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Review: Fabrication of Engineering Ceramics by Injection Moulding. II. Techniques

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SUMMARY

The development of injection moulding techniques and their application to ceramic suspensions is described, with particular attention being paid to the mixing of suspensions prior to moulding and to the origin of moulding defects. Methods for the removal of the organic component of the injection moulding blend are reviewed.

1. INTRODUCTION

The injection moulding process evolved from metal die-casting technology and has been used for over a century for shaping polymers. The first ceramic articles were produced in this way half a century ago. Today, many substantial research programmes worldwide aim to perfect the fabrication of fine engineering ceramics by this versatile technique.[1]

A ceramic blend must be prepared prior to injection moulding and therefore dispersive mixing of the ceramic powder in an organic vehicle is an important initial step. Technical developments in mixing therefore impinge on ceramics fabrication by determining the uniformity of particle assemblies in prefired bodies and therefore uniformity and extent of shrinkage.

In the present review the main technical developments in injection moulding machine design are described, including recent developments which allow control over solidification in the mould.

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The process of flow of the suspension into the cavity and of solidification is qualitatively described. The complexity of such processes still prevents the development of models which yield useful information for the practitioner. It is at this stage that moulding defects or residual stresses develop in moulded parts.

The polymer removal stage is often considered the most challenging technical aspect of the process. This may be because detailed study of this complex process has only recently begun. The techniques that have been applied to the problem, in so far as they have been published, are discussed below.

2. MIXING OF CERAMIC INJECTION MOULDING BLENDS

2.1. Characteristics of mixtures

The mixing of polymer–ceramic blends for injection moulding has received scant attention in ceramic literature but is considered of great importance in the preparation of filled polymers and polymer blends.[2–4] It will be shown below that it is also of considerable importance to ceramists because failure to disperse ceramic powder in a vehicle at an early stage in the process may result in non-uniform shrinkage at a microscopic or even macroscopic scale during subsequent sintering. The principles of mixing in so far as they apply to ceramic systems in general have been reviewed by Messer.[5]

It is generally insufficient to consider ceramic injection moulding blends as simply two-phase systems of ceramic in a polymer matrix. It has been shown[1] that the matrix is frequently a multicomponent polymer blend itself. Frequently it consists of a low-viscosity polymer or oil and a viscous thermoplastic. In most cases incomplete solubility can be expected to prevail and the degree of dispersion of one polymer phase in the other will influence the properties of the blend; in particular its decomposition kinetics. Thus the mixing of ceramic injection moulding blends involves the dispersion of ceramic particles and a minor polymer binder in a continuous matrix of the major polymer binder.

Mixing is defined as a process that reduces compositional non-uniformity and in viscous polymeric fluids the influence of molecular and eddy diffusion is generally negligible for useful timescales, leaving forced convective flow as the main mixing process.[2] If convection causes the movement of fluid or solid particles from one spatial location to another such that the interfacial area between liquid particles and the matrix increases, or that solid particles are distributed throughout the matrix, then *distributive* mixing is said to have occurred.

Distributive mixing is influenced by the strain imposed on the mixture. However, in the case of viscoelastic polymers and agglomerated fine particles which show yield point characteristics, the application of strain is necessary, but insufficient, to achieve mixing. The strain rate and hence shear stress imposed on the material determine the extent of mixing and this is known as *dispersive* mixing.[2]

The importance of dispersive mixing in ceramic systems is illustrated by the recent work of Lange[6] on uniformity of prefired density in ceramics. If agglomerates start at a different prefired density from the dispersed particles in a ceramic body then very high stresses are set up during firing[7] and these can produce circumferential or radial cracks in the region of agglomerates[8] depending on whether the agglomerates shrink faster or slower than the matrix respectively.[9] Furthermore failure to disperse agglomerates may influence the sintering kinetics and reduce the fired density by leaving thermodynamically stable pores with a large grain co-ordination number.[10]

In defining mixture quality the *characteristic volume*, sometimes called the *scale of segregation*, is an important parameter. Characteristic volume may be defined[5] as the amount of material at every location throughout the mixture within which the position of individual particles is unimportant. Its size depends on the properties demanded of the mixture. For example the characteristic volume of an engineering ceramic injection moulding composition could be calculated from the dimensions of the flaw size defined by Griffiths' equation for a desired mechanical strength. This would mean that compositional uniformity would be expected among random samples of typically 1000 μm^3 volume. Since such samples are well below the limits of practical analysis, resort to microscopical methods[11,12] is necessary in defining mixture quality. Since flaws produced by firing agglomerated powders are typically of the same dimensions as the starting agglomerates[9] the characteristic volume will be smaller than the volume of agglomerates often found in ceramic powders.[12] The breakdown of agglomerates in shear flow is described quantitatively by Tadmor and Gogos.[13]

There is increasing interest in ultrafine monosized spherical powders which can be packed into ordered arrays for ceramic fabrication.[14,15] In this case the characteristic volume would be of particle dimensions. The best that can be expected from injection moulding of such particles is a uniform random packing throughout.

Numerous indices to quantify the extent of mixing have been proposed and these are reviewed by Fan and co-workers.[16,17] In general these are based on the standard deviation s or the variance s^2 of the composition of spot samples taken from the mixture. The simplest such index[18] is given by

$$m_1 = \frac{\sigma_R}{s}$$

when σ_R is the standard deviation of composition for a random homogeneous mixture (RHM). A RHM is defined as a mixture in which the probability of finding a particle of a given component is the same at all locations in the mixture and σ_R is equal to $\sqrt{P(1-P)/n}$ for a binary mixture of particles. P is the proportion of one component and n is the number of particles in the sample.[18] The sampling of mixtures and treatment of results is extensively reviewed by Weidenbaum.[19]

A further aspect of mixture quality is the distinction between *ordered* and *random* mixtures. Ordered mixing occurs when fine particles of one component find interstices between large particles of another component.[5] Another example of interest in ceramics fabrication is where fibres mixed into a ceramic moulding composition exhibit preferred orientation or texture in the product. For single crystal fibres X-ray diffraction methods allow fibre orientation to be defined by a stereographic projection. For fibres amorphous to X-rays the preferred orientation in two dimensions can be defined by microscopical or microradiographical methods and the orientation in the third dimension is defined by the aspect ratio of the elipse created in the section plane by the fibre and can be found by quantitative microscopy.

