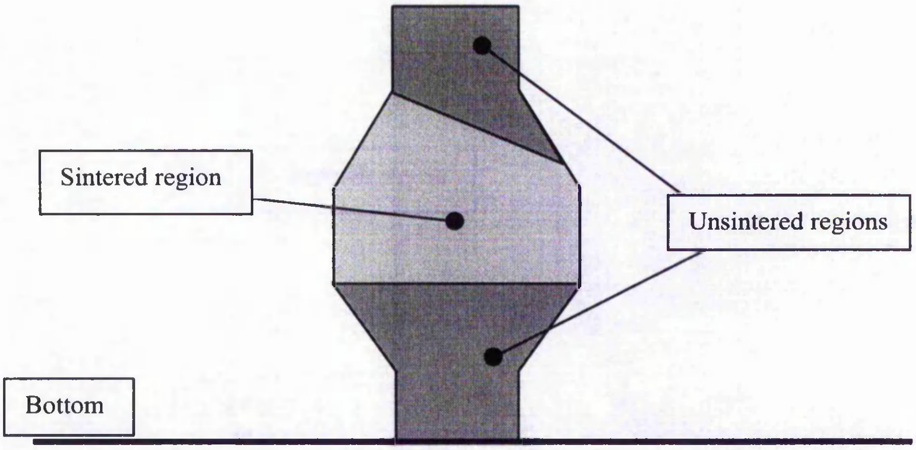


Figure 72. Diagram showing sintered and unsintered regions of the heart valve

It was unknown why the powder did not fully sinter throughout the component, but a probable cause related to the furnace. The graphite core within the furnace was sufficiently large to accommodate the geometry of the heart valve. However, the coil had three windings that covered a large proportion of the core, but not the entire length. Therefore, the region that was not covered would not heat to the same extent as the remainder of the core, and hence, may not have attained the temperature required to thermally activate mass transfer. This suggestion relates to the unsintered regions of the valve, because the top and bottom portions were outside the heating area of the coil. This effect was apparent since there was a well-defined section of the valve, below which there appeared to be a relatively low amount of evidence that supported sintering.

A solution may be to either raise the sintering temperature or increase the period that the valve is heated. Either way, the remainder of the valve should sinter, because the middle section had densified without any problem.

In conclusion, these results confirmed the suitability of the powder injection moulding process for creating a complex geometry such as the heart valve.

Chapter 6 – Flow Analysis of the Moulding Process

6.1 Introduction

A moulding system has been developed for creating a seamless conduit heart valve from a ceramic material with a reactive binder. The mould for the system was designed using an alloy insert that was melted out to produce a conduit shape. However, problems were experienced when moulding, in particular the internal collapse of the feedstock when the core was removed. A novel method designed to reduce this effect was implemented using a wax-based ‘skeleton’ that surrounded the moulded feedstock. When the wax was melted out (before removal of the insert) water entered the mould and polymerised the feedstock where the skeleton had been. This prevented the feedstock from collapsing when the insert was subsequently melted out, and so produced a conduit heart valve with minimal surface defects. It was clear that the process was a success, but the reasons why were not, because there was no scientific data available from the moulding process such as feedstock velocity and pressure when the mould was full. Therefore, it was decided to perform an investigation using a computational fluid dynamics (CFD) analysis to determine the feedstock pressure.

An analysis using CFD cannot be regarded as accurate unless the geometric model used for the flow domain is validated by comparing results with an actual fluid flow investigation. A plastic model of the heart valve mould was therefore manufactured to investigate flow pressure using water. The static head was measured at strategic positions associated with the mould inlet and outlet. The measured pressure from the plastic mould was compared to results from the computational analysis model at the corresponding measurement positions, and, hence, the CFD model was validated.

This chapter details the development of the models used with the CFD analysis, the model validation, and finally the resulting pressures within the heart valve mould using computational analysis. The key steps in the work were:

- The use of PHOENICS CFD code for developing a solution for the moulding process

- The development of two CFD models that represent the alloy mould and the alloy mould including a wax skeleton.
- The validation of these models by comparing CFD results to actual measured data from a plastic mould
- The measurement of density, flow rate and pressure measurements whilst a heart valve mould was filled
- A CFD flow analysis of the feedstock using the validated models, and a comparison to the pressure data measured whilst a heart valve mould was filled

6.1.1 Problem solving with PHOENICS

PHOENICS 3.1 CFD code was used for the investigations performed in this study, because of the versatility and support that this technique offers. This code was used for two investigations: validation of the heart valve models; and for performing an analysis of the feedstock pressure when the alloy mould was completely filled. Therefore, analytical models and algorithms were selected to be used within PHOENICS code on a trial and error basis, as opposed to a complete analysis where a specific equation was developed for the process under investigation. The intention of the feedstock analysis was to investigate *regions* of pressure within the mould, by using a basic model. If accurate values of pressure at specific points within the mould were required, then this analysis could not be guaranteed. Nevertheless, when the heart valve model was validated using a plastic mould to find pressure values at specific points (section 6.2.4) the PHOENICS analysis was accurate, because the measured data agreed with the basic code used by this technique.

Ideally, the alumina feedstock analysis required a specifically developed analytical model for a thorough investigation. This was because the feedstock viscosity not only changed with relation to the power law model (equation 12), it also changed with respect to the high moulding pressure, dependent on the relationship shown in equation 14(37).

$$\eta = \eta_j \exp^{(J(P-P_0))} \qquad (14)$$

Where,

η = *Dynamic viscosity (Pa.s)*
η_j = *Reference viscosity (Pa.s)*
J = *Pressure coefficient (N/m^2)*
P = *Pressure (N/m^2)*
P_0 = *Reference pressure (N/m^2)*

Integration of equation 14 into a CFD algorithm within PHOENICS code is a complex process, which involves changing the standard code by writing a script file. A pressure correction factor of 6% has been suggested for use in similar situations (37), but this factor is normally used with conventional moulding processes that typically experience pressures of 60x10^6 N/m^2, which is much higher than the mould resistance noted by this investigation. Moreover, if both the investigated models were adjusted by such a factor, then the pressure difference would not be affected, so the use of pressure correction factors was therefore considered insignificant within this study.

6.1.2 Creation of a model for use in PHOENICS

Two different alloy mould configurations have been investigated for creating the conduit heart valve, as discussed in chapter 3. The first mould arrangement had a single inlet and outlet, and the second included a wax skeleton that provided two extra vents. Models of these moulds were created for use within the PHOENICS CFD software, and were aptly identified as Novent and Twovent.

The two models were developed using Pro-Engineer, which is a fully parametric computer aided design (CAD) package. The designs were based upon a simple geometry that would support the creation of a CFD mesh. On this basis, the models were created with two mould halves and a single block, which incorporated the inlet, outlet, and vents as shown in appendix B.

The CAD models were exported from Pro-Engineer as STL files, which were imported into the pre-processor used within PHOENICS. When the files were exported, the Pro-Engineer package assigned a three dimensional co-ordinate system (x,y,z) with the z plane representing the vertical axis of the models.

The next stage of model design involved creating a grid for the models. This was created within the PHOENICS pre-processor using the same co-ordinate system produced by Pro-Engineer. The grid formed the basis of the domain for application of the finite volume method.

The finite volume method involves dividing the domain into discrete control volumes. The boundaries of the control volumes are positioned midway between adjacent nodes, which are placed at intervals corresponding to the domain size. An example of a control volume is shown in figure 73.

The governing equations are integrated over the control volume to yield a discretised equation at the nodal point ‘p’. These equations are then solved for a flow parameter such as pressure at each nodal point. A large amount of iterations will therefore reach conservativeness at nodal positions, which is marked by consistent expressions for fluxes of flow variables at the boundaries (or faces) of control volumes. The greater the number of nodes, the more reliable will be the solutions to the algebraic equations.

On this basis, the models included sufficient nodes to enable the solution to converge at a reasonable value within a realistic time constraint, and an empirical investigation with the models found that 40 nodes were sufficient for each axis of the domain. This provided a solution that converged within a reasonable period, and the results profiled the heart valve geometry with sufficient resolution.

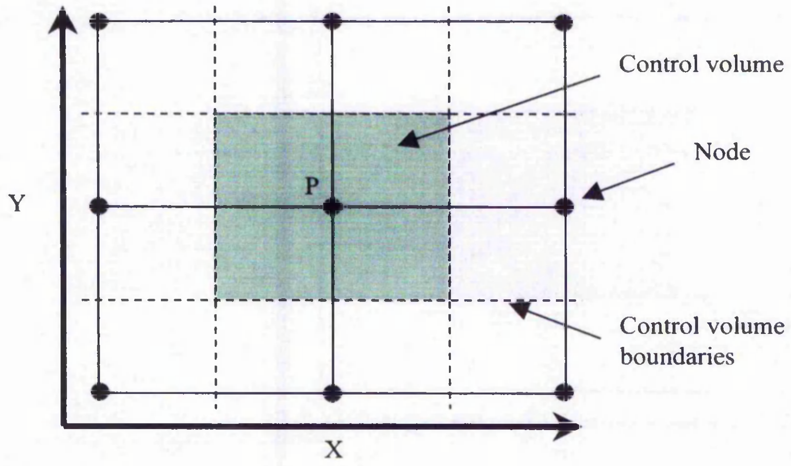


Figure 73. An example of a control volume used with the finite volume method

6.2 Validation of the Novent Model

The Novent model was verified by comparing the measured static pressure head in a plastic mould with the results of a CFD analysis using the same fluid. Parameters required for the CFD verification were as follows:

- Flow rate of the domain fluid (CFD boundary condition)
- Inlet and Outlet velocity
- Pressure measurement at positions around the mould
- Type of flow (laminar or turbulent)
- Outlet pressure of the mould (CFD boundary condition)

It was intended to perform a simple CFD analysis by using a laminar flow model. On this basis, four sets of pressure measurement were taken at a broad range of flow rates, and hence, any subsequent results that were considered turbulent were eliminated.

6.2.1 Measurement of Pressure and Flow Rate

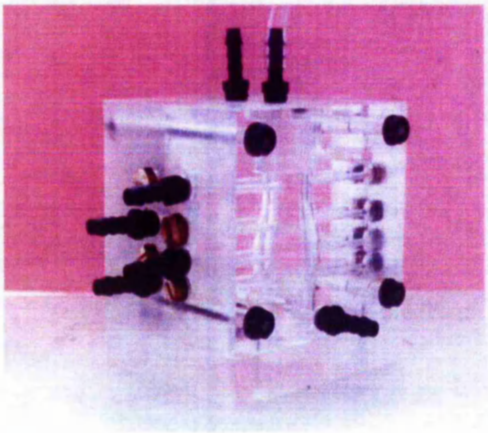


Figure 74. Perspex heart valve mould used for flow investigations

The main aim of this investigation was to find the pressure values at different positions around a mould replicating the Novent geometry. The mould was designed and manufactured from clear Perspex (figure 74), (as detailed in the CAD drawings in appendix B) thus enabling the liquid to be observed whilst flowing. Trapped air could be seen and removed by 'tapping' the mould before pressure measurements were taken, so as not to affect the values.

The mould was drilled at various positions that coincided with a region of interest for pressure measurement. A length of transparent tubing was attached to these positions, and raised above the mould.

The fluid used for the investigation was water, because a large quantity was required to enable steady, fully developed flow. The water was contained in a tank with a variable drain, so that the pressure head and flow rate could be altered by adjusting the drain height. A schematic representation of the apparatus is shown in figure 75.

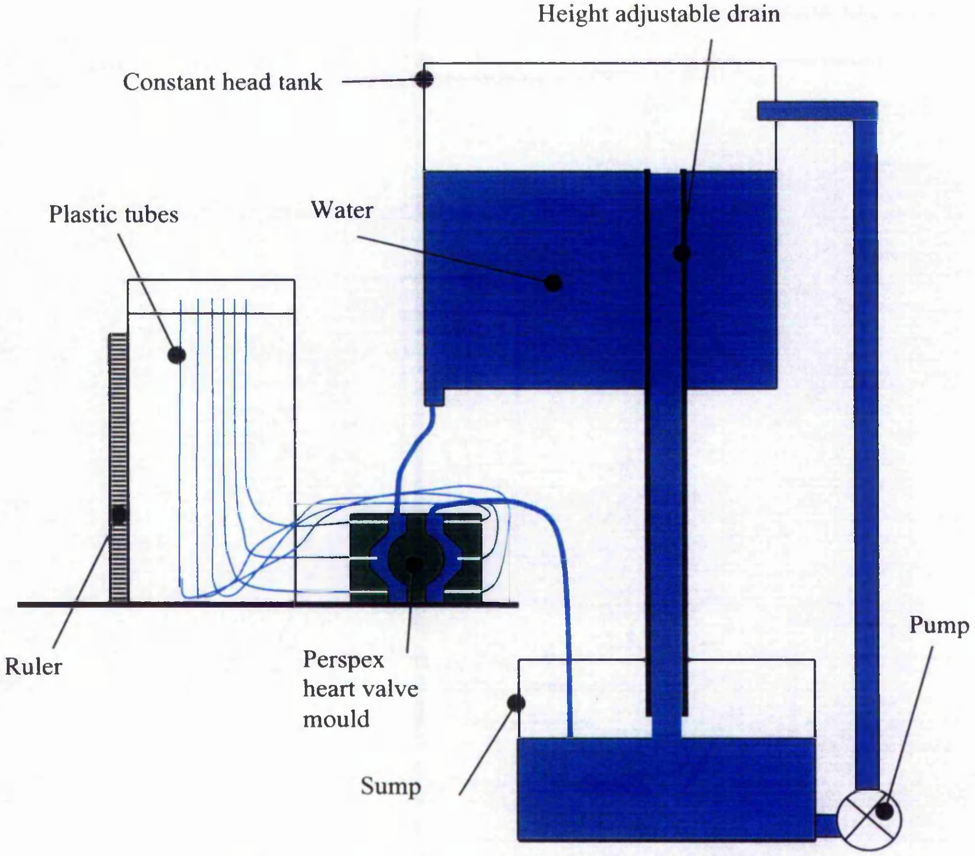


Figure 75. Apparatus for measuring pressure head

The drain height was adjusted to take four sets of readings at a constant fluid temperature of 20°C. The flow rate was measured by placing a 100cm^3 cylinder beneath the outlet pipe from the mould, whilst the fill time was noted using a digital timer. Ten measurements were taken and averaged at each flow rate, thus obtaining a fill time, which was used to find the volumetric flow rate (Q). The velocity of the fluid was calculated at the 3mm-diameter outlet by applying the flow rate to the continuity equation. Data collected from this investigation is listed in table 23.

Table 23. Flow rates measured from the Perspex mould investigation

Identification	*Fill Volume (m^3)*	*Fill time (s)*	*Fluid velocity (m/s)*	*Flow rate (Q) (m^3/s)*
Perspex 1	0.0001	5.3	2.67	$1.89\text{x}10^{-5}$
Perspex 2	0.0001	6.6	2.15	$1.52\text{x}10^{-5}$
Perspex 3	0.0001	5.2	2.73	$1.93\text{x}10^{-5}$
Perspex 4	0.0001	4.7	2.99	$2.11\text{x}10^{-5}$

The pressure head at each pressure point on the mould was found by measuring the fluid level in the transparent tubes. These heights (or heads) were taken from a datum position situated at the bottom face of the Perspex mould. Hence, the actual head at any particular position on the mould was determined by taking away the

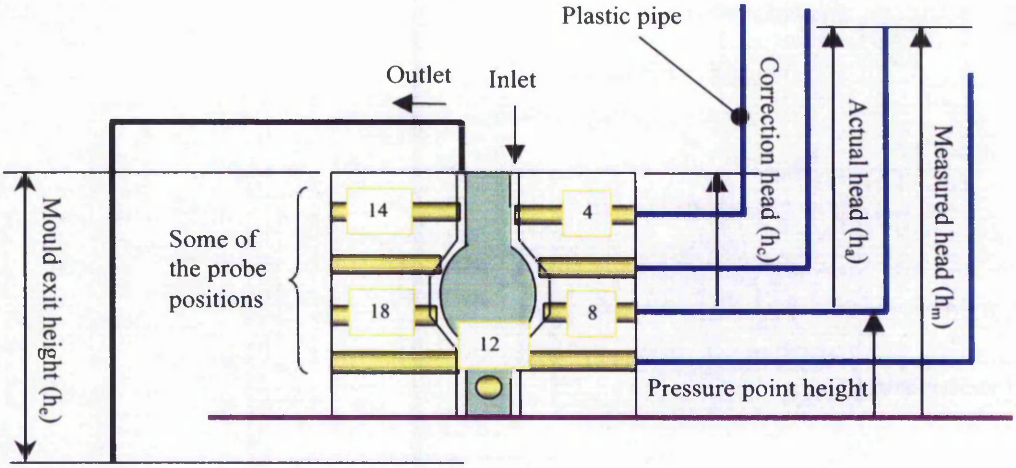


Figure 76. Measured positions on the Perspex mould

pressure point height from the measured head. The measurement points are shown in figure 76.

The CFD analysis (6.2.4) calculated mould pressure without the effect of gravitational forces, and the measured results were adjusted similarly. This involved ignoring the head due to gravity within the mould. Therefore, the correction head (h_c) was taken away from the actual head (h_a) producing a height (h_h) that was used to calculate corrected pressure. Table 24 details the corrected pressure measurements at four flow rates that correspond to those in table 23.

Table 24. Head and pressure values taken from the Perspex mould investigation

Probe position	*Perspex 1*		*Perspex 2*		*Perspex 3*		*Perspex 4*	
	h_h (m)	*Pressure (N/m^2)*	*h_h (m)*	*Pressure (N/m^2)*	*h_h (m)*	*Pressure (N/m^2)*	*h_h (m)*	*Pressure (N/m^2)*
3	0.446	4367	0.274	2683	0.536	5249	0.657	6434
4	0.453	4436	0.282	2761	0.544	5386	0.668	6542
5	0.445	4358	0.273	2673	0.531	5200	0.655	6414
8	0.448	4436	0.277	2761	0.530	5190	0.665	6512
9	0.446	4367	0.274	2683	0.528	5171	0.657	6434
11	0.464	453	0.285	2800	0.547	5357	0.682	6679
12	0.450	4416	0.280	2752	0.536	5249	0.667	6532
14	0.440	4309	0.270	2644	0.519	5082	0.652	6385
18	0.445	4407	0.274	2683	N/a	N/a	0.656	6424
19	0.446	4367	0.276	2703	N/a	N/a	0.659	6453

It was anticipated that the flow rates that were investigated could potentially cause turbulence, which would invalidate the results. This is because turbulent flow arises from high fluid velocity and low viscosity, producing volatile pressure variations at a single point and making it impossible to measure the static head. Therefore, the results that related to turbulent flow were identified and eliminated from this study.

The type of flow was determined by finding the Reynolds number at the four investigated flow rates, and hence, a decision was made to disregard certain results for use with the CFD analysis.

6.2.2 Measurement of Reynolds Number

The transition between laminar and turbulent flow can be determined by calculating the Reynolds number for a flow situation. For a general application Reynolds has stipulated that disturbances are always present, and transition will occur at values between 2000 and 4000. The onset of turbulence is influenced mainly by velocity and viscosity, and hence these factors need to be stable to establish when this will occur. If extreme care is taken, however, then laminar flow can be maintained at much higher values than Reynolds suggested.

The Reynolds number would normally be determined from a particular position in the fluid that represented a linear measurement. Therefore, in a circular pipe, the diameter would be used for this, because it represents a consistent component of the geometry. However, the mould geometry was a conduit without a constant factor such as the diameter, and another term had to be derived that represented a stable portion of the conduit section. This parameter, known as the hydraulic mean depth (d_m), was defined by using equation 15.

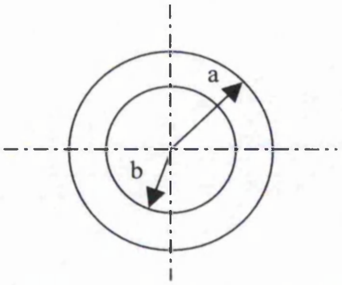
$$d_m = \frac{area}{perimeter} \qquad (15)$$

Where,

d_m = *Hydraulic mean depth*

The fluid in the Perspex heart valve mould was investigated at four flow rates. It was not known whether the flow at these rates was laminar or turbulent, but so that the results could be compared to the Novent model used in PHOENICS it was necessary for the flow to be laminar when the measurements were taken. This is because turbulent models can be difficult and time consuming to develop when using CFD, whereas laminar models are simple and well understood. Therefore, the Reynolds number was determined, after the hydraulic mean depth was calculated for the Perspex mould.

The annular area of a position close to the mould inlet was calculated, as shown in figure 77.



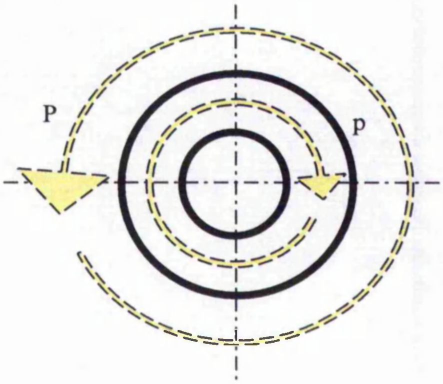
$$area = \pi(a^2 - b^2)$$

Near the mould inlet, a=13mm and b=10mm.

$$\therefore area = 2.167x10^{-4}m^2$$

Figure 77. Calculation for annular area of a position close to the mould inlet

The hydraulic mean depth was the ratio between the annular area and the perimeter of the mould that was in contact with the fluid. Therefore, the mean depth (d_m) for the Perspex mould was calculated, as shown in figure 78.



$$d_m = \frac{area}{perimeter}$$

Where, P=2πa and p=2πb

$$\therefore d_m = \frac{2.167x10^{-4}}{\pi(26x10^{-3} + 20x10^{-3})}$$

Hydraulic mean depth (d_m) = $1.5x10^{-3}$m

Figure 78. Calculation of the hydraulic mean depth for the Perspex mould

Table 25. Reynolds numbers for the flow rates investigated

No.	Inlet velocity (m/s)	Dynamic Viscosity of water (Pa.s)	Mean depth (d_m) (m)	Density of water (kg/m^3)	Reynolds Number (Re)
Perspex 1	2.67	0.001	0.0015	998.2	3998
Perspex 2	2.15	0.001	0.0015	998.2	3219
Perspex 3	2.73	0.001	0.0015	998.2	4088
Perspex 4	2.99	0.001	0.0015	998.2	4477

Table 25 details the attributes that were required to calculate the Reynolds number. It can be seen that all of the four investigated flows could be turbulent, because they have a Reynolds number greater than 2000. However, the Perspex 1 and Perspex 2 readings were within the transition zone between laminar and turbulent flow, and could, therefore have been taken whilst the flow was laminar. Accordingly, they were used for the comparison with the computational investigation.

6.2.3 Measurement of Mould outlet Velocity and Pressure

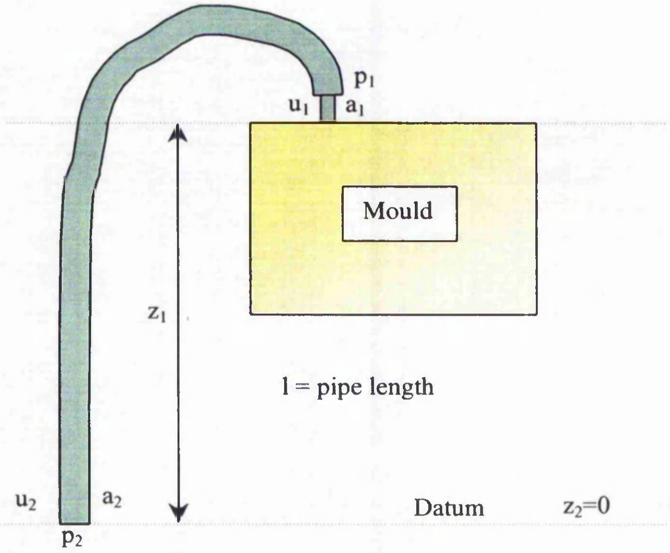


Figure 79. Attributes used for calculation within Bernoulli's equation

The gauge pressure at the outlet of the Perspex mould was unknown, because the outlet was not vented to atmosphere. Therefore, a boundary condition existed for the CFD model, and required calculation.

The two laminar flow rates were investigated to find the outlet pressure, and Bernoulli's energy equation was applied to the moulding apparatus, using the measured attributes shown in figure 79.

There was an abrupt expansion of the pipe at the mould exit, as shown in figure 79. This expansion and the pipe friction caused the fluid to lose energy when it flowed through the pipe, and the energy losses were considered as a reduction in the fluid head (h_l). The head loss equation was developed as shown in equation 16, where (f) was the fanning friction factor. This factor was found to be 0.01 at the pipe exit, for both investigated flow rates.

Head loss (h_l) = Pipe friction + abrupt pipe enlargement

$$h_l = \frac{4flu_2^2}{2d_p g} + \frac{u_2^2}{2g}\left(\frac{a_2}{a_1} - 1\right)^2 \qquad \text{———} \qquad (16)$$

$$p_1 = \left(\frac{u_2^2}{2} - \frac{u_1^2}{2} - z_1 + \frac{4flu_2^2}{2d_p} + \frac{u_2^2}{2}\left(\frac{a_2}{a_1} - 1\right)^2 \right)\rho \text{—} \quad (17)$$

Where,

h_l = *Head loss (m)*

f = *Fanning friction factor (n/a)*

l = *Outlet pipe length (m)*

u_2 = *Velocity at pipe exit (m/s)*

a_2 = *Area of pipe exit (m^2)*

d_p = *Exit pipe diameter (m)*

g = *Acceleration due to gravity (m/s^2)*

a_1 = *Area of mould outlet (m^2)*

p_1 = *Pressure at mould outlet (N/m^2)*

u_1 = *Velocity a mould outlet (m/s)*

z_1 = *Mould exit height to a datum (m)*

ρ = *Density (kg/m^3)*

The pressure at the mould exit was calculated by substituting the head loss equation into Bernoulli's equation, to produce an equation 17 for the outlet pressure (p_l).

The mould outlet pressure was calculated for each of the laminar flow rates and the results are shown in table 26.

Table 26. Attributes and Perspex mould exit pressure

Attribute	Perspex 1	Perspex 2
u_l (m/s)	2.67	2.15
u_2 (m/s)	0.67	0.54
z_l (m)	0.141	0.141
F	0.01	0.01
d (m)	0.006	0.006
l (m)	0.952	0.952
a_l (m^2)	$7.1x10^{-6}$	$7.1x10^{-6}$
a_2 (m^2)	$2.8x10^{-5}$	$2.8x10^{-5}$
Re	3999	3217
h_l (m)	0.350	0.226
p_l (N/m^2)	-1308	-1334

The outlet pressure (p_l) was negative, and therefore it was used as an outlet boundary condition for use with the Novent CFD model.

6.2.4 CFD Analysis of Pressure Within the Novent Model

The effectiveness of the Novent model was uncertain, and the model required a CFD analysis to validate the flow domain. This was achieved by introducing known boundary conditions previously determined from the Perspex mould investigation. Subsequently, the mould pressure was analytically resolved from the model, and a direct comparison was made with the measured pressure detailed in section 6.2.1. If there was a significant difference when the results were compared, then the Novent model would be unsuitable for further use, whilst a similarity of results would validate the model for an additional analysis using the alumina/cyanoacrylate feedstock.

The computation was performed using data collected from the two mould flow investigations that were considered laminar, hence the CFD results were named Perspex 1 and Perspex 2 (as detailed in table 26). The fluid properties and boundary conditions were entered into the pre-processor within PHOENICS, as detailed in table 27.

Table 27. Domain boundary and fluid properties for the Novent CFD model

Property or Variable	*Value*
Domain fluid	Water at 20°C
Reference pressure	$1x10^5$ N/m^2
Equation	Elliptic-CCM
Solution	Velocity and Pressure
Model	Laminar
Iterations	1000
Density	998.2 Kg/m^2
Viscosity (Kinematic)	$1.006x10^{-6}$ m^2/s
Gravitational forces	Not used

An elliptical algorithm was used for the CFD analysis, because the flow situation was considered as steady state. Moreover, this type of equation will resolve a computational anomaly such as a localised pressure gradient within the solution. If disturbances such as this were ignored, then the solution accuracy would be affected at all other nodal points (102).

The equation was run for 1000 iterations, which provided adequate convergence with residuals lower than two percent. This was an acceptable result, since the residuals were a measure of the overall conservation of flow properties.

The solution produced from PHOENICS was analysed using the post-processor facilities. The resulting velocity and pressure distributions were plotted for a general comparison with the Perspex mould investigation.

The three-dimensional velocity distributions that were found from the Novent model using Perspex 1 and Perspex 2 flow data are shown in figure 80. It was noted from these results that both solutions show a flow re-circulation around the central region of the mould. This same phenomenon was also noticed when the Perspex

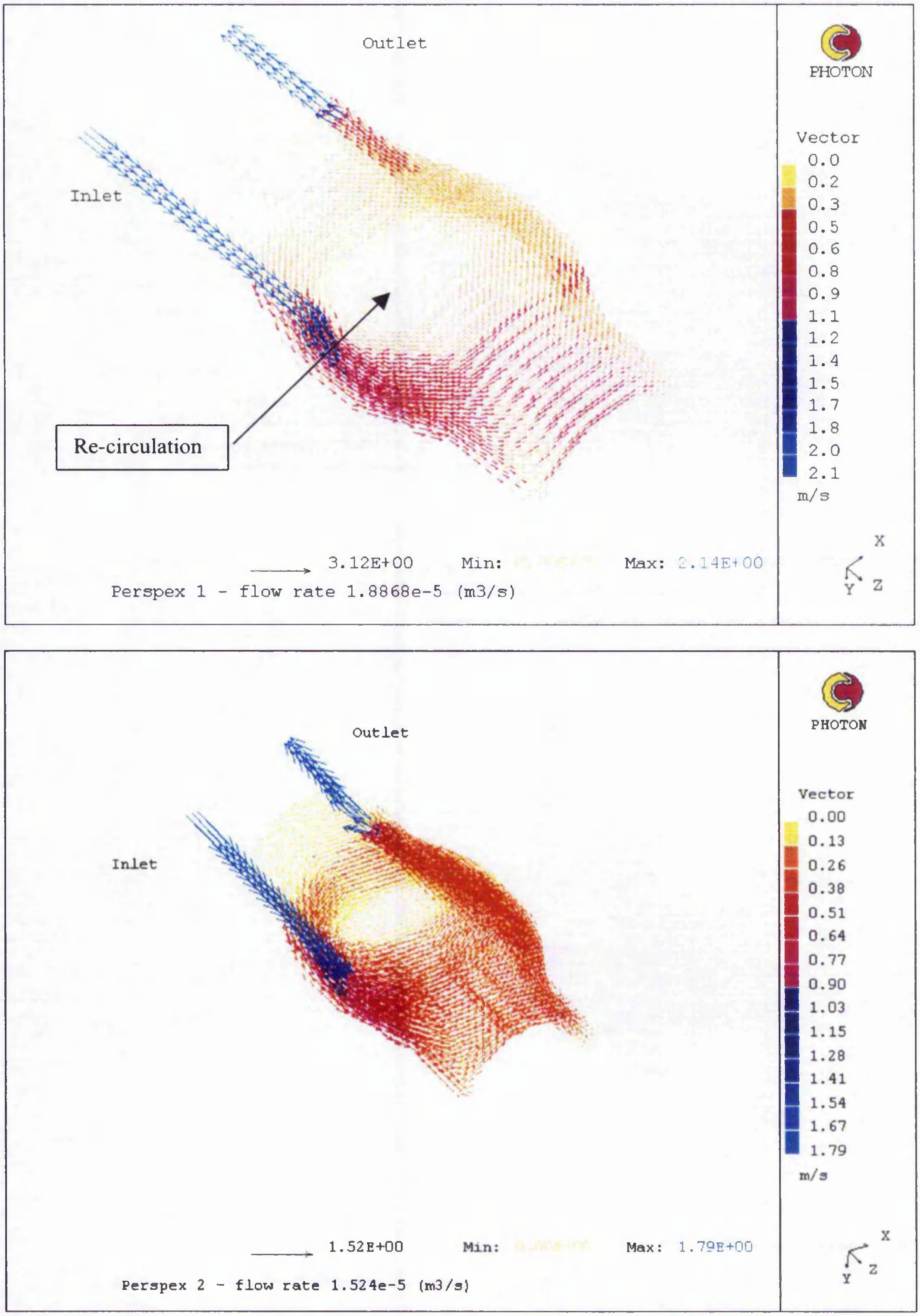


Figure 80. Velocity distribution through Perspex 1 and Perspex 2 Novent model

mould was analysed at these particular flow rates. Evidence such as this supports a comparison between experimental and computational data.

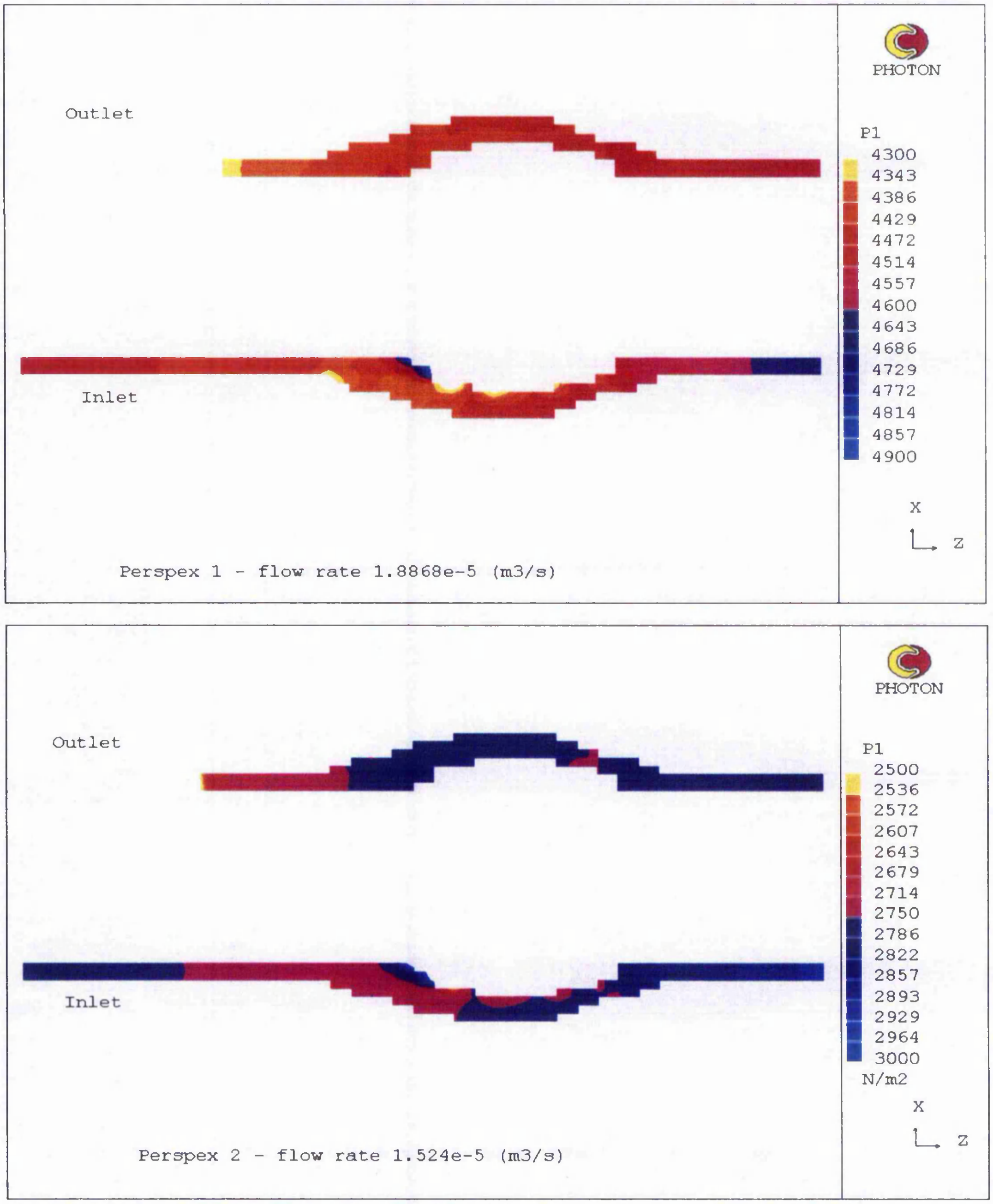


Figure 81. Pressure distribution around the Perspex 1 and Perspex 2 Novent model

The resulting pressure distributions from the computational analysis are shown in figure 81. It was observed from these images that the largest pressure occurred at the same position for both Perspex 1 and Perspex 2 solutions. This was expected, because this region was the first contact point for the fluid within the mould. However, the flow rate was relatively high, thus causing many pressure fluctuations in a small area. On this basis, the plots were useful for an overview but not as precise as results from the VR viewer, which provided spot values of pressure.

The VR viewer was used to position a probe at a particular region of interest within the Novent model, and hence, the calculated pressure was found at that point. Values were taken from the solution with relation to the measuring positions used with the Perspex mould, so that a comparison could be made for verifying the CFD model. Pressure results from this investigation are listed for the Novent model in table 28.

Table 28. CFD values of pressure for the Novent model, with Perspex 1 and Perspex 2 flow parameters.

Probe position (in relation to Perspex mould)	*Perspex 1*	*Perspex 2*
	Pressure (N/m^2)	*Pressure (N/m^2)*
3	4413	2747
4	4416	2748
5	4386	2732
8	4416	2749
9	4388	2733
11	4544	2850
12	4469	2783
14	4278	2657
18	4428	2757
19	4385	2729

6.2.5 Comparison of CFD and Measured Pressure Results

The Novent model was verified by comparing data collected from the Perspex mould flow experiment and the computational analysis. Once verified the Novent model was suitable to be used for the analysis with the viscous feedstock consisting of alumina and cyanoacrylate. The pressure values were compared from both CFD and practical investigations, and detailed in table 29 as a percentage error.

Table 29. Percentage error of pressure between Perspex mould and computational analysis

No	*Probe position (in relation to Perspex mould)*	*Perspex 1 percentage error (%)*	*Perspex 2 percentage error (%)*
1	3	+1.05	+2.39
2	4	-0.45	-0.47
3	5	+0.64	+2.21
4	8	-0.45	-0.43
5	9	+0.48	+1.86
6	11	-0.20	+1.79
7	12	+1.20	+1.13
8	14	-0.70	+0.49
9	18	+0.48	+2.76
10	19	+0.41	+0.96

N.B. error=(CFD-Perspex flow)/Perspex flow

The largest error of 2.76% was very low, suggesting that the CFD model was acceptable for estimating flow data. These results also suggested that the pre-processor attributes, such as domain size and fluid properties, were defined correctly.

The CFD analysis used a laminar flow model, which assumed that the Perspex mould flow characteristics were laminar, although the data could have been turbulent. The data in table 29 revealed close correlation between both investigations, suggesting that the choice of flow model was correct even though the Reynolds number was in the transition zone.

Another method of comparing the data was to analyse the error level at different points within the mould, and the errors for both the CFD and perspex mould were plotted as shown in figure 82.

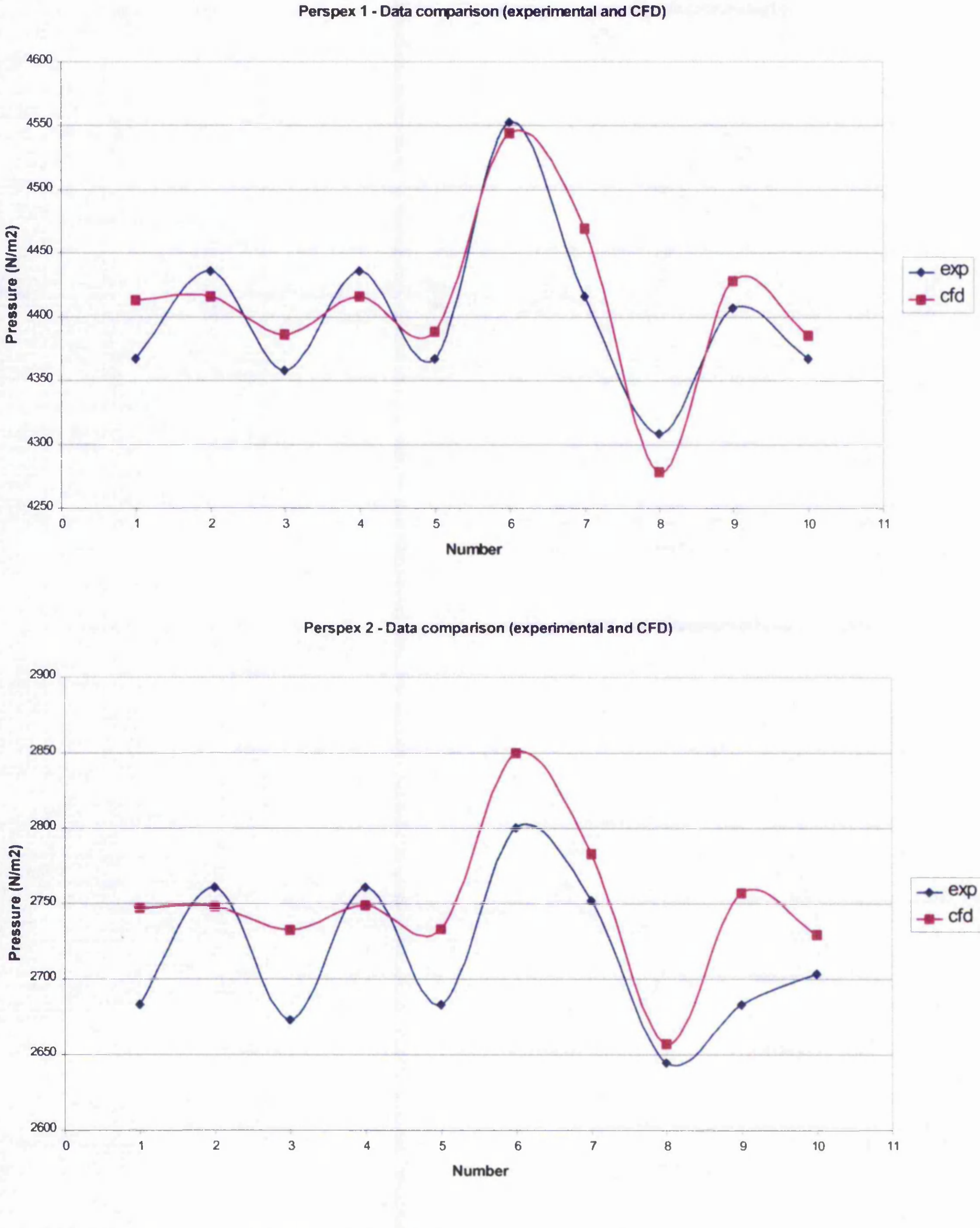


Figure 82. Pressure data comparison between CFD and Experiments

Figure 82 shows that the results at the various measured pressure points were similar to the CFD prediction. In particular, the data shows that the pressure distribution has been modelled correctly, because the measurements follow a matching trend. The findings confirmed that both the Novent model and subsequently the Twovent model were acceptable for use in a CFD analysis with another fluid. Accordingly, further CFD investigations used the alumina\cyanoacrylate feedstock, to predict pressure in the moulds that were to be used to create ceramic heart valves.

