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INJECTION MOULDING OF CO-CR-MO ALLOY POWDER

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ABSTRACT

The Powder Injection Moulding (PIM) process is briefly reviewed with regard to its technology and process requirements. Powder injection moulding based on a new binder system, and using a Co-Cr-Mo alloy powder as a test material, is described. The binder system comprises a major fraction of a water-soluble oligomer and a minor fraction of a polymer incorporated in the form of an emulsion. Various processing stages of the PIM process, i.e. feedstock preparation, injection moulding, debinding and sintering have been discussed.

BACK GROUND

Powder Injection Moulding (PIM) is a fast growing modern process for the consolidation of metal and ceramic powders. The PIM process combines the plastic injection moulding technology and the conventional powder metallurgy principles. The combination of these technologies allows the complex-shapes to be produced to high densities and with uniform mechanical properties. Some of the advantages of PIM over conventional powder metallurgy are that it allows more design flexibility, closer tolerances and gives more uniform shrinkage during sintering.

Historically, the concept of injection moulding originated from the metal die casting industry wherein the technology of injecting molten metal into closed dies to obtain desired shapes evolved. Later, this moulding concept was successfully exploited in the plastic industry [1,2]. Powder injection moulding is an extension of the plastic injection moulding process. Since the late 1920's, PIM has been applied principally to the manufacture of ceramic components. As early as in 1929, patents were granted for ceramic injection moulding [3]. By 1937, the AC Spark Plug Division of General Motors was producing spark plugs insulators using injection moulding. The earliest paper that appeared in the open literature was by Schwartzwalder [4] in which he discussed the injection moulding of ceramic materials. Since then, engineers and technologists have strived to improve this process and make it acceptable for large-scale industrial applications. Following the publication of patents by River [5] in 1976 and Wiech [6-9] in 1980, 1981 and 1983, commercial development of metal injection moulding occurred rapidly, initially in the USA and then in Japan and Europe. PIM is commonly applied to produce a variety of components in the automotive, aerospace, electronic, industrial equipments and consumer products and medical/orthodontic industries.

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UET, Lahore since June, 1996. The main objective is to develop the PIM facilities in the Department and optimize the process for the cost-effective production of various industrial components. Moreover, the students will be trained for this new forming technology.

PROCESS OUTLINE

The PIM process involves mixing selected metal and ceramic powders with a suitable combination of binders, lubricants and plasticisers to produce a mixture (feedstock) that can be shaped by injection moulding. The shaped parts removed from the die contain, ideally, a uniform dispersion of powder and must have an adequate green strength and stiffness to be handled. Subsequently, the binder and other unwanted additives are removed from the compacts by a process known as "debinding". Then, the parts are sintered to densify the resulting porous compacts to yield near-net shape components. The parts shrink considerably during sintering and the final product is a reduced version of the as-moulded green shape. The product can be used without further processing or it may be further densified, heat-treated, machined or surface treated.

Fig. 1 shows a flow chart depicting the key steps involved in the PIM process. As noted in the figure, the basic stages involved in forming a component by PIM include the following [10,11]:

1. Selecting and tailoring a powder for the process;
2. Mixing the powder with a suitable binder for producing either a homogeneous slurry or grannular pellets of mixed powder and binder (i.e. feedstock);
3. Injection moulding of the feedstock to obtain the required shape;
4. Removing the binder from the moulded parts (debinding);
5. Densifying the compact by high-temperature sintering;
6. Post-sintering processing, as appropriate, including machining, heat treatment, surface finishing or further densification.

MATERIALS FOR PIM

The feedstock for powder injection moulding consists of two components, i.e. (a) the particulate materials and (b) the binder and other additives.

Particulate Materials

Generally, the PIM process begins with very fine metal/ceramic powders, typically less than 20μm in diameter, preferably 8 to 10μm for metals and 1 to 3μm for ceramics and cermets. There are several reasons for this requirement. One is to encourage a homogeneous dispersion of particulate matter in the mixed feedstock so that it should have suitable rheological properties to obtain uniform mould filling during injection moulding. Secondly, after moulding and debinding, shrinkage and densification during sintering should proceed faster with very fine powders since the rate of diffusion is inversely proportional to the square of the particle size [12]. Thus, finer powders have the advantage of better sinterability and ease of moulding and they expose the injection moulding machine screw to less risk of damage.

Almost any metal, alloy or ceramic which can be obtained in fine-particle form and which can be densified by sintering, can be shaped using injection moulding. There is considerable information available on powders that work well in powder injection moulding [13-15], but there are some apparent conflicts in the powder characteristics needed. For example, an irregularly shaped or ligmental powder will raise the viscosity of feedstock mixture and yield a lower packing density during injection moulding. This requires more binder (i.e. low powder loading) and results in more sintering shrinkage; however, due to particle interlocking, the shapes produced will have a high green strength increased compact strength after binder removal and better shape retention during sintering. On the contrary, a spherical powder results in high packing density and offers comparatively less resistance to flow during injection moulding, thereby minimizing the amount of binder that must be added as well as reducing the sintering shrinkage. However, because there is no mechanical interlocking between spherical particles, the green part will have a comparatively lower strength, especially after removal of the binder.

Binder and other Additives

The binder is not only a necessary aid for promoting viscous flow in the feedstock during injection moulding, but it should also maintain the shape of the green part after removal from the mould. After moulding, the binder has to be removed carefully without impairing the integrity of the moulded part. Even though the binder is just an intermediate processing aid, it has considerable influence on the success of the PIM process. A binder system that may produce excellent flow characteristics during moulding, but presents difficulties during its subsequent removal is not suitable for PIM purposes. Binder requirements have been discussed in various publications [16,17].

Generally, a binder system consists of the following components [18]:

1. Major binder component: This is responsible for holding the compact in shape during debinding until the commencement of sintering and determines to a large extent the final binder properties. It is normally a high molecular weight thermo-plastic; such as, polystyrene, poly-propylene and paraffin wax.
2. Minor binder component: This is generally added to alter the viscosity of the binder system and is removed early in the heat treatment (debinding). If this component, which is usually a thermo-plastic or an oil, forms a continuos separate phase, then its removal would create pore channels throughout the moulded product to facilitate the removal of the evolving gas(es). Examples are paraffin wax and beeswax.
3. Plasticisers: These minor additives are included to enhance the mouldability of the feedstock mixture. Examples are carnauba wax and glycerine.
4. Processing aids: Some minor additives (surfactants) are included to improve the wetting between the binder and powder. Other minor components may be used to facilitate release of the product from the mould.

There are a number of patented binder systems in use, but detailed information about their composition and mixing is generally not revealed. The most widely practiced are the Weich, the Rivers and the BASF systems.