2.2. Mixing techniques

Mixing devices for high-viscosity fluid are reviewed in several reputable texts.[4,20,21] The simplest mixers are so-called motionless mixers in which a fluid is pumped through intricately designed internal passages which create strain in the fluid and induce distributive mixing. Such mixers consist of a battery of mixing elements and these introduce a substantial pressure drop. The high viscosity of polymer–ceramic blends has thus restricted the use of such mixers.

Lower-viscosity fluids (10–100 Pa s) are frequently mixed in single-blade stirred tank devices which incorporate either propellers, turbines or paddles and produce distributive mixing.[4]

An advance on this process is the range of double-blade batch mixers such as the 'Z' or 'sigma' blade mixers which have been applied extensively to the blending of ceramic injection moulding material. Blade profiles and power requirements of such mixers are detailed by Irving and Saxton.[20]

Early experts on ceramic injection moulding such as Schwartzwalder[22] and Taylor[23] favoured such mixers and some recent research has also relied on these types.[24] The limitations of the double-blade mixers are the tendency for filled thermoplastics which show yield point behaviour to reside in dead spaces in the mixer and there is insufficient dispersive mixing to break down ceramic powder agglomerates.[12]

Banbury-type mixers provide higher intensity batch mixing and are used on high-viscosity fluids for pigment and filler dispersion. They consist of a figure-of-eight section mixing chamber containing two counter-rotating lobed rotors. Quackenbush *et al.*[25] employed a torque rheometer of similar design to prepare ceramic moulding compositions.

The two-roll mill is also a mixer ideally suited to the processing of high-viscosity materials. It consists of two counter-rotating differential speed rolls with an adjustable nip and imposes intense shear stresses on the material as it passes the nip. There is little transverse mixing and thus constant operator attention is needed to displace the strip transversely. This process can be partially automated for polymers. A two-roll mill was used by Birchall *et al.*[26] to produce very high solids content mouldable cement pastes.

Two types of extruder are used for mixing: single- and twin-screw extruders. Single-screw devices with a helical screw rotating inside a heated barrel are not efficient mixing devices[20] and are sometimes enhanced by the incorporation of mixing discs, torpedoes or planetary gears into the screw configuration. The total strain imparted to an element of material is strongly dependent on its position and therefore mixing tends to be non-uniform across the screw channel. Unlike the more complex extruders the helical flow behaviour in single-screw machines is well characterized[27] and machines are well documented in textbooks.[28,29]

Flow in single-screw extruders relies on adhesion of the material to the barrel wall and it was to overcome this limitation that twin-screw extruders evolved.[30] There are four types depending on whether the screws co-rotate or counter-rotate and whether the screws intermesh or not. The first device was an intermeshing co-rotating extruder invented in 1939, and patented in 1949.[31] Considerable variation of screw design is possible to balance pumping and mixing characteristics.[32] Intermeshing extruders provide positive displacement pumping unlike single-screw machines and the output in volume per unit time is given by the difference between the theoretical flow rate and the sum of the leakage flows described in Fig. 1:

$$Q = Q_{\mathrm{th}} - Q_{\mathrm{L}} = 2mNV - (Q_{\mathrm{f}} + Q_{\mathrm{c}} + Q_{\mathrm{t}} + Q_{\mathrm{s}})$$

where m is the number of thread starts per screw, V is the volume of the 'C'-shaped channel between the flanks of successive flights and N is the

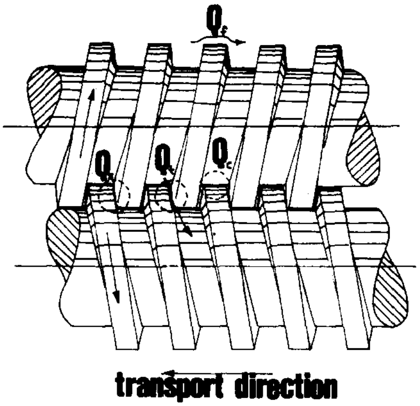

Fig. 1. Leakage flow paths in an intermeshing twin-screw extruder; after Janssen.[30]

rotation rate. Q_f is the leakage between screw flight and barrel wall, Q_c is the leakage between the screw flight and the other screw, Q_t is the leakage between the flanks of screw flights and Q_s is the leakage between flanks perpendicular to the plane through the screw axis.[30] The leakage paths have a strong influence on residence time in the extruder. Flow characteristics of such extruders have not been well defined and machine development has been largely empirical. As with single-screw devices mixing discs and kneading discs can be incorporated into the screw configuration.[33]

Twin-screw extrusion has been used for the preparation of particle-filled polymers[11] for reinforcement, flame retardancy, fabrication of prosthetic materials[34] or incorporation of magnetic or dielectric solids. The polymer degradation during processing can be controlled by screw design[35] and is found to be less severe than degradation induced by two-roll milling.[34] The degree of dispersive mixing obtained by twin-screw extrusion compounding is greater than that achieved by using a double-blade mixer.[12]

2.3. Composites

Of particular recent interest is the fabrication of ceramic matrix composites. This involves particular problems of mixing in which ceramic fibres or whiskers are dispersed along with ceramic powder in a fluid phase.

The theory of ceramic matrix composites was reviewed by Donald and McMillan in 1976.[36] Since then the reinforcement of engineering ceramics with ceramic fibres has acquired renewed interest as a toughening method.[37] Injection moulding has been used for short fibre reinforced polymers for many years[38,39] and considerable control is now possible over fibre orientation.[40] The main problem to be overcome when fibres or whiskers are incorporated in a ceramic suspension is control of fibre length degradation during the mixing process and during flow in the moulding machine. This difficulty has led to interest in fabricating ceramics from polymeric precursors.[41]

3. DEVELOPMENT OF INJECTION MOULDING TECHNOLOGY

A study of the adaptation of metal die-casting technology to polymer moulding shows how the problems of defective mouldings were slowly overcome as attention was directed to key components of the moulding machine. Many of the problems associated with that technology transfer were similar to those encountered in modern attempts to mould ceramics.