6.3 Investigation to Determine the Feedstock Pressure Distribution when Moulding

The Novent model had been validated for use in PHOENICS for predicting the pressure within geometry representing the heart valve mould. This model had identical flow geometry to the Twovent model, and hence, it was assumed that both models would provide a further understanding of the moulding process. It was the aim of this investigation to determine how the mould pressure distribution was affected by different mould venting locations. The results from this analysis would provide information to help evaluate the success of the wax skeleton mould (represented by the Twovent model).

Although the CFD model had been verified for use, it was not known if the model would work correctly with the viscous two-phase feedstock. Therefore, the inlet pressure was measured when filling a heart valve mould, so that the result could be compared with the CFD prediction.

Finally, the CFD calculation required the feedstock flow rate and density to produce a solution, and these two attributes were determined before the analysis.

6.3.1 Measurement of the Feedstock Density

The compressibility of the alumina/cyanoacrylate feedstock was investigated at a range of pressures, and the density was determined for use with the CFD analysis. This study was specifically designed to provide the following:

- Compressibility of the feedstock
- Variation of density with pressure
- The feedstock density at the moulding pressure

The force required to compress the feedstock was supplied from a hydraulic press. This force was measured on a 50kN load cell that was placed between the hydraulic ram and the piston that compressed the feedstock. The load cell was essentially a large strain gauge that measured compression as a percentage of the cell rating; its readings were limited to 5 tonnes (100%). Figure 83, shows a schematic arrangement of the apparatus.

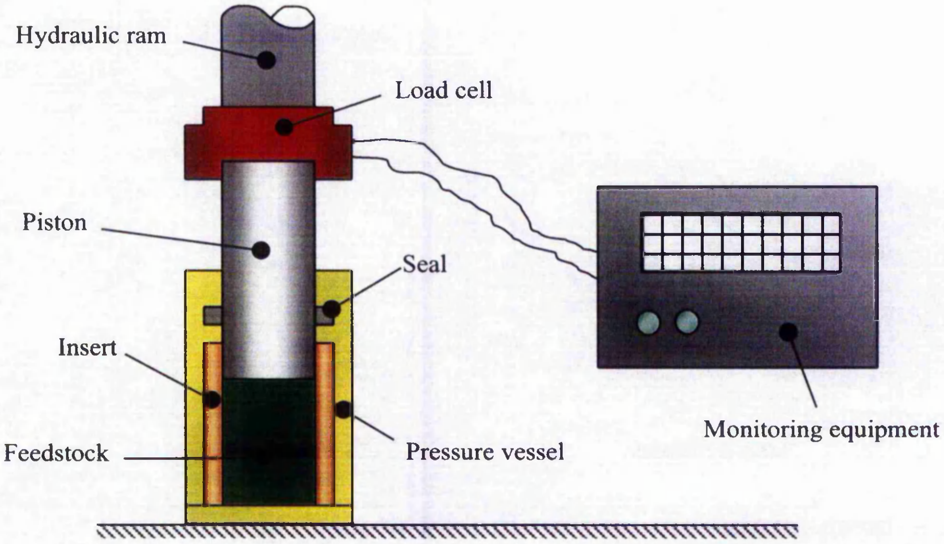


Figure 83. Apparatus used for determining density variation with pressure

A steel vessel was designed and manufactured with sufficient capacity to contain a polypropylene sleeve loaded with feedstock. The vessel contained a steel piston machined to a similar diameter to the sleeve, thus sealing the fluid within the container. In case the piston failed to provide a seal, an additional rubber seal was included in the upper portion of the vessel.

The apparatus was designed to withstand forces in the working range of the load cell. However, the maximum applied force was limited to 4 tonnes since this would provide sufficient information.

Feedstock was mixed with a composition including 0.48 (by volume fraction) of powder. The binder was inhibited by using a relatively large amount of acid, to prevent the likely occurrence of a polymerisation reaction. This mixture represented a typical feedstock that was used for creating the heart valve. The mass of the insert alone and the mass of the insert loaded with feedstock were measured, and the feedstock mass was obtained by taking the first value from the second. The insert was completely filled to avoid the entrapment of air before the piston was placed in position. Although this helped to minimise error, nevertheless, the feedstock would still include air from the mixing stage.

The change in volume of the feedstock was measured by noting the displacement of the piston at 5kN intervals, from 0kN to 40kN. The density of the feedstock was calculated from the changing volume and the constant mass. Table 30 shows the equipment data and table 31 details the results of this investigation.

Table 30. Equipment and feedstock data for density investigation

Variable	*Value*
Volume fraction of Alumina	0.48
Acid inhibition level	9%
Mass of Polypropylene insert	25.9g
Mass of feedstock and insert	65.4g
Fill height of the insert	51mm
Load cell capacity	50KN
Piston start height	180mm
Piston area	0.0003685m^2

Table 31. Result from the density variation with pressure investigation

Load (%)	*Load (KN)*	*Load (Tonnes)*	*Piston height (mm)*	*Sample volume (m^3)*	*Sample Density (kg/m^2)*
0	0	0.0	180.0	1.879×10^{-5}	2101
10	5	0.5	176.0	1.732×10^{-5}	2280
20	10	1.0	176.0	1.732×10^{-5}	2280
30	15	1.5	176.0	1.732×10^{-5}	2280
40	20	2.0	176.0	1.732×10^{-5}	2280
50	25	2.5	176.0	1.732×10^{-5}	2280
60	30	3.0	176.0	1.732×10^{-5}	2280
70	35	3.5	176.0	1.732×10^{-5}	2280
80	40	4.0	176.0	1.732×10^{-5}	2280

Initially the volume changed up to a load of 5kN, as the air compressed within the chamber. However, after the air had compressed, the volume did not change, and the density was calculated and plotted as shown in figure 84.

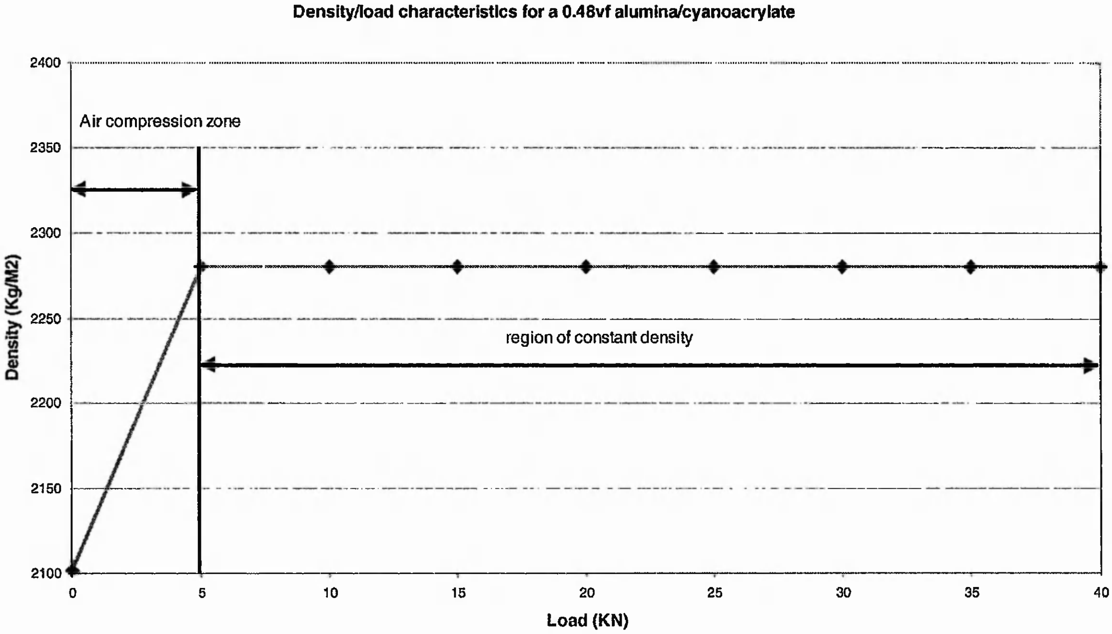


Figure 84. Density variation with load on an alumina\cyanoacrylate feedstock

6.3.2 Moulding Pressure and Flow Rate

Two parameters were required from this investigation: firstly, the feedstock flow rate; and secondly, the mould fill pressure. The rate that feedstock entered the mould was used as an inlet parameter for the computational analysis, and the fill pressure was compared to the computational results.

The feedstock flow rate and pressure were investigated whilst a heart valve mould was filled. The aims of this particular investigation were to:

- Determine the volumetric flow rate for the filling of the heart valve mould
- Calculate the inlet and outlet velocities from the flow rate
- Determine the fluid pressure when the mould was filled
- Determine a pressure that was related to the mould resistance, which would provide a comparison for computational results
- Compare the feedstock pressure when filling a mould with and without a wax skeleton

The two types of alloy heart valve mould were investigated, one with a wax skeleton, and the other without. Therefore, the three investigations required were:

(1) Feedstock pressure whilst filling the alloy mould *without* a wax skeleton
(2) Feedstock pressure whilst filling the alloy mould *with* a wax skeleton
(3) Feedstock flow rate in either alloy mould (because the flow rate was the same for the two moulding operations).

Flow rate was determined by measuring the change in piston height over time, whereas the pressure was evaluated by measuring the required force through a load cell. Although these were two separate investigations, both of these measuring methods can be realised on one diagram shown in figure 85.

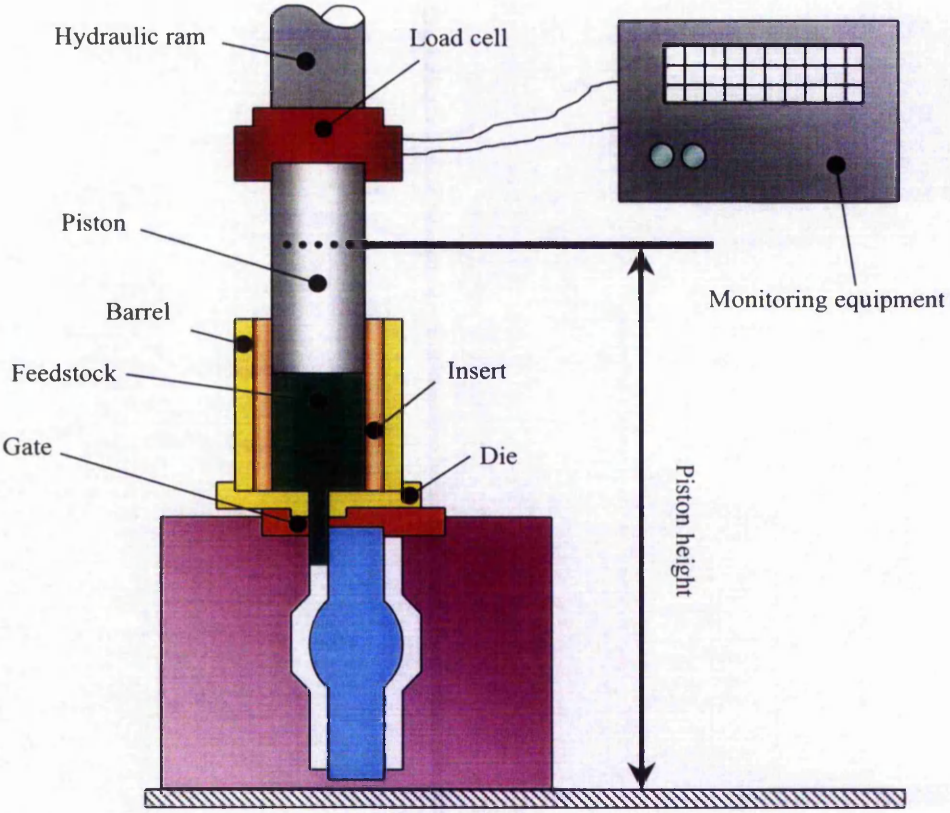


Figure 85. Apparatus used for determining the moulding pressure and flow rate

The heart valve moulds were cast and assembled using alloy inserts, and feedstock was mixed consisting of a high volume fraction of powder (0.48). This feedstock was loaded into a polypropylene insert that was placed inside the moulding barrel. Finally, the apparatus was assembled as shown in figure 85.

Force was applied by the use of a hydraulic ram, which provided enough pressure to fill the mould. Whilst under pressure, the flow rate was calculated by measuring the change in feedstock volume over time. The change in piston height was measured three times at intervals of 10 seconds and averaged to find the piston velocity. Multiplying the velocity by the piston area provided the flow rate (Q), which was constant throughout the whole moulding process. The continuity equation was used to determine the velocity at the mould inlet and vents, which had either a 3mm or 4mm diameter.

Table 32. Parameters used and calculated for flow rate investigation

Parameter	*Value*
Diameter of piston	21 mm
Area of Piston	3.464×10^{-4} m^2
Area of 3mm section	7.07×10^{-6} m^2
Area of 4mm section	1.26×10^{-5} m^2
Piston velocity	2.80×10^{-3} m/s
Feedstock flow rate	9.70×10^{-7} m^3/s
Velocity at 3mm section	0.1372 m/s
Velocity at 4mm section	0.0771 m/s

Mould pressure was measured from the output of the load cell, as a percentage of the cell rating. This data was taken every three seconds whilst each mould was filled until a steady flow occurred after feedstock had exited from the vents. Each reading was separated into one of three groups that outlined the stages of moulding, namely, 'start', 'filling' and 'full'. The data was averaged for that particular mould stage and converted into a pressure by dividing the force by the piston cross sectional area. These stages were marked by the change in force required to maintain the flow rate throughout the mould.

Initially, the feedstock was only forced from the barrel, and this force was associated with the 'start' stage. Next, when the mould filled, a back pressure was formed within the feedstock, which increased the force requirement. Finally, when the mould was full, this pressure increased a final time, because of the restriction caused by the exit vent(s). Therefore, the three stages were described by the following force equations:

START

Force = *Piston friction + Barrel inlet flow*

FILLING

Force = *Piston friction + Barrel inlet flow + Partial mould resistance*

FULL

Force = *Piston friction + Barrel inlet flow + Mould resistance*

Therefore,

Mould resistance (pressure) = FULL (pressure) – START (pressure)

Mould resistance was calculated by taking the start pressure from the full pressure. This was because the mould contributed to the flow resistance after the feedstock had left the moulding barrel, until the feedstock flowed out the exit vent(s). The measured pressure difference was compared to the analytical results obtained through the computational analysis, detailed in section 6.3.3. Table 33 shows the results from this investigation.

Table 33. Pressure measurement results

Fill stage	*Mould type*	*Average load (% of 50kN)*	*Load (kN)*	*Load (Tonnes)*	*Pressure (N/m^2)*	*Pressure (Bar)*
Start	Novent	21	10.5	1.05	30.3×10^6	303
	Twovent	21	10.6	1.06	30.5×10^6	305
Filling	Novent	28	14.0	1.40	40.4×10^6	404
	Twovent	27	13.8	1.38	39.8×10^6	398
Full	Novent	31	15.2	1.55	43.9×10^6	439
	Twovent	30	14.7	1.50	42.5×10^6	425

There was a noticeable difference in pressure between the Novent and Twovent moulding arrangements, especially at the full stage. This was expected because the Twovent mould had extra venting, which helped reduce the feedstock pressure.

The mould resistance was easily calculated by taking the start pressure from the full pressure. These values were high, but this was expected when moulding with a viscous feedstock at relatively low rates of shear. These results were the only values that could be obtained from a practical mould fill analysis, since an investigation with transducers situated within the mould was difficult using a cyanoacrylate binder. Therefore, CFD was used to find the mould pressure, using the measured mould resistance for a data comparison.

- Mould resistance (Novent) = 136 Bar
- Mould resistance (Twovent) = 120 Bar

6.3.3 CFD Analysis of the Feedstock Moulding Pressure

The fluid dynamics of the mixed feedstock were investigated as a steady, fully developed flow through models representing the alloy heart valve mould. These models, namely Novent and Twovent, were validated to work correctly by the work described in section 6.2. Hence, an analysis was carried out with PHOENICS CFD code, to produce a greater understanding of the moulding process. This involved investigating the following aims:

- Determine the role that the wax skeleton plays within the alloy heart valve mould
- Determine regions of pressure and picture how the pressure is distributed with the two models
- Determine how the extra vents in the Twovent model effect the feedstock pressure distribution with respect to the Novent model
- Determine the highest feedstock pressure within the mould, and determine whether this will cause the internal collapse of feedstock (when the core is removed in the moulding process)

The fluid had to be assessed to determine whether the feedstock flow was either laminar or turbulent. This involved substituting the appropriate fluid properties into the Reynolds equation, to evaluate the Reynolds number.

The feedstock had been characterised in section 3.2.4.2 as a power law fluid, thus the viscosity was calculated by using an apparent shear rate that was typical for the moulding process. It was known that the shear rate changed at different positions around the mould. Hence, the apparent shear rate was determined using equation 18 at the mould inlet, because most of the flow parameters were known at this point.

$$\nabla_a = \frac{4Q}{\pi r_2^3} \qquad (18)$$

Where,

∇_a = *Apparent shear strain rate* (s^{-1})
Q = *Volumetric flow rate* (m^3/s)
r_2 = *Radius of flow area (m)*

The apparent shear rate was substituted into equation 12 to find the apparent viscosity at the mould inlet, as shown by the following calculation.

Apparent shear rate at the heart valve mould inlet,

$$\nabla_a = 366 s^{-1}$$

By substitution in the viscosity equation,

$$\eta_a = 179 Pa.s$$

After substituting the fluid parameters into the Reynolds equation, the Reynolds number was very low. Nevertheless, this was expected, because the fluid was very viscous at the low shear rates associated with moulding. Therefore, the feedstock was modelled as a laminar fluid, since there was no risk of turbulent effects.

The CFD code required a kinematic viscosity model, which would have involved dividing the dynamic viscosity by the feedstock density. However, the feedstock used in this investigation was two-phase and the binder was the only fluid constituent. Therefore, the density of the feedstock was not used to find the kinematic viscosity because the powder constituent was not a fluid. On this basis, the binder density was used for determining the kinematic viscosity, because it was assumed that this was the only fraction of the feedstock that promoted flow when the dynamic viscosity model was created from the cone and plate rheometer. Furthermore, the ceramic powder particles were only 2μ-8μm in size, which was very small in comparison to the distance between the cone and plate. Thus, the effect of these powders was ignored for this investigation.

Another factor that could have effected the CFD model was related to the volume fraction of the feedstock when the viscosity model was determined. The cone and plate rheometer sheared the feedstock between two surfaces. Therefore, it can be assumed that only a fraction (relative to the solid loading) of the feedstock was sheared because it was a fluid, as shown in figure 86. Hence, the binder fraction was also used to correct the density used for finding the kinematic viscosity. The binder fraction was typically 0.52 for creating heart valves, and it was therefore used as the correction factor.

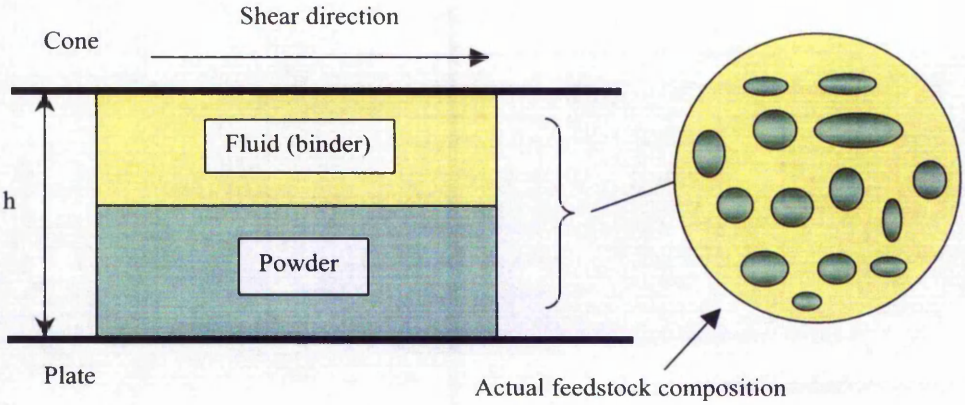


Figure 86. Diagram showing the feedstock constituents when sheared with the cone and plate rheometer.

Two viscosity models were created for the CFD analysis, to determine the effect of using the volume fraction correction. The first model incorporated the binder and volume fraction correction, whilst the second model included only the binder correction. The pre-processor in PHOENICS used an equation for kinematic viscosity that already included the feedstock density, and as this density could not be changed within the software, a correction factor was included to adjust the dynamic viscosity. Therefore, the viscosity equation 12 was adjusted to create two new equations 19 and 20.

(1) Volume fraction and binder density corrected equation

$$\eta_{kinematic} = \frac{16102.\nabla^{(0.48-1)}}{\rho_{feedstock}} \quad \text{———————} \quad (19)$$

(2) Binder density corrected equation

$$\eta_{kinematic} = \frac{8373.\nabla^{(0.48-1)}}{\rho_{feedstock}} \quad \text{———————} \quad (20)$$

Where,

$\eta_{kinematic}$ = *Kinematic viscosity* (m^2/s)

$\rho_{feedstock}$ = *Feedstock density* (kg/m^3)

∇ = *Shear strain rate* (s^{-1})

The CFD analysis was performed with both of these viscosity equations applied to the geometry models, Novent and Twovent, and four solutions were determined as detailed in table 34.

Table 34. Models Investigated with CFD

Model Name	*Details*
Novent	Heart valve model with one outlet. Kinematic viscosity model based on binder viscosity and volume fraction correction.
Novent 2	Heart valve model with one outlet. Kinematic viscosity model based on binder viscosity only.
Twovent	Heart valve model with a wax skeleton included, hence providing two extra vents (three outlets). Kinematic viscosity model based on binder viscosity and volume fraction correction.
Twovent 2	Heart valve model with a wax skeleton included, hence providing two extra vents (three outlets). Kinematic viscosity model based on binder viscosity only.

The CFD domain used with the four models had 40 nodes in each axis direction, which was based upon the high resolution achieved with the Perspex 1 and Perspex 2 models (section 6.2.4). The fluid properties were entered into the pre-processor, including the density determined in section (6.3.1), and the viscosity models detailed in equations 19 and 20.

The boundary conditions for each model were entered as an inlet flow rate and outlet pressure. Feedstock was vented to atmosphere in all cases, and therefore the outlet pressure was set to zero. The reference pressure within the pre-processor was set at $1x10^5$ N/m^2, and all results were based on gauge pressure.

The domain boundary conditions and fluid parameters that were used for the four investigations are detailed in table 35.

Table 35. Domain boundary conditions and fluid properties for the CFD models Novent, Novent 2, Twovent, and Twovent2.

Property or Variable	*Value*
Domain material	Feedstock used for heart valve with the following constituents by volume fraction, Alumina-0.48 Butyl-Cyanoacrylate-0.52
Reference pressure	$1x10^5$ N/m^2
Equation formula	Elliptic-CCM
Solution	Velocity and Pressure
Model	Laminar
Iterations	1000
Density	2280 kg/m^3
Viscosity	Power law with corrections detailed in table 34
Gravitational forces	Not used

As with the Perspex 1 & 2 investigation, the alumina\cyanoacrylate models would not converge within an acceptable time with gravitational forces applied to the model. Therefore, the gravitational forces were ignored, because the resulting pressure was insignificant in relation to the large pressures induced through the moulding process, and the solver was run for 1000 iterations without gravitational effects. This was sufficient to converge the numerical models.

After the CFD calculation, the results file was observed using the VR viewer. Exact pressure readings were not taken from different parts of the model, because they were not specifically accurate. Instead, regions of pressure were analysed to produce the observation required for this investigation.

On the other hand, the *maximum pressure* was taken as a value from the resulting solutions, because it was acceptable to use as a comparison to the pressure data measured when the heart valve moulds were filled. Table 36 includes the data retrieved from the four CFD results, and the measured mould pressure (section 6.3.2) for a comparison.

Table 36. Pressure data retrieved from the CFD investigation and pressure measured from the moulding investigation.

Model	Maximum pressure (N/m^2)	
	CFD	Practical
Novent	126x10^6	136x10^6
Novent 2	66x10^6	
Twovent	109x10^6	120x10^6
Twovent 2	57x10^6	

The models that included only the binder viscosity without a volume fraction correction produced results with a large variation from the measured pressure. On the other hand, the results that considered the volume fraction correction were similar to the measured results from the mould fill investigation. Based on this observation, the results from the Novent2 and Twovent2 models were ignored.

There was a low difference in error between the Novent, the Twovent, and the physical investigation. For example, Novent had an error of 7.6%, whilst Twovent was 10.1%. It was therefore concluded that these models suited the physical data within an acceptable limit for the purposes of this investigation, and hence, pressure regions were determined from these models and comparisons made.

The pressure within the Twovent model was significantly lower than the pressure in the Novent model, because of the extra venting. The extra vents provided a pressure reduction of 15.6%, which was probably sufficient to stop the phenomenon of feedstock collapse when the insert was removed in the moulding process. It was apparent that the vents had made a large difference to the regions of pressure within the moulds, as shown in figure 87. Pressure within the Novent model was high around a large proportion of the mould, particularly the upper regions. This would probably explain why the lower halves of moulded heart valves were always in a good condition when using the mould without a wax skeleton (3.4.6).

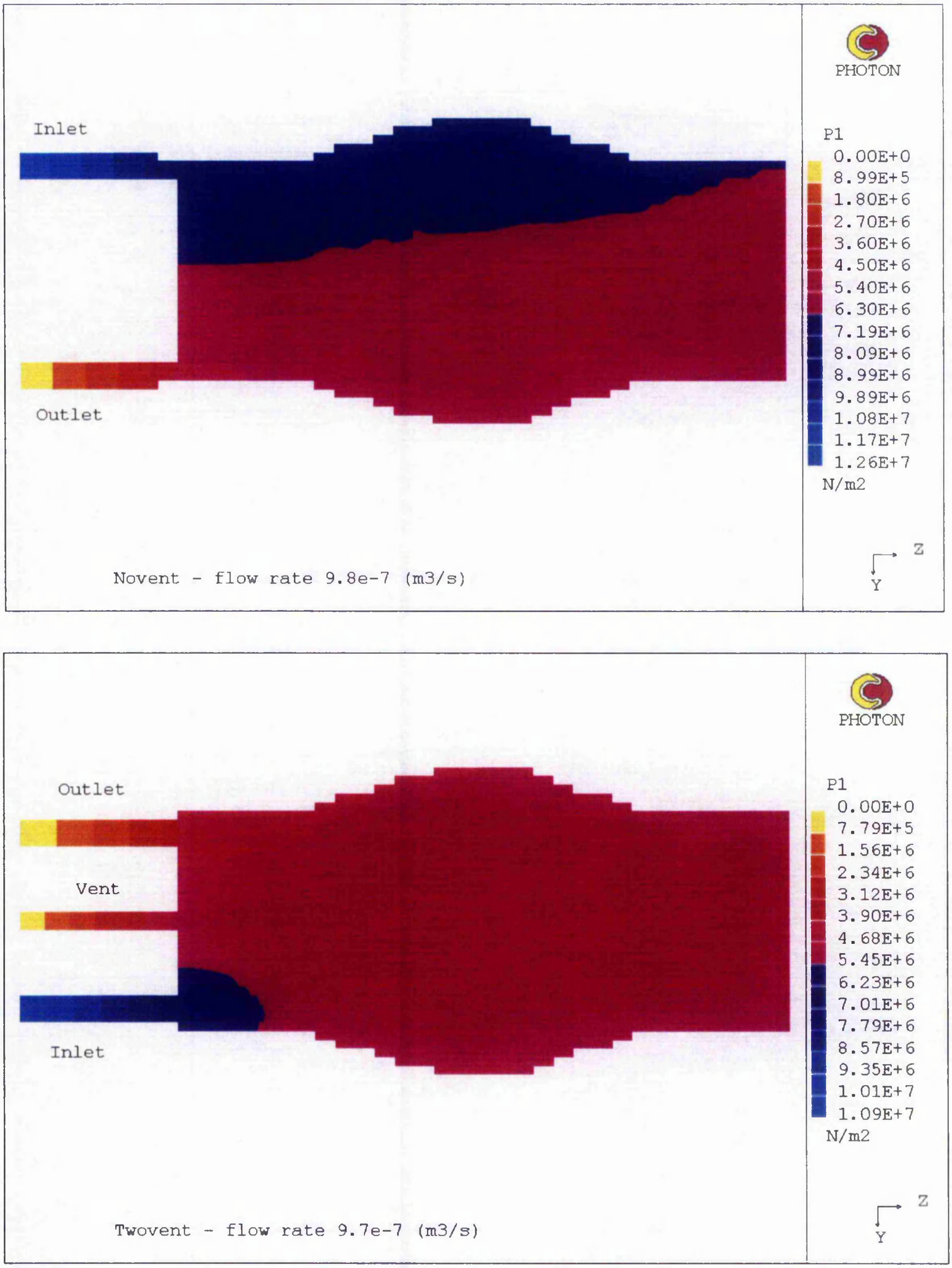


Figure 87. CFD result of pressure distribution through the conduit heart valve mould when the mould was full of feedstock

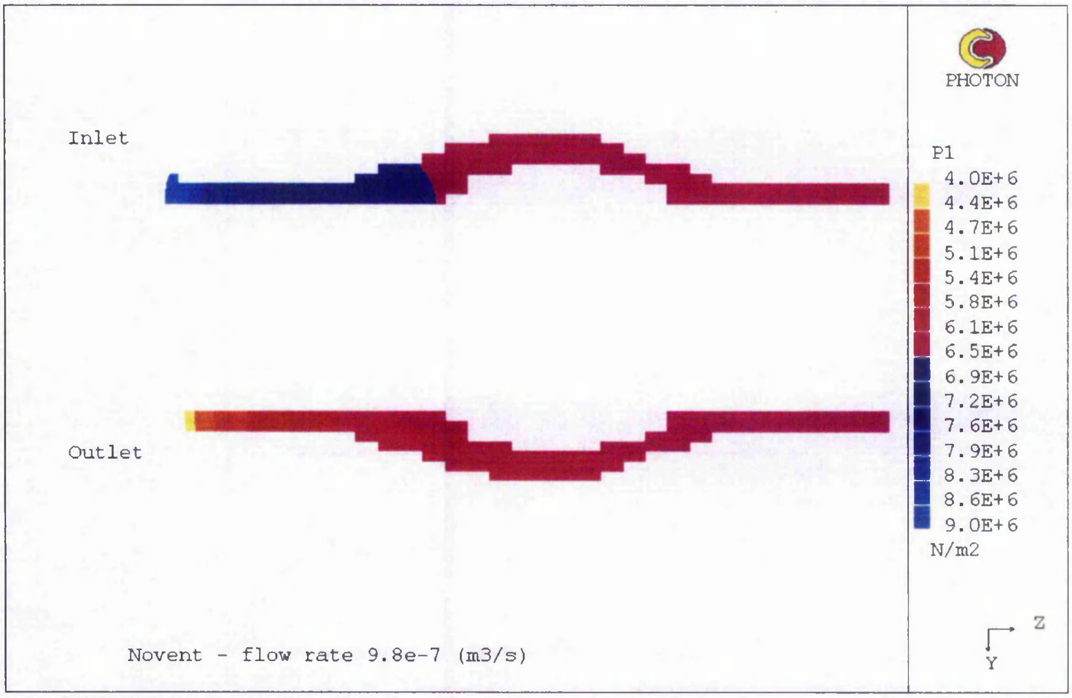


Figure 88. Pressure distribution throughout the Novent model at an increased resolution

The Twovent model did not show signs of this high pressure region. In fact, the pressure was reduced significantly at the upper regions of the mould near the inlet. Hence, the venting positions (associated with the wax skeleton) were probably located in the correct position for the heart valve mould. This observation probably provided a partial explanation as to why the wax skeleton mould prevented internal collapse of the feedstock.

The highest pressure region was the same for both models, near the inlet, which was expected for these moulds. On neither model was there a zone of very high pressure that would affect the moulding process. The Novent model was analysed at an increased resolution to determine any area that had a specifically high pressure. As shown in figure 88, the pressure tended to drop to approximately 60×10^5 Pa with no adverse pressure regions. Hence, the only major difference between the Novent and Twovent models was the pressure relief caused by the additional venting.

6.3.4 Summary

Flow regions have been identified with the Novent and Twovent models, proving that the extra venting arrangement has contributed to a substantial pressure relief within the heart valve mould.

The kinematic viscosity model within PHOENICS required a binder and volume fraction correction to produce reasonable results. Although, these corrections were assumed from the rheological data, the error was no higher than 10%, which was acceptable for an investigation such as this.

The internal collapse of the moulded components was probably associated with the large expanse of high pressure as shown with the Novent model. The lower regions of the model did not seem to accumulate pressure regions, which probably explains the improved quality at the bottom half of the heart valves formed with this mould. The Twovent model showed no signs of this pressure, demonstrating that the extra vents had provided adequate pressure relief. Hence, it was thought that pressurised air from the moulding process remaining in the mould would relieve more easily with these vents, thus reducing the risk of the feedstock collapsing when the insert was removed.

Finally, whilst the two extra vents may have promoted a pressure relief that helped to prevent internal feedstock collapse; the physical support provided by the polymerisation associated with removal of the wax skeleton was probably more significant.

Chapter 7 – Discussion

7.1 Overview

This project investigated the use of powder reaction injection moulding to manufacture a novel seamless conduit heart valve. Two chemicals were investigated and compared as binders for the aluminium oxide powder, butyl-cyanoacrylate, and methyl methacrylate. Butyl-cyanoacrylate satisfied the moulding requirements when included in a feedstock with alumina, and was adopted, but methyl methacrylate could not mix to the required volume fraction of alumina powder.

The cyanoacrylate binder was highly reactive, and chemicals were investigated to delay the polymerisation. This posed problems when mixing and handling feedstock that included the reactive monomer. Hence, inhibition levels were investigated to determine a safe level that would prevent the feedstock polymerising prematurely when moulding, and a working window was developed for inhibiting cyanoacrylate to a safe level. However, the monomer was inhibited to such an extent for moulding that initiation was a problem. Therefore, catalysing mediums were investigated to find which one instigated a successful reaction within an acceptable period of time. Steam and boiling water were found the best mediums and were later used in moulding investigations.

The mixture of cyanoacrylate and alumina was very viscous and this could have affected the moulding process. Therefore, the rheological properties were investigated and it was found that the viscosity was within acceptable limits for injection moulding. Furthermore, the feedstock behaved like a power law at the investigated shear rates; hence, a model was developed. The model was used to predict viscosity at high shear rates, which could be experienced within a standard injection moulding machine. At these high levels of shear, the viscosity fell to within 100 Pa.s, which was reasonable for moulding.

When the material properties were understood, a moulding process was developed to form the feedstock into a recognisable shape. A moulding arrangement was devised to inject the viscous, highly adhesive binder into a mould. This involved using a recyclable polypropylene barrel-insert for containing the feedstock within the moulding barrel, otherwise the binder tended to polymerise before extrusion. Mould materials were investigated, and it was found that the best arrangement was using an alloy mould and core. Both the mould and core could withstand moulding pressures, and by melting them after moulding the heart valve could be released without any damage. This method, along with the use of a wax skeleton within the mould was unique for injection moulding. Hence, a patent was developed throughout this study, encompassing the use of a novel feedstock and moulding technique for producing conduit articles.

If required, the internal surface of the moulded heart valve could be improved by machining to a tolerance that was appropriate to a prosthetic component of this nature. On this basis, moulded feedstock was investigated when the binder had polymerised, and it was noticed that the binder provided a high green strength. Cylindrical samples were moulded and polymerised for use as test pieces for ceramic machining. The samples turned exceptionally well using a standard lathe, which was much simpler and cheaper than expensive physical and chemical machining techniques. Hence, moulded articles produced by reaction moulding with a cyanoacrylate binder could be machined as part of a post processing technique, which would normally be used to increase tolerance of high quality components, or to remove surface defects that have arisen from a poorly moulded batch. These results suggested that green machining of PRIME feedstock would provide many benefits to a production process, in terms of cost, production time, and a reduction in scrapped materials.

The novel moulding technique using a wax skeleton produced heart valves to an acceptable standard, but no physical data was recorded to explain the successful results. In order to understand exactly how the moulding process worked, a computational analysis was used to determine the pressures inside the mould and highlight possible areas of increased pressure. The CFD model that was developed was validated by analysing Newtonian fluid flow through a Perspex heart valve mould and comparing pressure results from the practical and computational investigation.

The analysis highlighted areas of high pressure within the mould that were inadequately vented. The mould that included the wax skeleton had two extra vents and flow pressure was reduced significantly, explaining why the mould worked without producing failed components. It was also found that when the wax skeleton was removed by melting with hot water or steam, more feedstock was polymerised within the mould and helped to prevent an internal collapse when the insert was removed.

This introduction has given a general overview of the investigation. Sections 7.2 to 7.6 consider the findings from each area of the work in more detail.

7.2 Material Processing

It has been demonstrated that alumina powder is bio-compatible and useful as a material for heart valve prostheses, and, on this basis, three types of medical grade alumina powder with a purity greater than 99.8% were investigated. The powders were selected with a range of features, including certain characteristics that were known to assist powder injection moulding (such as particle size, shape, and distribution). It was found that an alumina powder that has a rounded shape and a small particle size with a relatively wide distribution had the best mixing characteristics.

The success of powder moulding is dependant on the feedstock volume fraction being greater than 0.45 so that components will sinter to an acceptable density. The three powders were investigated to find the tap density, which produced results that suggested powder number three had the potential to mix to the highest volume fraction. This observation was later confirmed when powder number three was able to mix with cyanoacrylate to a volume fraction of 0.5.

Binders for injection moulding had to have a viscosity lower than 10 Pa.s at the moulding temperature and pressure, otherwise, when a powder is included, the combined viscosity would be too high for moulding. Therefore, two reactive binders with a low viscosity were selected for study, methyl methacrylate (MMA), and cyanoacrylate. It was found that butyl-cyanoacrylate had a lower viscosity than ethyl- and methyl-cyanoacrylate, and for that reason, it was used throughout this investigation.

The polymerisation of MMA was found to be dependent on parameters such as catalyst level and temperature. The monomer was investigated by adjusting these parameters, and it was found that initiation of polymerisation could be controlled to promote a reaction within a period as low as 20 minutes. However, MMA could not be mixed with alumina to a powder volume fraction that was acceptable for injection moulding. MMA was therefore eliminated from this study, and cyanoacrylate was investigated further.

Cyanoacrylate is a highly reactive monomer that polymerises with the addition of a simple catalyst such as water. This caused difficulties when mixing feedstock because of the water vapour in the alumina powder and surrounding atmosphere. It was also found that high concentrations of powder caused rapid polymerisation when mixed with cyanoacrylate, and so the alumina powder was dried before mixing to remove any water content. In addition to drying the alumina powder, p-toluene sulphonic acid was used as an inhibitor to prevent a reaction, whilst the feedstock was mixed.

Alumina powder mixed with the cyanoacrylate binder to volume fractions as high as 0.5, and based on German's recommendations (37) was, therefore, acceptable for injection moulding investigations.

The cyanoacrylate polymerised when the acid inhibitor was neutralised by water to a pH level of 5.5. To judge the extent of polymerisation, batches of feedstock were polymerised in hot water, cold water, steam, and warm air moisture (hot oven). By investigating the polymerised surface hardness with Vickers Hardness tests, it was found that the steam and hot water mediums provided the most suitable neutralisation of the acid within a five hour period. On this basis, water was placed in the oven to accelerate binder polymerisation, whilst moulds were being thermally removed after feedstock injection.

7.3 Design for Moulding

The rheological properties of cyanoacrylate and alumina were investigated, because the feedstock for moulding had to have a viscosity level that would allow it to flow under high pressure. The rheological characteristics were also needed for other investigations such as computational analysis where a model of the viscosity was required.