Wiech suggested [6-9] a multi-component binder consisting of a mixture of low molecular weight polygropylene, paraffin wax, carnauba wax and stearic acid (PP/PW/CW/SA=20/66/10/4). The Wiech type binder system is widely employed for PIM with certain modifications and compositional changes. The binder system used in the Rivers process [5] is composed of methyl cellulose, glycerine, boric acid and water. A typical composition in terms of weight percentage is 25% methyl cellulose, 13% glycerine, 6% boric acid and 56% water. The composition of the BASF binder system is proprietary; however the essential component is a long-chain polyacetal polymer [19-21]. Recently, it has been reported[20] that the main binder component of the BASF system is a modified polyoxymethylene (POM), which can be removed at a much faster rate using a catalytic debinding process.

PREPARATION OF FEEDSTOCK

Once a powder and binder have been selected, the next concern is to mix these ingredients to produce an appropriate feedstock. In order to do this, the selected powders are mixed in precise proportions with suitable thermo-plastic binders and other additives. These polymeric additions often comprise as much as 30-40 volume percent of the feedstock. To obtain high density green compacts and reproducible results, it is essential to optimize the composition of the powder-binder mixture. In general, it is considered best to use the minimum amount of binder that gives good flow behavior since the binder must eventually be removed from the powder. However too little binder results in a highly viscous mixture causing mould filling difficulties and voids formation. During debinding, these voids can cause cracking due to internal vapor build-up, as a result of degradation of polymers. On the other hand, an excess of binders is wasteful and requires comparatively longer debinding times and also results in greater dimensional shrinkage during sintering. During moulding, excess binder can separate from the powder, leading to inhomogeneities in the moulded compact and possible dimensional control problems. Moreover, excessive binder loading levels usually cause deformation, sagging and blistering during subsequent binder removal stage. The ideal corresponds to the case where particles are coated with a uniform and very thin layer of binder and with no voids in the binder. Thus, it is necessary that the binder fills all of the void space between the particles while maintaining a reasonably low viscosity [22]. Different types of mixers are employed in the PIM industry. These include mixers incorporating plug extrusion, double planetary, twin-screw extrusion, sigma-blade, Z-blade, rolling mill and impeller concepts.

MOULDING

In its simplest form, moulding consists of heating the feedstock pellets/granules to a sufficiently high temperature such that the binder is melted and making the mixture fluid, then forcing this mixture into a cavity where it cools and forms and compact shape. The objectives is to attain the desired shape free of voids or other defects and with a homogenous

distribution of powder. The feedstock must therefore have sufficiently low viscosity at the moulding temperature to flow freely into the mould and subsequently to leave minimal residual stresses.

PIM processors have adopted the principles and equipment used in plastic injection moulding. Since the material properties and moulding requirements of PIM parts are substantially different from those of plastics, the injection moulding machines and techniques for PIM parts require modification. For example, the screw of a reciprocating injection moulding machine is usually made to rotate very rapidly at about 200-300 RPM in order to melt plastics efficiently by generating heat in the highly viscous plastics. Such high screw RPM would cause severe wear of the barrel because of the abrasive nature of the powders. As feedstocks loaded with metal powder have much higher thermal conductivities than those of polymers, it is easier to obtain a uniformly heated mass in the barrel of the moulding machine using heaters mounted on the barrel. However, when moulding metal powder mixtures, incomplete mould filling may occur due to premature freezing because of the more rapid heat transfer to the cold mould. Thus, excessive mould cooling must be avoided and precise control of the mould temperature is required. Some differences in mould design, and especially in the gating system, are needed to accommodate the highly viscous PIM feedstock provide.

DEBINDING

The binders have additives used in the moulding steps are removed by a processing which has come to be known as "debinding". Thus, a major difference between polymer injection moulding and powder injection moulding occurs after moulding, when the binder is removed from the compact prior to sintering.

German [23] has identified six debinding techniques which may be used in PIM, broadly categorized as either solvent or thermal processing, as shown in Fig. 2.

The debinding process may be a combination of more than one of these processes. Commercially, total thermal debinding and solvent extraction followed by thermal debinding are the two popular debinding methods. Recently, another techniques known as 'catalytic debinding' has been reported [19-21], whereby acidic vapors are used to remove the binder from green compacts produced from BASF feedstocks.

Solvent debinding generally offers better shape retention as well as a shorter cycle time compared to thermal debinding. The binders used in the common solvent debinding approach have an inherent disadvantage in mouldability, making it difficult to mould highly complex used debinding solvents. However, the recent trend is to use water-soluble binders [25-27]; thus water leaching is employed to remove a major proportion of the binder, which is quite a safe practice. Amaya [28] has reviewed the principles of solvent extraction and described its advantages and disadvantages with respect to thermal debinding.

Thermal debinding uses very low heating rates and thus requires long debinding times. High heating rates can results in distortion, slumping or even complete failure of the

component. For thermal debinding concurrent use of wicking enhances the shape retention. However, the removal of wicking powder after debinding is a time-consuming practice; therefore, the use of wicking may not be practicable in some commercial production [24]. The debinding temperatures and atmospheres have a great influence on the mechanical properties of the sintered compacts. For examples, if the debinding atmosphere contains some oxygen then there is always a possibility of formation of oxides. High temperatures accelerate the formation of oxides which may precipitate along the grain boundaries and also within grains. On the other hand, debinding in a reducing atmosphere [high h_2] may result in unwanted decarburisation.

Several methods have been developed in order to overcome the problems associated with classical thermal debinding. They are mainly based on the principle that a major fraction of the binder is removed chemically followed by a short thermal debinding treatment. With the solvent extraction method, the green component is immersed in a suitable organic fluid, which dissolves the binder partially. This results in the formation of open pore channels. Thus, the remaining binder partially. This results in the formation of open pore channels. Thus, the remaining binder fraction can be removed relatively easily and in a shorter time through the open pore structure by thermal means. In a recent development [19-21], a highly concentrated acid is added to the gas atmosphere in order to remove a binder based on polyoxymethylene by catalytic phase erosion, known as catalytic debinding. During debinding this binder develops formaldehyde. Thus, one problem with these methods is that they have to use special devices and/or chemical substances, which are partially hazardous for health and the environment.

SINTERING

Sintering is the bonding together of particles when heated to a high temperature. Though moulding and debinding steps are vital to the manufacture of parts, the final mechanical properties are dependent on the starting powder chemistry and sintering temperature, time and the atmosphere gases. Sintering is generally done in an appropriate atmosphere to prevent either the loss of critical elements such as carbon in steel or the contamination of the material by oxygen, nitrogen, or other materials which may be present during processing. Sintering can not correct defects introduced in earlier steps such as mixing, moulding, or debinding. The result of the sintering process is a near fully dense part with relatively low porosity.