The injection moulding process had its origins in the die-casting technique invented by Sturges in 1849[42] for non-ferrous alloys and therefore the designs of the first injection moulding machines for polymers were based upon die-casting methods. The first machine was used to fabricate cellulose nitrate plasticized with camphor and was patented by Hyatt in 1872.[43] In this machine a ram applied pressure to the material in a heated chamber, extruding it through a nozzle into a cooled mould to produce continuous rod, sheet or tube. The first moulding process used a multi-cavity mould to coat metal parts with Celluloid.[44,45] The key early developments were by Richards,[46] Eichengrun[47,48] and Buchholz,[49] and a more detailed account of early work is reported in several texts.[50-52] Some of the first materials moulded were filled with glass but the filler was abandoned because of poor results![50] The first semi-automatic machines emerged in Germany and America in 1929 and were activated by compressed air.[50] Although suitable for small articles these devices were limited by low material and clamp pressures.

An hydraulically activated machine appeared in 1934[53] and in the same period British machines appeared with hydraulic or pneumatic ram pressure.[50] Hydraulic mould clamping was introduced by Piperoux and Radburn in 1933[54] and this overcame the flashing inherent in earlier designs. The introduction of toggle mould clamping on the Isoma machines (1936) allowed superior mould locking. Uniform heating of the material was a problem in these early ram machines but improvements were achieved by incorporating a spreader into the flow channel patented by Gastrow.[55] Many of the characteristics of modern machines appeared in the rapid developments of the 1930s, including early automation made possible by temperature controllers, timers and dosing devices. Better control over injection pressure, mould closing and barrel heating facilitated the fabrication of large components. This in turn gave rise to larger moulding machines, including the large multi-nozzle machines with vertical clamping which appeared in 1936. Serious problems of reproducibility of components remained, and to solve this problem an early automatic machine was patented by Burroughs.[56] Thus by 1940 machines had developed to include an hydraulic ram acting in a heated thermostatted cylinder with an internal spreader and injecting into a vertically or horizontally clamped mould with hydraulic and toggle clamping and automatic ejection.

By 1944 a machine was available capable of moulding both thermoplastic and thermosetting materials.[50] Mould closing and clamping by hydraulic and toggle methods were perfected by 1944. Large scale machines for thermosets were developed at this time,[57,58] and a device combining injection and compression moulding was in use.[59]

Machines are characterized by the injection end rather than the clamp geometry and two major classes of machine are commonly used: the plunger machine and the reciprocating screw machine.[45]

A typical single-stage plunger machine is shown in Fig. 2(a). A metered quantity of material enters the heated barrel from the feed hopper and, as the piston advances, flows over a torpedo or spreader designed to improve heat transfer.[60] Such machines suffered from the following disadvantages.[61] There was little mixing of the molten material, giving rise to inhomogeneity. The pressure at the nozzle could vary considerably from cycle to cycle as the plunger compressed material which ranged from solid granules to viscous fluid. Since viscosity of polymer melts is pressure sensitive, erratic pressures increased the mould filling variability. The torpedo caused a significant pressure drop. The shot size was difficult to meter accurately.

A preplasticizing system overcame some of these disadvantages.[62-64] Such machines had twin barrels and in the case of a two-stage plunger device material was plasticized in the first barrel before being fed into the second barrel via a non-return valve. The torpedo could then be omitted from the injection barrel. Homogeneity was assisted by passing the material

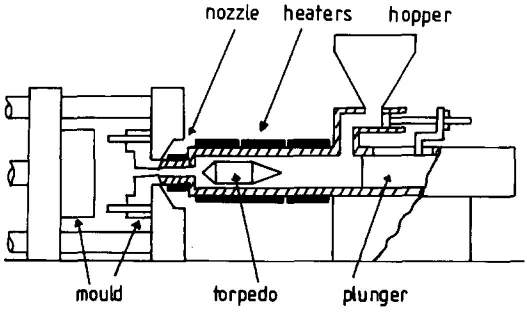

Fig. 2(a). Plunger-type injection moulding machine.

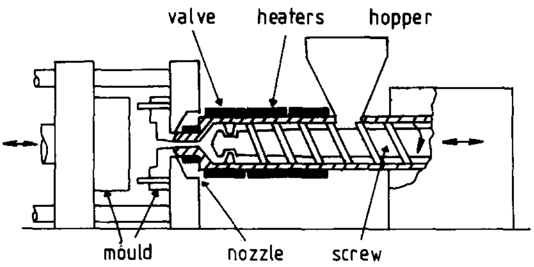

Fig. 2(b). Reciprocating screw-type injection moulding machine.

through the interconnecting nozzle. Shot size was metered by using limit switches on the primary barrel. In screw-plunger machines the primary plunger was replaced by a rotating screw.

The development of the reciprocating screw machine overcame many of the problems of plunger machines. The use of a rotating screw to heat and convey material was first introduced in Germany in 1943.[65] A typical reciprocating screw machine is shown in Fig. 2(b). Adhesion to the barrel wall allows the rotating screw to pump material forward, simultaneously mixing and heating the fluid to achieve uniformity. An adjustable pressure applied to the screw controls the reverse drift of the screw in the barrel and thus the plasticization of the material. The screw then ceases to rotate and behaves as a plunger, injecting material into the mould. A check ring or ball valve prevents leakage of material past the end of the screw. The screw remains in the forward position applying a hold pressure to compensate for shrinkage of the material in the cavity. The screw then again rotates recharging the injection chamber while the mould remains closed.

The fundamental improvement in the screw machine is the preplasticizing action[66-68] which causes direct Joule heating of the material. High shear rates produce lower viscosities in pseudoplastic fluids. Lower injection and clamp pressures can be used because of greater homogeneity of the material resulting from non-laminar flow. Degradation problems are less severe because of lower residence times and better heat transfer. This is especially advantageous in the processing of heat-sensitive materials. Finally, screw machines are more efficiently purged as the material is changed.

4. TECHNICAL DEVELOPMENTS IN MOULDING OF CERAMICS

One of the earliest reported applications of ceramic injection moulding was the manufacture of spark plug insulators in 1937.[22] Since then there has been considerable and varied experimentation with different moulding techniques.