The feedstock rheology was determined using a cone and plate rheometer. It was found that the feedstock behaved like a power law fluid, which is typical of thermoplastics used for injection moulding. The investigated volume fractions of powder ranged from 0.4 to 0.48 and the viscosity increased with each fraction. At low shear rates, the viscosity was very high for all investigated samples. In fact, the volume fraction of 0.48 had a viscosity similar to PIM feedstock at a loading level of

0.6. This suggested that the powder had a high amount of agglomeration, or that processing aids were required such as stearic acid. However, some agglomeration was considered to be of benefit in the context of the heart valve, because it enabled the moulded parts to have an inherent porosity.

The volume fraction of powder is related to the feedstock viscosity. At powder levels reaching the critical loading point, the feedstock will have a viscosity that rapidly reaches an asymptotic level. For the heart valve moulding it was found that the volume fraction of powder should not be increased over 0.48, because the critical loading was then slightly greater than 0.5.

Shear rates as high as $10^5 s^{-1}$ are associated with injection moulding at high flow rates. When the power law model found for this feedstock was used to predict the viscosity in similar conditions, it was found that the viscosity reduced to approximately 100 Pa.s for all investigated volume fractions (this assumed that the power law model worked with the feedstock at higher shear rates).

A model was constructed from the results to enable calculation of the viscosity at a range of shear rates. This model was used for finding the Reynolds number within the heart valve mould and for predicting viscosity within the computational fluid analysis.

Moulding of the cyanoacrylate binder was made difficult by the monomer's ability to rapidly polymerise when in contact with certain materials. To overcome this, a polypropylene sleeve was incorporated within the barrel of a specially designed moulding system. The mould was filled by inserting a piston in to the barrel, and forcing down with a hydraulic press, which provided adequate pressure to inject the feedstock.

Mould materials such as teflon and nylon were investigated, because it was thought that cyanoacrylate would not adhere to these surfaces. After moulding, the cyanoacrylate did adhere to the surface, but only because the machined surface was not adequately polished. This could have been resolved, but a second observed problem was of greater significance and caused the moulding materials and techniques to be changed. A range of cylindrical shapes was moulded from the feedstock with diameters less than 25mm as solid components. After opening the mould, parts had not polymerised. This observation suggested that solid components with a large circumference could not be moulded because a catalyst cannot enter the mould when it is sealed. Therefore, a novel technique was devised using an alloy-moulding platform. Alloy moulds were melted from the component thus removing the problem of adherence to the mould surface. Furthermore, removal of alloy moulds within an oven allowed the ingress of air moisture to the surface of components. However, this was not sufficient to polymerise the entire feedstock, and collapse of the moulding occurred when the core was removed. A solution was therefore developed, using a wax skeleton within the heart valve mould. The wax was removed by water that was above the wax melting temperature, thus polymerising most of the component surface before removal of the alloy moulds.

The technique of removing the mould and polymerising the component using the wax skeleton method was novel, and has become the subject of a patent developed throughout this investigation.

7.4 Ceramic Machining

Ceramic machining is normally difficult because of the material hardness and equipment availability, and grinding techniques are typically employed.

The feedstock, after moulding was observed to have a high strength that could probably withstand traditional machining operations. Hence, the heart valve could be machined to improve tolerance and surface finish.

Complex equipment such as that involved with non-traditional machining was not required for the alumina/cyanoacrylate feedstock. Instead, a simple traditional machining arrangement was used, which makes this process more flexible because of the availability and low cost of equipment. Moreover, the non-traditional techniques would probably not machine a complex geometry, such as that associated with the conduit heart valve, unless complex tooling was developed. If an alternative machining route was preferred, then ultrasonic machining would probably be the most realistic selection for cutting the geometry, however, traditional machining techniques are readily available, so this decision would never have to be made.

Green compacts for machining tests were made using polypropylene moulds because the moulds were readily drilled to allow the ingress of steam to polymerise the binder. Furthermore, the mould was easily turned down to the required diameter of the compact.

Samples turned with ease, suggesting that the binder material had sufficiently high fracture toughness for green machining. Furthermore, chip formation whilst machining suggested that the compacts had a brittle nature. Inspection of the chips and the compact surface showed no sign of debinding, therefore, no coolant was required whilst turning at the investigated cutting speeds and feeds. The compacts turned with similar characteristics to mild steel; hence, when the cutting speed was increased at a low feed rate the surface finish subsequently increased.

The surface of the green compacts had a roughness (R_a) less than 10μm, with some samples approaching 2μm. These are acceptable limits for turning operations, indicating a good surface finish. Although large deviations were found between the R_a values for the green compacts, caused by 'pull outs' from the material, adjusting the powder parameters such as volume fraction, particle size and shape would reduce this.

Post processing of the sintered conduit heart valve could involve a number of techniques based on particle removal or addition. Particle addition could be used to coat the surface of the valve with a dense ceramic by a process such as plasma spraying or a sol-gel operation. This would indeed increase the overall mass of the product at a small increase in volume, which in turn would increase the density of the part and provide extra strength. On the other hand, the heart valve may have sufficient strength, and techniques could be used to improve the service reliability by increasing the tolerance of the fired component. This would involve machining a dense ceramic, which is becoming increasingly popular with diamond grinding methods and even more so with non-traditional material removal techniques. However, the tolerance would also be improved by machining the moulded heart valve before the debinding stage of the PRIME process, which is considered the most rational approach. Moreover, since the feedstock is unfired, the amount of available machining techniques is increased, thus providing a more suitable selection of equipment based on cost and complexity.

This exercise has proved that there is a good potential for the green machining of an alumina/cyanoacrylate composite produced by PRIME. Combining moulding and machining routes without the investment of expensive physical & chemical machining equipment will create complex articles that require a good surface finish.

7.5 Heat Treatment

Heat treatment was required to remove the binder from the moulded heart valve, and to sinter the powder to a desired porosity. When mixed with alumina and inhibited with p-toluene sulphonic acid, it was found that cyanoacrylate would debind most efficiently between 210°C and 230°C. This information was collected from a Differential Scanning Calorimeter, which provided endothermic heat flow against temperature.

The weight loss of the feedstock was measured against temperature using a thermogravimetric analyser. This proved that the mixed volume fraction was correct, because the weight loss could be compared to the volume of binder removed. For example, feedstock was mixed by measuring concentrations to a certain volume fraction, and removal of the binder provided the binder mass loss as a percentage of remaining powder, hence the actual volume fraction.

The heart valve mouldings thermally debound within two hours at a heating rate of 5°C/min up to 220°C. The samples did not crack or show any sign of slumping or distortion, and the heating parameters were considered to be adequate for this stage of the investigation.

The second phase of heat treatment is sintering. Before any work was done with the heart valve, itself, small circular samples were sintered to measure porosity at a fast heating rate and high temperature. It was found that the samples sintered with porosity ranging from 44% to 53%, by sintering at 1750°C with a hold time of either 60 or 100 minutes. The level of porosity that would be required for the heart valve was unknown at this stage. However, if the porosity was too high then sintering for a longer period would increase the density.

The heart valve was sintered using the same heating profile as the small circular samples, with the intention of creating a similar level of porosity. However, the heart valves did not fully sinter in the induction furnace that was used for the investigation. It was thought that the furnace did not provide sufficient heat transfer to all areas of the large heart valve geometry. A recommended solution would be to increase the temperature, hold time, and lower the heating rate. However, this would increase the density of the component, which is undesirable.

Sintering was the final stage of the injection moulding process. A partially sintered heart valve had been produced without any sign of distortion and little shrinkage. It had been proved that a desirable porosity could be produced by sintering with a low volume fraction of powder, and further work could remedy the partial sintering.

7.6 Analysis of Mould Flow

The unknown effects that produced an adequate moulding using the wax skeleton were investigated by computational analysis. PHOENICS 3.1 code was used to determine the pressure formed within the mould when the flow was steady after a complete fill.

Two models (called Novent and Twovent) were developed within a CAD package and used in PHOENICS to produce pressure values at points around the model, which represented the heart valve mould. The models had to be verified by an agreement between experimental and computational analysis, and a Perspex heart valve mould was designed to find pressure values using a fluid with known properties. The Perspex mould investigation found that actual measured values compared with very little error to the computational analysis using PHOENICS. In fact, errors were below 2.1% for the Novent models, which is acceptable for verifying the model for use in another analysis with the heart valve feedstock.

It was found by practical investigation that the moulding pressure was approximately 425 Bar. However, when the inlet and outlet pressure were taken into consideration, the mould resistance was only 136 and 120 Bar for the Novent and Twovent models respectively. From these experimental results, it was apparent that the extra venting arrangement typical with the Twovent model had reduced the pressure.

Before the heart valve mould was investigated, certain moulding parameters were identified for the CFD boundary conditions. The first parameter found was the volumetric flow rate. The velocity of feedstock was only 0.1372m/s at the mould inlet, which equated to a flow rate of $9.707\times10^{-7}m^3/s$. This was a relatively slow velocity in comparison to a typical injection moulding feed rate.

The density of the feedstock combination was calculated as 2280 kg/m^3, by compressing feedstock of known mass with a hydraulic press. This was an expected value because the measured density was between the limits of the feedstock constituents. Once the density was determined, the flow type was investigated by using the Reynolds equation. The flow was found to be laminar, because of the extremely low Reynolds number, which was typical for a viscous fluid being sheared at a low rate.

The shear rate near the inlet of the mould when being filled with feedstock was 366s^{-1}; therefore, the viscosity was calculated as 179 Pa.s by using the equation determined from the rheological data. This shear rate and viscosity were within acceptable limits for moulding using a typical injection moulding machine, indicating that the feedstock has the flexibility to be used with other processing equipment.

The feedstock required two viscosity models, because of correction factors involved with the kinematic viscosity. It was found that a model that corrected for the fluid volume fraction and binder density produced results similar to the empirical pressure investigation with an error of 10.1%. Therefore, the CFD analysis was used to find regions of pressure within the moulds.

The pressure region within the mould that had a single outlet was much larger than in the model with two vents and an outlet. It was thought that this region of pressure compressed the remaining air within the mould, and after moulding ceased, feedstock polymerisation at the vents prevented this air from being released. Subsequently, the core was removed and the compressed air released into the mould cavity, thus damaging the moulded components. This suggestion was verified by examining the moulded heart valves before the wax skeleton was introduced. The valves had collapsed at regions that coincided with the pressure region discovered by the Novent CFD analysis. On the other hand, in the Twovent model, the pressure was reduced by 15.6%. This was because of the extra venting caused accidentally by having a wax skeleton inside the mould: when the mould filled, the vents originally designed for wax removal were burst by the pressure of the feedstock, thus relieving internal pressure. The heart valves created in the mould incorporating a wax skeleton had a very good internal surface, showing no signs of internal collapse. It is thought that the venting aided this, which was noted by the pressure reduction from the CFD Twovent analysis.

It was thought that the moulding success was based on two suggestions, although the weighting was, however, unknown:

- Reduction of pressure due to venting
- Greater physical strength of the feedstock due to more complete polymerisation over a greater surface area

7.7 Summary

This investigation has proved that a seamless conduit product, such as the heart valve, can be made from the PRIME process using a cyanoacrylate binder. In particular, the binder has introduced a different moulding practise in comparison to a standard PIM cycle with factors including, mould material, moulding temperature, pressure, and debinding. Because of these differences, there are many conclusions drawn from this research, which are listed in Chapter 8 as bulleted statements that are relevant to each chapter.

Chapter 8 – Conclusions and Further Work

8.1 Conclusions

This research project has found many conclusions that are specifically associated with the chapters of this thesis. On this basis, the chapter titles are used as headings for those particular findings, which are listed within this summary. The main conclusions that re-iterate the facts found from this investigation are bulleted below:

- Alumina powder mixed with cyanoacrylate to combine as a suitable feedstock for powder reaction injection moulding
- A moulding system incorporating a polypropylene sleeve was found to be suitable for transferring PRIME feedstock into an alloy mould incorporating an insert at low pressure and room temperature
- The conduit geometry of the heart valve was successfully moulded using alloy moulds (the alloy moulds contained a wax substrate in the shape of a skeleton, which, after melting, allowed ingress of an aqueous catalyst that polymerised the cyanoacrylate binder proportion of the feedstock)
- A computational analysis of feedstock flow was produced and used as evidence to prove that the pressure within the moulds was reduced by up to 15% when extra venting was utilised

8.1.1 Materials Processing

- Alumina powder with a rounded shape and small particle size with a relatively wide distribution was found to have the best mixing characteristics
- Alumina powder mixed to the cyanoacrylate binder to volume fractions as high as 0.5, which was acceptable for injection moulding investigations
- It was found that steam and hot water mediums contributed to polymerising cyanoacrylate binder faster than water at room temperature

- Initiation of MMA monomer could be controlled, causing a reaction within a period as low as 20 minutes
- MMA was unable to mix with alumina to a powder volume fraction that was acceptable for injection moulding and sintering

8.1.2 Design for Moulding

- The cyanoacrylate/alumina feedstock behaved like a power law fluid
- High mixed volume fractions of powder contributed to an increase in feedstock viscosity
- At low shear rates, the viscosity was very high for all investigated samples
- The volume fraction of powder within the feedstock should not be increased over 0.48 for the heart valve as this was close to the critical loading level
- By prediction, the viscosity reduced to approximately 100 Pa.s for all investigated volume fractions of powder
- It was found that a polypropylene sleeve was best suited for containing the feedstock when incorporated within the barrel of a specially designed moulding system
- Low melting alloys were found to be the most suitable materials for the heart valve mould and insert
- Processing temperatures were determined as follows; 100°C (insert) and 140°C (mould half)
- A removable 'wax skeleton' was used in the heart valve mould, which (when removed) allowed a catalyst to contact the surface of the feedstock. The feedstock subsequently polymerised

8.1.3 Ceramic Machining

- Polypropylene was found to be a valuable material for the moulding and machining of green compacts

- Samples turned with ease, suggesting that the cyanoacrylate binder had sufficiently high fracture toughness for green machining
- Chip formation whilst machining suggested that the compacts had a brittle nature
- The compacts turned with similar characteristics to mild steel, and hence, when the cutting speed was increased at a low feed rate the surface finish subsequently increased
- The surface of the green compacts had a roughness (R_a) less than 10μm, with some samples approaching 2μm
- Some deviation was found between the R_a values for the green compacts, caused by 'pull outs' from the material

8.1.4 Heat Treatment

- It was found that cyanoacrylate would debind most efficiently between 210°C and 230°C when mixed with alumina and inhibited with p-toluene sulphonic acid
- The heart valve mouldings thermally debound within 2 hours at a heating rate of 5°C/min up to 200°C, the mouldings did not crack or show any sign of slumping or distortion
- Samples sintered with porosity ranging from 44% to 53%. This was achieved by rapid sintering at 1750°C with a hold time of either 60 or 100 minutes

8.1.5 Flow Analysis of the Moulding Process

- The Perspex mould investigation found that actual measured pressure within the mould compared with very little error (2.1%) to the computational analysis using PHOENICS
- It was found by practical investigation that the heart valve mould pressure resistance was only 136 and 120 Bar for the Novent and Twovent models respectively
- The density of the feedstock combination was calculated as 2280 Kg/m^3, by compressing feedstock of known mass with a hydraulic press

- It was found that a model that corrected for the fluid volume fraction and binder density produced results similar to the empirical pressure investigation with an error of 10.1%
- The CFD analysis showed that the pressure region within the mould with a single outlet (Novent) was much larger than the model with two vents and an outlet (Twovent)
- The Twovent model managed to reduce the level of pressure by 15.6%

8.2 Recommendations for Further Work

The further work that could be applied to this project is concerned with producing a working a heart valve and simplifying the moulding process. This involves producing new techniques for analysing parameters that are particular to this project. Therefore, these recommendations are bulleted as simple statements that indicate the specific areas that require further investigation.

8.2.1 Feedstock Development

- Development of a model that describes cyanoacrylate polymerisation when mixed with aluminium oxide. Such a model would need to include parameters like inhibition level, initiator concentration, powder surface area, and powder acidity. A model would enable the moulding process to be more reliable and consistent.
- Development of a mixing method or machine so that feedstock can be formed within an inert atmosphere. This is because a side reaction can occur when the powder is dispensed into cyanoacrylate solution in air. Because of this, the viscosity would increase and it could even promote complete polymerisation.
- Design a feedstock that contains a time dependant catalyst, which would polymerise cyanoacrylate after moulding by the addition of an external influence such as heat. This could reduce the problems associated with catalyst entering the mould, and hence reduce moulding time.

8.2.2 Design

- Mechanical testing of the moulded feedstock to find the ultimate tensile strength, Youngs modulus and fracture toughness. These parameters will aid the machining of ceramics, because different feedstock compositions have different properties and thus require alternate traditional machining techniques.

- A computational analysis using a two-phase equation that is time dependent to allow for polymerisation. This could produce results with a greater accuracy for mould flow analysis using CFD. This could not have been developed within this investigation, as there was no model available to determine the feedstock polymerisation characteristics.
- Determine the exact mould pressures within a mould when the mould is filled with feedstock. This involves the use of a specially designed transducer that cannot be damaged by cyanoacrylate. The results from this investigation would aid the design of mould venting and produce values for direct comparison with a CFD model.
- The heart valve geometry used in this investigation did not include a 'seat' for an occluder to rest on when the valve is in the *fully open* position. Therefore, this requires designing and implementing into the mould, followed by a computational stress analysis. The analysis would provide information about the strength of the struts.
- The heart valve mould developed within this investigation used an insert that did not represent the exact heart valve geometry, because the main concern of this study was to develop a processing method. Therefore, a mould needs to be developed that represents the spline that forms the internal surface of the heart valve. Furthermore, the spline is a complex shape that would require machining by a computer controlled operation.

8.2.3 Moulds and Moulding

- Develop a moulding process that uses a single component, instead of multiple parts used within this investigation. The barrel, mould, and press could be incorporated into a machine that could produce batch components instead of a single part. The piston requires a sealing method, to prevent feedstock gathering in the annular gap between the piston and polypropylene insert. Furthermore, it would be advantages if the inserts could be supplied and loaded as a 'cartridge' into the machine. This would increase production and make the process more commercially attractive.

- Re-design the heart valve mould, to include a proper venting arrangement. The mould that incorporated the wax skeleton used vents that were created by feedstock pressure 'blowing' the wax out. Therefore, a new design could be implemented by analysing pressure output from a CFD analysis.

8.2.4 Miscellaneous

- Develop a process for measuring mass loss of a heart valve whilst debinding. Thermogravimetric analysis is normally performed on a small sample that is supposed to represent a larger model. However, the results from a full-scale TGA investigation would provide information on the exact debinding time, which in effect would reduce the processing time.
- Investigate a sintering process that will completely sinter the heart valve. This may involve using a furnace that has a larger chamber, but it could involve investigation of the thermal transfer methods. The internal surface of the valve only received heat by conduction and convection within the induction furnace. If another furnace arrangement were used, then radiation could be used as a main heating method for the internal surface of the heart valve.
- Determine the porosity requirements for tissue growth. This would involve sintering Alumina to a range of porosity, and culturing tissue on to the surface.
- Determine the strength of sintered heart valves. It is currently unknown what the strength of the heart valves are when sintered. The valves are difficult to break by applying pressure by hand; however, an empirical investigation would provide detailed information.
- Determine the life of the heart valve. This would involve performing an accelerated wear test on the heart valve by pumping fluid around with a peristaltic pump. Before this parameter can be investigated, other components have to be designed or completed such as, correct sintering of the valve, correct valve geometry using an insert, design and mould an occluder seat.

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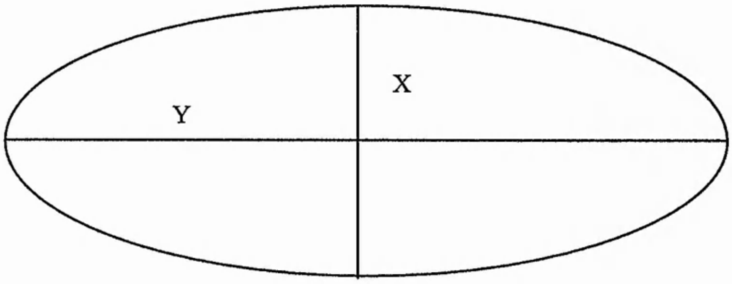
APPENDIX A

Alumina Powder Data

Following data based on the model below,



Powder Number 1,

10micron
histogram

qfreq = Cumulative frequency
freq=Frequency

x(µm)	y(µm)	y/x ratio	Value (µm)	x distribution qfreq	qfreq (%)	freq	y distribution qfreq	qfreq (%)	freq
13	15	1.15	0	0	0.00	0	0	0	0
2	13	6.50	1	6	10.00	6	4	6.67	4
7	10	1.43	2	16	26.67	10	7	11.67	3
7	11	1.57	3	26	43.33	10	14	23.33	7
7	13	1.86	4	33	55.00	7	22	36.67	8
8	11	1.38	5	39	65.00	6	27	45.00	5
2	10	5.00	6	44	73.33	5	35	58.33	8
3	12	4.00	7	51	85.00	7	40	66.67	5
6	8	1.33	8	55	91.67	4	44	73.33	4
10	9	0.90	9	57	95.00	2	46	76.67	2
8	7	0.88	10	58	96.67	1	49	81.67	3
6	5	0.83	11	59	98.33	1	54	90.00	5
3	7	2.33	12	59	98.33	0	55	91.67	1
9	10	1.11	13	60	100.00	1	58	96.67	3
7	15	2.14	14	60	100.00	0	58	96.67	0
6	9	1.50	15	60	100.00	0	60	100.00	2
11	4	0.36	16	60	100.00	0	60	100.00	0
3	7	2.33	17	60	100.00	0	60	100.00	0
2	1	0.50	18	60	100.00	0	60	100.00	0
4	3	0.75	19	60	100.00	0	60	100.00	0
7	3	0.43	20	60	100.00	0	60	100.00	0
6	5	0.83	21	60	100.00	0	60	100.00	0
3	11	3.67	22	60	100.00	0	60	100.00	0
2	1	0.50	23	60	100.00	0	60	100.00	0
3	13	4.33	24	60	100.00	0	60	100.00	0
4	6	1.50	25	60	100.00	0	60	100.00	0
6	5	0.83	26	60	100.00	0	60	100.00	0
3	5	1.67	27	60	100.00	0	60	100.00	0
5	11	2.20	28	60	100.00	0	60	100.00	0
2	11	5.50	29	60	100.00	0	60	100.00	0
5	8	1.60	30	60	100.00	0	60	100.00	0
8	4	0.50	31	60	100.00	0	60	100.00	0
3	7	2.33	32	60	100.00	0	60	100.00	0
3	6	2.00	33	60	100.00	0	60	100.00	0
4	6	1.50	34	60	100.00	0	60	100.00	0
5	7	1.40	35	60	100.00	0	60	100.00	0
4	4	1.00	36	60	100.00	0	60	100.00	0
5	6	1.20	37	60	100.00	0	60	100.00	0
3	2	0.67	38	60	100.00	0	60	100.00	0
4	3	0.75	39	60	100.00	0	60	100.00	0
2	3	1.50	40	60	100.00	0	60	100.00	0
1	3	3.00	41	60	100.00	0	60	100.00	0
5	5	1.00	42	60	100.00	0	60	100.00	0
2	4	2.00	43	60	100.00	0	60	100.00	0
7	3	0.43	44	60	100.00	0	60	100.00	0
1	4	4.00	45	60	100.00	0	60	100.00	0
1	2	2.00	46	60	100.00	0	60	100.00	0

				X distribution			Y distribution		
x(μm)	y(μm)	y/x ratio	Value (μm)	qfreq	qfreq (%)	freq	qfreq	qfreq (%)	freq
3	4	1.33	47	60	100.00	0	60	100.00	0
4	6	1.50	48	60	100.00	0	60	100.00	0
8	6	0.75	49	60	100.00	0	60	100.00	0
2	3	1.50	50	60	100.00	0	60	100.00	0
2	4	2.00	51	60	100.00	0	60	100.00	0
4	6	1.50	52	60	100.00	0	60	100.00	0
1	1	1.00	53	60	100.00	0	60	100.00	0
1	2	2.00	54	60	100.00	0	60	100.00	0
9	6	0.67	55	60	100.00	0	60	100.00	0
5	8	1.60	56	60	100.00	0	60	100.00	0
7	8	1.14	57	60	100.00	0	60	100.00	0
2	4	2.00	58	60	100.00	0	60	100.00	0
1	1	1.00	59	60	100.00	0	60	100.00	0
Average									
4.62	6.45	1.74							

Powder number 2,

150micron
histogram

qfreq = Cumulative frequency
freq=Frequency

				x distribution			y distribution		
x(µm)	y(µm)	y/x ratio	Value (µm)	qfreq	qfreq (%)	freq	qfreq	qfreq (%)	Freq
250	375	1.50	0	0	0.00	0	0	0	0
188	225	1.20	15	0	0.00	0	0	0.00	0
188	313	1.66	30	0	0.00	0	0	0.00	0
225	250	1.11	45	0	0.00	0	0	0.00	0
250	290	1.16	60	0	0.00	0	1	1.67	1
200	290	1.45	75	5	8.33	5	5	8.33	4
163	150	0.92	90	7	11.67	2	6	10.00	1
175	175	1.00	105	9	15.00	2	9	15.00	3
160	163	1.02	120	15	25.00	6	12	20.00	3
160	290	1.81	135	20	33.33	5	17	28.33	5
150	300	2.00	150	33	55.00	13	27	45.00	10
200	225	1.13	165	45	75.00	12	31	51.67	4
138	150	1.09	180	46	76.67	1	37	61.67	6
150	175	1.17	195	52	86.67	6	38	63.33	1
160	210	1.31	210	55	91.67	3	43	71.67	5
150	250	1.67	225	58	96.67	3	47	78.33	4
150	175	1.17	240	58	96.67	0	47	78.33	0
100	210	2.10	255	60	100.00	2	52	86.67	5
113	125	1.11	270	60	100.00	0	53	88.33	1
125	210	1.68	285	60	100.00	0	54	90.00	1
160	150	0.94	300	60	100.00	0	58	96.67	4
150	210	1.40	315	60	100.00	0	59	98.33	1
113	125	1.11	330	60	100.00	0	59	98.33	0
163	175	1.07	345	60	100.00	0	59	98.33	0
163	250	1.53	360	60	100.00	0	59	98.33	0
138	150	1.09	375	60	100.00	0	60	100.00	1
220	213	0.97	390	60	100.00	0	60	100.00	0
138	138	1.00		0	0.00	-60	0	0.00	-60
200	250	1.25		0	0.00	0	0	0.00	0
125	125	1.00		0	0.00	0	0	0.00	0
138	200	1.45		0	0.00	0	0	0.00	0
125	138	1.10		0	0.00	0	0	0.00	0
188	163	0.87		0	0.00	0	0	0.00	0
163	163	1.00		0	0.00	0	0	0.00	0
113	88	0.78		0	0.00	0	0	0.00	0
125	138	1.10		0	0.00	0	0	0.00	0
160	113	0.71		0	0.00	0	0	0.00	0
163	175	1.07		0	0.00	0	0	0.00	0
188	138	0.73		0	0.00	0	0	0.00	0
150	260	1.73		0	0.00	0	0	0.00	0
113	113	1.00		0	0.00	0	0	0.00	0
138	138	1.00		0	0.00	0	0	0.00	
63	100	1.59		0	0.00	0	0	0.00	
75	75	1.00		0	0.00	0	0	0.00	
75	100	1.33		0	0.00	0	0	0.00	
88	100	1.14		0	0.00	0	0	0.00	
113	150	1.33		0	0.00	0	0	0.00	

					x distribution			y distribution	
x(µm)	y(µm)	y/x ratio	Value (µm)	qfreq	qfreq (%)	freq	qfreq	qfreq (%)	freq
100	50	0.50		0	0.00	0	0	0.00	
88	75	0.85		0	0.00	0	0	0.00	
188	125	0.66		0	0.00	0	0	0.00	
63	75	1.19		0	0.00	0	0	0.00	
63	63	1.00		0	0.00	0	0	0.00	
113	125	1.11		0	0.00	0	0	0.00	
125	113	0.90		0	0.00	0	0	0.00	
163	188	1.15		0	0.00	0	0	0.00	
188	163	0.87		0	0.00	0	0	0.00	
150	280	1.87		0	0.00	0	0	0.00	
138	175	1.27		0	0.00	0	0	0.00	
163	225	1.38		0	0.00	0	0	0.00	
225	250	1.11		0	0.00	0	0	0.00	
Average									
148.5	176.6	1.19							

Powder number 3,

MM
histogram

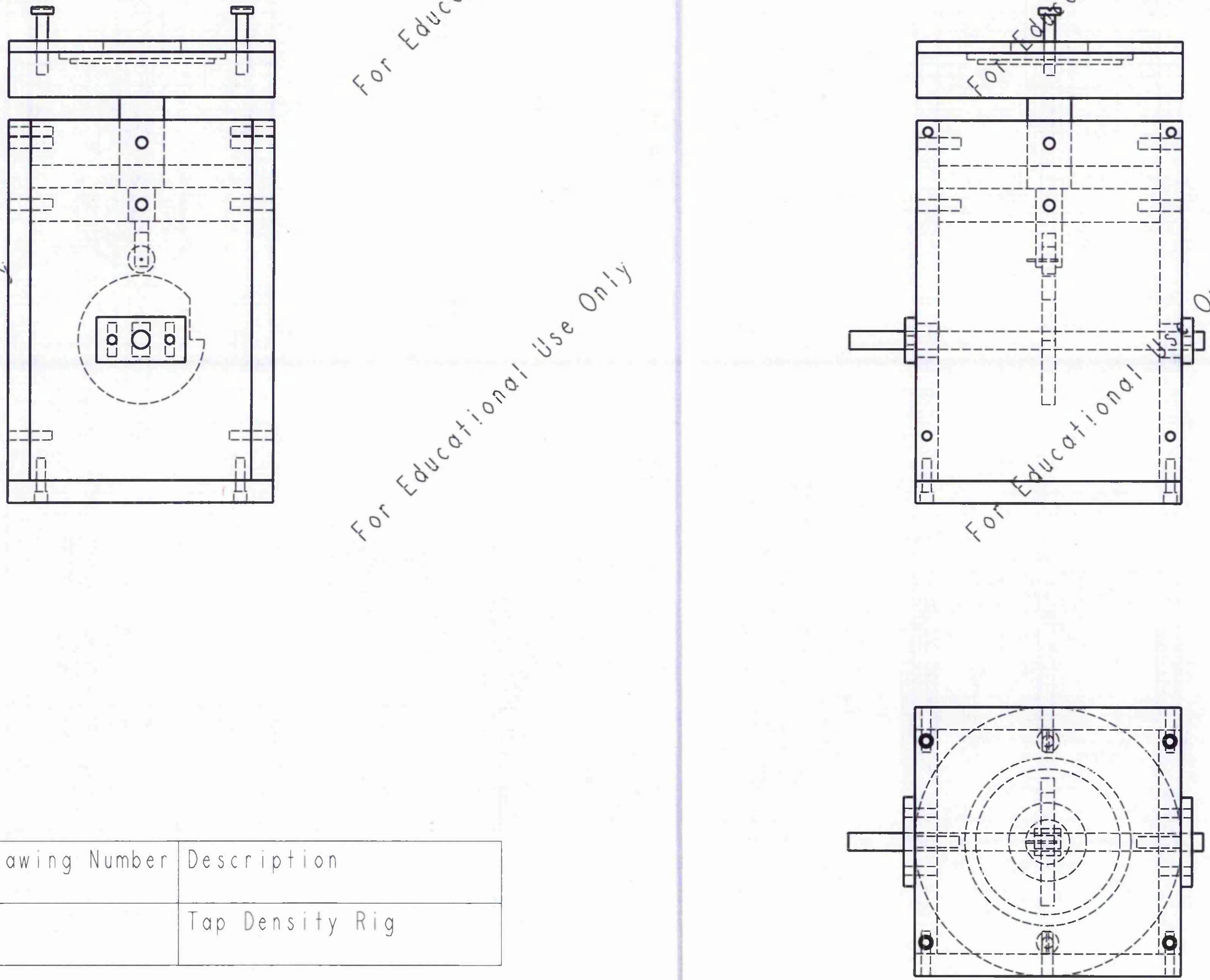
				x distribution			y distribution		
x(µm)	y(µm)	y/x ratio	Value (µm)	qfreq	qfreq (%)	freq	qfreq	qfreq (%)	freq
5	6	1.20	0	0	0.00	0	0	0	0
2.5	3.5	1.40	0.5	0	0.00	0	0	0.00	0
2	3	1.50	1	1	1.67	1	0	0.00	0
3	4	1.33	1.5	4	6.67	3	0	0.00	0
4	4.5	1.13	2	13	21.67	9	0	0.00	0
2.5	3.5	1.40	2.5	29	48.33	16	1	1.67	1
2	3	1.50	3	40	66.67	11	11	18.33	10
3	4	1.33	3.5	47	78.33	7	22	36.67	11
6	8	1.33	4	52	86.67	5	36	60.00	14
2.5	4.5	1.80	4.5	55	91.67	3	45	75.00	9
4.5	5	1.11	5	58	96.67	3	51	85.00	6
3	5	1.67	5.5	59	98.33	1	54	90.00	3
1.5	3	2.00	6	60	100.00	1	56	93.33	2
3.5	3.5	1.00	6.5	60	100.00	0	58	96.67	2
3	4	1.33	7	60	100.00	0	58	96.67	0
2.5	4	1.60	7.5	60	100.00	0	59	98.33	1
4	5	1.25	8	60	100.00	0	60	100.00	1
4	5	1.25	8.5	60	100.00	0	60	100.00	0
2	3	1.50	9	60	100.00	0	60	100.00	0
1.5	3	2.00	9.5	60	100.00	0	60	100.00	0
2	3.5	1.75	10	60	100.00	0	60	100.00	0
5	5	1.00	10.5	60	100.00	0	60	100.00	0
3.5	4	1.14	11	60	100.00	0	60	100.00	0
2.5	3.5	1.40	11.5	60	100.00	0	60	100.00	0
2.5	3	1.20	12	60	100.00	0	60	100.00	0
3.5	4	1.14	12.5	60	100.00	0	60	100.00	0
5.5	6	1.09	13	60	100.00	0	60	100.00	0
3	4.5	1.50	13.5	60	100.00	0	60	100.00	0
2	3.5	1.75		0	0.00	-60	0	0.00	-60
3	4	1.33		0	0.00	0	0	0.00	0
2.5	4.5	1.80		0	0.00	0	0	0.00	0
4	5.5	1.38		0	0.00	0	0	0.00	0
2.5	4	1.60		0	0.00	0	0	0.00	0
2	3.5	1.75		0	0.00	0	0	0.00	0
2.5	4	1.60		0	0.00	0	0	0.00	0
3	4.5	1.50		0	0.00	0	0	0.00	0
3	4	1.33		0	0.00	0	0	0.00	0
3.5	4.5	1.29		0	0.00	0	0	0.00	0
2	3.5	1.75		0	0.00	0	0	0.00	0
2.5	4	1.60		0	0.00	0	0	0.00	0
4	4.5	1.13		0	0.00	0	0	0.00	0
4.5	5.5	1.22		0	0.00	0	0	0.00	
2	3	1.50		0	0.00	0	0	0.00	
1.5	3	2.00		0	0.00	0	0	0.00	
2.5	4	1.60		0	0.00	0	0	0.00	
3.5	4	1.14		0	0.00	0	0	0.00	

					x distribution			y distribution	
x(µm)	y(µm)	y/x ratio	Value (µm)	qfreq	qfreq (%)	freq	qfreq	qfreq (%)	freq
3	3.5	1.17		0	0.00	0	0	0.00	
2.5	3.5	1.40		0	0.00	0	0	0.00	
5	5.5	1.10		0	0.00	0	0	0.00	
4.5	7.5	1.67		0	0.00	0	0	0.00	
3.5	6.5	1.86		0	0.00	0	0	0.00	
2.5	4.5	1.80		0	0.00	0	0	0.00	
3	3	1.00		0	0.00	0	0	0.00	
3	6.5	2.17		0	0.00	0	0	0.00	
3.5	5	1.43		0	0.00	0	0	0.00	
2.5	3	1.20		0	0.00	0	0	0.00	
2.5	3.5	1.40		0	0.00	0	0	0.00	
2	4.5	2.25		0	0.00	0	0	0.00	
1	2.5	2.50		0	0.00	0	0	0.00	
2.5	4	1.60		0	0.00	0	0	0.00	
Average									
3.02	4.24	1.48							

APPENDIX B

Technical Drawings

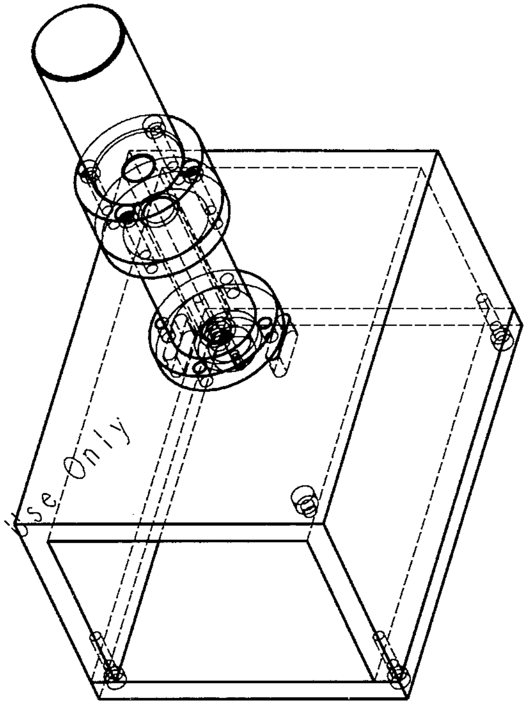
Drawing Number	*Description*
1	Tap density apparatus
2	Piston and Barrel
3	Conduit heart valve
4	Heart valve mould
a	Mould half mould
b	Outer mould
c	Outer mould lid
d	Outer mould endplate
e	Mould half with skeleton provision
5	Insert mould
6	Novent model
7	Twovent model
8	Perspex mould



500

Drawing Number	Description
1	Tap Density Rig

2



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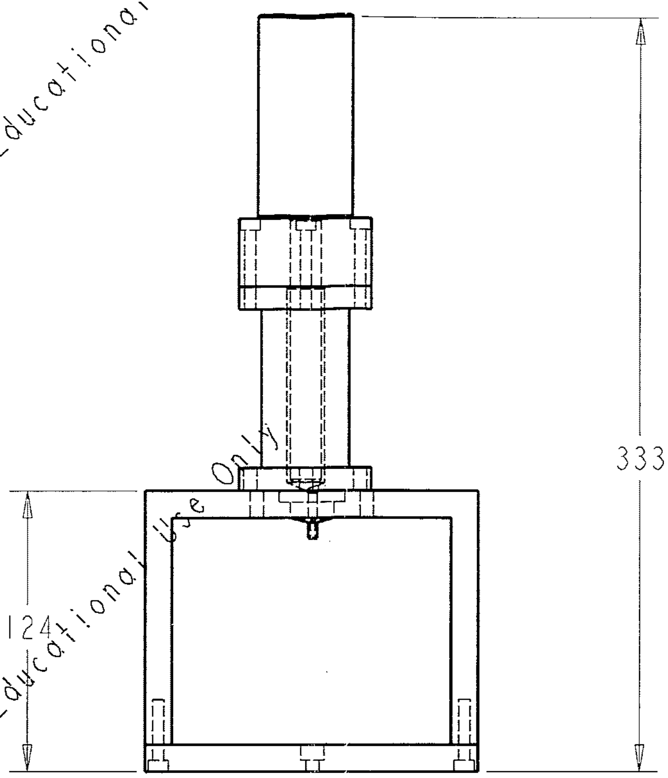
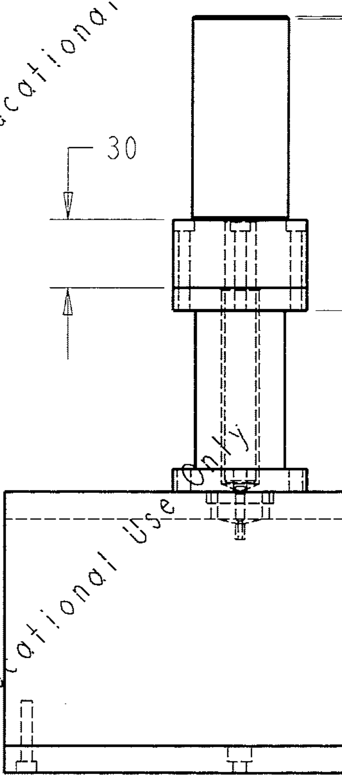
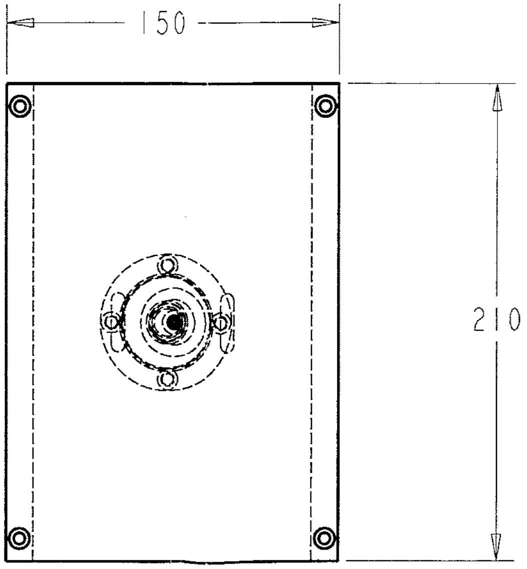