Different types of furnaces and atmosphere are used for sintering, initially, parts were sintered in batch furnaces, but nowadays most fabricators are using continuos high temperature sintering furnaces. Once sintered, PIM parts can be used as such or may given supplementary treatments like machining, surface treatment or heat-treatment.

OBJECTIVE

The main objective of the present study was to develop a simple composite binder system which would fulfill the requirements of the PIM process and overcome certain problems associated with the conventional systems, such as the long hot mixing stage

typically required to form a homogenous feedstock and the long times required for removal of the polymeric binders and other additives.

GENERAL EXPERIMENTAL PROCEDURES

Materials, Feedstock Preparation and Moulding

A gas-atomised, sub 45μm, Co-Cr-Mo alloy powder, supplied by Scientific Metal Powders Ltd., Sheffield, UK was used during the present study. The chemical composition of the powder is given in Table 1. The theoretical bulk density of the alloy is 8.5 Mg m^{-3}.

Table 1. The chemical Composition of Co-Cr-Mo Alloy powder.

Cr	Mo	Mn	Ni	C	Si	N	Fe	Co
27.6%	5.7%	0.68%	0.4%	0.17%	0.07%	0.16%	.23%	Bal.

Scanning electron microscopy was used to study the general shape of the powder particles. Test specimens were prepared by sprinkling a small portion of the powder onto double-sided self-adhesive carbon discs (previously attached to different Al stubs). The excess powder was tapped away and then specimens were coated with carbon using a SpeediVAC Carbon Coating Unit, Model 12E6/1598. A Cambridge Instrument CamScan microscope was used for examining these specimens and a few photomicrographs were taken for a permanent record. The average particle diameter and size distribution was also measured using a Coulter LS130 Particle Size Analyser, which in turn was interfaced to a Viglen III microcomputer with appropriate software. Approximately 5 gram of the powder was dispersed in about 250 ml of de-ionised water and exposed to ultrasonic vibrations for about one minute prior to pouring into the sampling vessel. A number of repetitive tests were conducted with and without a dispersion agent (Dispex N40).

A two-component binder was used, comprising a major fraction of polyethylene glycols (PEGs) of various molecular weights, and a minor fraction of very finely dispersed polymethyl methacrylate (PMMA) incorporated in the form of an emulsion. PEGs of different molecular weights (i.e. 400, 600, 1000, 1500) were considered for investigation and supplied by Honeywill and Stein Ltd. Surrey, UK. The emulsion was specially prepared for this work by Scott Bader Co. Ltd, Wellingborough, UK, and contained 40 wt. % of approximately 0.2 m PMMA particles dispersed in water and stabilized by a soap solution. The estimated molecular weight of the PMMA was $\sim 10^6$. For the present study, the binder was consisted of 8 wt. % PEG_{600}, 8 wt. % PEG_{1000}, 64 wt. % PEG_{1500} and 20 wt. % PMMA. The procedures for the selection of the binder system and choosing the binder composition and volume fraction have been discussed elsewhere [29,30].

Several ways of preparing feedstocks of different composition were investigated. These included changing the sequence in which the binder constituents were added, their amounts and the temperatures used during mixing. After a number of experiments and extended study, the mixing procedure shown in the flow diagram given in Fig. 3 (Method 1)

was carried out manually on small quantities of material and was found to be the most effective for obtaining a homogeneous feedstock.

A 65 Vol. % powder loading was used for preparing the feedstock for the present study. The feedstock was mixed in two steps. In the first step, the powder was gradually added and mixed into the emulsion to form a homogeneous mix (Mixture 1). The PEGs were dissolved in warm water and mixed into Mixture 1 to form a thick slurry. This was then dried at 50-60°C. It was frequently mixed during drying to avoid sedimentation of the metal powder and segregation of the PEGs to the surface from which evaporation was occuring. The dry mixture was shear mixed while cooling to room temperature using a pallet knife, to overcome any demixing that had occurred during drying. The mixture was extruded at 130 to 140 °C using the injection moulding machine. The extruded material was then chopped into small pieces of about 4-5 mm in size. Hot extrusion was employed to reduce entrapped air in the feedstock.

In method 2, as shown in the flow diagram given in Fig. 4, the PMMA emulsion was heated to evaporate the water to obtain the fine PMMA particles. These were dry blended with the metal powder. The PEGs dissolved in the methanol were mixed into this blend to form a thick slurry. The methanol was evaporated at 40°C and the feedstock was again mixed on cooling to overcome and demixing that might have occurred during drying. Finally, the mixture was hot extruded at 130 to 140°C and chopped into small pieces. The procedure for the evaluation of the feedstock has been discussed elsewhere [30].

To injection mould, a simple plunger-type of machine was employed. This was a vertical system with a plunger operated pneumatically. The mould was clamped mechanically. The barrel was 185mm long and had an internal diameter of 20mm. It was heated electrically using a heater jacket. The nozzle orifice was 3.75 mm. Simple bar-shaped test specimens having dimensions 5x5x55 mm were produced. A maximum moulding pressure of 50 MPa was always applied and the mouldability of the feedstock mixtures was assessed at various moulding temperatures.

The moulded samples were physically and macroscopically examined for defects such as cracking, surface voids, shrinkage and distortion. Destructive testing was conducted on selected mouldings to reveal any major internal defects, such as voids or cracks. This involved fracturing the mouldings and inspecting the fractured surfaces at low magnifications. The moulding temperature and pressure were maintained constant and moulding reproducibility was assessed by monitoring the variation in density of the consecutive mouldings.

Debinding

Debinding of the injection moulded green parts was performed in two steps, i.e. (I) Solvent extraction and (ii) Thermal pyrolysis.

Initial debinding was accomplished using a solvent extraction approach to remove the major binder component i.e. PEGs were extracted using water leaching at different temperatures.

In one set of experiments, de-ionised water was used in order to reduce the possibility of any rusting of the stainless steel powder. Trials were performed at different temperatures. Leaching was carried out within a rectangular water bath of dimensions 100 x180 x 230 mm, which was in turn immersed in an isothermal oil bath. The specimens were normally placed on a flat surface during leaching whereas, for the experiments determining the kinetics of the PEGs removal, the specimens were suspended in water in order to expose the whole surface area. The leached specimens were dried in an oven at 50-60°C for one hour and then the remaining binder, i.e. PMMA, was removed by thermal pyrolysis.

To determine the rate of removal of PEGs as a function of time and temperature, the moulded bars were cut into test specimens of about 20mm long. Each specimen was carefully cleaned to remove any loose particles from its surfaces and weighed before leaching using an electronic balance capable of weighing up to four decimal places. Then, the specimens were suspended in de-ionised water and leached at room temperature (~20°C), 40, 60 or 80°C, for various time intervals. The leached specimens were dried at ~60°C for 24 to 30 hours for complete removal of the water. The amounts of the PEGs removed were determined from the weight losses of the dried samples. These experiments were carried out twice and the mean weight loss was determined.