4.1. Machine types

The ideal design of moulding equipment depends on the nature of the organic vehicle system and this can be classified as[69] thermoplastic, thermoplastic wax or thermosetting.

Both plunger and reciprocating screw injection moulding machines routinely used for unfilled polymers are also used for ceramic suspensions after minor modification.[25,40,69–73] Reciprocating screw machines are often favoured[71,73] as they provide better metering, homogeneity, injection pressure control, reproducibility and lower cycle time. In plunger machines flow moulding is not possible and part size is limited by the maximum volume of the plunger stroke.[72] Nevertheless plunger-type machines are often favoured on the grounds of longer machine life because of less wear.[25,69,70] They also tend to require less capital investment.[70]

Plunger machines can be vertical injection, vertical press type with attainable cavity pressures up to 170 MPa[69] or of the horizontal type.[70] They are generally fully microprocessor controlled and equipped with a shuttle table to allow die transfer.

Reciprocating screw machines specifically developed for ceramic injection moulding are also currently marketed.[70,71] These are based on conventional designs and are again fully automated. Some machines contain circuits which permit fine control of injection and hold pressures which is considered essential for ceramic moulding.[74]

Wax-based systems tend to have much lower viscosities (<200 Pa s) than high polymer systems and are often injection moulded on plunger machines[69] known as wax injectors.[75] The suspension is stored in an agitated heated chamber prior to transfer to an injection chamber where an hydraulically controlled piston injects it into a mould. Such machines vary in size from the small (12 000 kg) horizontally clamped devices to 300 000 kg vertical press machines.

Thus for thermoplastic and wax systems direct injection processes are used in which the heated suspension is forced into a colder mould under pressure and then subjected to a hold pressure as it solidifies.[69,76] For thermosetting systems, however, transfer moulding is used in which the softened suspension is transferred by a plunger or screw to a heated mould where the resin cross-links.[69,77,78] In both cases the polymer phase undergoes a shrinkage as it changes state and this can introduce defects.

4.2. Process control

There is considerable interest in modelling the flow of non-Newtonian unfilled polymers under non-isothermal conditions through sprue and runners of varying dimensions but the problems are considerable. It is an achievement to be able to predict approximately the flow behaviour of polymers[79] and ceramic suspensions are complicated by the reduced thermal capacity and increased thermal conductivity which causes rapid cooling in the runner and mould. Furthermore the yield point behaviour of the suspension changes the flow behaviour at low shear rates. Viscosities of suspensions tend to be much higher than of unfilled polymers[80] and for these reasons the correct choice of machine parameters is important if sound mouldings are to be obtained.[71]

Peshek[69] has listed several requirements for ceramic moulding; optimization of pressure, temperature and injection speed is essential. Quackenbush *et al.*[25] pay particular attention to mould temperature and pressure hold times. It is thought that injection speed has a pronounced effect on ceramic moulding[71] because of the rapid chilling of the melt, described above. Reliability of temperature control is important with correct choice of thermocouple locations to avoid hot or cold spots. Pressure control mechanisms should be hydraulic and allow repeatable and accurate control over a wide range. Injection pressures are typically in the range 35–140 MPa.[72]

Internal stresses in moulded ceramic articles can produce internal defects both during solidification in the cavity or shortly after removal. This is enhanced by the solidification and cooling of a pocket of fluid trapped in the moulding after the sprue or gate has frozen off. Attempts to solve the problem therefore centre on ways of keeping the sprue molten until the interior of the moulding has completely solidified.

Extremely high pressures should compensate for thermal contraction[81] and this approach has been used to produce polyethylene mouldings with net internal compressive stresses.[82] However, the pressures used (up to 450 MPa) are impractically high.

Hot runner moulds have been used for moulding plastics[83] and these allow the moulding to solidify completely under the applied hold pressure.[84] However, they generally demand very small gates which are unsuitable for ceramic suspensions.

Menges *et al.*[85] used an oscillating hold pressure for polymer mouldings designed to compensate for internal shrinkage. Another design for applying oscillating pressure to a ceramic suspension in the mould is described in a German patent.[86] The reciprocating screw is bored to receive an oscillating piston activated from the screw drive end of the machine. Another part of the device applies oscillating pressure to the ceramic material in the mould and this oscillation is claimed to enhance pressure transmission.

Oscillating pressure applied to the moulded material in place of a static hold pressure was used by Allan and Bevis[87,88] to keep the sprue and runners molten during mould cooling and thereby to make 40 × 50 mm thick section mouldings of unfilled polyethylene without sink marks or internal voiding. The oscillating pressure causes viscoelastic heating in the sprue and runners and this allows the interior of the moulding to be filled, compensating for shrinkage. Continuous monitoring of cavity pressure allows the process to be controlled.

The same technique has been applied to short fibre reinforced thermoplastics[89] and ceramics[90] although the device is subject to wear when used with ceramics.

Defects introduced by entrapped air or adsorbed moisture in ceramic injection moulding mixtures have been overcome by using an injection moulding machine in which the feed reservoir and the mould are held under vacuum by a series of valves, a vacuum pump and vacuum reservoir.[91,92]

4.3. Tooling

Design of injection moulding tooling plays a major role in ceramic fabrication. Stanciu[93] outlined the main parameters in tool design. These include a consideration of flow in runners, part geometry, ease of automation and cost. In addition, tool wear is an important factor when moulding abrasive materials.

Incorrect mould design is one of the main causes of weld or knit lines in single gated moulds although incorrect machine settings can also cause this defect. Ideally the gate should be in a position where plug flow into the main part of the moulding is preferred.[25] Stanciu[93] suggests that gates should be placed at the bottom of the cavity to ensure flow against gravity and thus avoid air entrapment, but this is likely to be important only for low-viscosity fluids or low injection speeds. Venting of the die is important in avoiding air entrapment. Venting can proceed through ejector pin clearances or through machined grooves on the die face. Quackenbush *et al.*[25] have suggested that die design should incorporate overflow chambers beyond the die cavity. This allows the initial chilled material entering the mould to be excluded from the moulding.

The conventional mould clamping arrangement of hydraulic ram and toggle has been dismissed by some manufacturers who prefer simple mechanical mould locking for ceramic materials.[94] This is claimed to simplify the machine frame and allow greater versatility in mould design.