SCALE 0.400





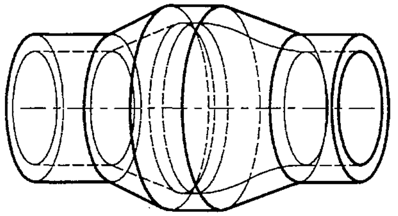
Drawing Number	Description
2	Piston and Barrel

all dimensions in mm

3

Drawing Number	Description
3	Conduit Heart Valve

All dimensions are in millimetres



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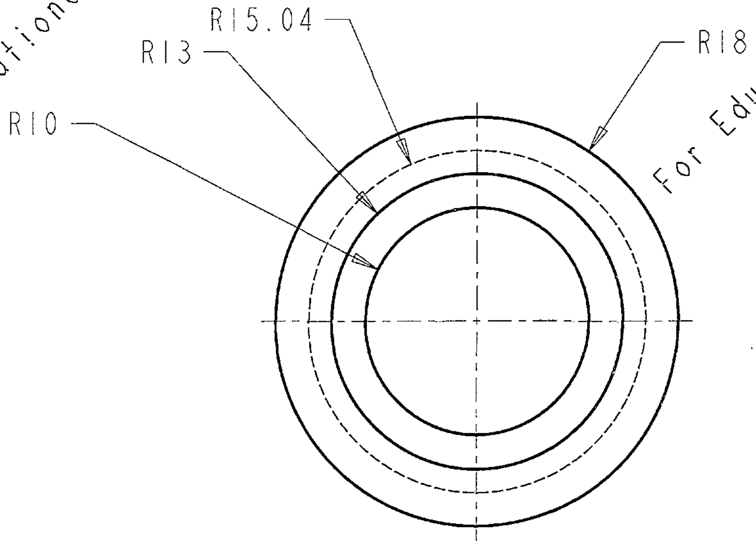
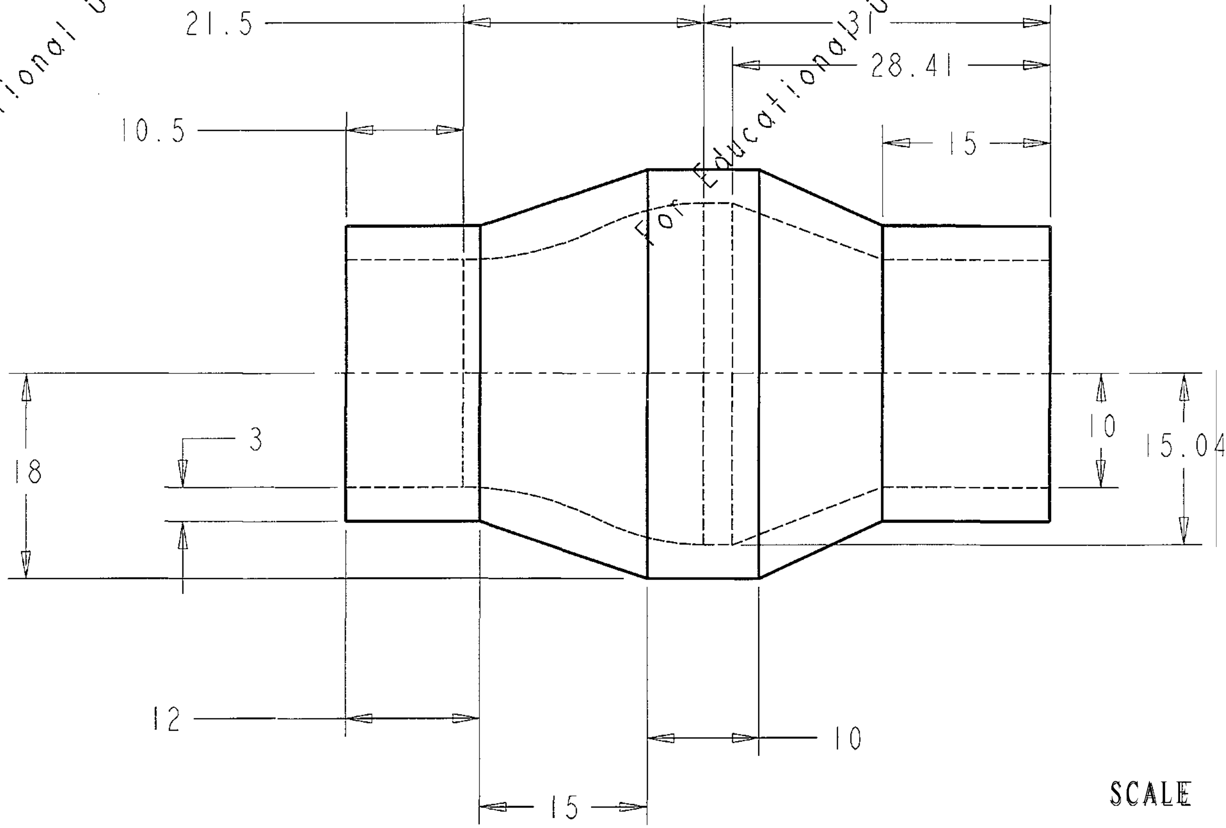
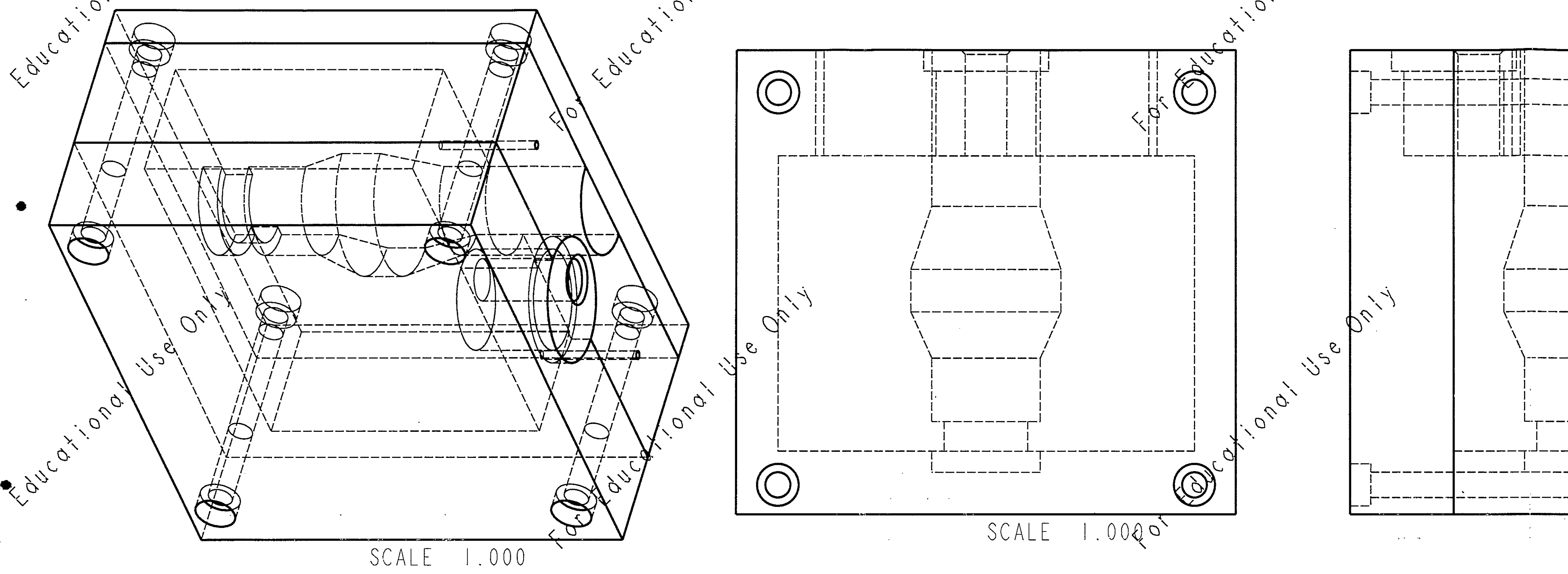
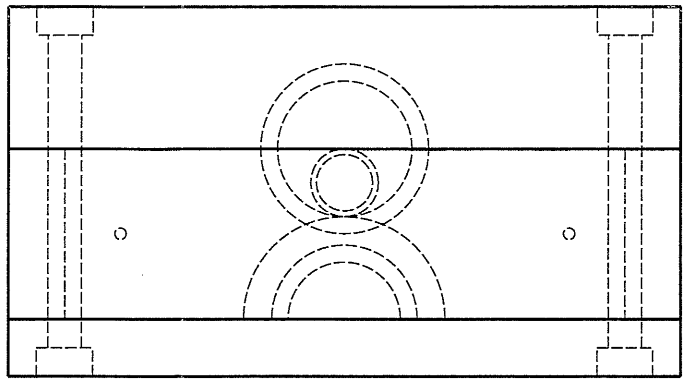


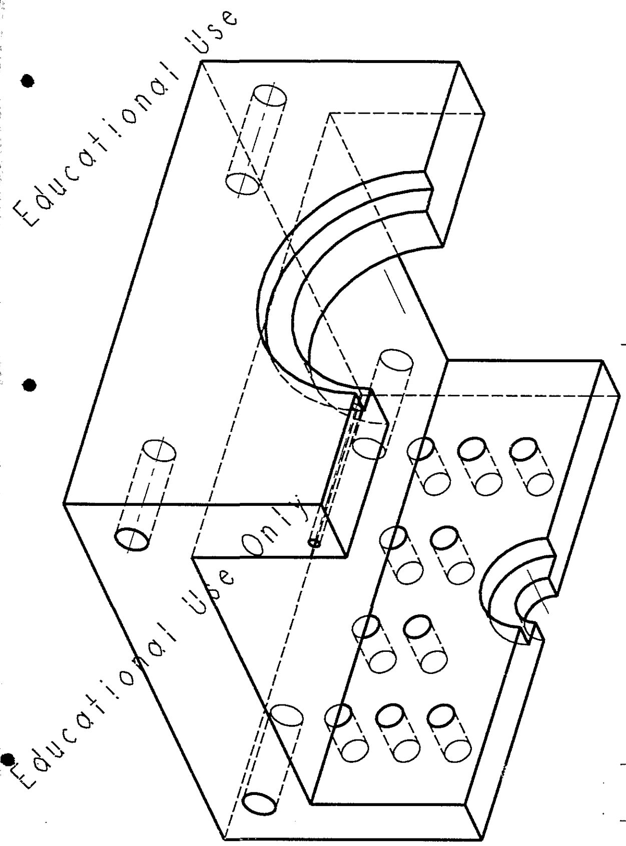


SCALE

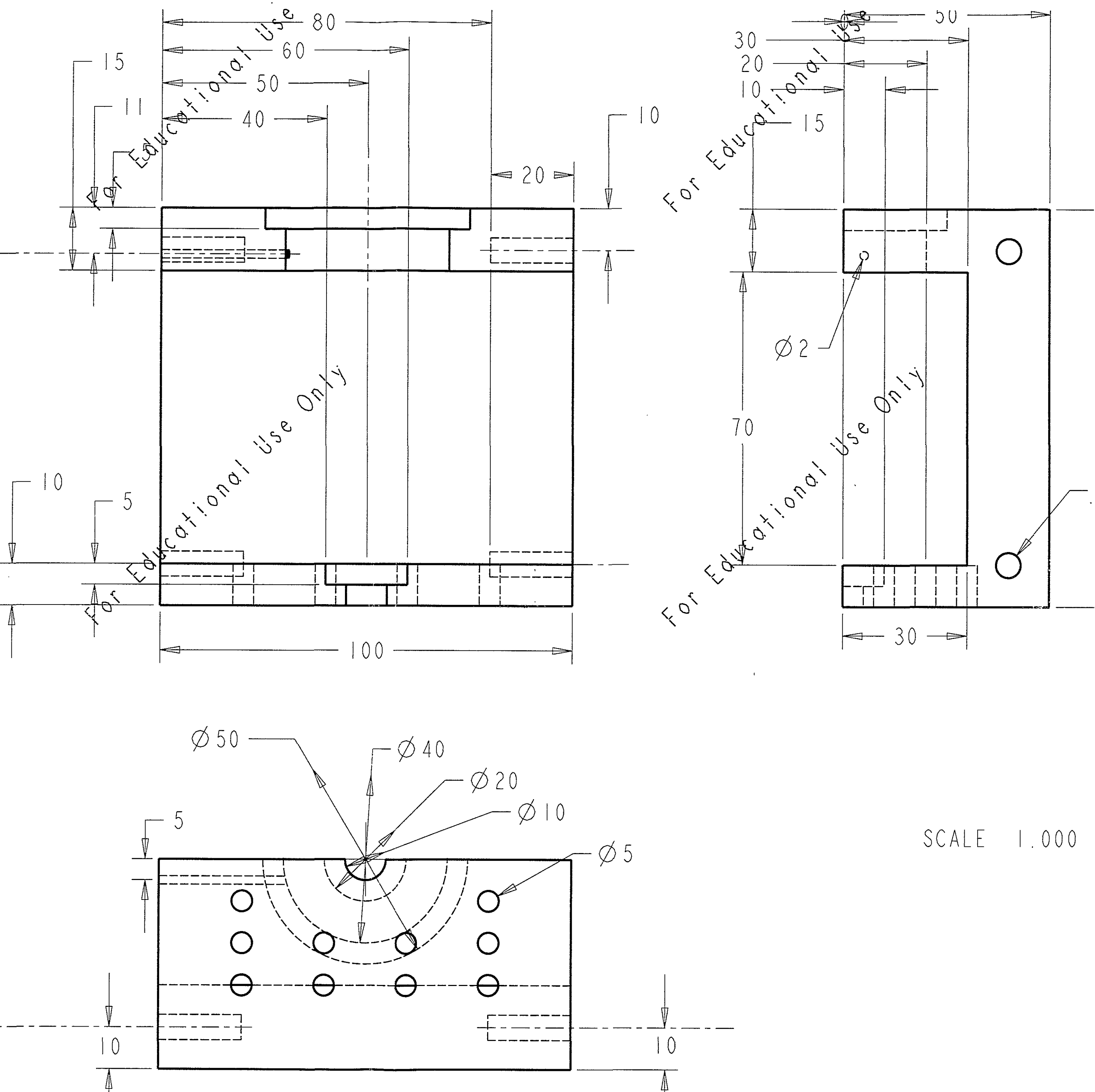




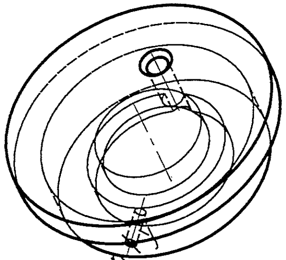
Drawing Number	Description
4a	Mould-half Mould



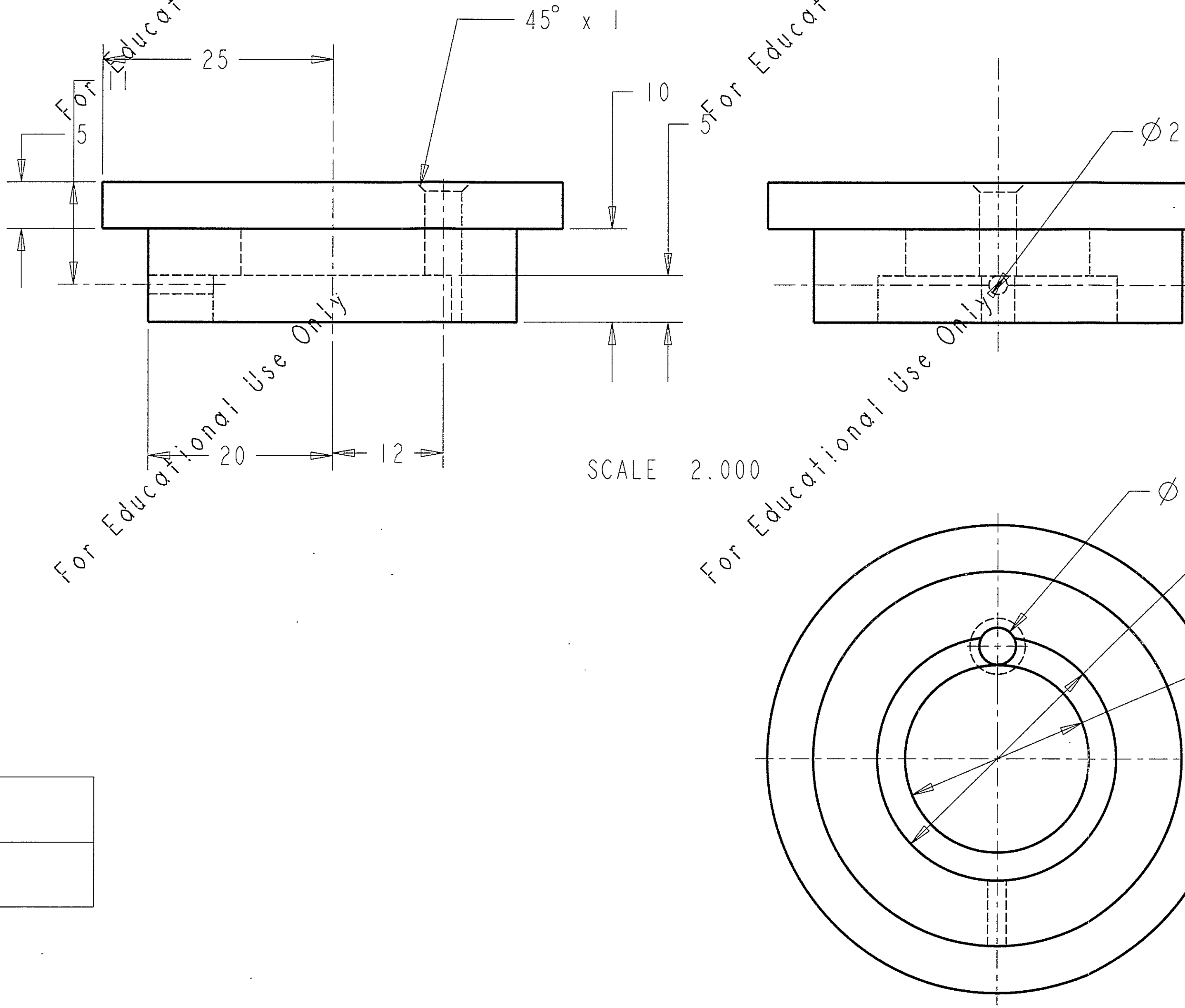
SCALE 1.000



SCALE 1.000



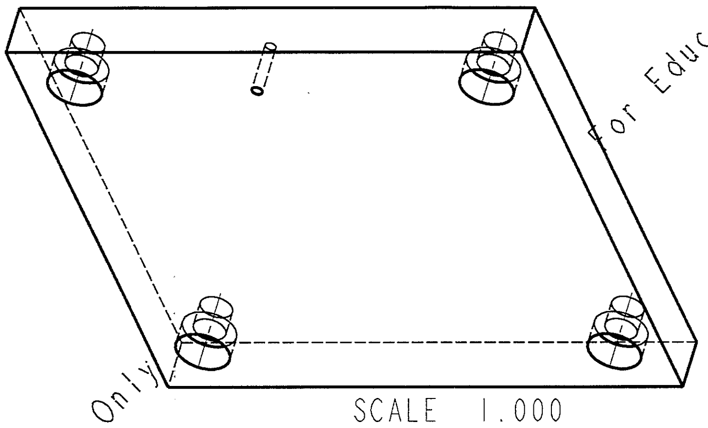
SCALE 1.000

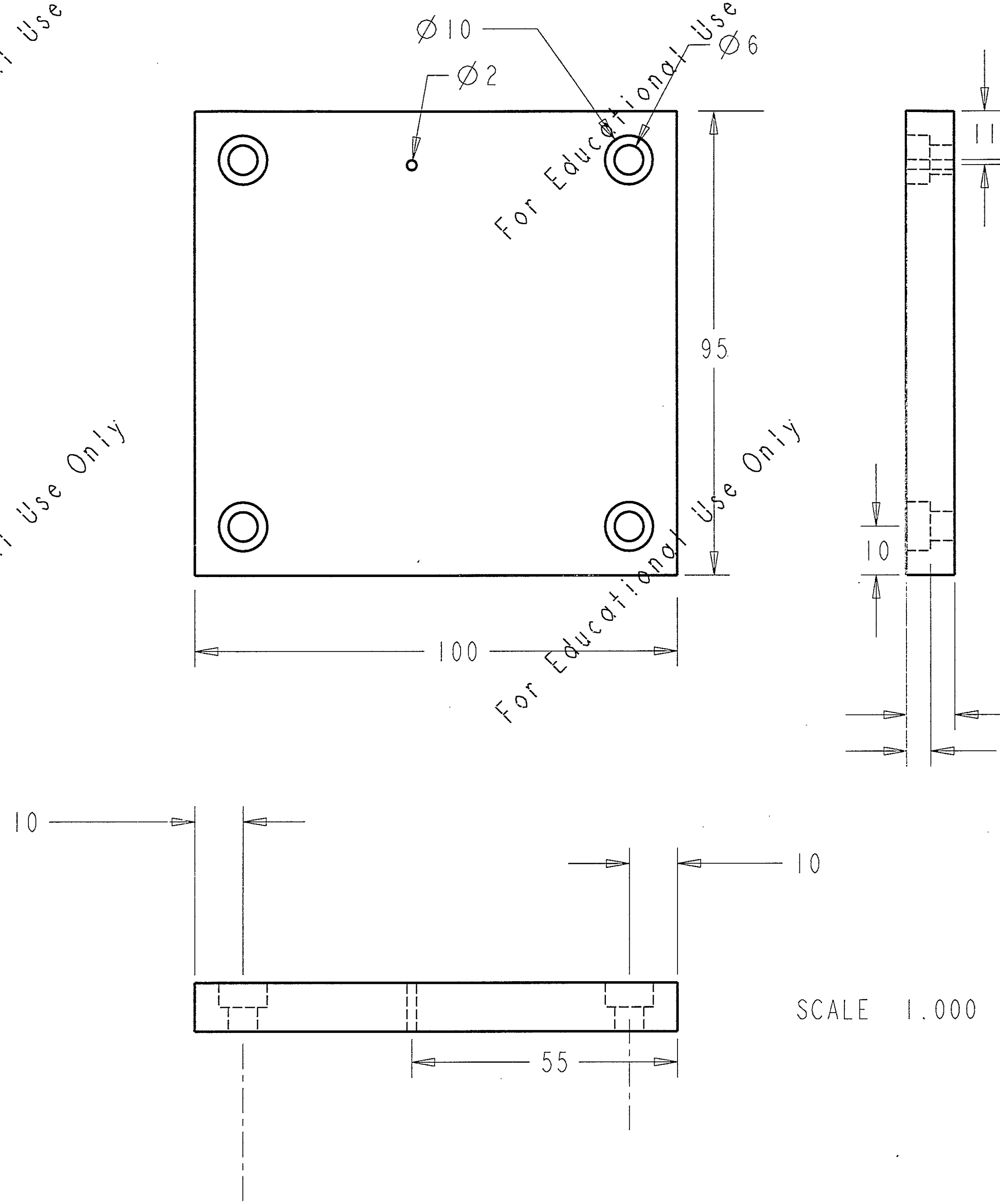


SCALE 2.000

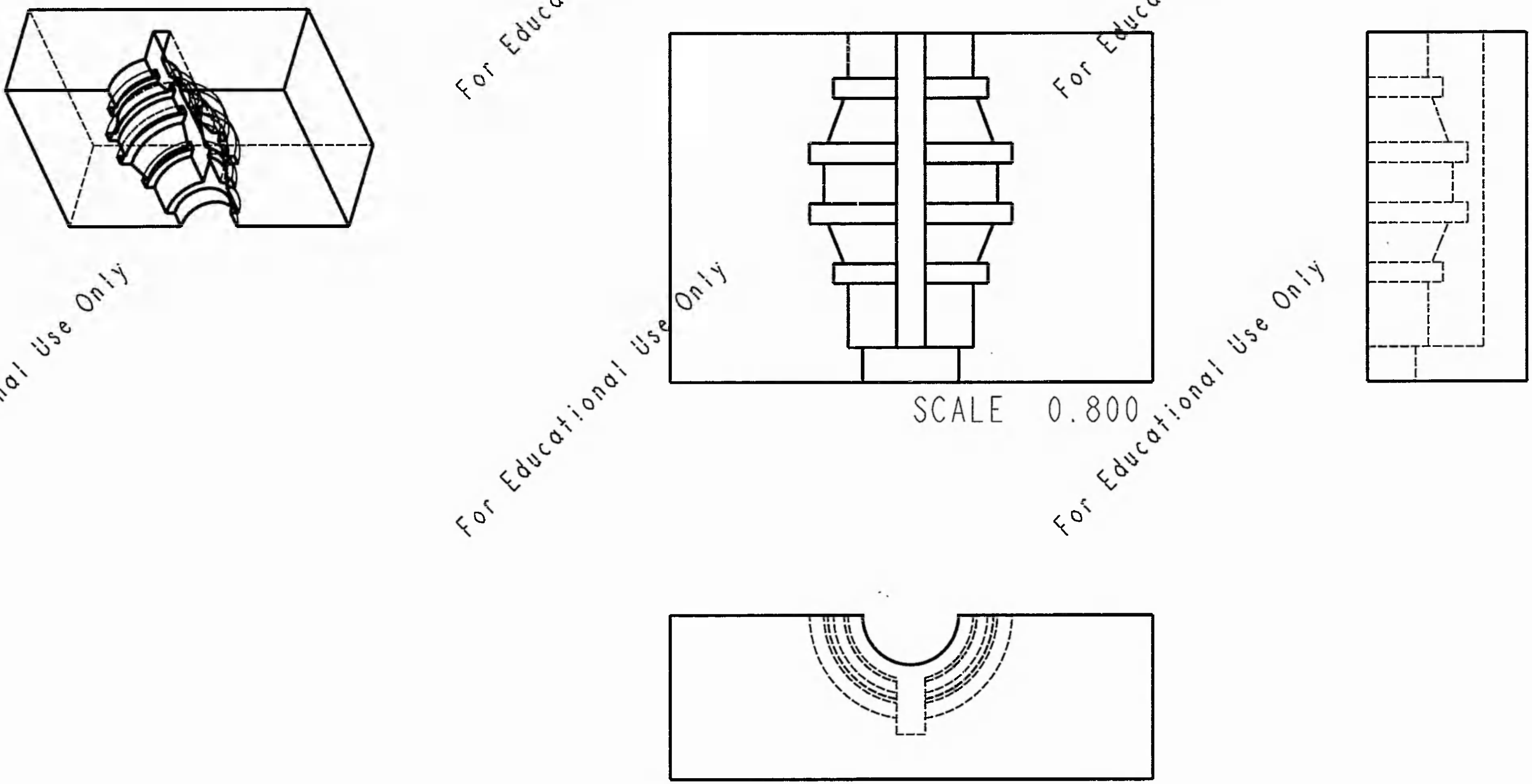
Drawing Number	Description
4c	Mould Casing Lid

all dimensions in millimetres

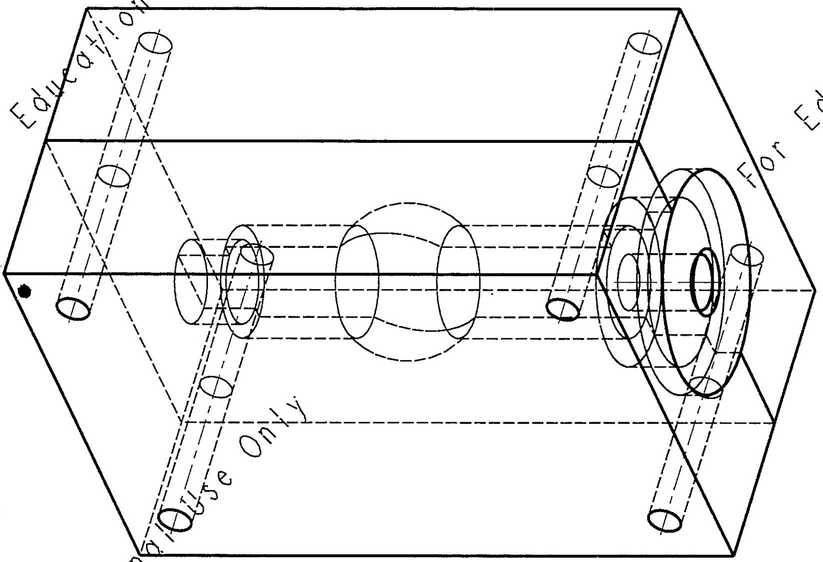


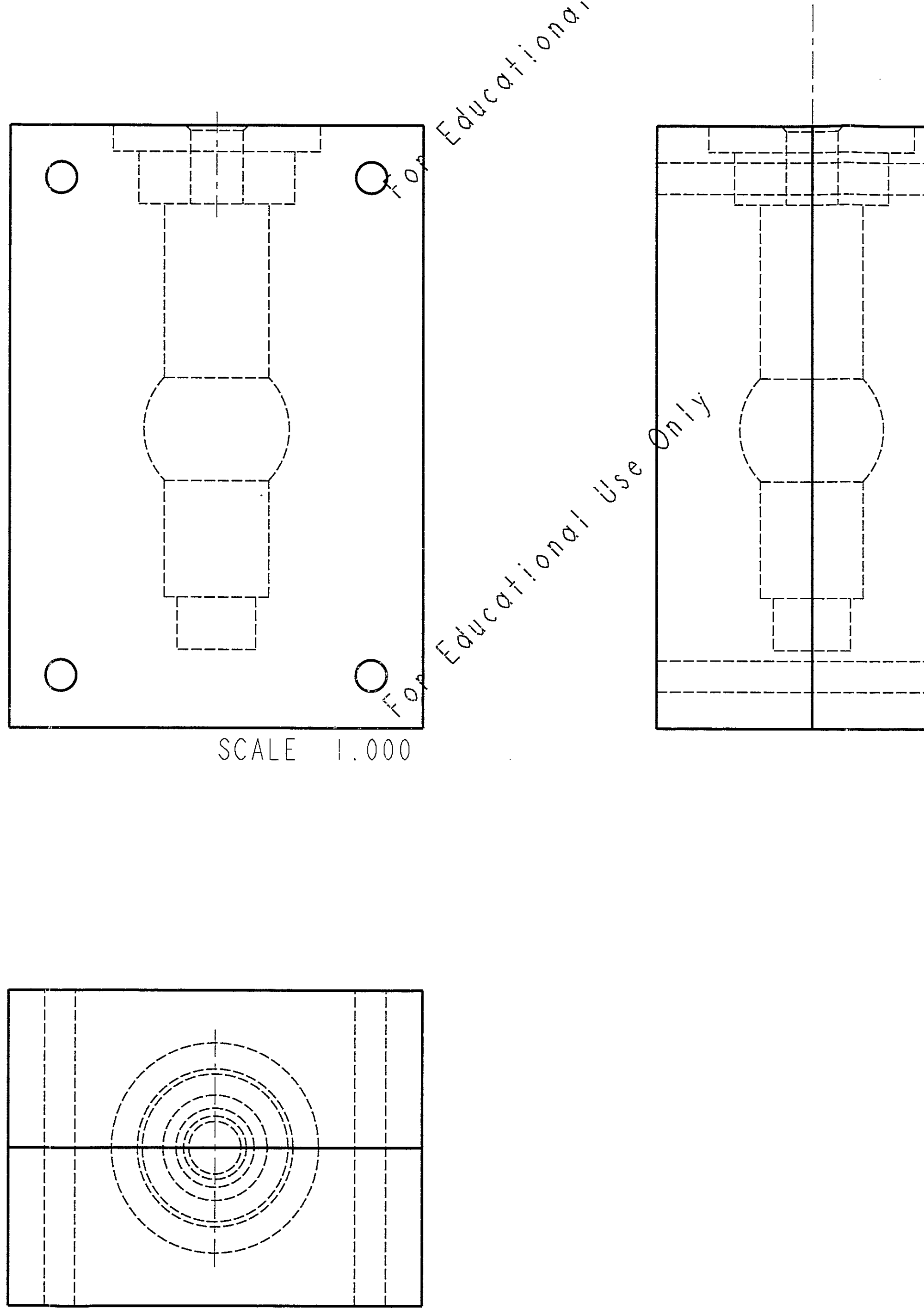


Drawing Number	Description
4d	Mould Casing Endplate

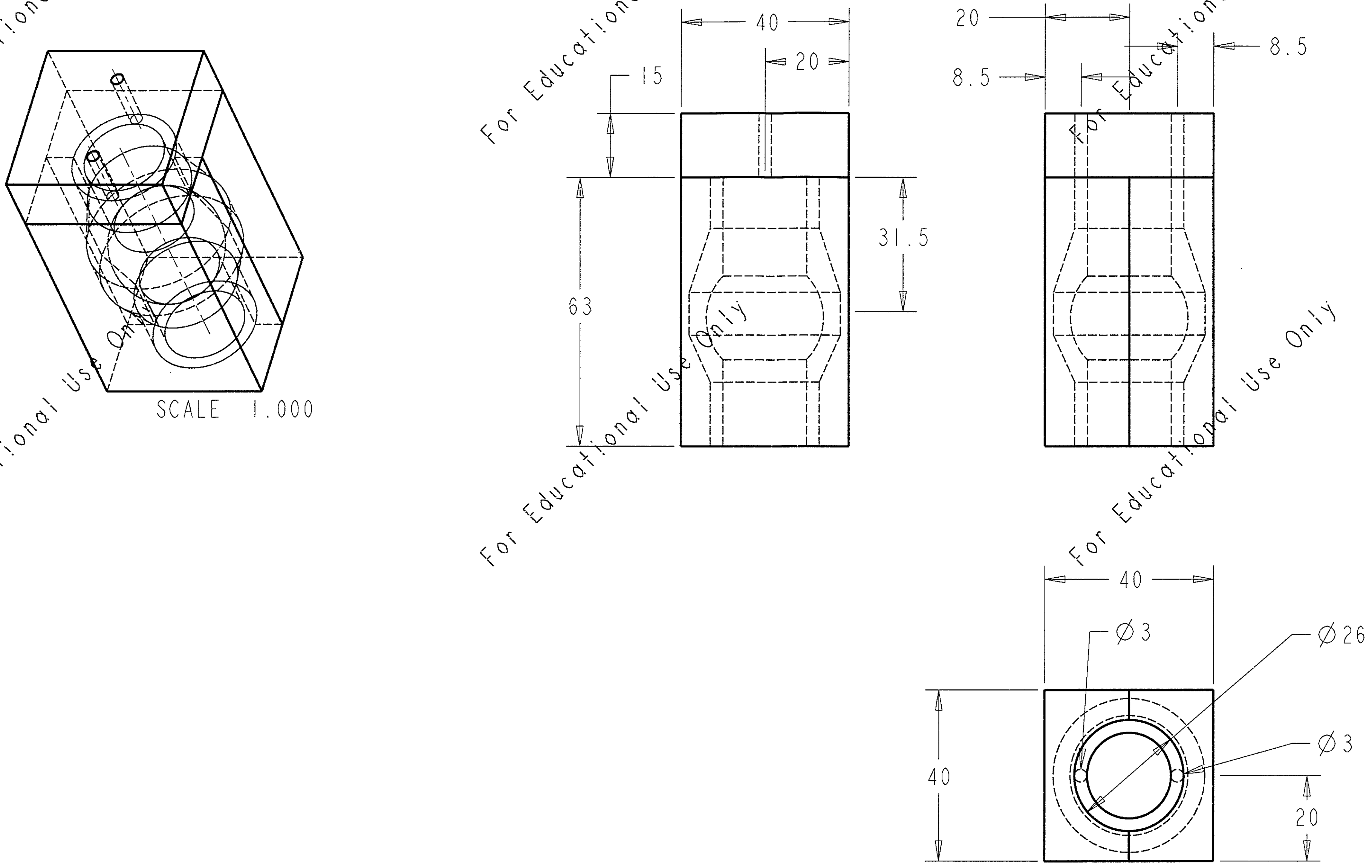


Drawing Number	Description
4e	Mould Half with Wax Skeleton Provision

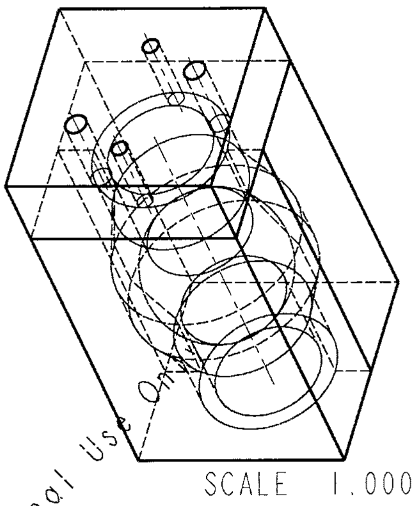


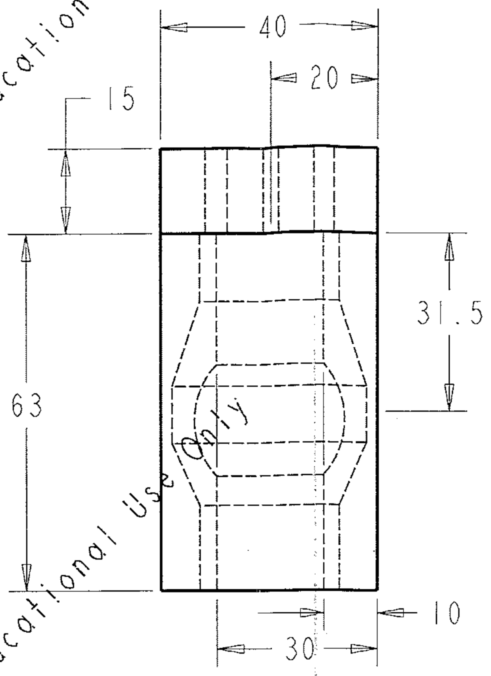


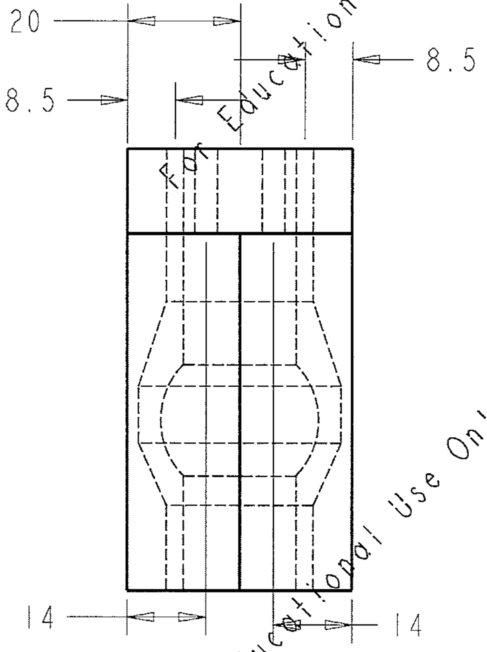
Drawing Number	Description
5	Insert Mould

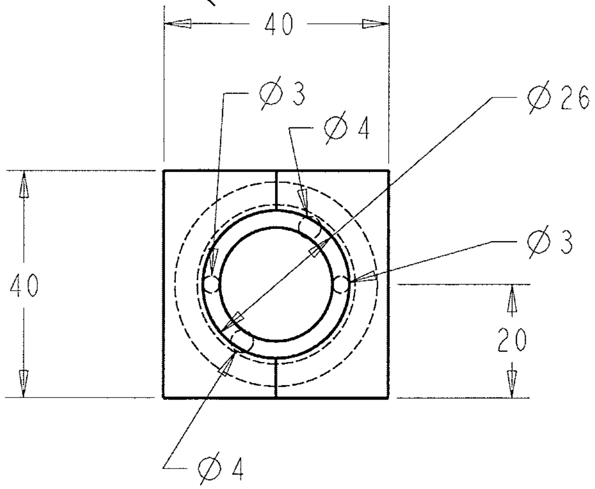


Drawing Number	Description
6	Twovent CFD model

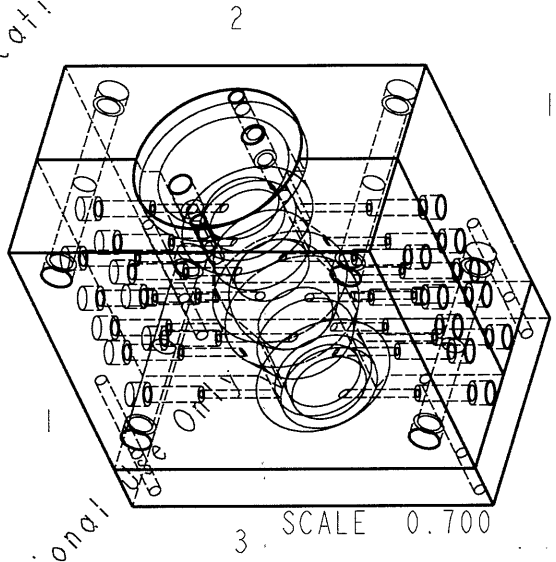


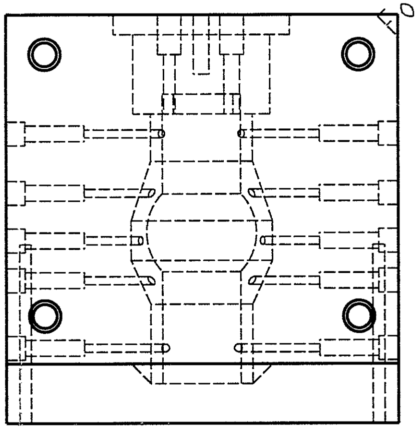






Drawing Number	Description
7	Two vent CFD model

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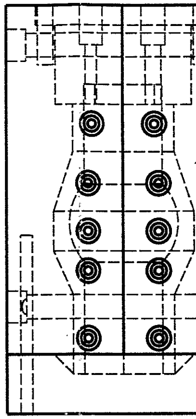

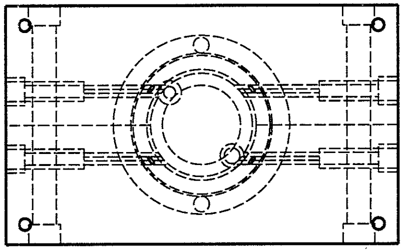

Drawing Number	Description
8	Perspex Mould

Number	Part	Material
1	p2half1	perspex
2	p2top	perspex

APPENDIX C

Software

Introduction

This section contains the software that was written for calculating the shear stress and strain developed from shearing fluid with the Rheotest 2 rheometer. The software was written using BASIC, as listed in the following section.