Scanning electron microscopy was used to study the development of pore channels resulting from the progressive removal of the PEGs during leaching.

Recycling of PEGs

Since, a high proportion of binder (35-40 vol. %) is used in PIM, it constitutes a major part of the cost. Thus, recycling of the binder or a part of the binder could produce worthwhile savings. During the present study, the major component of the binder (i.e. PEGs) was dissolved in water during leaching. The water was evaporated and the PEG was recovered in a solid form.

Thermal Pyrolysis

To remove the binder remaining after solvent extraction, i.e. PMMA, the dried specimens were heated in a tube furnace under different flowing gas mixture of 95% N_2/5% H_2. Various heating schedules were tried.

Sintering

Finally, the debinded parts were sintered in the same debinding furnace with the same atmosphere, and a variety of cycles were studied to achieve rapid sintering and high sintered densities. Sintered densities of various representative specimens were measured. Sintered

samples were also checked for shrinkage and distortion. The defects and pore morphology of the sintered specimens were investigated by optical and scanning electron microscopy.

RESULTS AND DISCUSSION

Materials, Feedstock Preparation and Moulding

The Co-Cr-Mo alloy powder was used due to its good corrosion resistance an wide applications in PIM, especially in surgical instruments and implants. The general particle shape and surface morphology of the powder are shown in a scanning electron micrograph, Fig. 5. The cumulative particle size distribution measured with a coulter LS130 Particle Size Analyser is given in Table 2, and is plotted in Fig. 6. Spherical shaped particles are considered favourable for enhancing the mouldability of the feedstock whereas, a wide particle size distribution results in relatively higher packing densities of the moulded parts and, thus, in less shrinkage during the debinding and sintering stages.

Table 2. The cumulative particle size distribution of Co-Cr-Mo alloy powder

% >	10	25	50	75	90
size μm	30.94	22.26	13.74	8.31	5.09

The procedure for choosing the binder composition and volume fraction has been discussed elsewhere [29,30]. However, some of the important characteristics of both constitutes of the binder are given here:

Poly (ethylene glycols) have good stability, good lubricity and can be mixed with water or a number of other solvents to give a wide range of viscosities. The higher molecular weight PEGs are solids. With increasing molecular weight, their crystallinity increases and they change from viscous liquids to soft solids to crystalline solids. Solubility is dependent on temperature and, generally, the lower molecular weight PEGs are more soluble. Solubility in polar solvents is good, but solubility in hydrocarbons and other solvents of low polarity is low. On oxidative degradation, they give low boiling compounds, which vaporise, leaving no sludge, gum or residue [31].

PEGs are non toxic and are readily excreted in urine. They have low vapour pressure, and no acute or long-term problems are expected from inhalation; however, respiratory protection is advised in the presence of heated mists or vapours. They are neither skin nor eye irritants; allergic skin reactions have not been reported [31].

A specially formulated emulsion containing 0.2 m PMMA particles dispersed in water, and stablised by a suitable agent, was used. Some of the important properties of the PMMA are given below [32];

Glass transition temperature,	$^*T_g$ = 105°C
Ceiling temperature, T_c	= 220°C
Density at 20°C	= 1.190 g/cm^3

Max. monomer yield	$\geq$ 98%
Unzipping sequence	= 2-3000

*T_c = Ceiling temperature at which the polymerisation equals the rate of depolymerisation.

Above the flow temperature, the PMMA begins to break down chemically (pyrolysis). Normally, PMMA decomposes by an unzipping mechanism upon heating to $\geq$ 200°C to generate monomer.

With Method 1 (Fig 3) used for feedstock preparation, when the emulsion is mixed with the metal powder, the fine PMMA particles are easily dispersed between the powder particles. SEM examination of dried samples of Mixture 1 revealed the presence of fine PMMA particles attached to the surfaces of the steel particles. In some cases, the steel particles appeared to be joined to each other by PMMA particles. When the solution of the PEGs in water is mixed into Mixture 1, they are obviously uniformly dispersed on a very fine scale. On drying the slurry, segregation of the binder components, which was considered possible, was not observed. This suggests that the mixing carried out during drying and cooling was effective.

With feedstock preparation Method 2 (Fig. 4), very fine PMMA particles were obtained after drying the emulsion. The particles were agglomerated but the agglomerates were not strongly bonded. For examples, they could be broken up and dispersed by being gently rubbed between two fingers. Some dispersed of these fine particles between the metal powder particles during dry blending should occur. When the solution of PEGs in methanol is mixed into this blend, the PEGs are obviously mixed on a very fine scale. Shear mixing of the paste helps to disperse further the PMMA particles. It is thought that the PMMA particles become sticky after mixing with PEGs and become attached to the powder particles; hence, this reduces the possibility of segregation of the PMMA. Heating at 40°C for one hour was found sufficient for removal of the methanol. As no water is employed during this mixing procedure, metals that react with water or oxygen in water can be processed using this approach.

The feedstock was easily injected within the temperature range of 130 to 150°C when using a cold mould and produced sound components. It is considered that the PEG_{600} will be a liquid at the mould temperature, which increases from ambient temperatures when hot feedstock is injected to it, so that a thin layer of liquid PEG is formed at the surface of the moulding. This acts as a lubricant and prevents the sticking of the component to the mould surface. A setting time of 12-15 second was found sufficient, as the components could be ejected from the mould without distortion after such a time lapse. The green density of most of the moulded parts was about 5.65 Mgm^{-3} . A part-to-part variation of about 5% was found in the green density of consecutive moulding produced from the same batch of feedstock. This variation may be due partly to inadequate control on moulding parameters. The green strength of these parts measured using 3 point bent test was about 12.5 MPa. The sprues, runners and as-moulded (green) scrap were recycled and could be moulded without any problem.

Debinding

1. Water Leaching

It was found that the rate of extraction of the PEGs from the green components (about 70% by weight in 16 hours) was very slow while leaching in still water at room temperature. However, the rate of removal was enhanced substantially by increasing the water temperature although the leaching temperature was limited by the requirement to avoid softening of the residual binder, which would cause slumping or distortion of the parts. The results of the water leaching study are given in Table 3, and the percentage weight loss of PEGs as a function of time at different temperature plotted in Fig. 7.