Injection moulding of detailed geometries is expensive to automate but automation has been achieved for complex silicon nitride stators.[95]

5. MACHINE WEAR

Wear and corrosion of machine parts and tooling is regarded as a problem in ceramics injection moulding.[69,71,93] The barrel, screw, non-return valve, nozzle and mould are areas especially at risk.[96] The difference in hardness between ceramic particles and metal or cermet parts (Table 1) is a main factor in abrasive wear.[97] A further factor in determining ploughing action is the particle size and size distribution of the ceramic.[98] Pressure on material has a pronounced influence on machine wear and this tends to localize the severity of damage.[98]

TABLE 1

A Comparison of Hardness Values for Typical Ceramics and Some Wear-resistant Materials

	Hardness (GPa)
Ceramics	
Zirconia	14
Sialon	20
Alumina	22
Silicon nitride	25
Silicon carbide	33
Wear-resistant metals and cermets	
Carbon tool steels	8·5
High-speed steels	9·0
Nitrided steels	10·0
Tungsten carbide—16% cobalt	11·5
Tungsten carbide—6% cobalt	15·5

Studies of machine wear caused by filled polymers[99] suggest that material hardness is not a good indicator of wear resistance. Particles produced more severe wear than fibres in the conveying zone but fibres were more damaging in the metering zone. On arrival in the metering zone it is considered that particles would be coated with molten polymer.

Nitrided barrels and chromium-plated steel screws were subjected to severe wear[71] and enhanced leakage flow between flights and barrel made process control impossible. Japan Steel Works incorporated corrosion–abrasion resistant screws although the material is not specified. The barrels were lined with a nickel-based iron–chromium boride composite with a hardness of approximately 7·6 GPa.[71] This reduced damage to the mating screw surfaces compared to metallic cylinders. Also barrel wear with a silicon carbide composition was 20% of that seen on nitrided steel.

Non-return valves of the check ring type have also been subjected to appreciable wear[100] as shown in Fig. 3. Nozzle and nozzle seat wear has been observed[98] on a carbon steel of hardness 4·7 GPa as shown in Fig. 4 but was considerably reduced by using a tool steel of hardness 7·5 GPa.

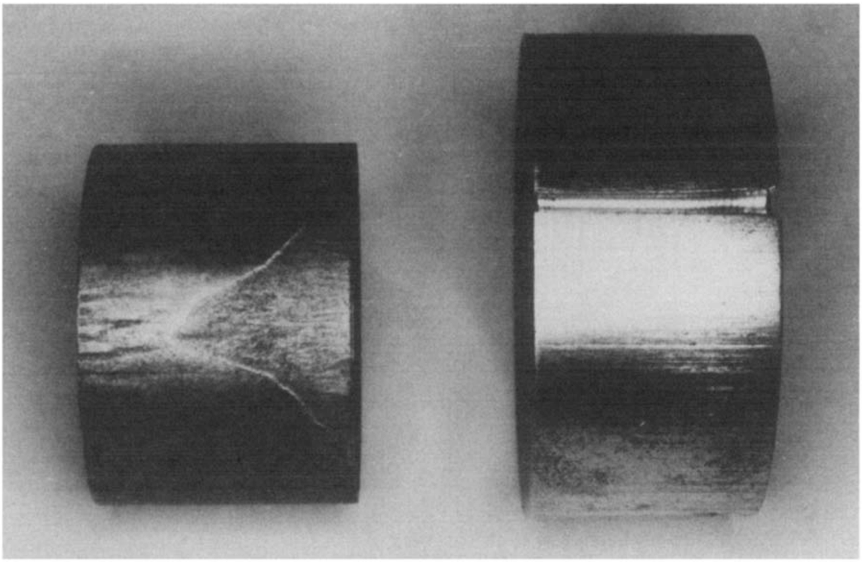

Fig. 3. Wear in check ring-type non-return valves.[100]

Tooling should also be constructed of wear-resistant material and resistance to chipping is also important.[93] Thus high carbon–chromium tool steels have been preferred to high wear-resistant but brittle carbide cermets and for the same reason steel-bonded carbide has been rejected.

Since 1974 high pressures (35–140 MPa) have been used extensively for ceramic injection moulding[101] and this tends to enhance machine wear. Furthermore, with incorrectly formulated compositions dilatancy effects can be induced by high material pressures causing separation of fluid from powder.[25,78] These difficulties have led to the use of lower pressures in the range 0·2–0·6 MPa.[72] The low pressure process originated over 30 years ago in the electronics industry[102] and machines using the same principles

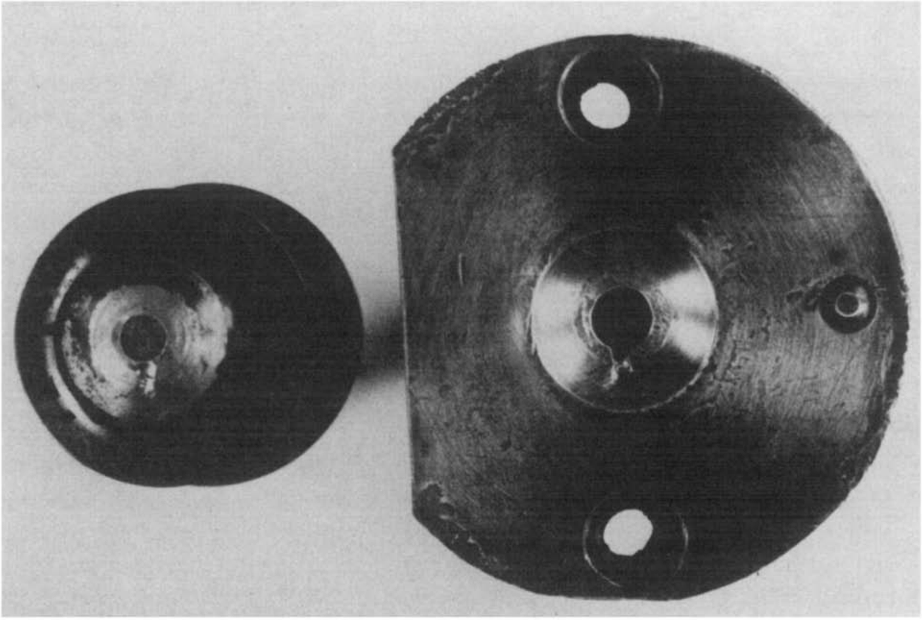

Fig. 4. Wear groove in nozzle and nozzle seat.