Program Listing

```
Rem software for determining the shear stress/strain for the Rheotest
2 rheometer
tmax = 0
old = 0
oldnum = 250
h = 6
DIM jot(1, h)
b = 640
s = 0

CLS
LOCATE 5, 10
PRINT "Welcome to Rheotest for the Rheotest II series........"
LOCATE 10, 10
PRINT "Department of Mechanical and Manufacturing Engineering"
PRINT "                       Nottingham Trent University"
LOCATE 25, 10
PRINT "     Programmed by Jonathan Ridgway.....October 1998"
DO
LOOP UNTIL INKEY$ = CHR$(27)
CLS

REM ****************************************
REM calibration data
REM grad = -.3379
REM inter = .7201
REM grad=-.3422
REM inter = .3159
grad = -.3409
inter = .5727
REM ****************************************

REM cone information
INPUT "Resistance Level (1 or 2):"; rlev$
INPUT "Cone (1,2 or 3)          :"; cone$
INPUT "Speed level (e.g 5a)     :"; speed$
INPUT "Cone calibration number  :"; cval
CLS
PRINT "to calibrate the monitoring device do the following:"
```

```
PRINT
PRINT "(a) remove the plate"
PRINT "(b) start the motor and measuring instrument"
PRINT "(c) reset the value on the analogue display using the
electronic adjustment"
PRINT
PRINT
PRINT "The following instructions are used to collect data....."
PRINT
IF cone$ = "1" THEN PRINT "(1) Place 0.1ml of material on the plate"
IF cone$ = "2" THEN PRINT "(1) Place 0.06ml of material on the plate"
IF cone$ = "3" THEN PRINT "(1) Place 0.04ml of material on the plate"
PRINT
IF cone$ = "1" THEN PRINT "(2) Set the micrometer to calibrated
level"
IF cone$ = "2" THEN PRINT "(2) Set the micrometer to calibrated
level"
IF cone$ = "3" THEN PRINT "(2) Set the micrometer to calibrated
level"
PRINT
PRINT "(3) Start the motor and measuring device"
IF speed$ = "1a" THEN speed = 11.1
IF speed$ = "2a" THEN speed = 20
IF speed$ = "3a" THEN speed = 33.3
IF speed$ = "4a" THEN speed = 60
IF speed$ = "5a" THEN speed = 100
IF speed$ = "6a" THEN speed = 180
IF speed$ = "7a" THEN speed = 300
IF speed$ = "8a" THEN speed = 540
IF speed$ = "9a" THEN speed = 900
IF speed$ = "10a" THEN speed = 1620
IF speed$ = "11a" THEN speed = 2700
IF speed$ = "12a" THEN speed = 4860
IF speed$ = "1b" THEN speed = 5.56
IF speed$ = "2b" THEN speed = 10
IF speed$ = "3b" THEN speed = 16.67
IF speed$ = "4b" THEN speed = 30
IF speed$ = "5b" THEN speed = 50
IF speed$ = "6b" THEN speed = 90
IF speed$ = "7b" THEN speed = 150
IF speed$ = "8b" THEN speed = 270
IF speed$ = "9b" THEN speed = 450
IF speed$ = "10b" THEN speed = 810
IF speed$ = "11b" THEN speed = 1350
IF speed$ = "12b" THEN speed = 2430


REM setup for data logging
LOCATE 20, 1
INPUT "File Name:"; file$
filename$ = "z:\" + file$ + ".txt"
OPEN filename$ FOR OUTPUT AS #1
PRINT #1, ""

50
REM setup of display
SCREEN 9
CLS
LINE (0, 250)-(640, 250), 6
LINE (0, 0)-(640, 0), 6
LINE (0, 0)-(0, 250), 6
LINE (639, 0)-(639, 250), 6

REM setup of timer

endval = 10000
sint = 1
c = 0
```

```
d = 0
a = TIMER
ON TIMER(sint) GOSUB timeupdate
TIMER ON
DO
ba = TIMER - a
c = INT(ba) + 1
d = d + 2
IF d = 620 THEN GOSUB refresh

FOR w = 1 TO h STEP 1
OUT b, 15
co = INP(b): s = 0
WHILE s = 0: s = INP(b + 1): s = s AND 1: WEND
A1 = INP(b + 2): a2 = INP(b + 3): a3 = a2 AND 15: a4 = a2 AND 32: n =
A1 + 256 * a3: IF a4 = 0 THEN n = n * (-1)
over = a2 AND 16
jot(1, w) = n

REM output
reading = ((average * grad) + inter)
IF reading < 0 THEN reading = 0
LOCATE 20, 1
IF reading > tmax THEN tmax = reading
shear = (cval * reading) / 10
visco = (shear / speed)
PRINT "Reading                :", USING "####.###"; reading
LOCATE 20, 45
PRINT "Shear Rate (s-1) :"; USING "####"; speed
LOCATE 21, 1
PRINT "Time   (s)             :", USING "####"; c
PRINT "Shear Stress (N/m2)    :", USING "######.###"; shear
PRINT "Viscosity   (Pa.S)     :", USING "######.###"; visco
NEXT w
total = 0
num = (249 - (reading * 2.5))
LINE (old, oldnum)-(d, num), 14
oldnum = num
old = d



REM *******************************************************
REM averaging technique
FOR count = 1 TO h STEP 1
total = total + jot(1, count)
NEXT count
average = total / h
REM ********************************************************



LOOP UNTIL INKEY$ = CHR$(27)

REM timer update
timeupdate:
PRINT #1, c; " "; speed, " "; shear, " "; visco, " "; reading
RETURN

refresh:
CLS
LINE (0, 250)-(640, 250), 6
LINE (0, 0)-(640, 0), 6
LINE (0, 0)-(0, 250), 6
LINE (639, 0)-(639, 250), 6
d = 0
old = 0

RETURN
```

APPENDIX D

Publications Related to This Research

J.S.Ridgway, J.B.Hull, C.R.Gentle (1997*), "Development of a novel binder system for manufacture of ceramic heart valve prostheses*", Proc.conf AMME'97, Wisla, Poland, pp165-169

J.S.Ridgway, J.B.Hull, C.R.Gentle (1997*), "Development of a novel binder system for manufacture of ceramic heart valve prostheses*", awaiting journal publication.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1998), "*Design and selection of an alumina-cyanoacrylate feedtock for porous conduit heart valve prostheses*", Proc.conf MID'98, Nottingham, England.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1998), "*Design for powder reaction moulding ceramic conduit heart valves*", proc.conf HC'Tech, Sofia, Bulgaria.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1998*), "Advanced moulding for reactive binders*", Proc.conf AMME'98, Zakopane, Poland.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1998*), "A P.R.I.M.E approach to moulding conduit ceramic parts*", *Journal of Materials Processing Technology, (to be published).*

J.S.Ridgway, J.B.Hull, C.R.Gentle (1998), "*Method and apparatus for moulding conduit articles*", Patent application.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1999), *"Machining of green ceramic compacts produced by powder reaction moulding*", Proc.conf TECOS, Rogaska Slatina, Slovenia.

J.S.Ridgway, J.B.Hull, C.R.Gentle (1999), *"Development of a rheological model for an alumina/cyanoacrylate feedstock*", Proc.conf AMME'99, Rdzyna, Poland.

J.S.Ridgway, J.B.Hull, C.R.Gentle (2000), *"Flow analysis of a powder reaction injection moulding process for manufacturing a ceramic heart valve"*, awaiting publication.

DEVELOPMENT OF A NOVEL BINDER SYSTEM FOR MANUFACTURE OF CERAMIC HEART VALVE PROSTHESES

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1.0 INTRODUCTION

The work so far at Nottingham Trent University has resulted in the design of a new valve prosthesis mounted in a conduit. This conduit can be used outside the heart as part of a surgical procedure to correct gross congenital anomalies in a child's cardiovascular system - essentially, a replumbing operation [1]. The success of this design is evidenced by the fact that an acrylic version has been adopted for the inlet and outlet valves of a novel ventricular assist device [2], which is under trials as a temporary mechanical heart to sustain heart failure victims until a transplant becomes available.

The most significant feature of the conduit valve, however, is the fact that it is to be made from alumina when intended for permanent implantation in children and adults. Early examples of the use of ceramics in biomedical implants relied simply on their resistance to wear and chemical attack. However, it has been documented that a fine covering of non-vascular tissue can grow on alumina when immersed in the blood stream [3]. This covering is thought to be sufficient to camouflage the prosthesis from any further interaction with the blood, but fine enough (<0.1mm thick) not to interfere with the mechanical function of the valve. This means that alumina valves will exhibit not just excellent wear properties but also unequalled biocompatibility that will obviate the need for continued anticoagulation.

Conventional powder processing is well established as a cost-effective method of producing net or near net shaped products. In recent years, there has been increasing research activity in the USA, Japan and Europe into the efficient production of sintered components from green compacts manufactured by metal or ceramic injection moulding. Injection moulding of polymers (binders) filled with dispersed metallic or ceramic powders has become a recognised route for the production of a large series of complex shaped parts at low cost and with a high degree of accuracy.

Current technology for powder moulding is based on dispersion in non-reactive carriers or binders, followed by shaping, de-binding and sintering. Many technical difficulties exist throughout the processing of powders by means of conventional polymer processing techniques, using polymers or waxes as binder/carriers. One of the major drawbacks is the long de-binding time, which can take hours or even days. Polymer or wax decomposition occurs relatively slowly, even at high temperatures. Attempts have been made to improve the de-binding times. Hull, Birkenshaw & Buggy [4] uses a reactive monomer, such as cyanoacrylate, which has a capability for rapid solidification through polymerisation. Subsequently, the binder can be removed in minutes from the powder compact, by thermal depolymerisation, and recovered for use.

The present study focuses on the development of a binder for compression/transfer moulding using a fine grade aluminium oxide powder in conjunction with a reactive monomer. This paper describes the outcome of experimental investigation into preparation, mixing and moulding characteristics of the reactive binders. A prototype heart valve mould has been developed to facilitate the assessment for various binder/powder mixes to create a similar shape to the final product.

2.0 FEEDSTOCK DESIGN

The feedstock consists of ceramic powder mixed with a binding agent. In order to mould a ceramic part, the feedstock needs to be carefully selected. The following sections describe the properties that each feedstock constituent requires for a suitable green part and the characteristics of the binder and powder.

2.1 Powder Selection

The selection of a suitable ceramic powder is a primary factor controlling the design of binder systems, as the sintered powder will form the final part. Criteria for selection includes particle size, size distribution, particle shape and packing density.

An aluminium oxide powder suitable for ceramic and refactory applications was selected for the study. A Scanning Electron Microscope (SEM) was used to characterise the properties of the ceramic powder. Particle size was found from the SEM micrographs to be on average 6μm with a distribution between 1μm and 15μm. This compares favourably with the widely accepted limits between 2μm and 8μm for powder injection moulding [5].

2.2 Binder Selection

For a moulded part to exhibit strong characteristics in its green state, (a green density is taken as sufficiently close to the theoretical density), the binder must hold a large volume fraction of ceramic powder. This can be investigated experimentally by mixing the binders with alumina. Two reactive thermoplastics have been investigated as suitable binders for alumina powder: methyl-methacrylate and Cyanoacrylate.

As a reactive substance, methyl-methacrylate (MMA) will readily polymerise under standard atmospheric conditions. However, this can be prevented by adding up to 0.1% by volume of an inhibitor such as Topanol or Hydroquinone to the monomer. Commercially free radical polymerisation techniques are employed, involving the addition of a catalyst such as a peroxide at temperatures up to 100°C (the boiling point of MMA is 100.5°C).

There are two potential problems with MMA as a reactive binder. Firstly, the rate of shrinkage after conversion from monomer to polymer can be as high as 20%. Secondly, the curing process is exothermic which adds an extra variable to the processing parameters. As an additional benefit, thermal de-binding of poly-methylmethacrylate leads to the recovery of the monomer, which can be recycled.

Three types of cyanoacrylate are commercially available and these are prefixed by Butyl, Ethyl, and Methyl. Each type exhibits different mechanical properties and there is a large range of viscosity between them - Methyl being the most viscous and Butyl the least.

The polymerisation of cyanoacrylate is rapid with free surface moisture being a suitable catalyst. Other research [6] has found potentially suitable surface catalysts including, caffeine, pyridine and t-butylamine. On the other hand, the use of a strong acid, such as p-toluene-sulphonic can inhibit the polymerisation. Cyanoacrylates will rapidly polymerise or 'zip' and also de-polymerise at the same rate. When the polymer is subjected to temperatures of approximately 180°C, the polymer breaks down to a monomer increasing the potential for re-cycling.

3.0 MOULDING

To test the mouldability of cyanoacrylates, a mould was designed accommodating a representation of the desired heart valve shape. Polytetraflouroethylene (PTFE) was used as the mould material to which the cyanoacrylate will not bond. A 0.4vf 4.5% acid inhibited sample was moulded using a hand extrusion machine. The mixture extruded easily with minimum force applied, and was left to cure. After 24 hours, the entry point to the mould had cured, however, no polymerisation had occurred beyond this point. The lack of 'reaction' within the mould may be attributable to two main factors: the lack of moisture to initiate a reaction, and the large cross section of the part. To ensure a complete polymerisation, the two halves of the mould were left exposed to atmospheric moisture until the mixture had cured. It was also found that the part was difficult to extract from the mould. A release agent such as a carbon spray may be required along with a high surface finish within the mould cavity.

4.0 CONCLUSIONS

The aim of this research was to find a suitable binder and ceramic powder as components of a powder moulding process, for manufacture of heart valve prostheses. Two reactive binders were investigated for fast processing performance, in conjunction with medical grade aluminium oxide powder (purity of 99.8%).

Methyl Methacrylate has the potential to be a binder for an alumina powder. Increasing the volume fraction from 0.3 would be a necessity to achieve a viable green part. This could be accomplished by using a different approach to mixing and possibly a powder dispersant. Polymerisation can be rapid enough to consider methyl methacrylate as a useful alternative to Butyl-cyanoacrylate, but lengthy debinding and processing at temperature make the cyanoacrylate a more attractive alternative.

Amongst the three variants of cyanoacrylate, butyl- is the most desirable due to its reduced viscosity, fast polymerisation, and rapid de-polymerisation. Reaction of the monomer has been investigated and proved controllable with addition of p-toluene sulphonic acid, to the extent of allowing the estimation of polymerisation time. Feedstocks created from cyanoacrylate need to be contained in an inert atmosphere to reduce pre-polymerisation effects caused by surface initiators, but with controlled inhibition and moulding conditions, workable parts can be created with a volume fraction up to 0.45.

Commercially, volume fractions of powder to binder are in the region of 0.5-0.8, producing parts with near net density after sintering. With the requirement to have an inherent porosity in the final product, a volume fraction of 0.45 is acceptable. After 55% binder has been extracted from the green body the part will be left with a large pore volume. This pore volume leaves scope for the designer to create a mechanism that will achieve the required variable porosity, which is a requirement for a heart valve prosthesis.

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Development of a novel binder system for manufacture of ceramic heart valve prostheses

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Abstract

Heart valve prostheses have become common since their introduction in the 1960's. Although prostheses work well in situ at the physiological site they are not designed for other applications such as conduits. Research at Nottingham Trent University has lead to the design of a conduit valve prosthesis to allow for correct arterial and valvular flow. Requirements are to have a porous internal structure to incur tissue in-growth, improve heamodynamic performance and longevity of the prosthesis. Powder reaction moulding technology has been implemented to create such a prosthesis from medical grade Aluminium Oxide.

Methyl Methacrylate and Cyanoacrylates were investigated as binders with aluminium oxide as the powder constituent. The production of samples with a small L/D ratio and analysis of reaction kinetics provided valuable evidence to support the role of these binders. It was found that Methyl Methacrylate can only mix to a powder volume fraction of 0.33, whilst cyanoacrylate can bind with alumina to a higher volume fraction of 0.45. With cyanoacrylate binding the largest fraction, samples were moulded from cyanoacrylate/alumina utilising a hand extrusion unit. The mould design represented the conduit heart valve and was manufactured from polytetraflouroethylene (PTFE). Investigation of the moulded bodies lead to two observations. Firstly, cyanoacrylate requires a surface initiation to polymerise within a mould cavity and secondly, mould release agents are needed to extract the part.

Preliminary investigation into thermal debinding of cyanoacrylate from alumina has been completed with promising results, proving that cyanoacrylate is a useful constituent for reaction moulding.

Keywords: Heart Valve, Moulding, Binder, Cyanoacrylate, Methyl-Methacrylate

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1.0 Introduction

Artificial heart valve design has progressed greatly since the first experimental surgical implants in the early 1960's. Current heart valve prostheses, both mechanical and biological, can be considered as one of the principal successes of biomechanical engineering. However, there is still significant scope for improvement, especially, in the treatment of children, where the need for refined flow characteristics, extended wear life and complete biocompatibility is most acute [1-2].

The work so far at Nottingham Trent University has resulted in the design of a new valve prosthesis mounted in a conduit. This conduit can be used outside the heart as part of a surgical procedure to correct gross congenital anomalies in a child's cardiovascular system - essentially, a replumbing operation [3]. The success of this design is evidenced by the fact that an acrylic version has been adopted for the inlet and outlet valves of a novel ventricular assist device [4], which is under trials as a temporary mechanical heart to sustain heart failure victims until a transplant becomes available.

The most significant feature of the conduit valve (figure 1), however, is the fact that it is to be made from alumina when intended for permanent implantation in children and adults. Early examples of the use of ceramics in biomedical implants relied simply on their resistance to wear and chemical attack. However, it has been documented that a fine covering of non-vascular tissue can grow on alumina when immersed in the blood stream [5]. This covering is thought to be sufficient to camouflage the prosthesis from any further interaction with the blood, but fine enough (<0.1mm thick) not to interfere with the mechanical function of the valve. This means that alumina valves will exhibit not just excellent wear properties but also unequalled biocompatibility that will obviate the need for continued anticoagulation. The problem remains, however, of making the conduit in alumina to the necessary high accuracy and finish.

Conventional powder processing is well established as a cost-effective method of producing net or near net shaped products. In recent years, there has been increasing research activity in the USA, Japan and Europe into the efficient production of sintered components from green compacts manufactured by metal or ceramic injection moulding [6-8]. Injection moulding of polymers filled with dispersed metallic or ceramic powders has become a recognised route for the production of a large series of complex shaped parts at low cost and with a high degree of accuracy.

Figure 1. 3D CAD model of Conduit Valve

Injection moulding is associated with the production of parts in large quantities, whereas compression moulding is a process used where tight control and high accuracy can be implemented to a single part. While a great deal of research efforts have been directed to powder injection moulding, less attention has been paid to the application of powder reaction compression moulding. Powder reaction compression moulding offers a novel approach to the manufacture of a single high tolerance heart valve.

Current technology for powder moulding is based on dispersion in non-reactive carriers or binders, followed by shaping, de-binding and sintering. Many technical difficulties exist throughout the processing of powders by means of conventional polymer processing techniques, using polymers or waxes as binder/carriers. One of the major drawbacks is the long de-binding time, which can take hours or even days. Polymer or wax decomposition occurs relatively slowly, even at high temperatures, because the rate controlling mechanisms are the rate of binder degradation, and the diffusion rate of the inherent volatile fragments. These are fundamental chemical limitations. Attempts have been made to improve the de-binding times. Hull, Birkenshaw & Buggy [9] uses a reactive monomer, such as cyanoacrylate, which has a capability for rapid solidification through polymerisation. Subsequently, the binder can be removed in minutes from the powder compact, by thermal depolymerisation, and recovered for use.

The present study focuses on the development of a binder for compression/transfer moulding using a fine grade aluminium oxide powder in conjunction with a reactive monomer. This paper describes the outcome of experimental investigation into preparation, mixing and moulding characteristics of the reactive binders. A prototype heart valve mould has been developed to facilitate the assessment for various binder/powder mixes to create a similar shape to the final product.

2.0 Feedstock Design

The feedstock consists of ceramic powder mixed with a binding agent. In order to mould a ceramic part, the feedstock needs to be carefully selected. The following sections describe the properties that each feedstock constituent requires for a suitable green part and the characteristics of the binder and powder.

2.1 Powder Selection

The selection of a suitable ceramic powder is a primary factor controlling the design of binder systems, as the sintered powder will form the final part. Criteria for selection includes particle size, size distribution, particle shape and packing density.

An aluminium oxide powder suitable for ceramic and refactory applications was selected for the study. A Scanning Electron Microscope (SEM) was used to characterise the properties of the ceramic powder. Particle size was found from the SEM micrographs to be on average 6µm with a distribution between 1µm and 15µm. This compares favourably with the widely accepted limits between 2µm and 8µm for powder injection moulding [10].

Information is also needed concerning the friction characteristics between powder particles through the measurement of the tap density. Tap density is defined as the highest density that can be achieved by vibrating a powder (by set standards) without any external pressure being applied. In theory, the numerical difference between the tap density and theoretical density represents a void which is to be filled with binder. A sample of alumina was vibrated for 145 minutes at 100rpm with an amplitude of 3mm. It was found to have a tap density of 1250kgm^{-3}, or 0.32 as a fraction of the theoretical density.

2.2 Binder Selection

The basis for the selection of a binder for this application necessitates the meeting of the following requirements.

- Fast polymerisation with a controlled reaction
- Thermally debind within a relatively short time period (compared to standard thermoplastic binder systems).
- Low viscosity to aid mixing

For a moulded part to exhibit strong characteristics in its green state, (a green density is taken as sufficiently close to the theoretical density), the binder must hold a large volume fraction of ceramic powder. This can be investigated experimentally by mixing the binders with alumina. Two reactive thermoplastics have been investigated as suitable binders for alumina powder: methyl-methacrylate and Cyanoacrylate.

2.2.1 Methyl-Methacrylate

As a reactive substance, methyl-methacrylate (MMA) will readily polymerise under standard atmospheric conditions. However, this can be prevented by adding up to 0.1% by volume of an inhibitor such as Topanol or Hydroquinone to the monomer. Commercially free radical polymerisation techniques are employed, involving the addition of a catalyst such as a peroxide at temperatures up to 100°C (the boiling point of MMA is 100.5°C).

There are two potential problems with MMA as a reactive binder. Firstly, the rate of shrinkage after conversion from monomer to polymer can be as high as 20%. Secondly, the curing process is exothermic which adds an extra variable to the processing parameters.

As an additional benefit, thermal de-binding of poly-methylmethacrylate leads to the recovery of the monomer, which can be recycled.

2.2.2 Cyanoacrylate

The anionic polymerisation of cyanoacrylate is inhibited at pH <5.5 [11]. Thus to prevent polymerisation, weak acids such as carboxylic are used to inhibit the monomer throughout storage. Hence to initiate polymerisation a base is required to neutralise this acid, with free surface moisture being a suitable catalyst. Other research [12] has found potentially suitable surface catalysts including, caffeine, pyridine and t-butylamine. On the other hand, the use of a strong acid, such as p-toluene-sulphonic can inhibit the polymerisation. Cyanoacrylates will rapidly polymerise or 'zip' and also de-polymerise at the same rate. When the polymer is subjected to temperatures of approximately 180°C, the polymer breaks down to a monomer increasing the potential for re-cycling.

Three types of cyanoacrylate are commercially available and these are prefixed by Butyl, Ethyl, and Methyl. Each type exhibits different mechanical properties and there is a large range of viscosity between them - Methyl being the most viscous and Butyl the least.

Binder viscosity plays a major role in the mixing process. When increasing the powder content of a binder the combined viscosity increases rapidly, rendering mixing impossible. For ease of mixing butyl-cyanoacrylate was preferred since its viscosity is 100 times less than that of methyl-cyanoacrylate.

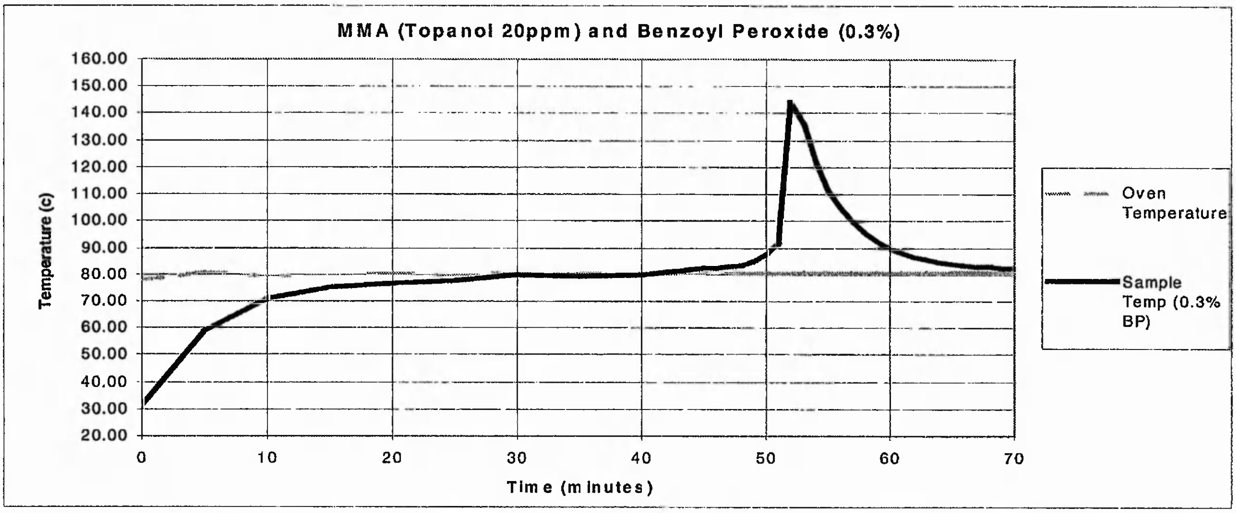

Figure 2. Plot of reaction temperature against time for methyl methacrylate

3.0 Mixing of Feedstock and Creation of Samples

The monomer solution was manually mixed with aluminium oxide powder by utilising a beaker and glass stirring rod. The following sections describe the results of mixing and the chemical reactions encountered.

3.1 Methyl-Methacrylate and Alumina

The Methyl Methacrylate used for the present study contained 20ppm of Topanol inhibitor. Benzoyl Peroxide was chosen as a catalyst to initiate the polymerisation.

In an attempt to understand the kinetics of polymerisation, varying concentrations of Benzoyl Peroxide ranging from 0.1%vol to 3%vol were mixed with MMA. The solution was cast into a mould with a small L/D (length/diameter) ratio and left to cure inside a pre-heated oven at 80°C. During curing, oven and sample temperatures were monitored and recorded.

From figure 2 it can be seen that once the mould heated up to the temperature of the oven there followed a period of about 10 minutes during which the temperature of the mould remained largely constant. It is believed that at this stage the inhibitor (Topanol) is being depleted and a small conversion of monomer to polymer is taking place. When about 20% of the monomer has polymerised, the reaction becomes auto catalytic and is accompanied by an exotherm where the majority of the conversion takes place. This effect is known as the 'gel effect', which is initiated by an increase in viscosity of the solution [13]. Figure 2 shows a typical curing process of MMA and benzoyl peroxide. It is also found that by increasing the catalyst concentration, the time period before the commencement of the gel effect decreased, whilst maintaining a constant oven temperature.

The temperature rise associated with the gel effect was observed to have no connection with the quantity of catalyst. With the boiling point of MMA being 100.5°C, whenever an exothermic reaction temperature increased over this value the sample boiled as it polymerised, giving rise to a sample full of air pockets. The method was modified, to control this effect, by decreasing the curing temperature.

A series of experiments was carried out in which alumina was mixed with MMA to find the maximum powder loading or 'volume fraction of powder (vf)'. Starting with a volume fraction of 0.2 samples were created by mixing alumina with MMA after the catalyst had been dissolved.

Table 1. An example of samples created with MMA and alumina

Sample	*Volume Fraction of powder*	*Oven Temperature (°C)*	*Benzoyl Peroxide (%)*	*Peak Temperature (°C)**	*Curing Time (minutes)*
1	0.2	80	0.5	91.4	80
2	0.2	80	0.7	87.2	70
3	0.2	80	3.0	96.2	50

**Maximum temperature due to the exothermic rise*

Table 1 details the curing times and exothermic rise associated with a selection of samples at 0.2vf. In all cases at 0.2vf samples exhibited a exothermic reaction temperature, fortunately below the boiling temperature of MMA. It was also noted that samples that had a concentration of catalyst greater than 0.5% contained voids, even though the reaction temperature did not rise above the boiling point. The volume fraction of 0.2 is below the limit for moulding acceptable green parts. When 80% binder is thermally degraded a sample would collapse under its own weight. Therefore increasing the packing density of alumina powder is vital to guarantee the structural properties needed for a green part. The maximum volume fraction that could be achieved by manual mixing samples was 0.33. At concentrations greater than this mixing became impossible with current techniques as the powder agglomerated and became too viscous to realistically continue. Samples cast at 0.2vf were investigated by scanning electron microscopy (SEM). It was observed that the MMA engulfs the alumina as shown in figure 3.

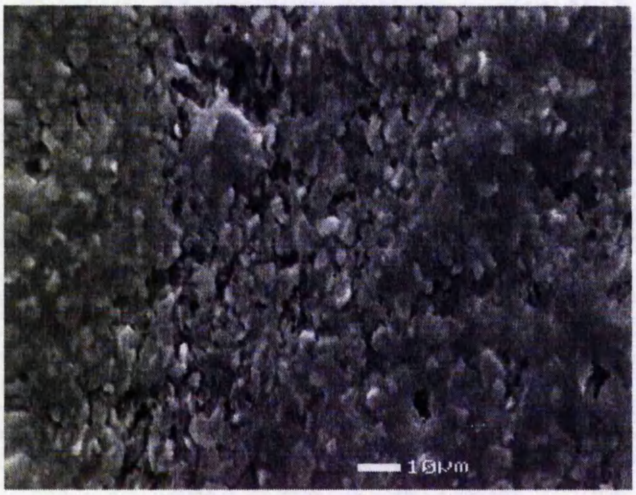

Figure 3. A SEM image of a 0.2vf MMA and alumina compact

3.2 Butyl-Cyanoacrylate and Alumina

Butyl-Cyanoacrylate is a highly reactive monomer. Three factors can effect the reaction kinetics of cyanoacrylate & alumina mixes: volume fraction of powder, extent of inhibition and the moulding environment. When exposed to surface moisture, the polymerisation process is both rapid and exothermic. However, the risk of initiation of polymerisation can be greatly reduced by keeping a sample within a sealed container such as a syringe.

Alumina powder was added to cyanoacrylate to observe the mixing characteristics. Polymerisation was instant indicating that the alumina powder contained surface moisture or other unidentified catalysts. Actions were taken to dry the alumina powder for 24 hrs at 180°C prior to experiments. The need to control polymerisation can also be achieved by the use of p-toluene-sulphonic acid, which has been shown to inhibit cyanoacrylate reactions [12]. The acid is supplied in powder form and requires mixing into the cyanoacrylate until fully dissolved. However, mixing at room temperature proved extremely difficult, as the powder acid would not dissolve, therefore the operation was performed in a water bath at 50°C for 15 minutes. Through the heating stage the colourless cyanoacrylate liquid changed its appearance to yellow indicating that the solution has been inhibited. Samples were then created by mixing small quantities of alumina to the inhibited cyanoacrylate.

Birkenshaw et al [12] found that larger volume fractions of powder caused cyanoacrylate to polymerise faster, thus requiring greater amounts of acid inhibition. In this context, attempts have been made to find the largest volume fraction of alumina, using 6% by vol of acid. The highest volume fraction attainable by manual mixing was 0.5. Above this level the viscosity increased beyond acceptable limits. The polymerised sample yielded cracks and regions of brittleness, which was also unacceptable. For practical reasons, it was decided to create samples with a 0.45 volume fraction in order to ensure that the fully polymerised samples were "crack free" and the moulded shapes were retained without any physical changes.

One of the factors to control polymerisation as previously mentioned is the inhibition times. Experiments were performed to investigate the cyanoacrylate inhibition with varying concentrations of acid at two of the largest volume fractions of powder: 0.4vf and 0.45vf. After mixing, the samples were loaded in to a 5ml syringe; this form of containment is comparable to the barrel of an extruding machine. Periodically a small quantity of the mix was extruded from the syringe; the extent of polymerisation was estimated by means of the resistance to extrusion.

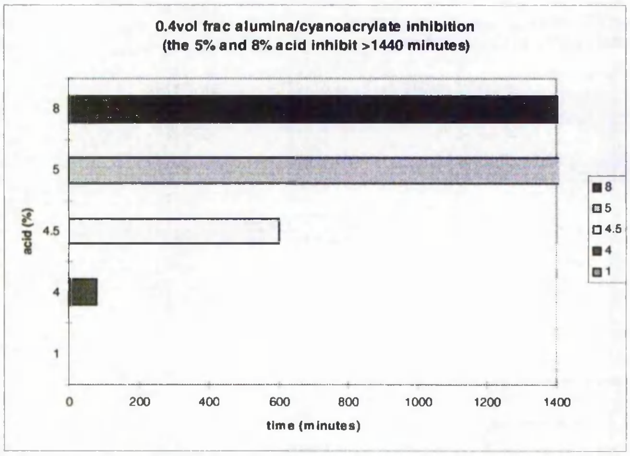

Figure 4. Inhibition characteristics for a 0.4 volume fraction

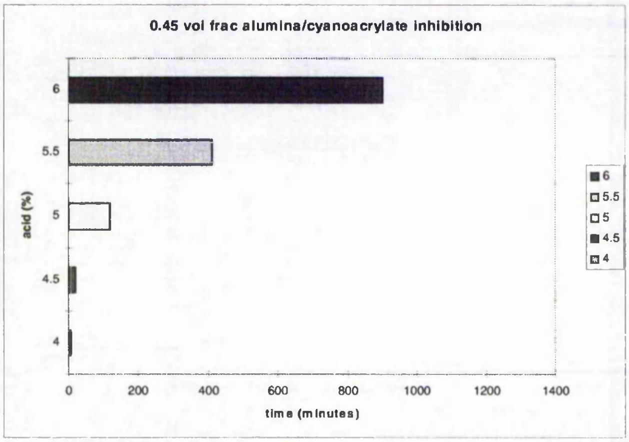

Figure 5. Inhibition characteristics for a 0.45 volume fraction

From the data an estimate can be made of the polymerisation times for individual tested samples, with a defined level of acid inhibition. Figures 4 and 5 show the inhibition characteristics for 0.4vf and 0.45vf respectively. As shown, a greater amount of inhibition is required for the higher volume fraction of powder. When extruding a feedstock, this data is required to ensure polymerisation will not occur prematurely within a moulding barrel.

Figure 6 shows a SEM image of a 0.4vf sample and two things are noted. Firstly the binder engulfs the alumina particles in the same way as the methyl-methacrylate does as shown in figure 3. Secondly, an increase in volume fraction suggests that the powder packing is of a greater density with an observable higher ratio of powder to binder.

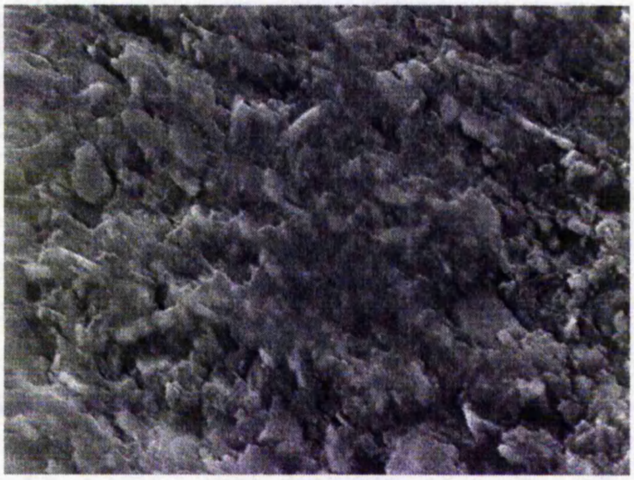

Figure 6. SEM of a 0.4vf cyanoacrylate and alumina compact

4.0 Moulding

Two of the main problems encountered in the operation of a powder moulding system are sintering and de-binding. Based on empirical data, German [14] suggested that the minimum solid loading for powder injection moulding is 0.45. For reasons outlined in section 3.1, the highest volume fraction requirement obviates the use of methyl- methacrylate as a binder for this system unless it can be increased. Furthermore, MMA also needs to be moulded at a raised temperature, thus introducing extra variables and complications due to the gel effect. This leaves butyl-cyanoacrylate as the remaining option to be investigated further.

To test the mouldability of cyanoacrylates, a mould was designed accommodating a representation of the desired heart valve shape (figure 7). Polytetraflouroethylene (PTFE) was used as the mould material to which the cyanoacrylate will not bond. A 0.4vf 4.5% acid inhibited sample was moulded using an APM ESGO 2071 [15] hand extrusion machine. The mixture extruded easily with minimum force applied, and was left to cure. After 24 hours, the entry point to the mould had cured, however, no polymerisation had occurred beyond this point. The lack of 'reaction' within the mould may be attributable to two main factors: the lack of moisture to initiate a reaction, and the large cross section of the part. To ensure a complete polymerisation, the two halves of the mould were left exposed to atmospheric moisture until the mixture had cured. It was also found that the part was difficult to extract from the mould. A release agent such as a carbon spray may be required along with a high surface finish within the mould cavity.

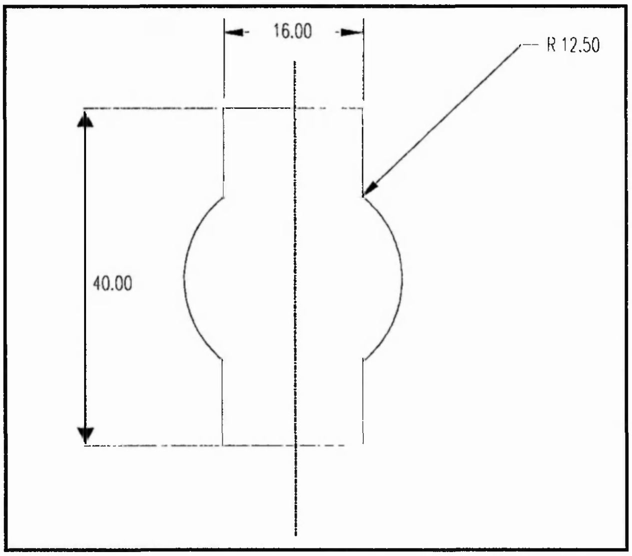

Figure 7. Outline detail of the moulded part

Previous research [16] has highlighted the fact that de-binding of moulded alumina parts with a cyanoacrylate can be achieved. Further experiments are planned to perform thermo gravimetric analysis (TGA) on moulded parts.

5.0 Conclusions

The aim of this research was to find a suitable binder and ceramic powder as components of a powder moulding process, for manufacture of heart valve prostheses. Two reactive binders were investigated for fast processing performance, in conjunction with medical grade aluminium oxide powder (purity of 99.8%).

Methyl Methacrylate has the potential to be a binder for an alumina powder. Increasing the volume fraction from 0.3 would be a necessity to achieve a viable green part. This could be accomplished by using a different approach to mixing and possibly a powder dispersant. Polymerisation can be rapid enough to consider methyl methacrylate as a useful alternative to Butyl-cyanoacrylate, but lengthy debinding and processing at temperature make the cyanoacrylate a more attractive alternative.

Amongst the three variants of cyanoacrylate, butyl- is the most desirable due to its reduced viscosity, fast polymerisation, and rapid de-polymerisation. Reaction of the monomer has been investigated and proved controllable with addition of p-toluene sulphonic acid, to the extent of allowing the estimation of polymerisation time. Feedstock created from cyanoacrylate need to be contained in an inert atmosphere to reduce pre-polymerisation effects caused by surface initiators, but with controlled inhibition and moulding conditions, workable parts can be created with a volume fraction up to 0.45.

Commercially, volume fractions of powder to binder are in the region of 0.5-0.8, producing parts with near net density after sintering. With the requirement to have an inherent porosity in the final product, a volume fraction of 0.45 is acceptable. After 55% binder has been extracted from the green body the part will be left with a large pore volume. This pore volume leaves scope for the designer to create a mechanism that will achieve the required variable porosity, which is a requirement for a heart valve prosthesis.

Moulding of cyanoacrylate as a binder has highlighted problems with initiation of polymerisation; observations with the preliminary moulding experiments have led to two recommendations for further work.

- Initiate the binder within the mould by use of surface initiation of the binder (use of caffeine, pyridine and t-butylamine)
- Use a releasing agent to coat the inner surface of the mould halves, to aid removal of the parts when cured.

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DESIGN AND SELECTION OF AN ALUMINA-CYANOACRYLATE FEEDSTOCK FOR POROUS CONDUIT HEART VALVE PROSTHESES

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ABSTRACT

A conduit heart valve prosthesis requires two basic elements. Firstly, an inherent porosity which will encourage fibrous tissue growth, thus dramatically reducing the risk of thrombosis. Secondly, a wear resistant body which will enhance haemodynamic performance and longevity of the patient.