Table 3. Rate or removal of PEGs at different leaching temperatures

Leaching Temperature, °C	PEGs removed (wt. %) after				
	30 min.	60 min	90 min	120 min	180 min
40	35	44	53	58	65
60	50	65	82	90	95
80	60	79	88	97	98

The results show that about 80 to 90% wt. % of the PEGs were removed during the first two hours of extraction at 60°C and 80°C, respectively, and that thereafter, the rate of extraction was very slow. After three hours at these temperatures about 95 wt. % could be removed. The samples did not show any noticeable dimensional change or deformation after leaching for three hours at 40°C, 60°C or 80°C. It was found that some voids were formed in the binder at the surface of the moulded components due to the shrinkage of the binder while cooling from the moulding temperature to ambient (Fig. 8), which created initial paths for the diffusion of the water into the body. Also, it is considered that during the initial paths for the diffusion of the water into the body. Also, it is considered that during the initial stage of water leaching the lower molecular weight PEGs are removed more rapidly and form additional crevices/cavities to further accelerate ingress of water into the green body which results in a higher rate of removal of the remainging PEGs. As there was little difference between amounts of PEGs removed after three hours at 60°C and at 80°C, to avoid the softening of the moulded components and oxidation of the PEGs, the lower temperature (60°C) was selected for subsequent leaching of the green samples. Thus, the samples were water leached at this temperature for three hours and subsequently dried at 60°C for one hour prior to thermal debinding. It is assumed that this treatment may also remove the stress developed in the components during moulding.

A SEM photograph of a water leached specimen (Fig. 9) clearly illustrates the open pore channels formed after the removal of the PEGs. These channels allowed more rapid removal of the remaining binder, without cracking, blistering or general swelling during subsequent thermal debinding. After the removal of the PEGs, the residual PMMA was found to be sufficient to bond the powder particles together to give adequate strength for

handling (Fig. 9). Leaching studies have also been undertaken using methanol and ethanol and no swelling or distortion or the parts was observed in these solvents [33].

2. Thermal Debinding

The volatilisation kinetics of the dried, fine PMMA particles and the binder (i.e. PMMA present in various water-leached and subsequently dried parts made from different feedstock mixtures) have been studies by the authors [30]. The data obtained from this study were used to establish the debinding cycles for the test specimens. Thus, the binder remaining after leaching (i.e. PMMA) was removed by heating and evaporation. The test samples were placed on a flat silica plate and heated at heating rates and evaporation. The test samples were placed on a flat silica plate and heated at heating rates of either 5, 8, or 10°C/min up to 350°C and were held at this temperature for either 15 min, 30 min. or 60 min. It was found that samples heated at the highest rate of 10°C/min. did not show any blistering, slumping or cracking after debinding and subsequent sintering. The PMMA decomposes to produce methyl methacrylate (MMA) monomer, which is gaseous at the burn-out temperature employed and thus rapidly escapes from the body through the open pore channels formed during leaching. Although no problem was apparent for specimens heated at 10°C/min. from ambient temperature to the sintering temperature, a holding time of 15 to 30 min. at 350°C is recommended to ensure removal of all the binder prior to the sintering. The following cycle was thus adopted for debinding of bars with a 5 x 5 mm^2 cross-section.

I) Heating up to 350°C at a rate of 10°C/min.
II) Holding at 350°C for 15 min.

Sintering

The sintering temperature for this Co-Cr based alloy was established by a trial and error method and 1300°C was found to be the most suitable and efficient sintering temperature for this powder. A number of test specimens were heated from the debinding temperature to the sintering temperature at a rate of 10°C/min. and were soaked at this temperature for either 30, 60 or 90 min. The sintered samples were examined macroscopically and microscopically and no cracking or distortion was observed. It was found that, as sintering time increased, the small pores were eliminated, while larger pores shrank and spherodized. The microstructures of various sintered specimens are shown in Fig. 10. The test samples, sintered at 1300°C for 90 min, had very fine, round and uniformly distributed pores, as shown in Fig. 11. A linear shrinkage of about 12.2% and a final density of about 99.5 percent of the theoretical value was measured for these samples. The corresponding mean pore size, measured with an image analyser was found to be about 4μm. The total water leaching, thermal debinding and sintering cycle time was about 7 hours, including 15 minutes hold at 350°C.

Control of Carbon

The likelihood of a change in the carbon level during water leaching is very remote. Moreover, as a major comonent of the binder is removed during water leaching, the amount

of binder removed during the thermal debinding stage is comparatively low. Thus, reducing the possibility of contamination by thermal decomposition products. Thermogravimetric studies of dried, fine PMMA particles showed that there was no residue left after thermal decomposition. Owing to the high heating rate used for debinding and sintering, the exposure time for the components at high temperatures and the resulting oxidation of carbon are much reduced.

Recycling of PEGs

Since a high proportion of the binder (35-40 vol. %) is used in PIM, this contributes towards a major cost of the process. The major component of the binder, i.e. PEGs was dissolved in water during leaching. The water was evaporated and the PEG was recovered in a solid form. The properties of this PEG are currently being studied. However, since no extended hot mixing was required and the, feedstock was heated at 130 to 150°C for only a few minutes during the hot extrusion and moulding stages, it can be assumed that there might be little change in properties of the PEGs due to oxidation.

SUMMARY

1. The mixing process is comparatively easy and a lengthy hot mixing stage can be avoided. By using the emulsion based binder system, the fine polymeic particles are easily dispersed uniformly throughout the feedstock on a fine scale of size. Mixing as a slurry can be carried out using a relatively small force; hence wear of the mixing equipment and contamination are reduced. The preliminary mixing is carried out at reactively low temperatures. Hot mixing, if used, would be short and hence cause minimum vaporisation or oxidation of the binder constituents. The short duration, with the particles already coated with the binder, should result in little wear of the mixer.
2. The feedstock produced by using the new binder system showed good mouldability in the range of 130 to 150°C; no binder separation was observed during moulding.
3. The moulded parts had adequate green strength for handling.
4. The sprues, runners and as moulded (green) scrap, if any, can be recycled.
5. The major components of the binder, i.e. PEGs, can e easily removed in a relatively short time (typically 2 to 3 hrs for 5mm thick sections) by water leaching at about 60°C. This opens up pore channels which allow much faster removal of the remaining binder during subsequent thermal debinding, without adverse effect on the integrity of the component. The components had sufficient strength for handling after the removal of PEGs.
6. Higher heating rates than for conventional binder systems can be used for the thermal debinding and sintering heat-treatment, which further shortens the total cycle time. Thermal debinding cycles of about 1 hour were successfully employed for $5mm^2$ cross-section bars. This is a much shorter time than the 12-18 hours, which is normally used for this cross-section with conventional binders.
7. The binder is a simple two component system. There is only one component to be removed during thermal debinding, therefore, a single debinding temperature can be selected.

8. Since ethanol or methanol can be used for solvent leaching, therefore, the powders sensitive to oxidation in water can also be processed, providing they are mixed in an non aqueous slurry.
9. Control of carbon level is comparatively easy.
10. A major proportion of the binder, i.e. PEG can be recycled.
11. Water is being used as a solvent for removing out PEGs which is considered to be a safe practice and no special equipment is required for this process. The binder components, i.e. PEGs and PMMA and their thermal degradation products are non-toxic.