are marketed today for ceramic injection moulding.[103] In such machines moving parts such as screws or plungers are absent and energy consumption is small (1–3 kW). Dies are generally small and may be constructed from aluminium or wood because of the low pressures.[72]

Low viscosities ($\simeq$100 Pa s) are achieved by using wax-based systems which are mixed in a thermostatted tank incorporating a planetary mixer. Injection of the die is achieved by imposing air pressure on the material in the tank causing it to flow along a feeder pipe into the mould. The method has been used for silicon nitride, silicon carbide and oxide ceramics[72] but it is not clear how shrinkage defects in thick section mouldings are avoided.

6. DEFECTS IN CERAMIC INJECTION MOULDINGS

Moulding defects may originate at the mould filling stage or during solidification in the cavity. The former include incomplete cavity filling and the incidence of weld or knit lines. The latter are defects which originate from volume shrinkage effects or from unrelieved polymer orientation and consist typically of voids, microvoids, gross cracking or microcracking. Such defects can provide initiation sites for defects found in powder assemblies after polymer removal.

6.1. Mould filling

The entry of fluid into a cavity in an injection moulding machine involves non-isothermal flow of a non-Newtonian fluid through a variety of channel sections under high pressure which itself influences both fluidity and crystalline melting point.[104] It is not therefore a process which can easily be modelled. The enhanced thermal conductivity and lower specific heat of a polymer which has been filled with large volume fraction of ceramic powder means that chilling of the melt is rapid. Incomplete mould filling, especially of thin sections, may result from low material fluidity, low mould temperatures, low barrel temperatures or low injection speeds or pressures. Material fluidity is limited by the need to incorporate large loadings of powder. Higher mould temperatures are limited by the need to eject the component without distortion and barrel temperatures are limited by the degradation of the vehicle during residence.

Filled polymers do not exhibit die swell[105] and show a greater tendency to jet into the cavity producing a coil and resulting in weld lines within the moulding.[71,106] Weld lines are regions of weakness and decrease the toughness.[107] They may persist as defects in the fired ceramic. They are almost inevitable in multi-gated cavities[108] but can also occur in single gated articles if the melt front splits to overcome an obstacle. Gate position can have an important bearing on whether or not welds will occur. In general welds can be avoided on single gated moulds by side gating the cavity to generate plug flow.[25,106]

6.2. Solidification

The development of cracking or voiding in ceramic injection mouldings is related to non-uniform shrinkage.[108] During the early stages of cooling the thickness of the solid skin of material adjacent to the mould wall increases and residual stress may appear, but volume shrinkage is compensated for by the static hold pressure on the fluid material imposed by the plunger or screw. However, at some time after injection the material in the gate freezes and the remaining pocket of fluid in the core of the moulding solidifies, undergoing crystallization and/or thermal contraction. The resulting stresses produce, in many thermoplastics, characteristic sink marks in the surface of the mouldings. In ceramic suspensions, however, such stresses are preferentially relieved by the appearance of voids or cracks. Examples of such defects in injection moulded modulus of rupture bars are shown in Fig. 5. The tendency to produce voids or cracks is influenced by the machine settings but also by the crack arrest temperature of the polymer.[109] The nucleation of voids is particle size dependent[109]

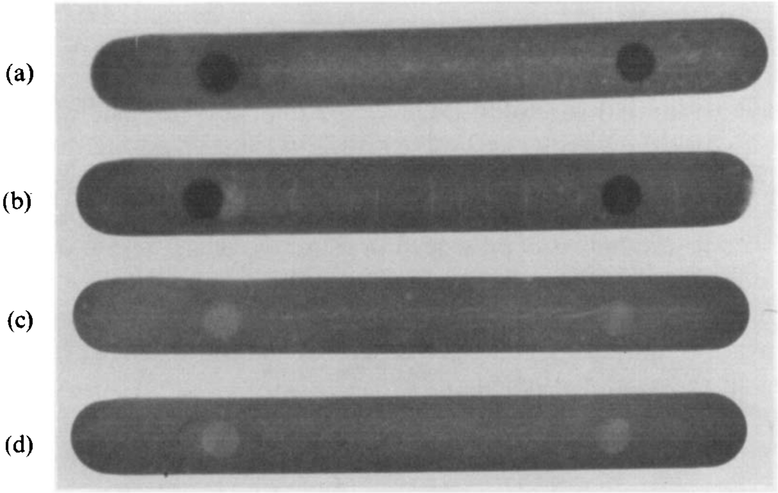

Fig. 5. Defects in injection moulded modulus of rupture bars revealed by X-ray radiography. (a) Shrinkage voids, (b) transverse cracks, (c) longitudinal cracks, (d) free of injection moulding defects.

and takes a Griffith form with stress to nucleate a void being proportional to the reciprocal root of the particle diameter.[110]

For these reasons, post injection hold pressure is an important parameter and indeed for unfilled materials very high pressures (450 MPa) have produced residual compressive stress in the centre of mouldings.[82] Runner and gate geometry is clearly important and large gates are favoured[81] to extend the freeze off time. Ram forward time should be sufficient to apply pressure until the gate freezes. High mould temperatures reduce the differential stresses resulting from rapid cooling rates.[81] High barrel temperatures reduce viscosity sufficiently to enhance pressure transmission.[81] The properties of moulding formulations themselves also influence the incidence of defects.[108] In particular a low temperature dependence of viscosity allows greater pressure transmission to the cavity.[81] These problems are enhanced in regions of mouldings with large sections.

Preferred molecular orientation combined with residual stresses can cause cracking or voiding.[108] During flow in the cavity polymer chains keyed by the solid skin are extended by polymer flow, producing alignment. Orientation is avoided by high melt and mould temperatures which allow recovery to take place. Reduction in injection pressure and speed also reduce the high shear stresses experienced by the material in the mould. In this case thick sections tend to suffer less from polymer orientation effects because of slower cooling.