These requirements have been met by using a hard wearing alumina ceramic in combination with powder reaction moulding technology. This technology involves mixing, moulding, de-binding and finally sintering the powder with a suitable binder.

A number of commercial alumina powders were selected and mixed with a butyl cyanoacrylate binder to develop the most effective feedstock. One particular powder proved superior. This alumina mixed to the binder with a ratio of 50/50, and further sintered to reveal an apparent porosity ranging from 44%. This level of porosity is readily increased by decreasing the powder loading.

This paper details the process and feedstock design which satisfies the basic requirements for a porous conduit heart valve prosthesis.

INTRODUCTION

Heart valve prostheses are quite varied in terms of both design and material. For example, the device range includes: Titanium caged silastic rubber ball valves, pyrolytic carbon/titanium tilting disk valves, porcine xenografts, polymeric cusp valves and human tissue valves. In certain cases, the patient requires not only a valve replacement but also a new artery to replace a diseased one. Current technology drives surgeons to select a prosthetic device like the aforementioned but attached part way along a section of dacron tubing which can then be sutured in position. This approach is unacceptable for correct haemodynamics and reliability as shown by Gentle and Leefe (1996). Therefore a conduit heart valve has been designed to specifically concentrate on improving these elements, as described by Gentle and Tansley (1995).

The new valve, designed through a computational flow dynamics package has proved itself to be a success in a novel ventricular assist device (VAD). The Chang VAD has adopted the new conduit ball valve as inlet and outlet valves made from an acrylic (CHAD Research Laboratories).

The most significant feature of the conduit heart valve, however, is that it will be made from aluminium oxide (alumina) for permanent implantation. Alumina is widely recognised as a biocompatible material and it is already used successfully in other prosthetics (Yamagami et al 1988)(Gentle 1986). However, it has been found that porous alumina can sustain non-vascular tissue growth on its surface when immersed in a blood stream (Juden et al 1983). This thin layer is thought to be sufficient to camouflage the valve from any other interaction with the blood, preventing the build-up of thrombosis which inevitably leads to life threatening embolisms. Hence, a process needs to be developed to create an alumina heart valve with a controlled porosity.

One possible method is powder reaction moulding, which can be used to create seamless ceramic parts. The ceramic powder is dispersed in to a fluid medium known as a binder or carrier. This is then moulded into the desired shape, where the binder commences to cure. The solid component, after extraction from the mould, is further treated to remove the binder. De-binding processes depend upon the type of binder used; they can vary from solvent wicking to thermal degradation, and the process can last for days. Finally the de-bound part (or green body) is sintered at elevated temperatures to create and strengthen particular bonds and achieve near net density.

Research by Ridgway et al (1997) has indicated that butyl cyanoacrylate can be used as an effective binder with aluminium oxide. Cyanoacrylate will readily polymerise (ZIP) with the addition of a catalyst at room temperature (~20°C), and rapidly revert back to monomer (UNZIP) when exposed to temperatures greater than 180°C. This method of room temperature processing, combined with rapid de-binding enables a simple approach to powder moulding, and decreased process times.

This paper investigates commercial alumina powders with a cyanoacrylate binder to develop porous conduit heart valves, using the powder reaction moulding process.

MATERIALS

ALUMINA POWDER

Alumina is available in a variety of grades: the powder purity is normally compromised by impurities and sintering aids such as magnesium oxide (MgO) or silica (SiO). For example, alumina powders used for prosthetics have a purity greater than 99.8% in order to achieve biocompatibility, and 0.1%-0.2% of processing aids. This grade of alumina was selected for the present study.

Some powder characteristics are critical to the success of a powder moulding process, the main ones being particle size and shape. However, the ceramic designer has to allow for conflicts between these characteristics. For example:

a) a small particle size is advantageous for faster sintering but has a slower de-binding rate and greater shrinkage upon densification

b) a spherical particle shape will give a higher packing density but the green body tends to slump during de-binding

German et al (1991) have highlighted that an ideal powder would therefore comprise a mixture of several fractions, with an average particle size in the range 2μm to 8μm and a length/width ratio of 1.2 to 1.5. Table 1 details the powders used for this study, with powder No.3 fitting German's recommendations.

Table 1. Properties of Alumina selected for study

Powder No	*Purity (%)*	*Particle Size (μm)*	*Particle Shape*	*Additional Information*
1	99.80	<10	Irregular	0.1% MgO
2	99.99	150	Rounded	
3	99.80	2-8	Rounded	0.1% MgO

Scanning Electron Microscopy (SEM) is a useful tool for identifying the shape and size distribution of the particles. Figure 1 shows a SEM image of powder No.3

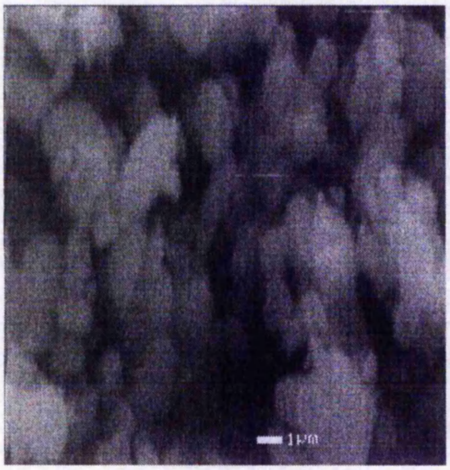

Figure 1. SEM image of powder No.3

BINDER

Butyl cyanoacrylate is a highly reactive monomer. If the pH exceeds an approximate value of 5.5 then an exothermic ionic polymerisation occurs. Therefore, to prevent curing, the monomer is stored with a small volume of acid (Cooke and Allen 1993). This method of inhibition is utilised when using cyanoacrylate as a binder. Alumina will rapidly initiate polymerisation of the monomer, thus demonstrating the need for a strong acid to reduce the pH below the threshold value. It is thought that this polymerisation may be caused by the entrapment of water between alumina powder particles, which neutralise the acid. The proportion of acid required for inhibition depends upon the type of powder being used and the volume fraction of alumina. It is thought that smaller particle sizes and higher powder volume fractions need greater inhibition due to the increased surface area. This inhibition factor is therefore crucial when designing a feedstock which includes a reactive binder; the monomer should not cure (or show signs of curing) before moulding is complete.

MIXING

The mixing process can be seen as the most important stage of a powder moulding cycle. Any flaws or inhomogenity are initially disguised when the mixture is moulded but de-binding would subsequently reveal the imperfections as cracks or warpage. Thus extreme care has to be taken to ensure the powder is thoroughly mixed.

This investigation is primarily concerned with determining mixing characteristics for a small quantity of feedstock representing the volume of a heart valve prosthesis. Therefore feedstock is simply prepared by thorough stirring in a beaker with a glass rod, as the shot capacity does not need to exceed 30ml. Before the powder is stirred in to the binder, a small quantity of acid is dispensed in to the solution in an attempt to inhibit a reaction. If too little acid is used then curing will occur before mixing is complete, while too much acid would prevent the feedstock from curing at all. The exact amount required to inhibit the cyanoacrylate satisfactorily is determined empirically. Table 2 details the sample compositions and their effects.

Table 2. Mixed compositions of alumina and cyanoacrylate

Sample No	*Powder No*	*Mixture Ratio (powder/binder) by volume*	*Acid Level (%)*	*Dissolving Time (minutes)*	*Notes*
1	1	40/60	4	15	mix ok, no agglomeration, no exotherm
2	1	40/60	3	15	mix ok, no agglomeration, exotherm
3	1	45/55	4	15	mix ok, no agglomeration, exotherm
4	1	45/55	5	15	mix ok, no agglomeration, no exotherm
5	1	50/50	6	20	mix viscous, no agglomeration, exotherm
6	1	50/50	7	20	mix viscous, no agglomeration, no exotherm
7	2	40/60	4	15	mix ok, no agglomeration, no exotherm
8	2	45/55	4	20	mix ok, no agglomeration, no exotherm
9	2	50/50	6	20	could not mix
10	3	45/55	6	25	mix ok, agglomeration, no exotherm
11	3	48/52	7	25	mix ok, agglomeration, no exotherm
12	3	50/50	7	25	mix ok, agglomeration, no exotherm

The aim of mixing is to achieve a workable volume fraction of powder to binder. A desirable level would be between 45/55 and 80/20 for conventional moulding as this yields sintered theoretical densities approaching unity. On the other hand, high densities are not required for a porous medium, hence feedstock were mixed to a maximum ratio of 50/50. At this ratio, the mixture viscosity had dramatically increased compared to a ratio of 40/60, as the powder was reaching its critical loading (German, 1990). Because of this, powder No.2 could not mix to the desired ratio of 50/50 without additional processing aids.

It was also observed that powder No.3 agglomerated when in contact with the binder. This attractive force between the particles contributes to voids within the part, as shown in figure 2.

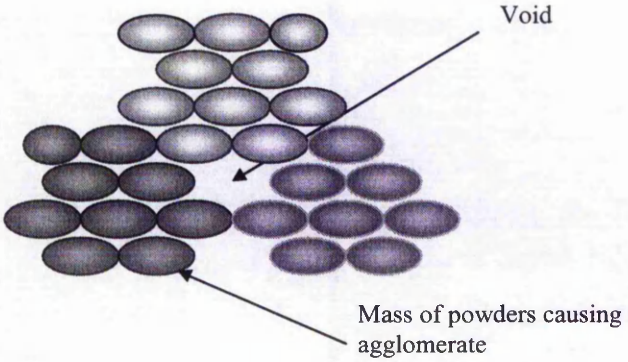

Figure 2. Agglomerates containing internal voids

It is thought that these voids would reduce a final sintered density, but enhance an apparent porosity level within a component. For this reason dispersants are not used in the feedstock as voids help provide the desired porosity for heart valves.

MOULDING

Historically cyanoacrylate was created as an adhesive, bonding most materials from metals to rubbers. It also works as a binder but it presents a problem with moulding. Conventional moulding machines cannot be used as the binder will adhere to the barrel or screw surface. This could be resolved if the surface was cleaned after every shot, but this is highly impractical. The shot capacity for a conduit heart valve prosthesis, however is less than 30ml and it is feasible to develop a simple system for moulding parts, as opposed to using a screw or plunger injection machine.

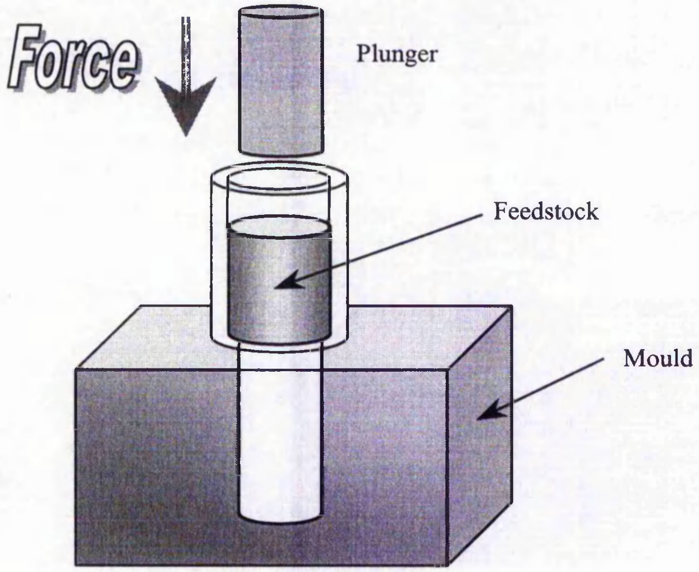

Figure 3. Simple moulding machine

The feedstock shown in Table 2 was loaded in to the barrel as indicated in figure 3. Direct pressure was applied via a manual press, to extrude the mixture in to a simple mould. After the binder had cured, the moulded part was sectioned using a diamond saw. These sections were then measured and prepared for de-binding.

At this stage powder No.2 was discarded. The mixture was too viscous to mould, and any attempt to reduce the powder loading ratio would have undesirable effects on the sintering ability of the powder. Figure 4 shows a SEM of a typical moulded cyanoacrylate/alumina.

Figure 4. SEM image of sample 1 moulded 40/60 alumina-cyanoacrylate

DE-BINDING

After moulding the part requires to be de-bound (removal of the binder). Failure to remove the binder at this stage would lead to cracks and deformities in the part if it were to be sintered. Traditionally waxes and other polymeric binders are used in powder injection moulding and de-binding is the lengthiest part of the process. Thermal degradation and solvent wicking of polymeric binders can take hours or even days, but cyanoacrylate is advantageous because of its ability to unzip in minutes when exposed to temperatures greater than 180°C. Other polymers such as poly-methylmethacrylate (PMMA) revert back to monomers and debind faster than a traditional binder/wax system. However, PMMA is too viscous to bind a useful powder loading, making sintering difficult.

Selected samples were thermally de-bound in a Binder-FED53 oven with a set heating rate of 5°Celsius/minute to determine the shrinkage, warpage and weight loss. Table 3 details the results.

Table 3. De-Binding results

Sample No.	*Debinding Time (hours)*	*Start Temperature (°C)*	*Set Point (°C)*	*Heating Rate (°C/min)*	*Start Mass (g)*	*End Mass (g)*	*Comments*
1	2	19	220	5	7.126	5.162	Large amounts of slumping & warpage
6	2	19	220	5	6.97	5.48	no slumping, no warpage, no shrinkage, vapour holes
10	2	20	220	5	5.4	4.30	no slumping, no warpage, no shrinkage, vapour holes
11	2	20	220	5	5.68	4.46	no slumping, no warpage, no shrinkage, vapour holes
12	2	20	220	5	5.29	4.17	no slumping, no warpage, no shrinkage, vapour holes

Sample 1 collapsed under its own weight when thermally de-bound. The powder loading was too low and when the binder was extracted there was not enough support from the suspended particles to retain any shape.

The other samples had powder loadings greater than 45/55 and they retained shape without shrinkage. Therefore it is acceptable to maintain this powder loading as the base level for integral parts.

Minor cracks and surface pitting was noticed on all parts. It is thought that the heating rate could be reduced along with the setpoint to eradicate the formulation of vapour blow holes contributing to surface defects.

When parts had fully de-bound (determined by no further mass loss) they were removed from the oven. Special care has to be taken when handling these parts as they are fragile and damage may result.

SINTERING AND DENSITY MEASUREMENTS

Sintering is considered a success in powder moulding if the part approaches the theoretical density of its constituent powder. After de-binding compacts are often near 60% dense while the final sintered density approaches 100% (German 1990).

A near net sintering density is possible by using a high powder packing density but a fully dense part is not required for a porous heart valve. A balance between sintered strength, porosity and sinterability needs to be determined from the packing density when the feedstock is initially designed. These factors can only be found by empirical investigation.

An induction furnace with an Argon atmosphere was used to sinter samples. The furnace was set to full gain whilst heating, arriving at operating temperature within 20 minutes. This is not normal practice but it gives an accelerated test of the sinterability of the powder. Figure 5 shows a heating profile for sample 12, which is typical.

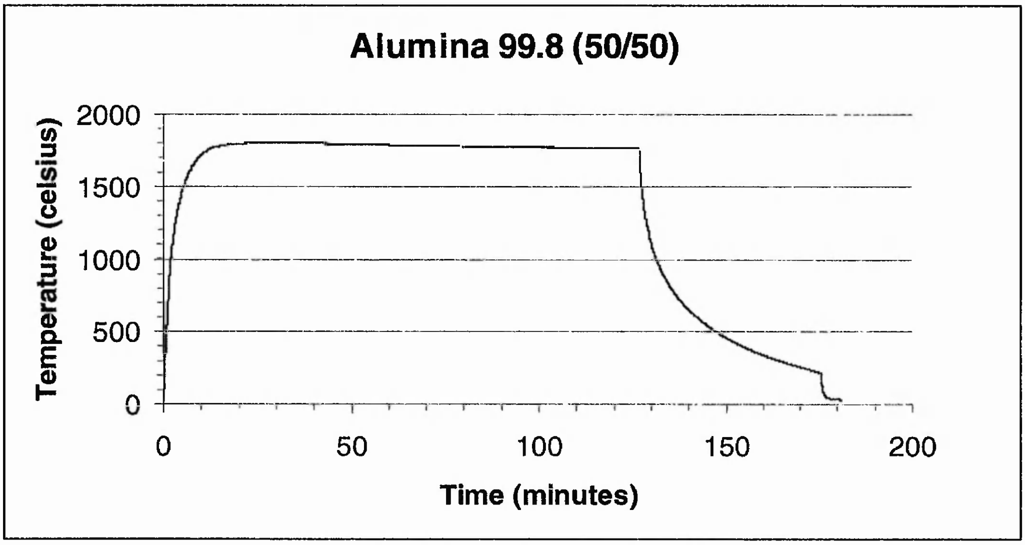

Figure 5. Heating profile of sample 12

Table 4. Sintering results for selected samples

Sample No.	Sintering Temperature (°C)	Hold Time (hours)	Comments
6	1750	1	Densified, very fragile, easily damaged
10	1750	1.5	Densified, hard wearing, strong
11	1750	1	Densified, hard wearing, strong
12	1750	1.5	Densified, hard wearing, strong

Table 4 highlights the results of sintering. A temperature of 1750°C was sufficient to densify parts and initiate grain growth, helped by the addition of the sintering aid. Although both powders used for sintering contained 0.1% MgO, powder No.3 maintained a sintered strength down to a loading level of 45/55. It is thought that the homogenous packing obtained by a rounded particle shape is one of the factors that contributed to this observation. Figure 6 shows the sintered surface of sample 11.

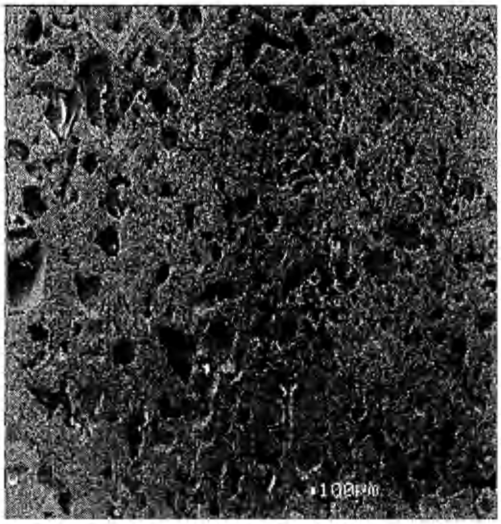

Figure 6. SEM image of surface from sample 11

One method of classifying the porosity is to utilise the Archimedian principle. Samples were boiled in distilled water for 2 hours so they were completely saturated. The suspended, dry and wet mass for each sintered sample was measured and the corresponding density and porosity was calculated.

Table 5. Density measurements of sintered samples

SAMPLE	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
10	1.5908	1.2076	2.0029	0.795	0.412	0.383	52	4.15	2.00	46.44
11	2.9037	2.1379	3.6263	1.488	0.717	0.770	48	3.77	1.95	49.01
12	4.0898	2.9791	4.9672	1.988	0.877	1.110	44	3.68	2.06	51.69

A - Dry mass (g)
B - Suspended mass (g)
C - Saturated mass (g)
D - Exterior volume (cm^3)
E - Volume of open pores (cm^3)
F - Volume of impervious parts (cm^3)
G - Apparent porosity (%)
H - Apparent S.G (%)
I - Bulk density (g/cm^3)
J - Relative density

Table 5 details the apparent porosity and relative density of the sintered parts. The porosity varies from 44% to 52% which should be sufficient for a porous heart valve. Adjustment of the porosity can be achieved by changing the powder loading of the feedstock, or supplying greater pressure whilst moulding to obtain a higher packing density.

CONCLUSION

Cyanoacrylate has proved to be a useful binder for a selection of commercial medical grade aluminium oxides. Careful consideration has to be given to selecting an inhibition level that will not cause premature or delayed polymerisation.

The common problem of agglomeration is welcomed in this particular application. Voids created between flocculated particles assist in creating a porous medium. Therefore no dispersants or anti-flocculation compounds are required as part of the feedstock.

Adjusting the powder loading at the mixing stage can control the final porosity of sintered parts. A higher powder packing density increases the final sintered density and reduces porosity. A balance is therefore required where feedstock will sinter with adequate strength and retain an integral porosity.

Powder with a small particle size and rounded shape proved to sinter with adequate strength. This is aided by the addition of up to 0.1% magnesium oxide which provides a liquid phase during sintering of alumina.

The moulding stage requires further development if this feedstock were to be used on a commercial basis. Unconventional materials would need to be incorporated in the die and barrel design of a conventional moulding machine. Alternatively a cleaning cycle could be included as part of the moulding cycle.

Finally, this investigation has proved that reactive binders in conjunction with alumina powders can be injection moulded to create a ceramic with a desired, controllable porosity which would be an ideal material for conduit heart valves.

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DESIGN FOR POWDER REACTION MOULDING CERAMIC CONDUIT HEART VALVES

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ABSTRACT: Heart valve prostheses have become one of the prime achievements in biomechanical engineering. Initially, in the 1960's heart valves consisted of a 'rubber ball and steel cage' design, which has progressed to a 'bi-leaflet pyrolytic carbon' valve in the 1990's. These valves were designed as aortic or mitral valve replacements, leaving a gap in the market for specifically designed conduit valves. Nottingham Trent University is developing a seamless porous ceramic conduit heart valve that targets requirements for correct heamodynamic performance and longevity.

Powder reaction moulding has been investigated as a process for moulding the conduit heart valve, to introduce an inherent porosity to the part and reduce production times. Cyanoacrylate was investigated as a binder with aluminium oxide as the powder constituent. After controlling the reaction kinetics, parts were created to determine the moulding characteristics. It was found that initiating polymerisation of the cyanoacrylate was difficult under the moulding conditions, therefore a novel moulding approach was used to initiate polymerisation in conjunction with creating a seamless part.

This work has proved that cyanoacrylate can be used as an effective reactive binder with aluminium oxide, and moulded to create seamless parts. This is a key stage to the development of a ceramic conduit heart valve.

KEYWORDS : Ceramic Moulding, Cyanoacrylate, Heart Valve, Binder.

INTRODUCTION

Prosthetic heart valve research has greatly improved quality of life since the first implants in the 1960's. Originally valves were of the caged ball type, but this design was later improved due to mechanical failures and clinical complications. New types of valve were designed utilising simple tilting disk configurations made from pyrolitic carbon. To date this is as far as mechanical heart valves have progressed commercially.

Certain cases of congenital heart disease require the replacement of the heart valve plus part of the aorta. Therefore, a prosthetic requirement would be a combination of valve and conduit. Surgeons overcome this by utilising a mechanical (or tissue) valve within a section of dacron tubing, since no commercial valve assembly is available. Problems therefore arise as the haemodynamics are incorrect and the valve does not function properly.

The work so far at Nottingham Trent University has resulted in the design of a new valve prosthesis mounted in a conduit. Computational fluid dynamics research by Wilson (1997) also indicates that this valve is an excellent replacement to valves currently on the market. The success of this design is evidenced by the fact that an acrylic version has been adopted for inlet and outlet valves for a novel ventricular assist device (VAD) in Australia (CHAD research laboratories). This is a mechanical device able to sustain heart failure victims until a replacement heart becomes available.

The most significant feature of the conduit valve is that it is to be made from Alumina, as a permanent implantation in children and adults. Examples of the use of ceramics in implants are more commonly noted in replacement hips or false teeth (Yamagami et al 1988), with the emphasis being wear resistance. However, it has been found that porous alumina can sustain non-vascular tissue growth on its surface when immersed in the blood stream (Juden et al 1983). This covering is thought to be sufficient to camouflage the valve from any other interaction with the blood, but fine enough (<0.1mm) not to interfere with the mechanical action of the valve. Alumina valves will therefore exhibit excellent wear properties plus an unequalled biocompatibility that will obviate the continued need for anticoagulation treatment. The only problem remaining is the manufacture of such a valve with a high accuracy, porous structure and excellent reliability. Thus, a requirement is a seamless valve with a variable porosity for structural integrity.

Conventional powder processing is well established as a cost-effective method of producing net or near net shaped products. In recent years, there has been increasing research activity in Japan, Europe and the USA into the efficient production of sintered components from green compacts manufactured by metal or ceramic injection moulding (Vervoort et al 1996, Hwang et al 1996 and Mutsuddy et al 1995). Injection moulding of polymers filled with dispersed metallic or ceramic powders has become a recognised route for the production of a large series of complex shaped parts at low cost and with a high degree of accuracy.

Current technology for powder moulding is based on dispersion in non-reactive carriers or binders, followed by moulding, de-binding and finally sintering. Many technical difficulties exist throughout the processing of powders by means of conventional polymer processing techniques, using polymers or waxes as binders/carriers. One problem is the long debinding time when the polymerised binder is leached out from the moulded body; this can take hours or even days. Attempts have been made by Hull et al(1996) to reduce the de-binding times by using a reactive monomer such as a cyanoacrylate. The reactive binder can be removed in minutes from the powder compact, by thermal depolymerisation, and recovered for use. Ridgway et al (1997) has investigated reactive binders with aluminium oxide, and the most efficient was found to be Butyl Cyanoacrylate for its powder loading capacity.

This study investigates the moulding and material selection for moulds to create a seamless part from a cyanoacrylate\Aluminium Oxide powder binder system.

MATERIALS

Aluminium Oxide (alumina) has been recognised as an acceptable choice of ceramic powder for heart valve prostheses (Gentle 1986). Along with properties such as its strength, fracture toughness and cost, alumina also has the ability to grow a fine covering of tissue.

A powder was selected with an average grain size of 6μm and a purity of 99.8%. Investigation by Scanning Electron Microscopy (SEM) shows that the particle shapes are irregular with a distribution between 1μm and 15μm. Irregular particles normally lead to a low packing density and agglomeration, however, a high density green part is not imperative as the heart valve needs to be porous. The particle size and shape can be estimated by examining a SEM image as in figure 1.

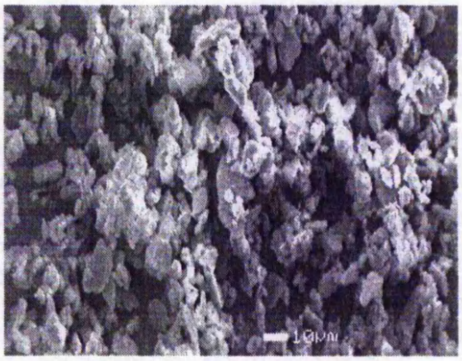

Figure 1. SEM image of Al_2O_3 powder

The two main requirements for a useful binder are firstly, a high loading capacity with low viscosity and secondly, an ability to rapidly debind. Butyl Cyanoacrylate exhibits these properties and therefore was selected for use. Cooke et al(1993) has highlighted that anionic polymerisation of cyanoacrylate is inhibited when the pH is reduced below 5.5. To prevent this value being overcome, a weak acid is mixed with cyanoacrylate monomer to maintain the shelf life of the product. Therefore, additions of a weak base such as water vapour will slowly neutralise the acid until the threshold of 5.5 is overcome, then rapid polymerisation (or zipping) will occur. If a stronger base such as water moisture or N,N-Dimethyl-p-toluidine is added to a cyanoacrylate then the rate of neutralisation of the acid is faster and polymerisation can seem to be instant.

Cyanoacrylate will readily adhere to metallic surfaces and most plastics, however, Nylon-66 and Teflon (PTFE) are an exception. It is intended to make a mould from either of these materials and further investigate the moulding characteristics of an alumina/cyanoacrylate feedstock.

An experiment was designed to investigate the reaction kinetics of the binder. This involved dispensing a small quantity of alumina into 3ml of Butyl Cyanoacrylate monomer at room temperature. Surface contact of the powder instigated rapid polymerisation of the binder, associated with an exothermic temperature rise as indicated in figure 2. This rate of reaction poses a problem when mixing feedstock, however, this can be overcome by utilising a strong acid to neutralise the catalysing alkalinity. P-Toluene Sulphonic acid has previously been used successfully to inhibit cyanoacrylate (Ridgway et al 1997 and Birkinshaw et al 1996) and on this basis, was selected. The quantity of acid mixed depends upon the volume fraction and quantity of cyanoacrylate, where volume fraction is defined as the ratio of ceramic powder to binder (equation 1).

$$vf = \frac{a}{a+b} \tag{1}$$

where: vf = volume fraction of powder
a = volume of powder
b = volume of binder

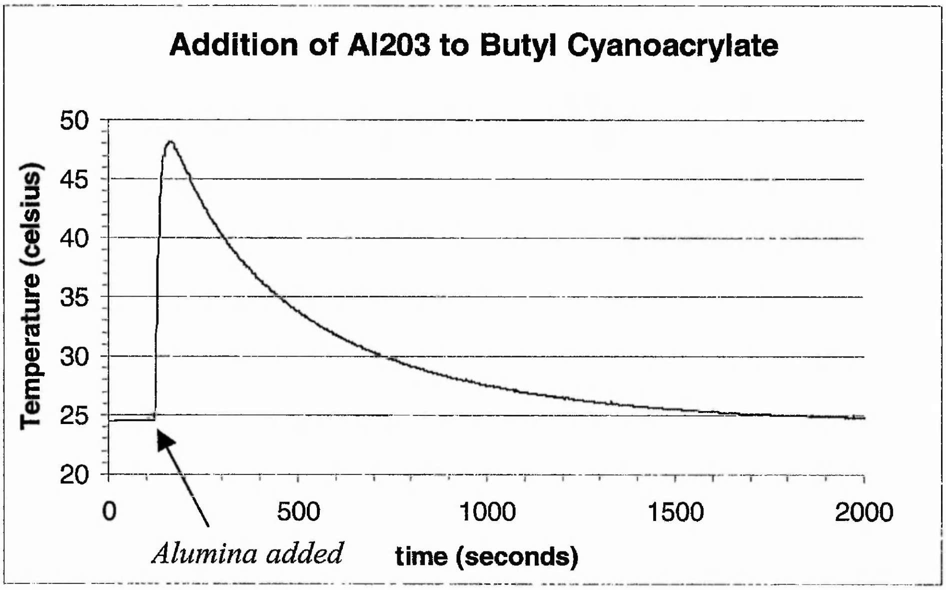

Figure 2. Reaction time and temperature of the addition of Aluminium Oxide to Butyl Cyanoacrylate

Table 1. Extrusion of feedstock with a 10ml syringe

Volume Fraction (vf)	*% acid inhibition (of binder volume)*	*Comment*
0.4	**3.5**	**No extrusion (sample set)**
0.4	**4**	**Easy extrusion**
0.4	**>4**	**Easy extrusion**
0.45	**4**	**No extrusion (sample set)**
0.45	**5**	**Not cured, greater force required**
0.45	**>5**	**Not cured, greater force required**

*All samples were mixed for 10 minutes before extrusion

MIXING AND EXTRUSION

The reactive monomer requires inhibiting before mixing can commence, otherwise when alumina is added to the solution an instant reaction will occur. P-Toluene sulphonic acid is dispensed in to a measured sample of cyanoacrylate, and dissolved at 50ºC for 15 minutes. As an indicator, the solution changes colour from transparent to a pale yellow as inhibition commences. At this stage the pH has reduced to form a strong acidic solution, and ceramic powder can now be introduced. Upto 0.45vf of Aluminium Oxide powder is thoroughly mixed in to the solution via a stirring rod. This is the highest volume fraction that the cyanoacrylate used for investigation can hold with the mixing method used. For a comparison, a volume fraction of 0.4 can also be used for experiments, as this is also an acceptable value for powder processing.

Ridgway et al (1997) found that the minimum amount of acid to be mixed for a volume fraction of 0.4 is 4% (of binder volume), and 5% for a volume fraction of 0.45. If less acid is used then polymerisation will occur before injection of the feedstock, however, the feedstock will take longer to cure if more acid is used. A balance has to be struck between these values for an economic processing time, this has to be found experimentally.

For a good representation of acid inhibition, samples can be extruded from a syringe. Table 1 shows the results of samples extruded from a 10ml syringe with varying acid concentrations. It can be noted that when the volume fraction (or powder loading) of the binder is increased, extra acid inhibition is required to counter act the extra base content.

From table 1 it can be seen that it is difficult to extrude from a syringe when the volume fraction increases over 0.4 resulting from a possible increase in viscosity. To overcome this a small extrusion machine can be used to supply the extra force required. Figure 3 shows an SEM image of mixed cyanoacrylate and alumina.

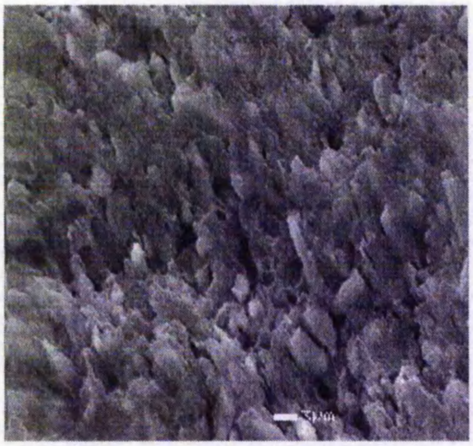

Figure 3. SEM image of mixed cyanoacrylate and alumina

MOULD DESIGN AND MOULDING

The basic moulding requirements for cyanoacrylate/aluminium oxide feedstock are as follows;

- Room temperature processing
- Syringe for mould injection of 0.4vf feedstock
- Extrusion machine for injection of >0.4vf feedstock
- Mould with a high surface finish
- Mould releasing agent
- Mould material compatible with the feedstock
- An injection point through a simple sprue bushing
- An exit point for air release
- Release pins

On the basis of the above requirements a polytetraflouroethylene (PTFE or Teflon) mould representing a solid model of a conduit valve was designed and manufactured. This design could test the mouldability of feedstock and provide useful information about curing. Figure 4 is a diagram of the design (no release pins were implemented at this preliminary stage of design).

The Teflon mould was pre-prepared for use by treating the inner surfaces with a silicon oil surfactant, preventing cyanoacrylate adhering to the mould, hence, aiding removal of the formed part. A feedstock consisting of 0.45vf powder and 5.5% acid (by volume of binder) was injected in to the mould cavity by utilising the efforts of an ESGO 2071 (Asmidar) hand extrusion machine. The mould was left at room temperature for 7 days whilst the feedstock cured.

On opening, the formed surface in contact with the mould displayed a close replication and showed satisfactory curing, however, inspection revealed that the cyanoacrylate had not fully polymerised at the centre of the part. This problem of incomplete curing could be associated with the large diameter of the part, leading to insufficient catalyst (or base) to initiate complete polymerisation.

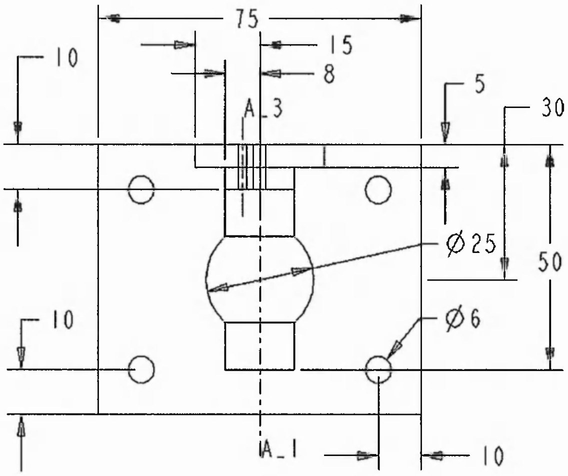

Figure 4. PTFE mould for solid conduit valve
(all dimensions are in mm)

Further investigation of the mould highlighted a problem with machining. The Teflon had warped whilst the mould was being manufactured, caused by high temperatures produced when cutting. Therefore, the inner surfaces did not seal correctly during moulding, producing a part with excess flash. This can be eradicated by either changing the material or bracing the mould before and after the machining process.
Three methods of eliminating the problems encountered with moulding the solid part from the Teflon mould are;

a) Provide a passage for a catalyst to enter the mould
b) Control levels of acid inhibition
c) Limit parts to a small thickness

CONCLUSIONS

The correct use of inhibition with cyanoacrylate leads to a suitable binder that will inject efficiently from a moulding machine or a syringe (for lower volume fractions). Further investigation of acid quantities and inhibition could lead to a more efficient moulding time and a more detailed understanding of the reaction kinetics.

PTFE is an effective mould material, parts can be removed from the mould with ease, but a problem exists with warping after machining. As mentioned in section 4, braces could be used to hold the material in place before and after machining, however this has to be investigated. Nylon-66 proved to be a useful mould material as there was no warping from manufacture but still it has its limitations. After moulding, parts were difficult to extract as they had adhered to the mould surface even though a silicon oil surfactant was used. Investigating alternative release agents could solve this problem.

This investigation has found that Teflon could be used as a material for moulding a heart valve from alumina; using a cyanoacrylate binder. However, further work in the field of polymerisation control and mould enhancement would be required to create a porous conduit part.

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ADVANCED MOULDING FOR REACTIVE BINDERS

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1. INTRODUCTION

The processing of advanced materials such as refractory ceramics and metallic alloy powders has been investigated intensely over the past two decades [1-2]. Ceramic injection moulding has therefore become a prime method for manufacturing complicated parts from a robust material. Typically, powder is dispersed within a thermoplastic carrier (or binder) before it is moulded at high temperatures and pressures. Further removal of the binder by thermal or solvent degradation methods yields a component that is suitable for sintering. Within industry, components have been manufactured with densities greater than 95% of theoretical [3], however this processing route has its drawbacks. De-binding can take days due to slow heating rates and changes in viscosity of the polymeric carrier which, can delay production and increase costs. A solution has been found by using a reactive binder that can polymerise within seconds and degrade back to a monomer within a fraction of normal de-binding times [4]. This technology known as Powder Reaction Injection Moulding Engineering (PRIME) has been developed using a cyanoacrylate binder that is commonly used as an adhesive thus introducing difficulties when moulding [5]. This extended abstract discusses the feedstock used for experimentation and mould design to create a conduit part.

2. FEEDSTOCK

Feedstock is a name given to the combination of a powder and binder matrix for injection moulding. This matrix is created by carefully mixing the powder in to a binder under a controlled atmosphere, typically a vacuum. A ceramic powder that can be satisfactorily mixed to cyanoacrylate is alumina (aluminium oxide). Alumina has inert properties and excellent wear resistance allowing it to be used in many applications including automotive components and medical prosthetics. However when alumina is mixed with cyanoacrylate a reaction occurs, instantly curing the binder. Therefore this polymerisation reaction has to be delayed until the feedstock has been moulded. A strong acid used in quantities above 0.1% by volume can be dissolved in to the monomer solution thus delaying a reaction. Para-toluene sulphonic acid is capable of preventing reactions and if used in greater quantities inhibition can be for hours [6], providing that a strong base initiator is not introduced to the monomer. Moreover polymerisation can be initiated by using surface catalysts such as caffeine, pyridine, t-butylamine and also free surface moisture.

Inhibition level is very important when the feedstock is moulded, premature polymerisation could ruin a moulding machine and take hours to clean, and therefore a balance has to be made. This leads to the development of a workable window for mixing feedstocks (figure1).

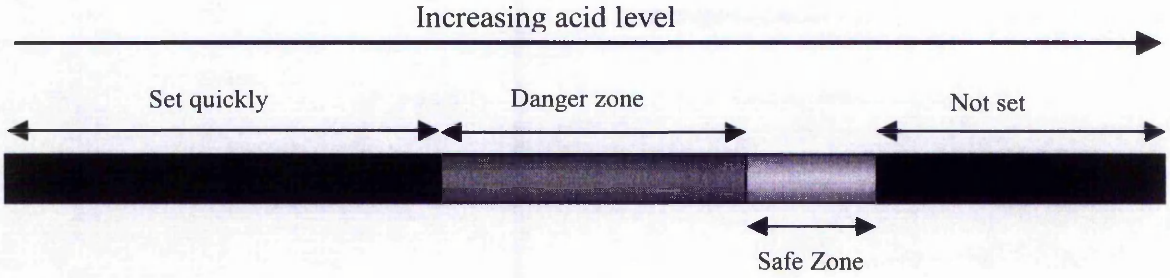

Figure 1. Working window for acidity levels of inhibited monomer

3. DESIGN FOR MOULDING

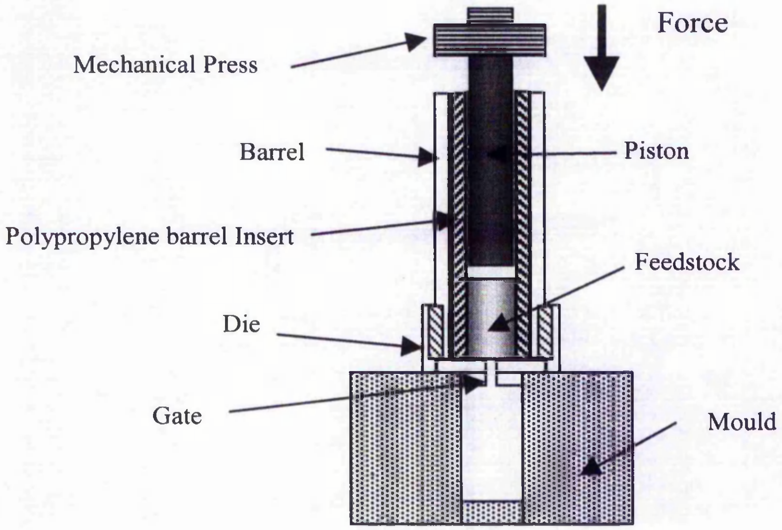

Figure 2. Moulding system

Historically cyanoacrylate was created as an adhesive, bonding a wide range of materials from metals to rubbers in seconds. When being used as a binder it presents a problem associated with processing. Conventional PIM machines cannot be used for moulding as the binder will adhere to the barrel or screw surface, therefore it is feasible to develop a simple system for manufacturing low volume parts. A barrel for such a machine should be made from a material that cyanoacrylate will not adhere to such as polypropylene or polyethylene. However a machine made from these materials would have little mechanical strength. A practical solution is to use a polymeric disposable barrel insert. Polypropylene tubing is relatively inexpensive and suited to the application, hence a method for moulding was developed as shown in figure 2.