From the above observations, it can be concluded that the new binder fulfills most of the requirements of a good binder system.

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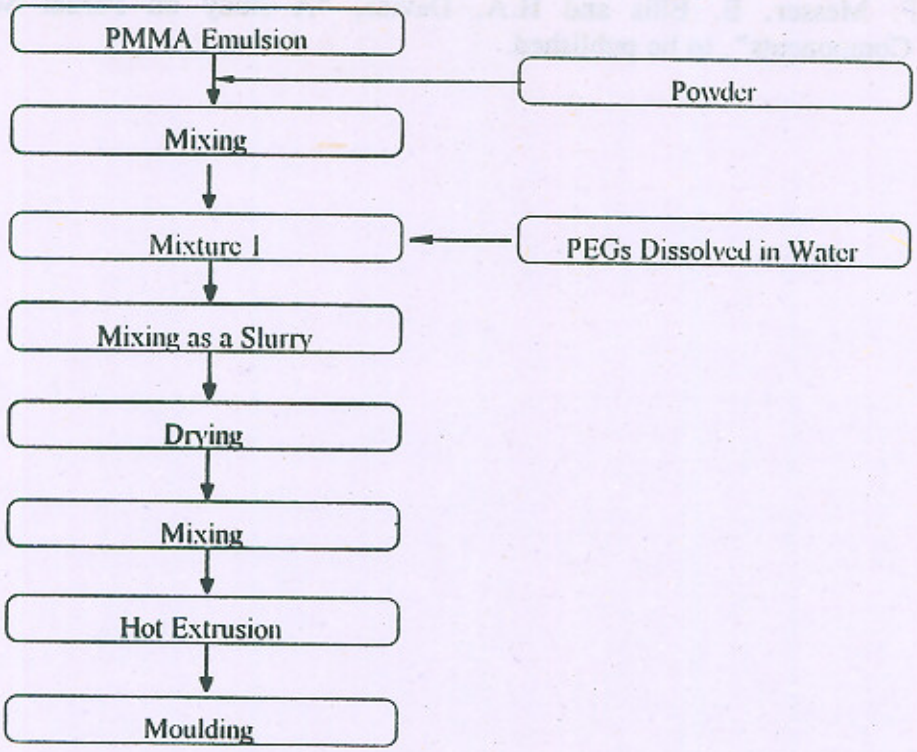


Figure 3 : Flow diagram for mixing of the feedstock.

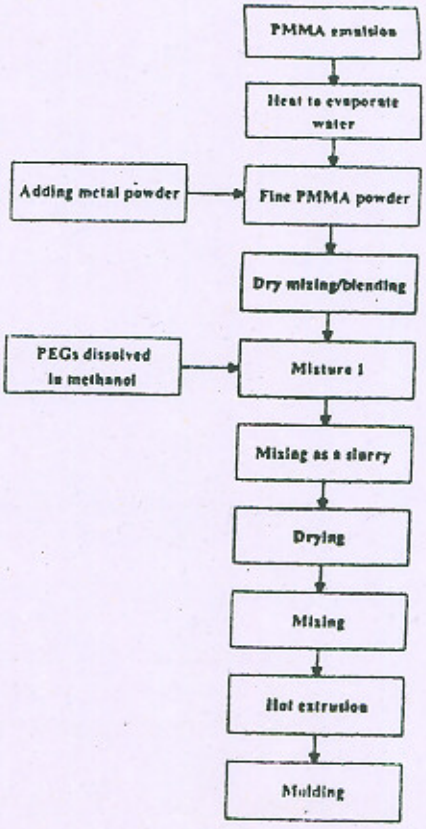


Figure 3 : Flow diagram for producing the feedstock with metals that react with water.