A recent technique which allows greater control over solidification in the moulding, and therefore allows the production of thick section thermoplastic mouldings, uses an oscillating rather than a static post injection pressure. The methods of achieving this effect are described above and have been used to mould large sections of polyethylene without sink marks or voids.[87,88] More recently short fibre reinforced thermoplastics[89] have been moulded in this way and the technique is being applied to ceramics.[90] The technique causes pressures in the sprue to oscillate at a preset frequency between predetermined limits. The energy absorbed by the material causes the sprue to remain molten and material to enter the interior of the moulding for long and controllable periods after injection. By constantly monitoring the cavity pressure, the shrinkage and resulting stresses in the moulded part can be controlled.

7. POLYMER REMOVAL TECHNIQUES

The thermal and oxidative degradation of polymers has been extensively investigated and is well reviewed.[111-113] Thermal degradation may involve depolymerization, in which the carbon–carbon backbone of the molecule is severed, decreasing the molecular weight, or substituent reactions in which side groups are attacked, typified by the stripping of HCl from polyvinylchloride. The former may occur either by a random process leaving large molecular weight fragments (and this is the case for most polyolefins) or by scission at reactive sites yielding mainly monomer but having little initial effect on molecular weight (and this is the case for polyoxymethylene). Polystyrene is intermediate in behaviour. If oxygen is present, a series of chemical reactions between the polymer and oxygen or oxygen-containing radicals becomes possible and these may be strongly exothermic.

The polymer removal stage of the process involves the extraction of typically 30–40 vol.% of vehicle. Five polymer removal techniques can be identified: (a) thermal degradation of the organic binder in an inert atmosphere,[114] (b) oxidative degradation,[115] (c) capillary flow into a finer powder,[72] (d) evaporation,[116] (e) solvent extraction.[117]

7.1. Thermal degradation

This is the most widely used technique. It involves a very slow heating rate and this leads to long cycle times which could be several weeks for complex shapes.[25,114] If the temperature is not accurately controlled, decomposition of the polymer occurs within a narrow temperature range resulting in high degradation product vapour pressures producing swelling and cracking.[71] Initially the moulding may be heated to its softening point fairly rapidly whereupon the vehicle becomes fluid.[25,118] An exception is where residual stresses are present in mouldings and a low temperature stress relieving treatment is preferred.[114] Subsequently an extremely slow heating rate is required at the early stages of decomposition.[114] Quackenbush *et al.*[25] heated articles at 10°C h^{-1} up to the flow point of the binder and then decreased the rate to 2°C h^{-1} between 150 and 450°C. The rate could be increased to 10°C h^{-1} towards the end of the process when a substantial void volume was present.

Vacuum or inert gas atmospheres are preferred[24,114] during polymer removal. Pressures of 7–14 Pa have been found acceptable.[114] This avoids the strong exothermic reaction of polymers with oxygen which hinders process control.

Attempts have been made to use a blend of polymers with different molecular weight characteristics in order to broaden the burn-out region.[114,119] It is significant that for nitrogen ceramics, carbon residue is undesirable. Similarly ash content of the polymer becomes important in some applications where very low silicate or sodium levels are required and in particular for optical property control.

It is a common practice to embed injection moulded articles in a fine powder such as alumina during polymer removal.[24,25,71,114,120–122] The powder bed may perform several functions. It may allow temperature uniformity in the furnace, avoiding surface radiant heating. It may, under certain circumstances, extract fluid from the article by capillary action. It may reduce the steep gas partial pressure gradients at the surface of the moulding. It may also support the moulding in its softened state and prevent sagging.[71] Unfortunately the condensation of polymer degradation products in the powder bed may give errors in weight loss measurements and thus interfere with process control.[114]

Peltsman and Peltsman[72] used a powder bed to extract binder from the component surface by capillary action. They used a low-viscosity wax but the same technique may be less effective with high polymers. They initiated the capillary extraction process between 50 and 60°C and continued heating to 120°C. Evaporation of the remaining binder continued up to 300°C. Ideally in this method the powder bed should be composed of a somewhat finer powder than that of the moulded article. Its success with mouldings of ultrafine precipitated powders has not yet been demonstrated.

The early Bendix process for polymer removal took many days. The binder was a blend of polyethylene, paraffin wax and beeswax[116] and speeding up the process resulted in cracking and blistering. Strivens[120] increased the burn-out rates of this process by incorporating thermosets into the formulation and reduced the removal time to 20 h. It is suggested that the incorporation of thermosetting resins increased the inter-particle adhesion at elevated temperatures. Thus Wiech[116] suggests that the internal energy of the binder decomposition products must be less than the cohesive energy of the particle assembly if defects are to be avoided at this stage.

7.2. Oxidative degradation

Mutsuddy[115] has reported that after investigating alternative approaches to binder removal, oxidative degradation of polyolefins is the most effective. Polyolefins, either as waxes or high polymers, have been used extensively as ceramic injection moulding vehicles[1] and their degradation,[123–125] reaction products[126–128] and catalytic influences[129,130] have been well documented. Some general points deserve emphasis. Although tacticity of polyolefins does not influence thermal degradation, atactic polypropylene reacts with more oxygen than the isotactic polymer because more tertiary carbons are accessible.[131] The tertiary carbons produced by side chain branching are very susceptible to attack and for this reason polypropylene is much less stable than polyethylene. Of particular interest is the influence of sample thickness on the oxidation of polyolefins. An effect of thickness caused by oxygen diffusion is found in degradation studies, when sample thickness exceeds 250 μm.[132] Not only does the rate of reaction depend on oxygen partial pressure but the nature of the reaction sequence also changes.[133] Since most injection moulded articles are much larger than 250 μm the oxygen diffusion step controls the kinetics and the complexity of reaction sequences and hinders the application of known kinetic data to the problem of process control. Thus Mutsuddy[115] states that temperature–time schedules have to be modified for changes in size and shape of component as well as minor changes in the binder. However, he has attempted to identify reaction sequences in polyethylene binder removal by gas analysis in order to help devise burn-out schedules.[115]

Johnsson *et al.*[114] used weight loss measurement to control the heating rate of a burn-out oven under vacuum. The temperature followed a preset ramp provided the weight loss was below a critical value. The furnace temperature was reduced if this value was exceeded. In this way 13 wt% of polyethylene was removed from silicon nitride mouldings in 30 h for 10 mm thick cylinders and 35 h for a 20 mm thick cylinder. This represents at least a 50% reduction in cycle time compared to linear heating rates. These authors claim that supporting the moulding in a powder bed was not necessary.