Conduit parts can be moulded by using the 'lost wax' process. The 'lost wax' process involves thermally removing a wax insert after the feedstock has been formed around it. The wax fits inside the mould and its profile is transferred to the internal surface of the final part. Thus, it is essential that the wax is moulded to a high tolerance with an excellent surface finish. Removal of the insert could be performed by suspending the sealed mould within a water bath at a temperature above the melting point of the wax. After leaving the mould for a period, the wax would melt out and evaporate exposing the inner surface of the moulded part. This then allows water to enter the mould and subsequently polymerise any remaining uncured feedstock. However wax is a soft material and it can warp or crack under injection moulding pressures, therefore an alternative to this material is required that can withstand this environment such as a metallic alloy.

A major concern when moulding cyanoacrylate feedstock systems is the problem of adhesion with the mould surface. As with the moulding barrel, adhesive forces can make it impossible to remove the cured part from the mould without causing severe surface damage. Therefore a novel approach to the process which involves melting away the mould after removal of the sacrificial core has been adopted. Figure 3 details this arrangement and highlights given advantages of this process over a normal moulding procedure.

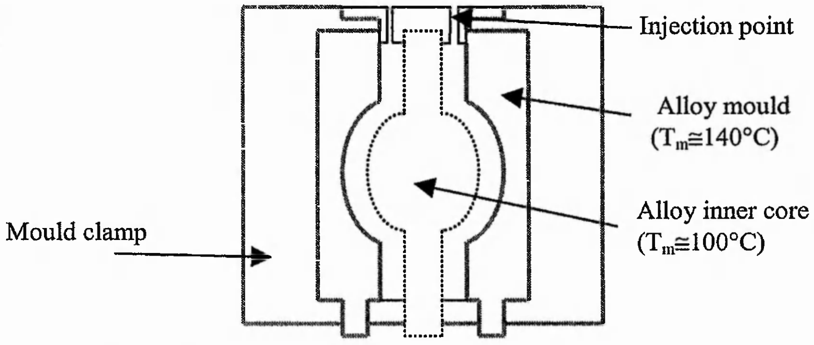

Figure 3. Moulding arrangement

- Melting of the mould material could allow the part to polymerise very quickly on the inner and *outer* surface, reducing processing time from days to within hours.
- The part can be easily removed after processing, as there is no surface contact with the mould.

- An alloy will not be damaged or collapse with the injection pressures associated with the process.
- The use of a mould material such as an alloy eliminates warping problems that can be encountered when machining Nylon or Teflon.
- No release pins are required.
- No mould release agent is required.
- The mould and core can be re-cycled

4. CONCLUSION

Powder reaction moulding is a novel process that requires a re-design of conventional moulding apparatus. High pressures and temperature control are not required for a low viscous cyanoacrylate feedstock, therefore a simple press is used to apply low forces within the injection cycle.

The volatile nature of cyanoacrylate has forced the requirement of a polypropylene insert within the moulding barrel. This novel approach to moulding has enabled a simplistic method of cleaning the apparatus after moulding, by disposal of the insert.

Nylon and Teflon are suitable mould materials as cyanoacrylate will not adhere to the surfaces, however these materials are expensive and difficult to machine. Therefore a system has been developed utilising a metallic alloy mould that is melted away after processing, thus eradicating any problems associated with adhesion of the binder. Removal of the mould and insert allows the ingress of a catalysing agent such as water.

The utilisation of an alloy moulding platform has enabled the creation of complex conduit parts which can be debound within minutes. This novel system is relatively simple and inexpensive in comparison to conventional moulding equipment, which has high costs and complexity.

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A P.R.I.M.E APPROACH FOR MOULDING CONDUIT CERAMIC PARTS

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Abstract

The processing of advanced materials such as refractory ceramics and metallic alloy powders has been investigated intensely over the past two decades. Ceramic injection moulding has therefore become a prime method for manufacturing complicated parts from a robust material. Typically, powder is dispersed within a thermoplastic carrier (or binder) before it is moulded at high temperatures and pressures. Further removal of the binder by thermal or solvent degradation methods yields a component that is suitable for sintering. Within industry, components have been manufactured with densities greater than 95% of theoretical. However, this processing route has its drawbacks. De-binding can take days due to slow heating rates and changes in viscosity of the polymeric carrier that can delay production and increase costs. A solution has been found by using a reactive binder that can polymerise within seconds and degrade back to a monomer within a fraction of conventional de-binding times. This technology known as Powder Reaction Injection Moulding Engineering (P.R.I.M.E) has been developed using a cyanoacrylate binder that is commonly used as an adhesive thus introducing difficulties when moulding. This paper describes the processing limitations of this binder and the method for moulding a conduit ceramic part.

Keywords: powder moulding, cyanoacrylate, binder, ceramic processing, Alumina.

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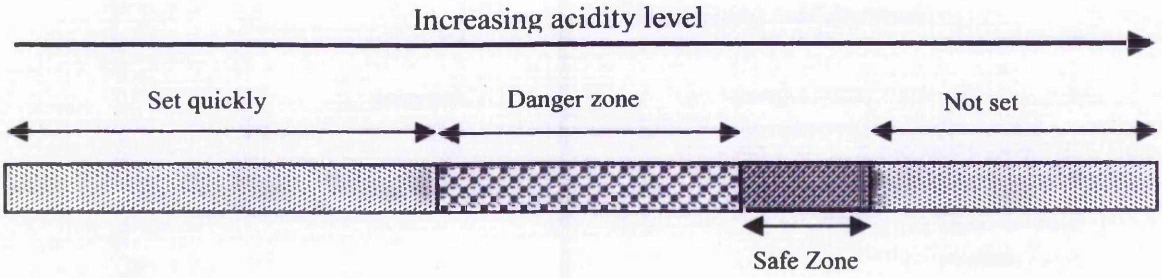
1. INTRODUCTION

Modern applications of technical ceramics such as automotive components and bio-prosthetics [1-6] have forced development and intensive research into alternate forming methods. Products within modern society can include complex shapes for mechanical and aesthetic reasons, but more importantly, there is a drive for wear resistance, longevity, economy and tolerance to harsh, volatile environments. Such components can be developed using a highly successful approach known as powder injection or compression moulding [7-12], combining traditional polymer injection moulding techniques with powder processing technology. Typically, a ceramic or metallic powder is dispersed within a molten polymer binder (or carrier) before it is formed under high pressure into a pre-heated mould. Thermal degradation or solvent extraction methods are then employed to remove the polymeric binder prior to firing, whereas the 'brown body' is sintered to near net density.

Whilst processing polymer melts, variables within the moulding cycle such as temperature and pressure have to be constantly measured, leading to a complex system with accurate control. A new technology developed by Hull et al [13] simplifies the PIM process by using a reactive binder. PRIME or Powder Reaction Injection Moulding Engineering is a method that relies on using a reactive monomer such as a cyanoacrylate to bind ceramic or metallic powders within the mould. It is well-documented [14-17] that when polymerised, cyanoacrylate can de-bind by reverting back to a monomer within minutes, thus significantly reducing processing time in comparison to viscous polymer melts used in PIM. Cyanoacrylate polymerisation reactions occur at room temperature thus simplifying the requirements for a moulding platform. However, problems can exist with this highly reactive binder when using conventional moulding apparatus. This paper demonstrates the use of PRIME to develop a conduit part, highlighting processing limitations and solutions.

2. FEEDSTOCK

Feedstock is a name given to the combination of a powder and binder matrix for injection moulding. This matrix is created by carefully mixing the powder in to a binder under a controlled atmosphere, typically a vacuum. A ceramic powder that can be satisfactorily mixed to cyanoacrylate is alumina (aluminium oxide). Alumina has inert properties and excellent wear resistance allowing it to be used in many applications including automotive components and medical prosthetics. However, when alumina is mixed with cyanoacrylate a reaction occurs, instantly curing the binder. Therefore, this polymerisation reaction has to be delayed until the feedstock has been moulded. A strong acid used in quantities above 0.1% by volume can be dissolved in to the monomer solution thus delaying a reaction. Para-toluene sulphonic acid is capable of preventing reactions and if used in greater quantities inhibition



(1) ***Set quickly***	This corresponds to an acid level that is too low. Feedstock will polymerise whilst mixing.
(2) ***Danger zone***	This area is associated with chance polymerisation whilst mixing. Sometimes the monomer will react and other times it will not, it is best to avoid this zone at all costs.
(3) ***Safe zone***	The acid level is just right in this portion. The feedstock will not set whilst mixing and it will remain fluid for a short period until moulding is complete.
(4) ***Not set***	If too much acid is dissolved into the monomer, the feedstock can take a long time to polymerise. For example, feedstock has been known to remain in a fluid state for 4 weeks without any signs of polymerisation (within a sealed container) [16].

Figure 1. Working window for acidity levels of inhibited monomer

can be for hours [14], providing that a strong base initiator is not introduced to the monomer. Moreover, polymerisation can be initiated by using surface catalysts such as caffeine, pyridine, t-butylamine and free surface moisture.

Inhibition level is very important when the feedstock is moulded, premature polymerisation could ruin a moulding machine and take hours to clean, and therefore, a balance has to be made. This leads to the development of a workable window for mixing feedstock as shown in figure 1. Use of the window is also useful when another parameter is introduced to a feedstock, such as a new powder. The alkalinity of individual powder batches is not discrete, thus changing the inhibition characteristics of a feedstock. Therefore, if parameters such as powder type are adjusted, acidity levels need to be empirically determined.

3. THE MOULDING PROCESS

Historically, cyanoacrylate was created as an adhesive, bonding a wide range of materials from metals to rubbers in seconds. When used as a binder it presents a problem associated with processing. Conventional PIM machines cannot be used for moulding because the binder will adhere to the barrel or screw surface. Therefore, it is feasible to develop a simple system for manufacturing low volume parts. A barrel for such a machine should be made from a material that cyanoacrylate will not adhere to such as polypropylene or polyethylene. However, a machine made from these materials would have little mechanical strength. A practical solution is to use a polymeric disposable barrel insert. Polypropylene tubing is relatively inexpensive and suited to the application, and hence a technique for moulding was developed as shown schematically in figure 2.

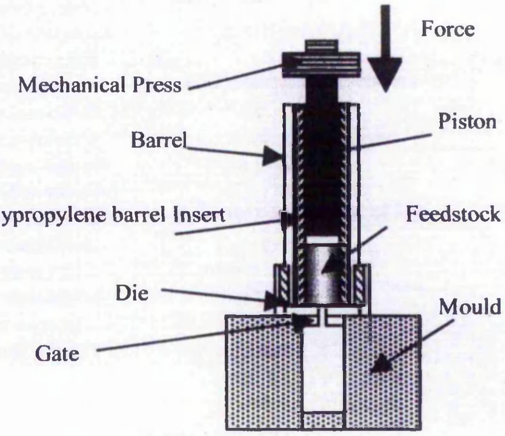


Figure 2. Moulding system

Part of the powder reaction moulding process is to react the feedstock within the mould. It is thought that this can be achieved by one of three methods. Firstly, surface initiation, secondly, a method of entering the catalyst in to the mould, or finally, air within the mould may be sufficient to cause a reaction. Each of these methods will be investigated to find the most efficient approach.

It is difficult to design a mould, because the rheological flow characteristics of the feedstock are unknown. Therefore, an empirical approach has to be employed. The basic requirements necessary in the mould design are as follows:

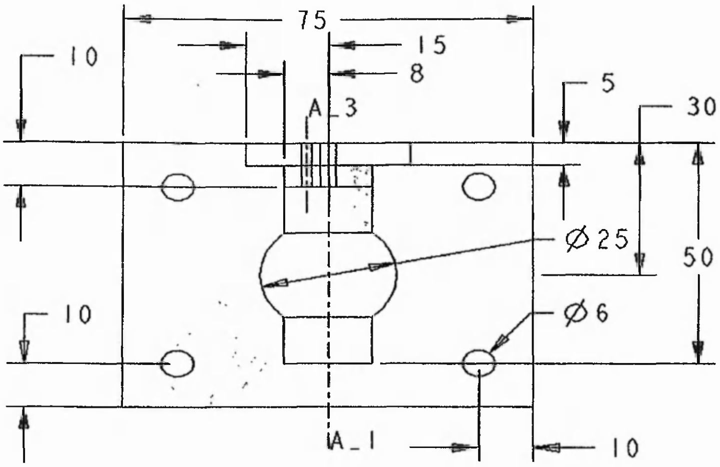


Figure 3. PTFE mould for solid conduit valve
(all dimensions are in mm)

- Sufficient mechanical strength to withstand moulding pressures
- Room temperature moulding
- Fixture of the moulding barrel to the mould inlet
- A high quality surface finish
- Releasing agent
- Material compatible with cyanoacrylate
- Inlet
- Vent(s)
- Release pins

4. MOULD DESIGN

Based on the above requirements a polytetraflouroethylene (PTFE or Teflon) mould representing a solid model of a conduit was designed and manufactured. This design was used to test the mouldability of feedstock and provide useful information about curing. Figure 3 is a diagram of the design (no release pins were implemented at this preliminary stage of design).

The Teflon mould was pre-prepared for use by treating the inner surfaces with a silicon oil surfactant to aid release of the formed part. A feedstock consisting of 0.45vf powder and 7% acid (by volume of binder) was injected in to the mould cavity using the arrangement shown in figure 2. The mould was left at room temperature for 7 days whilst the feedstock cured.

On opening, the formed surface in contact with the mould displayed a close replication and exhibited satisfactory curing. However, inspection revealed that the cyanoacrylate had not fully polymerised at the centre of the part. Further investigation of the mould highlighted a problem with machining. The Teflon had warped whilst the mould was being manufactured, probably caused by high temperatures produced when cutting. Therefore, the inner surfaces did not seal correctly during moulding, producing a part with excess flash. This can be eradicated by either changing the material to Nylon-66 or bracing the mould halves before and after the machining process.

Three methods of eliminating the problems encountered with moulding a ceramic part are;

(a) Provide a passage for a catalyst to enter the mould
(b) Control levels of acid inhibition using the working window method
(c) Limit parts to a small thickness

The development of a *conduit* part automatically meets two of the above recommendations. Firstly, a conduit could have a small thickness in its cross section and secondly, a sacrificial core similar to that used in mould manufacture in the 'lost wax' process will create a passage for a catalysing agent.

The 'lost wax' process involves thermally removing a wax insert after the feedstock has been formed around it. The wax fits inside the mould and its profile is transferred to the internal surface of the final part. Thus, it is essential that the wax be moulded to a high tolerance with an excellent surface finish. Removal of the insert was performed by suspending the sealed mould within a water bath, at a temperature above the melting point of the wax. After leaving the mould for a period, the wax melted out and evaporated exposing the inner surface of the moulded part. This then allowed water to enter the mould and subsequently polymerise any remaining uncured feedstock.

To test the process an aluminium mould was designed to create wax inserts with a diameter of 8mm. This insert was fitted inside a Nylon-66 mould with an internal diameter of 19mm, hence a hollow cylinder with a thickness of 5.5mm was created. Figure 4 is a CAD model of the aluminium mould for wax inserts, figure 5 details the arrangement of the wax insert inside the Nylon-66 mould.

Inserts were created by casting molten paraffin wax in a pre-heated mould, to eradicate distortion caused by rapid cooling. These inserts and the surface of the Nylon 66 mould

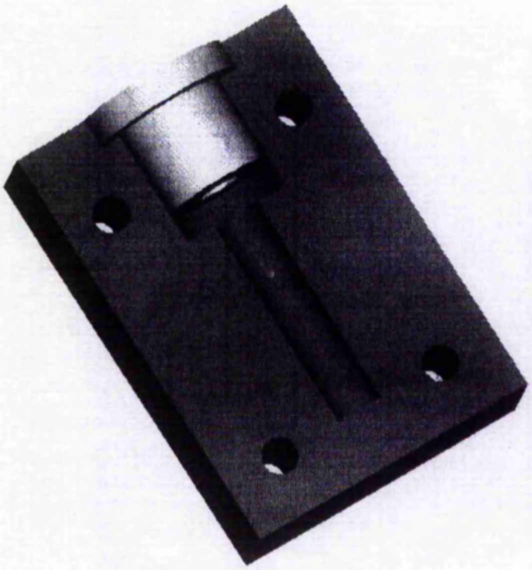


Figure 4. Aluminium mould half for wax inserts

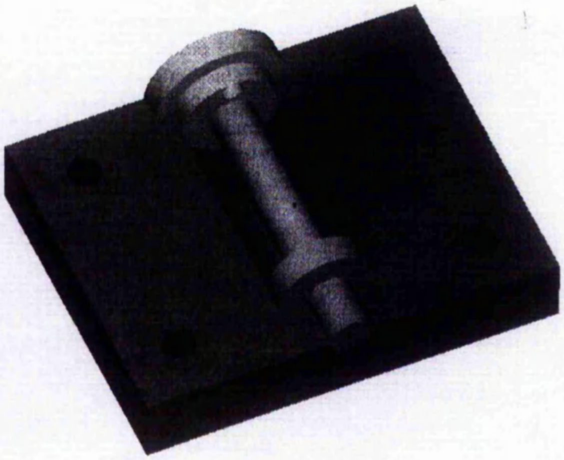


Figure 5. Nylon-66 mould half with wax insert included

were then treated with a silicon oil surfactant as a releasing agent. After the Nylon mould was clamped, a 0.45 volume fraction feedstock inhibited with 7% acid was injected via the standard method and left to cure for seven days.

Before opening the Nylon mould, it was suspended in a water bath at 90°C for 2 hours, subsequently the wax melted out. On opening, the part had adhered to the inner surface, but no flash was noticed at the joining seam. Slight tapping on a steel block released the part for further inspection.

Pitting was noticeable on the part surface due to the difficulty releasing the part from the mould. However, the feedstock seemed to have completely polymerised on the internal surface. The external surface still showed signs of fluidity caused by lack of polymerisation even though the mould was left undisturbed for seven days. The sample was dimensionally accurate to the mould showing no signs of shrinkage through polymerisation. Figure 6 shows a photograph of the finished part.

Figure 6. Photograph of moulded cyanoacrylate/alumina

5. IMPROVED MOULD DESIGN

Observations made with the Teflon\Nylon\wax technology highlighted problems that were overcome by changing the moulding process. A novel metallic alloy mould and core was designed to accommodate the form of a complex conduit part, offering many advantages over the basic mould design, as detailed below.

(1) Any mould material can be used with a melting temperature lower than the de-binding point such as a low melting alloy.
(2) Removal of the alloy mould and core by melting could allow the part to polymerise very quickly on the inner and *outer* surface, reducing processing time from 7 days to within hours.
(3) The part can be easily removed after processing, as there is no surface contact with the mould.
(4) An alloy material will not be damaged or collapse with the injection pressures associated with the process.
(5) The use of a mould material such as an alloy eliminates the warping problem encountered with machining nylon.
(6) A new material would be welcomed, as Nylon is expensive and prone to wear.
(7) No release pins are required.
(8) No mould release agent is required.
(9) The mould and core can be re-cycled

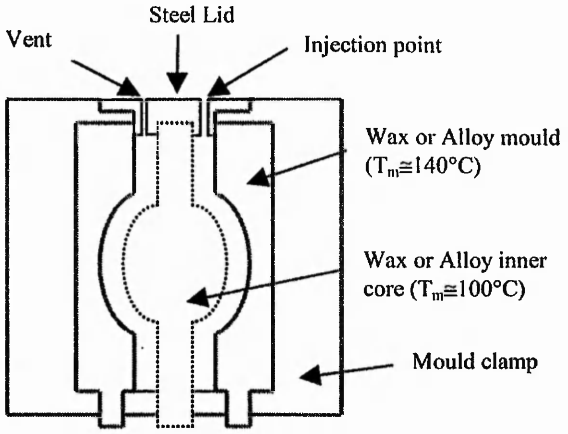


Figure 7. Moulding arrangement

Figure 7 is a schematic diagram of the mould arrangement, with the sacrificial core in-situ. The inner core was typically melted out at ≅100 Celsius and the outer shell at ≅140 Celsius to maintain integrity of the moulding prior to polymerisation. If the temperature raised above the latter value then the cyanoacrylate would start to thermally de-bind within the mould cavity.

Initially, wax was investigated as a material for the mould and insert because of its lower melting temperature. Five different waxes were compared for casting the shape of the outer mould. Table 1 details casting data and observations. The types of wax are detailed below.

Candelilla	Hard natural wax, very brittle and cracks easily
Carnauba -	Hard natural wax not as brittle as candelilla
Paraffin	Soft wax
Investment Casting	Mixture of polystyrene and paraffin wax

The wax inserts could not withstand the pressures of moulding and they cracked whilst feedstock was being injected. The observation highlights the fact that wax is an incorrect choice of material for the moulds even though the injection pressures are relatively low. Therefore, an alternative material such as a metallic alloy was investigated.

Two common types of alloy have melting temperatures below the de-binding threshold of approximately 150°C. These metals are alloys of tin/bismuth and tin/bismuth/lead, the latter having the lower melting temperature; indicating a suitable candidate for the insert. Table 2 lists casting temperatures and observations.

Table 1.
Wax casting information

No	Wax type	Melting Temperature (°C)	Casting Temperature (°C)	Mould Temperature (°C)	Observations
1	Carnauba	≈85	100	110	Little shrinkage, but cracks when cooling
2	Candelilla	≈85	100	110	Very brittle and cracks when cooling
3	Paraffin 1	52-65	80	90	Casts with little cracking but high shrinkage and very soft
4	Paraffin 2	75-82	90	100	Casts with little cracking but high shrinkage, soft
5	Investment Casting	63-70	90	65	Casts easier than natural waxes but cracks easy, extreme care required on cooling rates, very tough wax and malleable, noticeable shrinkage

Table 2.
Metallic alloys casting information

Alloy	Component	Melting Temperature (°C)	Casting Temperature (°C)	Mould Temperature (°C)	Observations
Tin/Lead/ Bismuth	Insert	104	120	85-90	Brittle but hard and dense
Tin/Lead	Outer mould	138	150	150	Hard dense material

6. RESULTS

Table 3
Moulding Observations

No.	Volume Fraction	Acid (%)	Insert Type	Mould Type	Insert melt temp (°C)	Mould melt temp (°C)	Observations		
							Cracks *1-bad 10-good*	Surface Quality *1-bad 10-good*	General
1	0.48	7	Paraffin Wax	Sn/Bi	95	155	8	6	Surface pitting related to internal collapse
2	0.48	6	Investment Wax	Sn/Bi	80	155	9	9	Internal collapse near injection point
3	0.48	6	Sn/Bi/Pb	Sn/Bi	110	150	3	6	Major internal collapse
4	0.48	6.2	Sn/Bi/Pb	Sn/Bi	110	155	8	5	Internal collapse, exotherm noted whilst moulding
5	0.47	8	Sn/Bi/Pb	Sn/Bi	110	150	N/a	2	Inversed mould whilst melted out core which caused serious collapse
6	0.48	7.5	Sn/Bi	Sn/Bi/Pb	N/a	110	N/a	N/a	Tried to melt outer mould first. Feedstock had not polymerised causing a termination
7	0.48	7.5	Sn/Bi	Investment Wax	N/a	N/a	N/a	N/a	Wax cracked whilst moulding even though supported by mould clamp

n.b. Surface quality represents pitting and smoothness

A feedstock consisting of 0.48vf alumina and 8% acid was used for moulding experiments. This level of inhibition is in the '*safe zone*' section of the working window, reducing the risk of premature polymerisation. Wax and alloy inserts were used for experimentation to find the one that produces the highest surface quality of the conduit part.

Table 3 details observations made from forming the feedstock around wax and alloy inserts. The moulding process was successful; each part was effectively removed from the mould without any external damage. However, the feedstock collapsed in all cases as the insert was melted out. Further investigation of the damaged parts indicated that the collapse is probably caused by the lack of support for the feedstock when the insert is removed. Hence, a method of accelerating the polymerisation reaction is required. Sample 2 and 3 were moulded with a surface initiator applied to the insert, however, it had no noticeable effect and other methods are required to polymerise the feedstock. Figure 8 shows sample 1 as moulded

A novel design has been implemented that uses a wax skeleton to surround and support the feedstock whilst in the mould. Removal of this skeleton allows the passage of a catalyst direct to the surface of the binder, causing polymerisation soon after contact. The feedstock then has extra support from the polymerised shell enabling the insert to be melted from the mould without dragging the binder and powder with it. Figure 9 demonstrates the new design with the cavity for a wax skeleton.

Figure 8. Moulded conduit (sample 1)

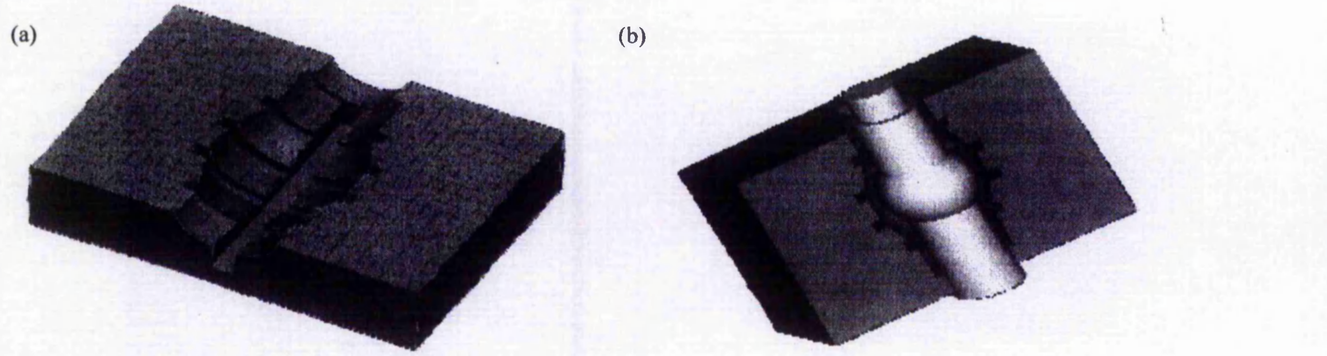


Figure 9. (a) the new mould showing the skeleton formation, (b) the new mould with an insert in position

Table 4
Moulding observations with wax skeleton included

No.	Insert Type	Mould Type	Skeleton type	Skeleton melt temp (°C)	Insert melt temp (°C)	Mould melt temp (°C)	Observations		
							Cracks *1-bad 10-good*	Surface Quality *1-bad 10-good*	General
8	Sn/Bi/Pb	Sn/Bi	Paraffin	85	120	155	10	8	Slight internal imperfections, paraffin wax compressed with moulding pressures indicated by raised lumps on outer surface
9	Sn/Bi/Pb	Sn/Bi	Investment Wax	80	120	155	8	9	Slight internal imperfections, investment casting wax caused little external surface imperfections
10	Sn/Bi/Pb	Sn/Bi	Investment Wax	80	120	155	10	9	Virtually no internal imperfections, although external pitting. Noticed that a large amount of feedstock appeared through wax injection points whilst moulding

n.b. Surface quality represents pitting and smoothness

This method works very well and the problem of massive internal collapse has been resolved as noted in table 4. However, there was still a slight imperfection near the injection and venting point of the mould, common to all the moulded conduits. This phenomenon is either connected to the venting position of the mould or an internal pressure build-up within the feedstock. The latter of these suggestions indicates that when the insert was removed a pressure relief caused slight collapse.

From these observations, the wax skeleton provides either,

(1) a passage for the catalyst to contact the surface of the part, polymerising the feedstock therefore supplying a structural support for the feedstock whilst the core is melted out

or

(2) two extra points of venting which may relieve the internal pressure built-up in the feedstock whilst moulding

7. CONCLUSIONS

(1) Powder reaction moulding is a novel process that requires a re-design of conventional moulding apparatus. High pressures and temperature control are not required for a low viscous cyanoacrylate feedstock. Therefore, a simple press is used to apply low forces within the injection cycle.

(2) The volatile nature of cyanoacrylate has forced the requirement of a polypropylene insert within the moulding barrel. This novel approach to moulding has enabled a simplistic method of cleaning the apparatus after moulding, by disposal of the insert.

(3) Nylon and Teflon are suitable mould materials because cyanoacrylate will not adhere to the surfaces, however, these materials are expensive and difficult to machine. Therefore, a system has been developed utilising a metallic alloy mould that is melted away after processing, thus eradicating any problems associated with adhesion of the binder. Removal of the mould and insert allows the ingress of a catalysing agent such as water.

(4) The utilisation of an alloy moulding platform has enabled the creation of complex conduit parts which can be debound within minutes. This novel system is relatively simple and inexpensive in comparison to conventional moulding equipment, which has high costs and complexity.

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METHOD AND APPARATUS FOR MANUFACTURING CONDUIT ARTICLES

This invention relates to an apparatus and method of producing articles. More particularly but not exclusively this invention relates to a method of moulding conduit articles.

It is known to produce articles such as artificial heart valves by conventional processing techniques. Such processes include injection moulding a polymer with dispersed metallic or ceramic powders. In powder injection moulding processors, temperature and pressure are varied to deliver feedstock to the die. A feedstock is mounted within a moulding barrel to inject a show of molten feedstock. Normally the feedstock is at a higher temperature than the mould tooling and as the feedstock cools the viscosity rises and therefore extra pressure is required to fill the cavity.

Powder injection moulding is a process usually employed with high volume production of articles and less suitable for small production numbers such as heart valves.

Another known method of production is powder reaction compression moulding. Powder reaction moulding is different to the conventional powder injection moulding technique in that the moulding takes place at a constant relatively low temperature and at a relatively low pressure. Moulding at a constant temperature reduces the complexity of the moulding process, for example no viscosity/temperature relationships need to be considered and the machine tooling is simplified as the thermal transfer coefficients are less important. Powder reaction moulding involves the dispersion of suitable metallic or ceramic powders within reactive carriers or binders followed by shaping and sintering the formed article. After injection of the feedstock into a mould, the carrier or binder must then be removed or 'debound' from the feedstock. When the binder is removed from the moulded article, the article is then sintered. The polymer or wax decomposition reactions occur relatively slowly and the mechanism and the rate of binding degradation and the diffusion characteristics of the volatile fragments determine the duration of this stage of the process.

Recent attempts have been made to decrease the debinding time. For example it has been proposed to use a reactive monomer such as cyanoacrylate, which has a capability for more rapid solidification through polymerisation. However, since the feedstock is contained within the mould it is difficult for a catalyst to contact it directly.

This is a particular problem with cylindrical moulded shapes since it is generally only possible to polymerise two surfaces and this propagation of the catalyst in to the moulded feedstock is time consuming. It may even be impossible for large depths.

The binder is removed, by polymerisation, from the moulded product and then reused. The binder may be removed by either dissolving it within a soluble solution or by heating the component to such a temperature that the binder has a sufficiently low enough viscosity to flow into a wicking substrate. A further method of binder removal is diffusion or permeation following depolymerisation or thermal decomposition of the binder. It is also known to combine these techniques to try and reduce debinding times.

Debinding is an important part of the moulding process although problems such as loss of shape, discolouration, cracks and surface pits are associated with it.

UK patent number 2 300 590 B discloses a powder injection moulding process employing a carrier having a ceramic or metallic powder dispersed therein. The monomeric or oligormeric composition is reversibly polymerisable so as to yield a solid polymer, which in turn is capable of undergoing a thermally activated depolymerisation reaction so as to provide the monomeric or oligormeric composition in fluid form. Thus the use of such a reactive monomer has the advantage of rapid solidification through polymerisation. The binder or carrier is a reactive monomer such as a cyanoacrylate. It has also been proposed to use ethyl cyanoacrylate or butyl cyanoacrylate.

However, cyanoacrylate was historically created as an adhesive (superglue) for bonding a wide range of materials in a very short period of time. Thus its use as a binder causes problems, since it has a tendency to adhere to the barrel or screw surface of the moulding apparatus.

It is also desirable for moulded articles such as heart valves to be seamless thus increasing the service reliability.

It is an object of the invention, therefore, to provide a method and apparatus for moulding articles, which attempts to alleviate the aforementioned problems and provide improvements generally.

According to the invention there is a provided a method of producing a moulded article comprising the steps of:

(a) providing a mould and a substrate in the mould;
(b) providing a feedstock in the mould and at least partially spaced from the internal surface of the mould by said substrate;
(c) moulding said feedstock;
(d) removing said substrate from the mould;
and
(e) providing a catalyst within said mould so as to polymerise said feedstock

Also according to the invention there is provided a mould comprising a internal hollow portion the walls of said hollow portion being formed with channels.

Also according to the invention there is provided a method of producing a moulded article comprising the steps of:

(a) providing a mould;
(b) providing a feedstock in the mould;
(c) moulding said feedstock;
(d) melting said mould such that said mould is removed from said feedstock

Also according to the invention there is provided apparatus for supplying feedstock to a mould comprising a hollow container, adapted to be connected to a mould, a removable sleeve located inside said container for receiving feedstock and pressure means for supplying said feedstock to said mould wherein said sleeve is provided as a carrier for said feedstock.

An embodiment of the invention will now be described by way of example, with reference to the accompanying drawings in which:

Figure 1 is a perspective view of prior art moulding apparatus;

Figure 2 is a perspective view of mould apparatus according to an embodiment of the invention;

Figure 3 is a pictorial representation of one half of a mould according to an embodiment of the invention;

Figure 4 is a perspective view of one half of a mould according to an embodiment of the invention;

And

Figure 5 is a perspective view of the mould half of figure 4 with a core insert in position.

A simple moulding apparatus 10 is shown in figure 1. A moulding mixture 12, commonly known as the feedstock, is positioned within a barrel 14 and pushed into a mould 16 by a piston 18. In powder injection moulding, the feedstock is heated within the barrel whilst mixing and pressurising it with a reciprocating screw. This embodiment of the invention refers to a powder reaction moulding but it is to be noted that the invention is equally applicable to injection moulding processes.

Referring now to figure 2 moulding apparatus shown generally at 18. A barrel 20 is generally cylindrical and mounted, at one end, within a die 22. A removable sleeve 24 manufactured from polypropylene or polyethylene is mounted within external barrel 20. This sleeve 24 is manufactured from a material that cyanoacrylate will not readily adhere to. Polypropylene or polyethylene are examples although other suitable materials may be employed.

The outer barrel 20 is required to have some mechanical strength and hence the sleeve 24 performs the function of supplying a 'non-stick' surface and being disposable or reusable itself. Feedstock 26 is mounted within the sleeve 24 and pushed into the lower end of the sleeve 24 by piston 28. The feedstock 28 formulation depends on the article to be moulded. With specific regard to heart valves the feedstock may comprise a mixture of cyanoacrylate and alumina powder particles.

The sleeve 24 is removable and may be reused. Advantageously, the sleeve ma also be moveable within the barrel so as to 'carry' the cyanoacrylate boxed feedstock. Without the use of a sleeve the feedstock comprising cyanoacrylate would have a tendency to adhere to the inner surface of the barrel 20. The sleeve is provided as a 'non-stick' carrier. It is envisaged that the sleeve 24 may also be moveable within the external barrel 20 if this is necessary during an injection moulding process for example.

Continued force of the piston 28 forces the feedstock 26 through the die 22 and into the mould 30 through gate 32.

Now referring to figures 3 to 6 mould 30 includes a wax or alloy inner core 32 housed within the mould 30. Mould 30 is also manufactured from wax or alloy itself and formed in two halves. A steel lid 34 is provided at one end of the mould and is positioned over the core 32. An injection point 36 is provided is provided in the top end of the core to allow ingress of the feedstock. The top portion of the mould is provided with a vent 38 to allow gases to escape and hence relieving internal pressure build up in the feedstock during the moulding operation. The two halves of the mould are positioned, in use, so as to abut one another by mould clamp 40.

The inside of the mould is formed with a series of channels 42. The channels are filled with investment casting wax or another suitable material and then the feedstock is poured or forced into the mould 30 around inner core 32. After the feedstock 26 has at least partially formed into its desired shape, the wax within the channels is removed by heating to a high enough temperature to melt the wax without affecting thee feedstock and core. This may be achieved by placing the mould in a water bath at approximately 10 degrees Celsius above the wax melting point. The investment casting wax is then melted out and water enters the void where the wax 'skeleton' was previously positioned.

Once the wax has been removed the moulded feedstock is then at least partially polymerised.

In an embodiment of the invention the channels are then filled with a suitable catalyst such as water which has the effect of initiating polymerisation of the cyanoacrylate or other similar feedstock material. Advantageously the catalyst can reach the surface of the feedstock. After polymerisation the polymer is at least semi-solid and is then removed from the mould 30 or the mould removed by melting.

In this embodiment of the invention the mould 30 itself is removed by placing the mould including the feedstock in an oven, for example, and melting the mould such that the feedstock 26 remains. The melted mould 30 may then be reformed to provide further moulds.

Once the polymerising process is complete the article is then removed from the mould 30 and then placed in an oven at a suitable temperature, for sintering so as to bind the particles of the moulded article.

Inner core 32 is manufactured so as to be 'sacrificial' in the moulding process. As such the melting point of the mould is higher than that of the inner core 32. In this embodiment of the invention the inner core melting point is approximately 100 degrees Celsius and the melting point of the mould 30 is approximately 140 degrees Celsius.

The core is removed from the moulded feedstock whilst the feedstock 26 is still in the mould 30. The core is removed by heating the mould and feedstock to a suitable temperature to melt the inner core and remove by draining away. The outer mould 30 is then removed.

The inner core is then placed in an oven, melted and re-cast for the next moulding operation/

Advantageously after the wax in the channels has been removed, the channels 42 allow the ingress of water or other suitable catalyst to perform the catalysing function. It had been previously difficult to both allow the feedstock to react with a catalyst coated on the inner surface of the mould, as is common in powder reaction moulding processes.

It is also envisaged that the catalyst could be applied to the feedstock in the mould by incorporating a suitable catalyst within the mould material.

The catalyst becomes reactive when the feedstock contacts the inner surface of the mould.

In an embodiment of the invention the moulded article is also easily removed from the mould since there is no surface contact with the mould 30 thus no mould release agent is required.

The moulded 'green' article may then be easily machined into its desired form.

CLAIMS

1. A method of producing a moulded article comprising:
    (a) providing a mould and a substrate in the mould;
    (b) providing a feedstock in the mould and at least partially spaced from the internal surface of the mould by said substrate;
    (c) moulding said feedstock;
    (d) removing said substrate from the mould
    and
    (e) providing a catalyst within said mould so as to polymerise said feedstock

2. A method of producing an article according to Claim 1, wherein said substrate is melted and drained from said mould.

3. A method of producing an article according to Claim 1 or Claim 2, wherein said substrate is wax.

4. A method of producing an article according to any one of the preceding claims wherein said moulding process comprises powder compression moulding.

5. A method of producing an article according to any one of the preceding claims wherein said moulding process comprises powder compression moulding.

6. A method of producing a mould article according to any one of the preceding claims wherein said feedstock is provided around a core such that the moulded article produced is a conduit article.

7. A mould comprising an internal hollow portion the walls of said internal hollow portion being formed with channels.

8. A method of producing a moulded article according to Claim 1 wherein said substrate is provided within channels formed within the internal walls of the mould.

9. A method of producing a moulded article according to Claim 1 wherein said substrate is provided within channels formed within the internal walls of the mould.

10. A method of producing a moulded article comprising steps of:

(a) providing a mould;
(b) providing a feedstock in the mould;
(c) moulding said feedstock;
(d) melting said mould such that said mould is removed from said feedstock.

11. A method of producing a moulded article according to Claim 10 wherein the melted mould is reformed into a mould shape.

12. Apparatus for supplying feedstock to a mould comprising a hollow container, adapted to be connected to a mould a removable sleeve located inside said container for receiving feedstock and pressure means for supplying said feedstock to said mould.

13. Apparatus according to Claim 12 wherein the internal surfaces of said sleeve are non-stick.

14. A method of producing a moulded article substantially as herein described with reference to the accompanying drawings.