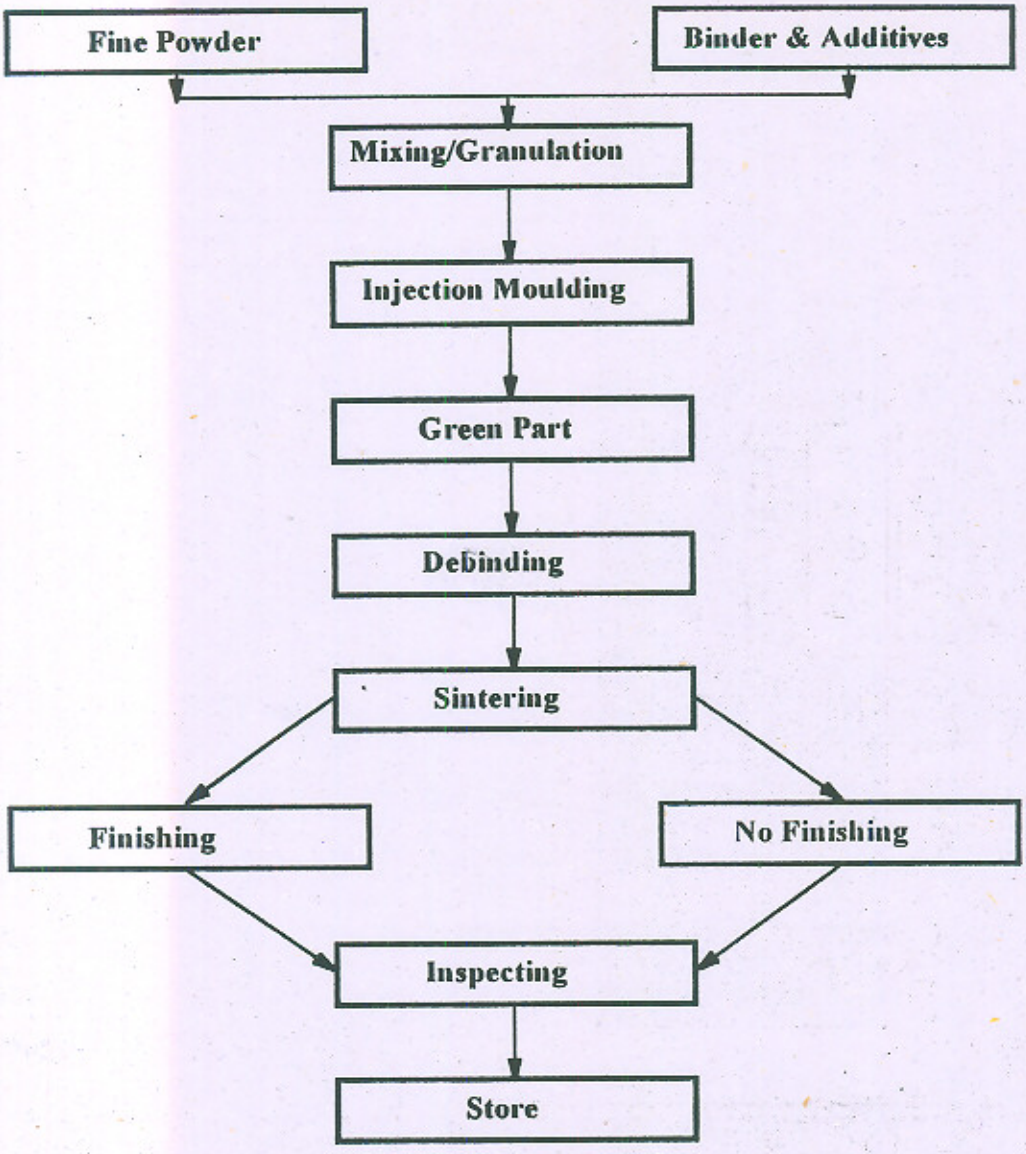


Figure 1 : Flow diagram of the PIM process

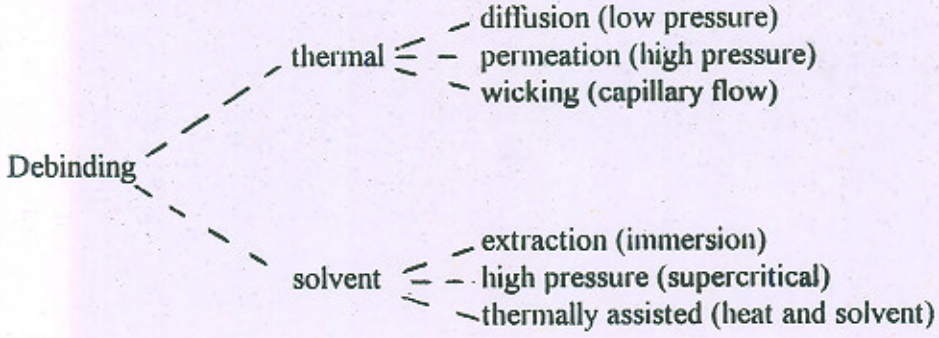
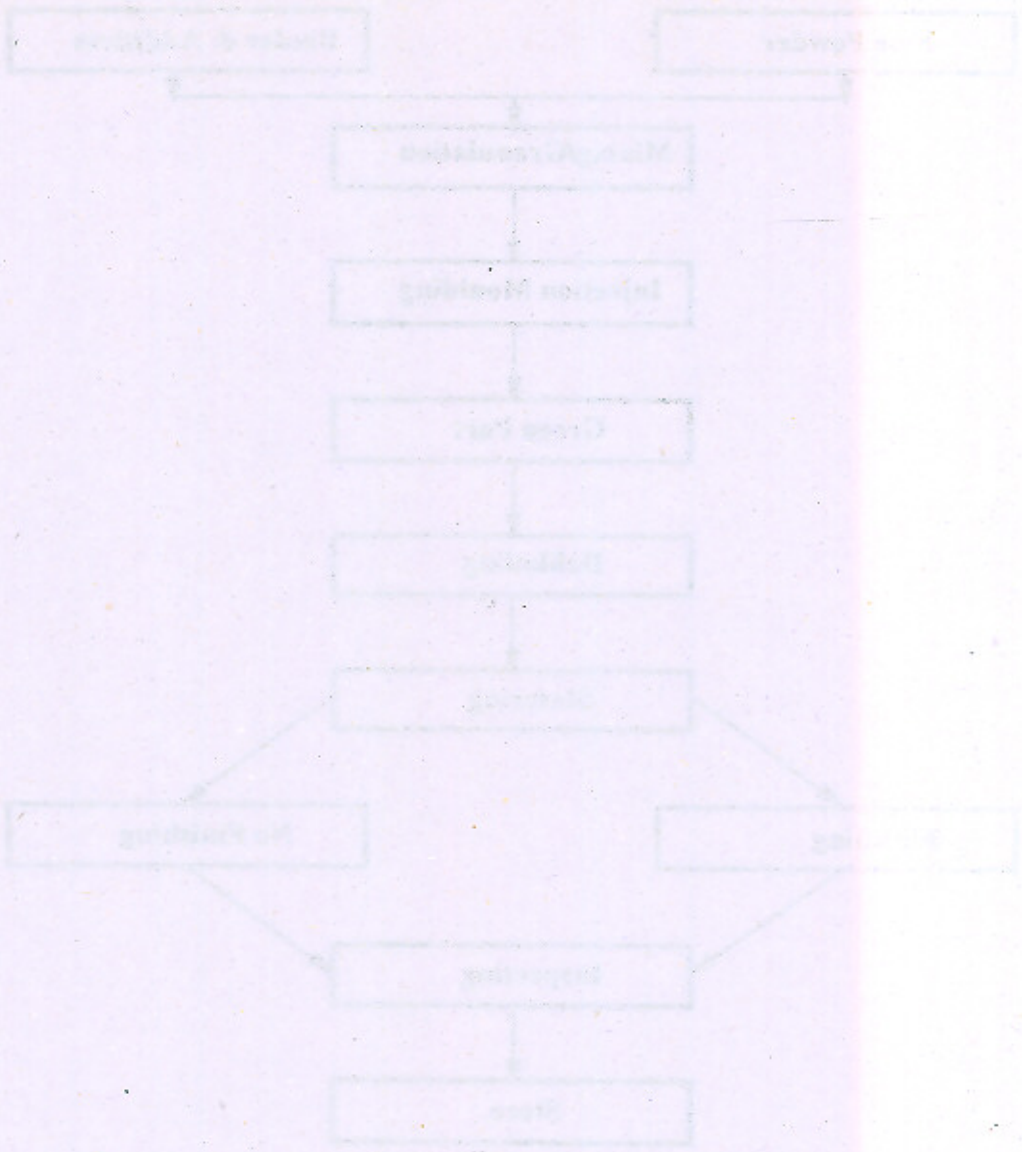


Figure 2: A schematic classification of the six key debinding processes based on either thermal or solvent approaches.



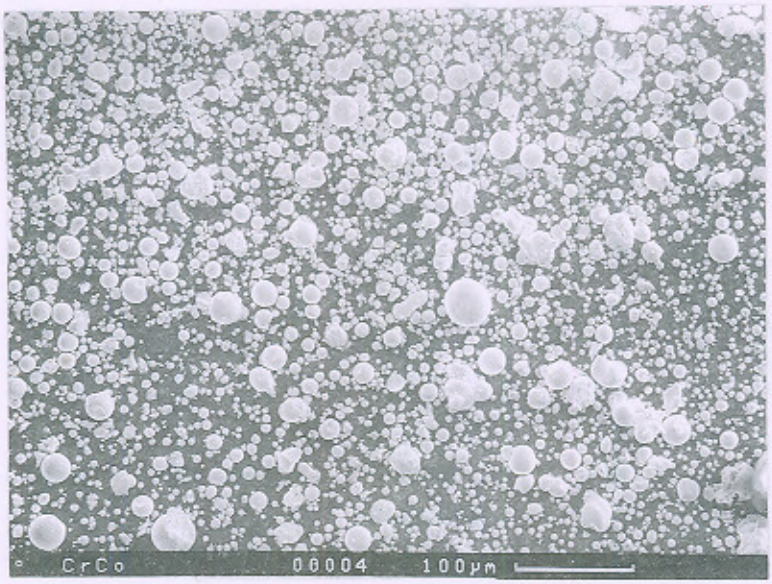


Figure 5: Scanning electron micrograph of the Co-Cr-Mo alloy powder, used for the experiments.

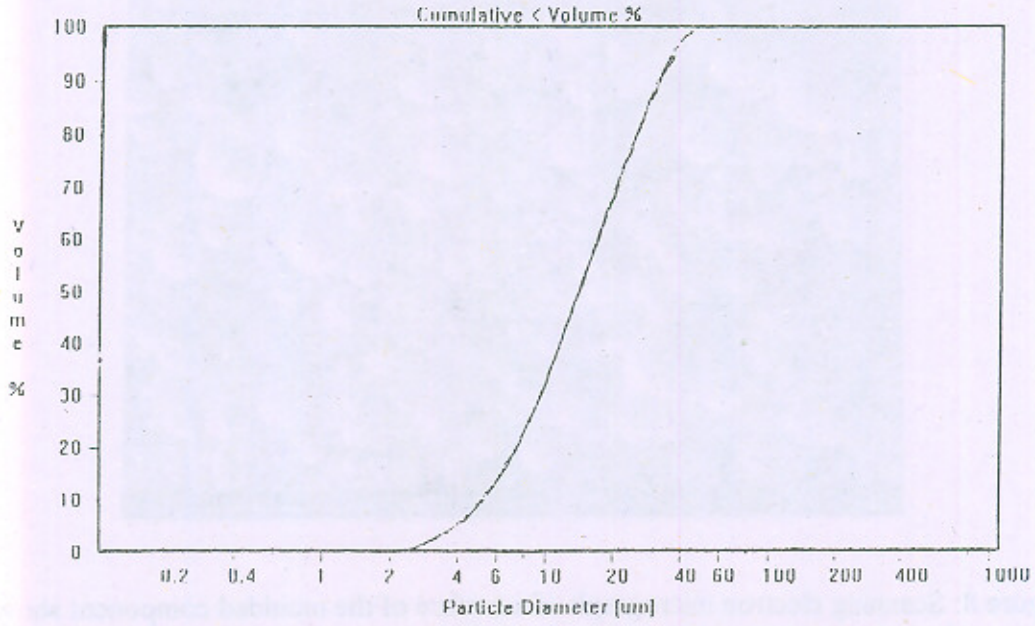


Figure 6: The cumulative particle size distribution of the powder.

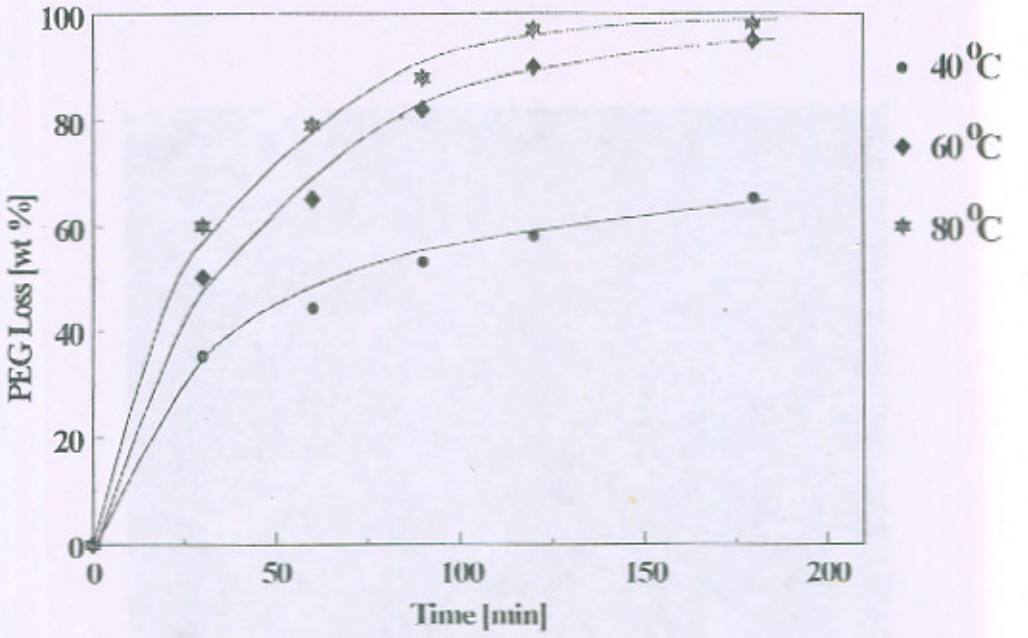


Figure 7: The percentage weight loss of PEGs as a function of time at different leaching temperatures

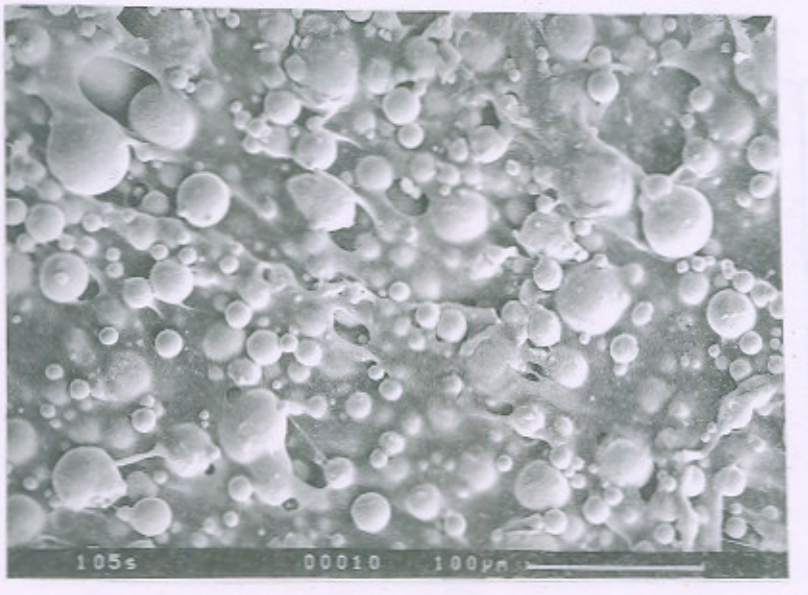


Figure 8: Scanning electron micrograph of a surface of the moulded component showing the formation of cavities as the binder shrinks during cooling from the moulding temperature.