15. A mould substantially as described herein with reference to the accompanying drawings.

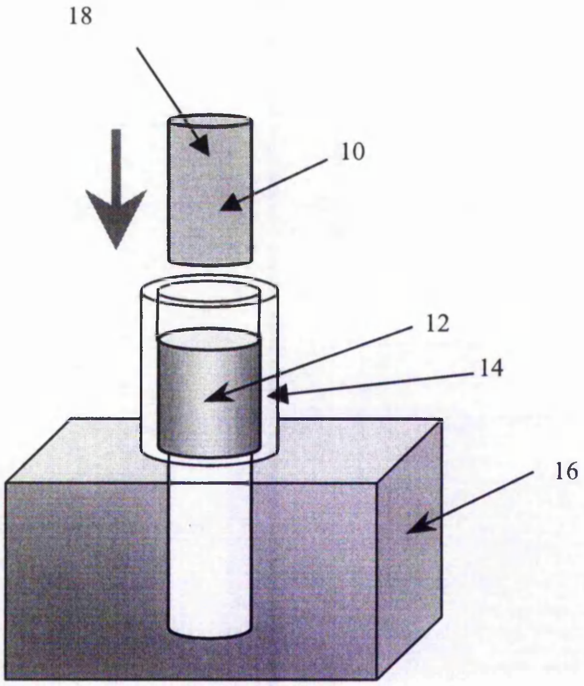

Figure 1

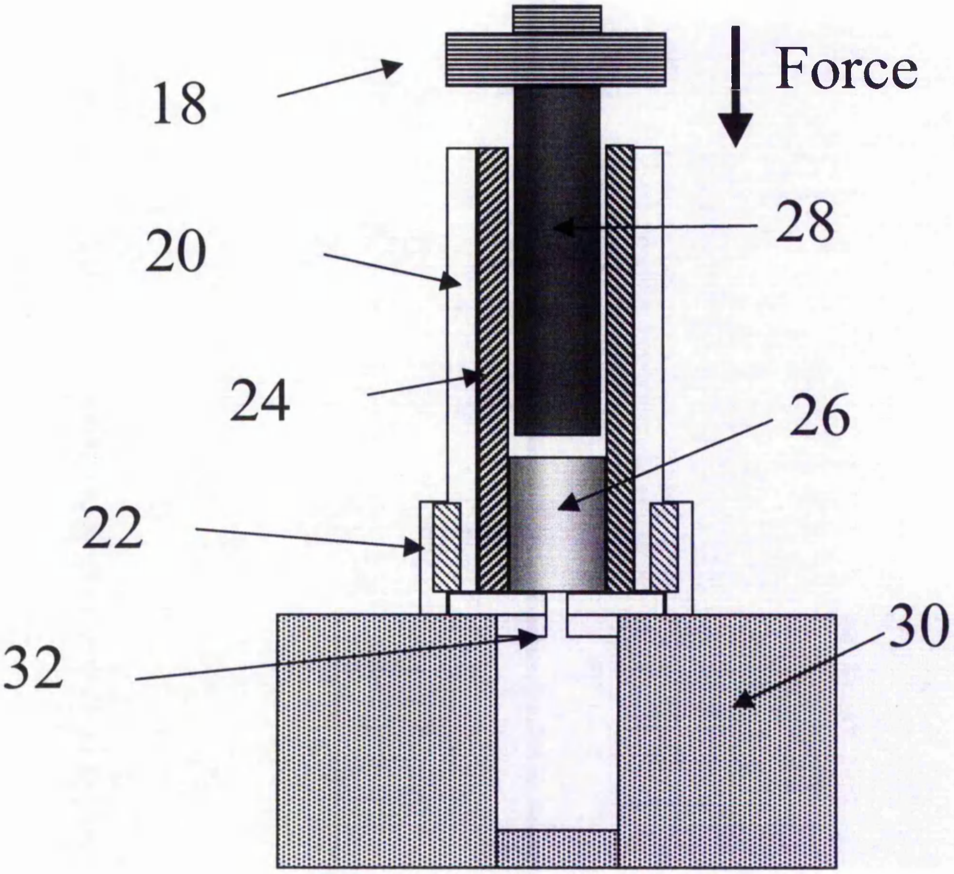

Figure 2

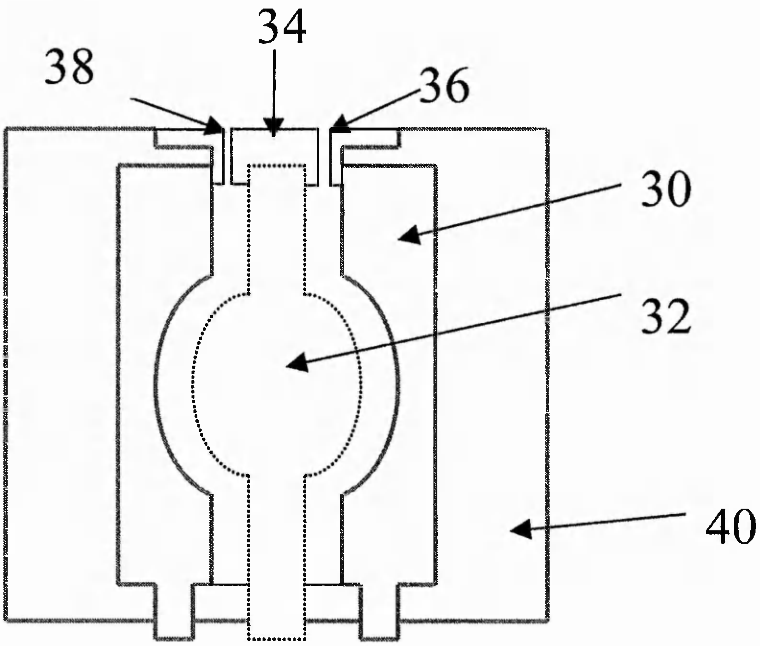

Figure 3.

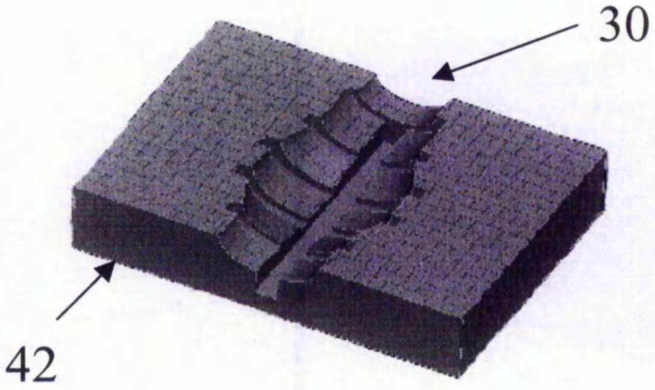

Figure 4

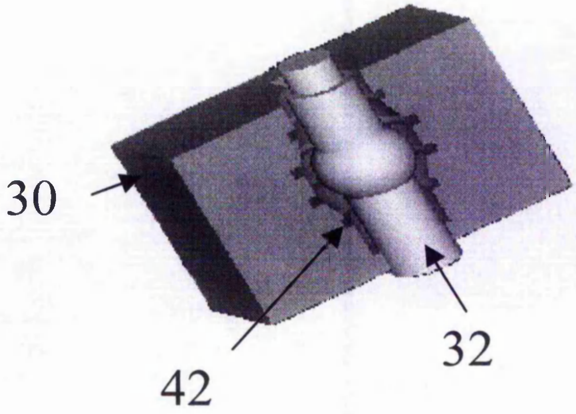

Figure 5

MACHINING OF GREEN CERAMIC COMPACTS PRODUCED BY POWDER REACTION MOULDING

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Abstract: Ceramic and metallic injection moulding has become a prime method for manufacturing complicated parts from a robust material. Typically, powder is dispersed within a thermoplastic carrier (or binder) before it is moulded at high temperatures and pressures. Further removal of the binder by thermal or solvent degradation methods yields a component that is suitable for sintering. Within industry, components have been manufactured with densities greater than 95% of theoretical. A new technology known as Powder Reaction Injection Moulding and Extrusion (P.R.I.M.E) has been developed using a cyanoacrylate binder that is commonly used as an adhesive. This new technology has been the basis of a major research program aimed at manufacturing artificial heart valves from alumina powders. A recent development is the ability to readily machine green compacts made in a similar way as the heart valve. This allows good tolerances to be attained and hence better control of the final dimensions of sintered components. This paper outlines the development of the machining process.

Keywords: Green Machining, Ceramic Processing, Moulding, Cyanoacrylate, Surface Roughness.

Introduction

Ceramics are being used more frequently for the production of engineering components and biomedical prosthetics. This increase in usage is directly related to the superior properties of this material such as resistance to wear, high temperature strength and resistance to corrosion. Applications that take advantage of these attributes are wide and varied, including, valves and valve seats, turbine blades and liners, cutting tools, artificial hip joints, dental prosthetics and artificial heart valves.

However, the properties of ceramics also have undesirable characteristics with respect to engineering fabrication. High hardness and low toughness present difficulties when machining monolithic ceramics. Therefore, bulk material removal is normally limited to the traditional approach of diamond grinding. Although diamond grinding is used for more than 80% of all machining performed on advanced ceramics [1], it is limited in the complexity of shapes that can be produced. Non-traditional machining techniques have been introduced to try and overcome this barrier. These processes rely on physical and chemical machining (P&C) to remove small, solid or gaseous particles from the part to be cut. P&C methods include ultrasonic machining, electrical discharge machining (EDM), laser beam machining (LBM) and electro chemical machining (ECM). However, these procedures have limitations in production, these include, a high initial investment cost and restrictions on the types of material that can be machined.

Currently only P&C and grinding techniques are employed to machine dense, sintered, ceramics. Therefore, the design of sophisticated ceramic components is limited to the complexity of P&C or the simplicity of grinding. An alternative approach to the forming of ceramics is to mould and then machine a component to a high tolerance prior to sintering, using a simple traditional technique such as turning. This process, known as ‘green machining’, occurs by particle attrition and is typically used for the production of spark plug insulators. However, ceramic binders cannot normally withstand the forces associated with traditional machining, this can often be attributed to the low fracture strength [2].

Powder Reaction Injection Moulding and Extrusion (PRIME) is a technique that involves mixing a reactive binder with a particulate material, moulding, debinding and finally sintering to near net density [3]. This process has proved to be successful for developing conduit articles out of ceramic, such as a prosthetic conduit heart valve [4]. The reactive binder used to create such components is butyl-cyanoacrylate. It has been possible to mould complex shapes when mixing this binder with aluminium oxide (alumina) powder at volume concentrations of ~50%. Components produced by this method appear to have substantial mechanical properties in the 'green' unfired state. Hence, the binder may provide adequate strength for green machining, which would enhance the possibilities of creating parts to a high tolerance, before being sintered. Articles produced by this method, including the prosthetic heart valve, would benefit greatly from this option, especially when surface finish is of prime concern.

This paper focuses on the machinability of an alumina/cyanoacrylate composite produced by PRIME, and investigates the obtainable surface finish from turning, in comparison to turning mild steel.

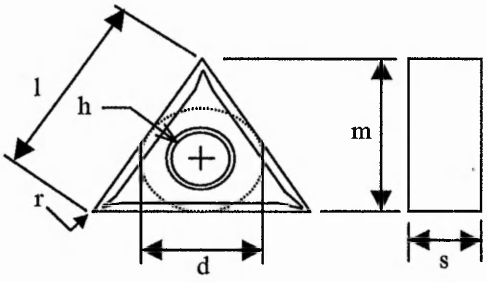
Experiments

Cyanoacrylate is an adhesive that is frequently used for its rapid ability to cure (or polymerise). When being used as a binder this will obviously cause severe problems whilst mixing, unless the reaction is inhibited. A strong acid, such as p-toluene sulphonic, is known to inhibit reactions allowing a sufficient quantity of powder to be mixed with the binder [5-6]. However, reaction can be initiated after moulding by introducing a catalyst to the mixture, such as water. The samples used for this study were inhibited with 8% acid by volume of binder, thus reducing the risk of polymerisation whilst moulding.

The moulding of samples required investigation with respect to the adhesive nature of the binder. Cylindrical compacts were needed for machining trials, thus the requirement of a simple mould that allows release of the part without damage. This ruled out a metallic mould because cyanoacrylate adheres quickly to the surface, especially if there are any pits or imperfections from fabrication. However, cyanoacrylate will not adhere to some polymeric materials such as polyethylene and polypropylene. Therefore, a polymeric (polypropylene) mould was selected for a moulding vessel, with a number of 1mm holes drilled throughout its entire length. This provided two advantages to processing,

(1) The part did not need to be removed from the polypropylene mould whilst machining. The mould was simply turned off, exposing the part for machining experiments.
(2) The 1mm holes in the mould allowed the ingress of a catalyst to the surface of the part, which would polymerise the binder.

Machining of the test pieces was performed on a Colchester Student 1800 series lathe. The required parameters included, tool type, tool material, tool geometry, cutting speed and feed rate. Ranges of feed rates at 3 cutting speeds were selected, along with a coated carbide tool with geometry as shown in figure 1. The tool was selected because of its suitability to small cuts below 2.5mm and feed rates up to 0.5mm/revolution. Furthermore, a nose radius of 0.4mm was selected for good chip control between the chosen feed rates of 28mm/min to 576mm/min.



l=16.5
d=9.52
s=4.76
r=0.4
h=3.81
m=13.89

All dimensions are in millimetres

Figure 1. Tool geometry

Green bodies (alumina\cyanoacrylate composites) were formed with a volume fraction of 0.48 (powder to binder) using the aforementioned moulding technique. The green bodies, and mild steel samples, were turned down to a diameter of 13mm (x), with a 0.5mm cut, and a 20mm(y) length for surface roughness inspection.

The surface characteristics of engineering materials have a direct effect on serviceability and thus cannot be ignored. There are many parameters that can be measured to characterise a surface, the most common being roughness, waviness and lay [7]. The net of the roughness and waviness is normally measured by a profileometer, which measures surface contours of the material. The arithmetic average or R_a of the peak to valley height of the surface is the most commonly used parameter to express a roughness value, usually measured in micrometres (µm). Therefore, the R_a value was determined for all samples, using a Taylor Hobson Tallysurf series. The profile of each sample was measured 4 times, and the high and low values of R_a were recorded.

The ideology behind the surface profile experiments was to form a basic understanding of the quality of surface that can be obtained, and a visual awareness of the fracture strength of this material.

Results

The green samples machined with ease, indicating that the fracture strength of the composite is within acceptable limits. However, the binder provides mechanical strength for the matrix, and if the volume fraction of powder were increased then the fracture strength will reduce significantly. Therefore, these results will change when parameters are altered such as powder type and loading.

The chips that were produced when machining can provide a basic indication of the machinability. Specimens were collected and examined under a scanning electron microscope for characteristics such as size and colour. Figure 2, shows the chip formation from a green machined sample.

Figure 2. Chips Produced from sample 4 (green)

The chips were discontinuous unlike the mild steel, which produced continuous chippings [8]. This indicates that the material is not as ductile as steel, probably due to the particulate nature of the green composite. Chips were not discoloured, and the workpiece had no evidence of excess friction. Moreover, it is known that cyanoacrylate will debind (de-polymerise) at temperatures exceeding 180 Celsius. As there was no indication of this on the surface of the samples, it can be concluded that coolant is not required whilst machining.

Table 1. Machining Data

Sample	Feed Rate (mm/min)	Cutting Speed (rpm)	Alumina/ Cyanoacrylate		Mild Steel	
			R_a High (µm)	R_a Low (µm)	R_a High (µm)	R_a Low (µm)
1	28	555	3.6	2.1	2.4	2.4
2	56	555	5.3	3.7	3.3	2.7
3	111	555	5.2	4.2	4.6	4.3
4	50	1000	3.4	1.9	0.9	0.9
5	100	1000	4.9	3.6	1.0	0.9
6	200	1000	5.6	3.2	2.5	1.9
7	108	1800	3.6	2.7	0.9	0.9
8	234	1800	7.0	4.6	1.8	1.7
9	576	1800	9.4	8.8	4.6	3.8

Table 1 details the surface roughness for the eighteen measured samples. Generally the surface quality of the green compacts is acceptable, with the roughness not exceeding 10μm. Furthermore, at 1000rpm, the average R_a value approached 2μm. A value below 2μm is considered to be a very good surface for a turning operation. Moreover, the mild steel proved to attain a good quality surface at the higher cutting speeds, whereas the green compacts were not as good, especially at higher feed rates.

The large deviation of R_a values for the green compacts is characteristic of particulate composites. At high speed and feed rates, particles of powder tend to 'pull out' of the surface, leading to pits, and subsequently a rougher surface. This phenomenon can be seen by examining the actual profile of the machined samples as shown in figures 3 and 4.

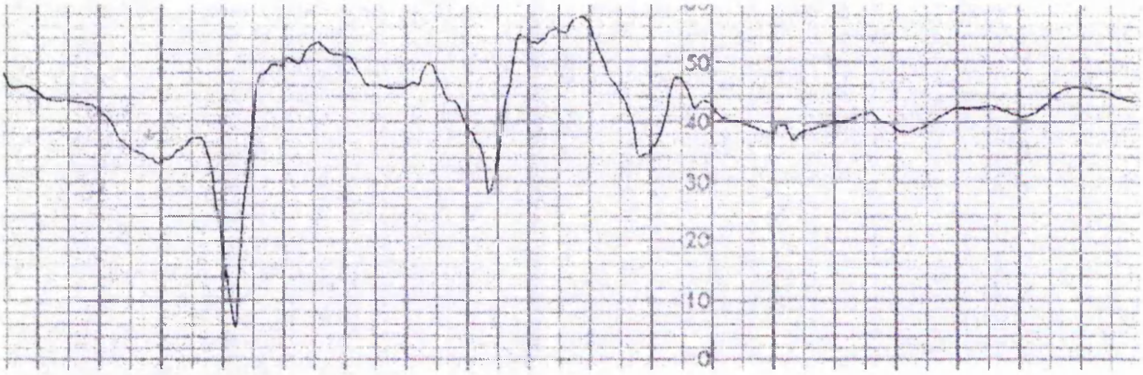


Figure 3. Surface profile of sample 8 (green compact)

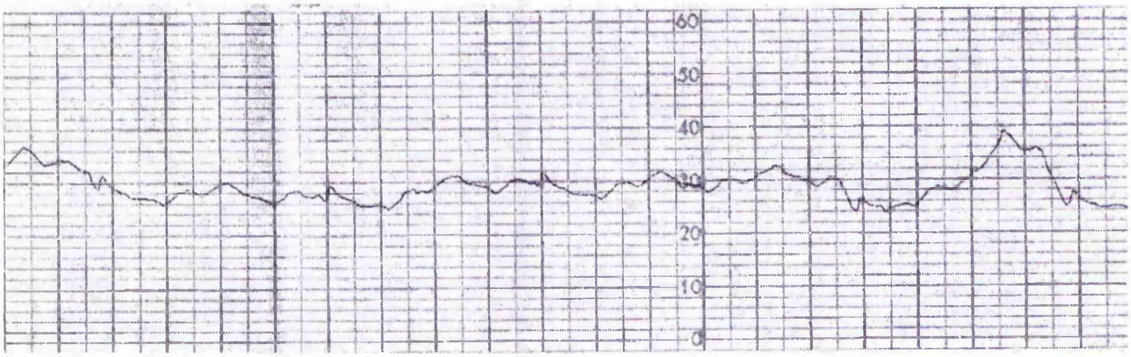


Figure 4. Surface profile of sample 6 (mild steel)

It can be seen that figure 3 has a much coarser surface, with large peaks and troughs, arising from 'pull outs' whilst machining. In comparison, figure 4 has a much smoother profile, which is characteristic of a good turned surface normally achieved with mild steel. A method to alleviate this problem would be to use a ceramic with a smaller particle size. Therefore, 'pull outs' would be limited to the size of the particles, and the surface quality may improve. However, smaller particles tend to agglomerate whilst preparing compacts, which lowers the attainable volume fraction of powder to binder.

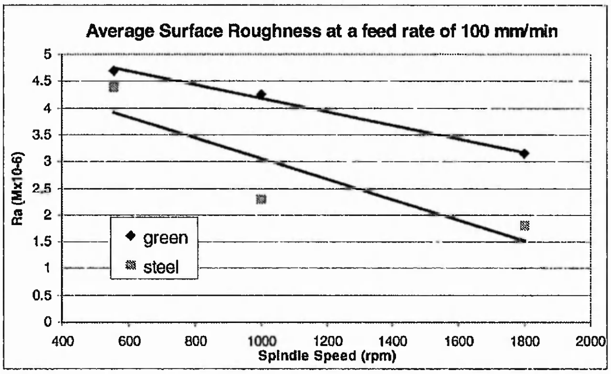


Figure 5. Average surface roughness at a feed rate of 100mm/min

Figure 5 is a plot of the roughness against cutting speeds at a feed rate of 100mm/min. It can be seen that the Ra value of the green compacts decreases as the speed increases. Therefore, as with steel, an increase in cutting speed and a low feed rate, is required to attain finer finishes.

Conclusions

(1) Polypropylene is a valuable material for the moulding of green compacts by PRIME.The moulds can be drilled to allow the ingress of a catalyst to polymerise the binder, and whilst machining, the mould can be turned down to the required diameter of the compact.

(2) Samples turned with ease, suggesting that the binder material has a sufficiently high fracture toughness for green machining.

(3) Chip formation whilst machining suggests that the compacts have a brittle nature. Inspection of the chips and the compact surface showed no sign of de-binding, therefore, no coolant is required whilst turning at these cutting speeds and feeds.

(4) The surface of the green compacts fell within a R_a range of 10µm, with some samples approaching 2µm. For turning operations, these are acceptable limits indicating a good surface finish.

(5) Large deviations were found between the R_a values for the green compacts, caused by 'pull outs' from the material. Adjusting the powder parameters such as volume fraction, particle size and shape can reduce this.

(6) The compacts turned with similar characteristics to mild steel, when the cutting speed was increased at a low feed rate the surface finish subsequently increased.

This exercise has proved that there is a good potential for the green machining of an alumina/cyanoacrylate composite produced by PRIME. Combining moulding and machining routes without the investment of expensive P&C equipment can create articles that require a good surface finish.

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DEVELOPMENT OF A RHEOLOGICAL MODEL FOR AN ALUMINA/CYANOACRYLATE FEEDSTOCK

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1. INTRODUCTION

Powder injection moulding (PIM) is a technique used to create complex parts from metallic or ceramic powders. The process involves mixing a polymeric binder and powder in a heated environment to form a paste. This paste is then forced under high pressure in to a mould, where subsequent cooling produces a shaped part. Thermal degradation methods are then employed to remove the binder from the powder, leaving a fragile shape. The final process involves sintering the powder to a level that normally approaches a near net density.

A novel method has been developed for moulding components using a technique similar to PIM [1]. In this process, ceramic powder is dispersed in to a reactive binder, such as Cyanoacrylate, which is then moulded to form a desired shape. The main difference with this method is that the binder cures within an alloy mould, which is subsequently removed from the component by a thermal technique [2]. Moreover, Cyanoacrylate is known to rapidly debind in comparison to polymeric binders, thus reducing processing time down to minutes instead of hours.

The feedstock used for PIM operations has sophisticated characteristics, because the paste contains powder particles mixed with a liquid binder. Therefore, it is useful to know the rheological properties of the binder when designing a component. Moreover, mould design and pressure analysis is normally difficult to assess, because of the viscous nature of a powder filled binder. Hence, research has been focussed on producing models to determine the flow behaviour, which will aid the design of PIM systems.

PIM feedstock are very complex, thus requiring a sophisticated model to determine the rheological behaviour, because the power law alone does not generally fit a powder system with multiple constituents. Therefore, a single binder system using a unique feedstock, such as Alumina/Cyanoacrylte, could be modelled using a simple relationship like the power law.

This paper investigates the rheological aspects of an Alumina/Cyanoacrylate feedstock to determine an equation that can be used to model flow properties. The binder used in this feedstock is different to standard polymeric binders, where the rheological properties are generally well understood. Therefore, this novel feedstock requires a practical investigation to determine a relationship between shear stress and shear rate, which will enable a general understanding of this novel system.

2. MEASURING EQUIPMENT

A range of techniques is available for measuring viscosity. PIM feedstock is typically non-Newtonian and the measuring equipment used normally reflects this. Testing techniques for non-Newtonian materials therefore include the use of, rotating coaxial cylinders, rotating parallel plates, mixing rheometers, and cone-on-plate rheometers. The latter is commonly used for measuring the rheological properties of PIM systems, but it is generally limited to shear rates of less than $5000s^{-1}$. Hence, a capillary rheometer is typically used, because it matches the range of viscosity and shear rates encountered in practise [3]. However, cyanoacrylate is an adhesive binder and a capillary rheometer would be severely damaged if used for an analysing tool. Therefore, a cone and plate rheometer is the only option for measuring shear stress at a range of strain rates, with a cyanoacrylate binder, because the equipment can be easily disassembled.

3. RHEOLOGICAL INVESTIGATION

The rheological characteristics of Cyanoacrylate mixed with Alumina powder are required to determine whether this material combination is suitable for an injection moulding feedstock. In order to understand the rheological properties of this feedstock, a thorough investigation at a range of solids loading and shear rates is required.

There is a suitable range that the viscosity must be for moulding, especially when considering the viscous nature of a fluid loaded with a powder. It has been suggested that the viscosity of a binder alone should not increase over 10 Pa.s whilst moulding, and the feedstock has to remain below 1000 Pa.s [3]. Therefore, the range of solids loading used for investigation represents an injection mouldable feedstock composition, starting with a volume fraction of 0.4, increasing to 0.48. The aims of this investigation are listed below,

- Determine whether the feedstock is mouldable
- Determine the rheological characteristics at a range of solids loading
- Find the rheological relationship (Newtonian or non-Newtonian)
- Determine an equation for the characteristics
- To predict what the viscosity will be at higher shear rates
- Determine the shear stress and viscosity at shear rates between 5 and $4860s^{-1}$

The equipment used for this investigation was a Rheotest 2 series cone and plate rheometer. Sample temperature was maintained on this rheometer by pumping water at 22°C around the plate section, which was monitored by a thermocouple within the plate.

4. RESULTS

The three volume fractions of powder investigate do not show an individual trend that will define the rheological characteristics of that particular system. As shown in figure 1, there is a range of results for each powder loading, because of a batch variation between samples. This phenomenon is typical of PIM feedstocks, especially when binders are loaded to a high powder level. Hence, external factors such as mixture inhomogeneity, chance polymerisation, temperature, and density can all effect the results. A controllable factor that has a large influence is polymerisation. Therefore, large quantities of acid were dissolved in to the binder before these investigations, because it is known that this will inhibit Cyanoacrylate, thus reducing the risk of polymerisation [4].

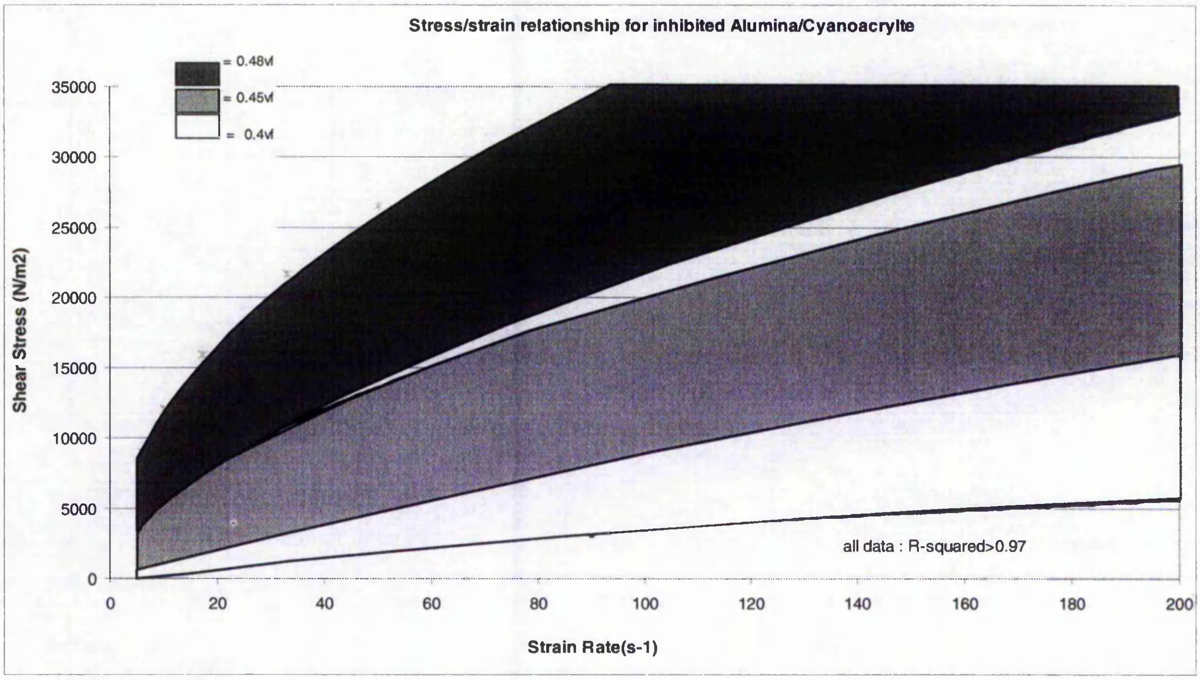

Figure 1. Rheological data from solids loading of 0.4, 0.45 and 0.48

The solids loading for mixed feedstock was limited to 0.48, because a higher loading will tend to increase the viscosity towards an infinite value, which is impractical for injection moulding. Unfortunately, a high solids loading, was difficult to measure at higher shear rates, especially with the cyanoacrylate binder. Samples mixed at a volume fraction of 0.48 caused extreme shear stresses when investigated, and the shear rate was limited to $90s^{-1}$. Moreover, mixtures with a low solid loading were measured at shear rates up to $270s^{-1}$, as torque became the limiting factor. However, the viscosity of the investigated samples was within limits for an injection moulding feedstock, except for the samples with a high solid loading at low shear rates below $10s^{-1}$, shown by the steep gradients in figure 1.

The feedstock experiences different flow fronts whilst being forced through a mould, such as corners, expansions and contractions. These changes obviously effect the rate of shear, which can be as high as 10^5s^{-1} when passing through a gate. Therefore, a prediction was made to find what the viscosity would be at a higher shear rate. It was found by interpolation that if the power law were maintained at a high rate of shear, then the viscosity would reduce to a level below 100 Pa.s. This value is very low in comparison to a highly loaded feedstock at low shear rates. A high solid loading is best suited to the moulding process, such as the sample that was mixed to a volume fraction of 0.48. Therefore, a rheological model was determined based on the results that experienced the highest viscosity at this level. The equations for shear stress and viscosity are shown in (1) and (2) respectively.

$$\tau = 3856 \,.\nabla^{0.48} \quad (\mathrm{N/m^2}) \tag{1}$$

$$\eta_a = 3856 \,.\nabla^{(0.48-1)} \quad (\mathrm{Pa.s}) \tag{2}$$

Where, ∇ = Shear rate (s^{-1})
η = Apparent viscosity (Pa.s)
τ = Shear stress (N/m^2)

5. CONCLUSIONS

(1) The results suggest that Alumina and Cyanoacrylate feedstock behave like a Non-Newtonian fluid, and agree to the power law at shear rates between $5s^{-1}$ and $270s^{-1}$.

(2) When making a prediction using the power law model, the viscosity reduced to 100 Pa.s compared to 1000 Pa.s at low shear rates. These levels are within an acceptable range for powder injection moulding. A high solids loading inevitably means a high stress when shearing a fluid. Therefore, the volume fraction of 0.48 for the Alumina powder was seen to be the limit for this feedstock combination.

(3) A power law equation has been developed, which is a good characterisation of this feedstock at high solids loading. If the characteristics change, such as particle shape, packing density, particle size, or processing temperature, then another feedstock would have to be investigated. However, this investigation was performed at 22C, which is similar to the processing conditions used for powder reaction injection moulding. Therefore, this model developed should stand whilst feedstock is being moulded.

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FLOW ANALYSIS OF A POWDER REACTION INJECTION MOULDING PROCESS FOR MANUFACTURING A CERAMIC HEART VALVE

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INTRODUCTION

A moulding system has been developed for creating a seamless conduit heart valve from an Aluminium Oxide powder mixed with a Cyanoacrylate binder [1]. The mould for such a system was designed using an alloy insert that was melted out to produce a conduit shape. However, problems were experienced when moulding, such as internal collapse of the feedstock when the core was removed. A novel method designed to reduce this effect was implemented using a wax-based 'skeleton' that surrounded the moulded feedstock. When the wax was melted out (before removal of the insert) water entered the mould and polymerised the feedstock where the skeleton was situated. This action prevented the feedstock from collapsing when the insert was melted out, thus producing a conduit heart valve with minimal surface defects. However, it was unknown why this process was successful, because it was difficult to obtain scientific data from the moulding process such as feedstock velocity and pressure when the mould was full. Therefore, it was apparent that an investigation was required using a computational fluid dynamics (CFD) analysis to determine the feedstock pressure.

METHOD

The aim of the investigation was to find the pressure distribution within the heart valve mould using CFD code. Therefore, a model of the mould was required to analyse the feedstock flow, and hence, produce a reasonable solution. The following items were thus investigated:

- CFD model
- Model validation using known flow data
- Application of the model to the alumina\cyanoacrylate feedstock

Two different alloy mould configurations have been investigated for creating the conduit heart valve. The first mould arrangement had a single inlet and outlet, and the second included the wax skeleton, which provided two extra vents for the feedstock. Models of these moulds were created for use within the PHOENICS CFD software, and hence, they were aptly identified as Novent and Twovent.

An analysis using CFD cannot be regarded as accurate until the geometric model used for the flow domain is justified with a comparison to a physical investigation. A plastic model of the heart valve mould was therefore manufactured to investigate flow pressure using water at various flow rates, by measuring the static head at strategic positions associated with the mould inlet and outlet. The measured pressure from the plastic mould was compared to computational analysis results using a laminar flow model, and hence, the geometric model was validated.

Before, the validated CFD model was used to find the pressure distribution within the heart valve, the feedstock pressure was investigated whilst a heart valve mould was filled. The heart valve moulds were cast and assembled using alloy inserts, and feedstock was mixed consisting of a high volume fraction of powder (0.48). This feedstock was loaded into a polypropylene insert that was placed inside the moulding barrel. Force was applied by the use of a hydraulic ram, whilst the feedstock pressure was measured from the output of a 50KN load cell, as a percentage of the cell rating. This data was taken every three seconds whilst each mould was filled until a steady flow occurred after feedstock had exited from the vents. Each reading was separated into one of three groups that outlined the stages of moulding, namely, 'start', 'filling' and 'full'. This data was averaged for that particular mould stage and converted into a pressure by dividing the force by the cross sectional area of the ram. These stages were noticed by the change in force required to maintain the flow rate throughout the mould. The results of this investigation are detailed in table 1. The mould resistance was calculated by taking the start pressure from the full pressure. These values were high but this was expected when moulding with a viscous feedstock at relatively low rates of shear. Nevertheless, these results were the only values that could be obtained from a practical mould fill analysis, since an investigation with transducers situated within the mould was difficult using a cyanoacrylate binder. Therefore, CFD was used to find the mould pressure, using the measured mould resistance for a data comparison.

Table 1. Pressure measurement results

Fill stage	Mould type	Average load (% of 50KN)	Load (KN)	Load (Tonnes)	Pressure (N/m^{2})	Pressure (Bar)
Start	Novent	21	10.5	1.05	30.3x10^{6}	303
	Twovent	21	10.6	1.06	30.5x10^{6}	305
Filling	Novent	28	14.0	1.40	40.4x10^{6}	404
	Twovent	27	13.8	1.38	39.8x10^{6}	398
Full	Novent	31	15.2	1.55	43.9x10^{6}	439
	Twovent	30	14.7	1.50	42.5x10^{6}	425

CFD ANALYSIS

The fluid dynamics of the mixed feedstock were investigated as a steady, fully developed flow through the models representing the alloy heart valve mould. The models had been validated to work correctly, and hence, an analysis was carried out with PHOENICS CFD code, to produce a greater understanding of the moulding process. This involved investigating the following aims:

- Determine the role that the wax skeleton plays within the alloy heart valve mould
- Determine regions of pressure and picture how the pressure is distributed with the two models

- Determine how the extra vents in the Twovent model effect the feedstock pressure distribution with respect to the Novent model
- Determine the highest feedstock pressure within the mould, and determine whether this will effect the internal collapse of feedstock (when the core is removed in the moulding process)

The rheological properties of the feedstock were determined using a Rheotest 2 series cone and plate rheometer [2]. A viscosity distribution was therefore developed that matched a power law at the investigated shear rates. This result was typical for a polymeric binder that would normally be used for powder injection moulding [3].

The boundary conditions and fluid properties for each model were entered into the pre-processor. The solver was run for 1000 iterations, which was sufficient for the numerical models to converge.

Regions of pressure were analysed from the post-processor, thus providing the maximum pressure data for the two mould configurations. This data was compared to the mould resistance, which was calculated from data in table 1, and hence, the results are detailed in table 2.

Table 2. Pressure data retrieved from the CFD investigation and pressure measured from the moulding investigation.

Investigation	Model	Maximum pressure (N/m^2)
CFD	Novent	126x10^6
	Twovent	109x10^6
Measured	Novent	136x10^6
	Twovent	120x10^6

There was a very low error between the CFD models, and the measured pressure values. For example, the Novent models had an error of 7.6%, whilst Twovent was 10.1%. It was therefore apparent that these models suited the physical data within an acceptable limit for the purposes of this investigation, and hence, pressure regions were determined from these models and comparisons made.

The pressure within the Twovent model was significantly lower than the pressure in the Novent model, because of the extra venting. The extra vents provided a pressure reduction of 15.6%, which was probably sufficient to stop the phenomenon of feedstock collapse when the insert was removed in the moulding process. It was apparent that the vents had made a large difference to the regions of pressure within the moulds, as shown in figure (1). Pressure within the Novent model was high around a large proportion of the mould, mainly around the upper regions. However, the Twovent model did not show signs of this high pressure region. In fact, the pressure was reduced significantly at the upper regions of the mould near the inlet. Hence, the venting positions (associated with the wax skeleton) were probably located in the correct position for the heart valve mould. This observation probably provided a partial explanation as to why the wax skeleton mould prevented internal collapse of the feedstock, because of the reduced pressure.

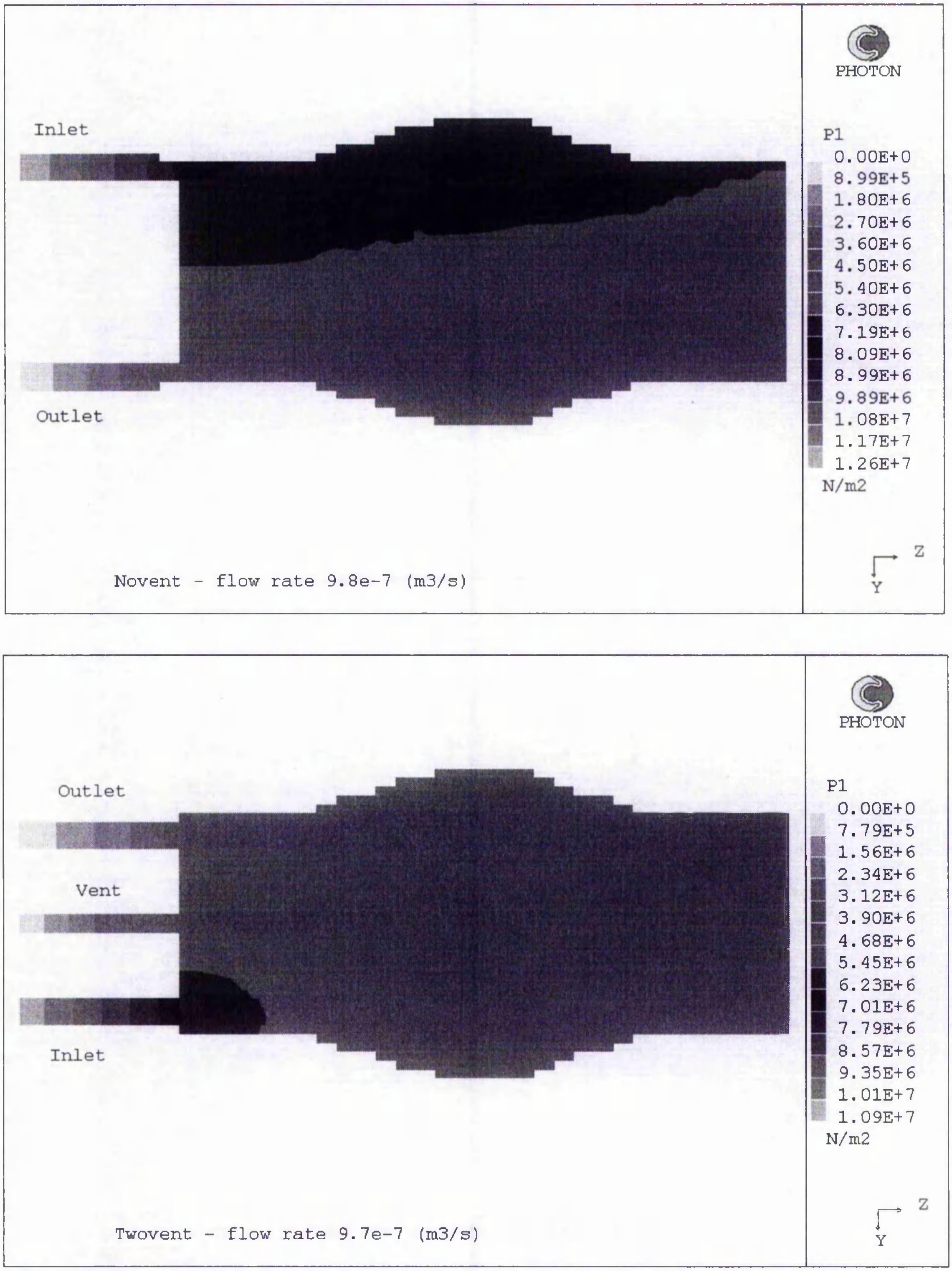

Figure 1. CFD result of pressure distribution through the conduit heart valve mould when the mould was full of feedstock

CONCLUSIONS

- Flow regions have been identified with the Novent and Twovent models, proving that the extra venting arrangement has contributed to a substantial pressure relief within the heart valve mould.
- The internal collapse of feedstock was probably associated with the large expanse of high pressure as shown with the Novent model. However, the Twovent model showed no signs of this pressure, thus proving that the extra vents had provided adequate pressure relief. Furthermore, it was thought that pressurised air in the Twovent mould would relieve more easily with the extra vents, thus reducing the risk of feedstock collapsing when the insert was removed.
- Finally, the two extra vents may have promoted a pressure relief preventing internal feedstock collapse. However, the polymerisation associated with removal of the wax skeleton probably provided the best support.

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