Flaw generation during binder removal by thermal degradation can occur early in the cycle.[25] When the binder becomes fluid, flaws can be generated by expansion of air compressed into the component during injection moulding. Blistering and cracking of the components can occur if the temperature is increased too steeply due to rapid evolution of volatiles.[25]

Delamination or internal cracking is a more serious type of burn-out flaw.[25] It is claimed to be independent of the binder removal rate and depends on powder loading and morphology of the powder.[25] It can also be related to the use of certain organic vehicle systems.[25] Control over this type of flaw has been achieved by modifying powder loading levels and by selecting suitable surfactants.[25] The binder is preferentially removed from the surface of mouldings but subsequently, as polymer emerges from the interior, the resulting slight shrinkage generates tensile stresses and causes internal cracks. 'Skin' formation is another defect frequently observed.[71] This can produce surface cracks and blistering. This has not been fully explained but may be related to preferential polymer degradation at the surface.

7.3. Evaporation

Weich[116] has preferred evaporation or sublimation of binders. The moulded articles were placed in a chamber with control of binder partial pressure and of temperature. Thus control of diffusion and evaporation was achieved. The volatile binder was recondensed and reused. This method has been demonstrated with 3–5 μm metal powders and low molecular weight organic binders. Controlled drying also becomes possible where water-soluble or water-based emulsion polymer systems are used.[1]

7.4. Solvent extraction

A two-component vehicle was used wherein one component was soluble in the extraction solvent and the other insoluble.[117] Combinations of thermoplastic waxes and thermosetting resins have been employed.[117,120] Extraction was effected by immersion in, or washing with, boiling solvent prior to drying. The process can be automated by using a conveyor belt which passes through a solvent wash and drying zones. A wide range of solvents have been used,[117] many of which require expensive plant to control.

The advantage claimed for solvent extraction was faster removal of the organic vehicle.[117] It was also claimed to be more economical, requiring less expensive plant. To meet modern safety regulations this may no longer be valid. The solvent can be distilled and reused.

7.5. Polymer precursors

It is natural to question the need to remove the fluid phase in its entirety from ceramic mouldings and for this reason the current interest in polymer precursors for ceramics[134] impinges on injection moulding. Silicone oils have been used in moulding compositions to produce silica in the fired ceramic.[135,136] The use of polymer precursors for ceramics was first suggested by Chantrell and Popper.[137] Such techniques have found most use in the fabrication of ceramic fibres.[138,139] There is, however, considerable interest in the fabrication of monolithic ceramics of silicon carbide and boron carbide from polymers.[140] The use of such materials in the binder formulation would have several major advantages; a reduction in the volume of gaseous product to be removed, an increase in the prefired strength of the powder assembly and a reduction in shrinkage during burn-out. Polymers which efficiently deposit ceramic residues are currently being developed[141–143] and this makes the direct fabrication of monolithic ceramics feasible. Such a procedure would avoid the rheological and mixing problems of moulding suspensions and it would eliminate the problem of severe machine wear.

8. CONCLUSIONS

The concept of injection moulding began with metals technology, was transferred to plastics engineering and is now increasingly used for ceramics fabrication. Many of the techniques developed for polymer, and especially reinforced polymer, processing can be applied to ceramics forming.

Dispersive mixing of powders in a polymer blend by machines whose configuration imposes high shear stress is the preferred mixing method. There are three common machine types and each uses two principal moving parts: two-roll mills, double-cam mixers and twin-screw extruders.

A wide range of injection moulding machines can be used for components of small cross-section but the real challenge to ceramic injection moulding technology is the ability to produce thick sections which will survive solidification in the cavity and subsequent polymer removal without the incidence of defects. Solutions to the former problem include techniques for keeping the sprues and runners molten during the post injection stage to allow extended mould filling and thus control shrinkage stresses during solidification and cooling.

Available reports suggest that the wear of ceramic moulding machinery tends to be localized and that specific machine parts require special and often expensive materials. The complex screw does not necessarily experience the most severe wear.

Numerous ingenious methods have been devised to remove the polymer vehicle. In addition to thermal and oxidative degradation, these include solvent washing, capillary extraction and evaporation or sublimation.

While each method has its disadvantages, thermal degradation has been the most frequently cited method. Weight loss–temperature control loops on furnaces allow the polymer extraction time to be minimized. There remains little quantitative understanding of the process; diffusivities of low molecular weight components or degradation products in molten polymer blends are largely uncharted. The mechanical strength of the powder assembly and the extent of shrinkage which it undergoes during polymer removal both influence the incidence of defects.

The problems presented by this technology impinge on many specialisms within materials technology, engineering and chemistry and thus skills in collaborative research planning have tended to yield the most significant developments.

REFERENCES

1. Edirisinghe, M. J. and Evans, J. R. G., Review: fabrication of engineering ceramics by injection moulding. I. Materials selection, *Int. J. High Tech. Ceram.*, **2** (1986) 1–31.
2. Tadmor, Z. and Gogos, C. G., *Principles of Polymer Processing*, Wiley, New York, 1979, Chapter 7.
3. Uhl, V. W. and Gray, J. B. (Eds), *Mixing: Theory and Practice II*, Academic Press, New York, 1967, Chapter 8.
4. Middleman, S., *Fundamentals of Polymer Processing*, McGraw-Hill, New York, 1977, Chapter 12.
5. Messer, P. F., *Milling and Mixing*, to be published.
6. Lange, F. F., Processing-related fracture origins I. Observations in sintered and isostatically hot-pressed Al_2O_3–ZrO_2 composites, *J. Am. Ceram. Soc.*, **66** (1983) 393–8.
7. Kellet, B. and Lange, F. F., Stresses induced by differential sintering in powder compacts, *J. Am. Ceram. Soc.*, **67** (1984) 369–71.
8. Lange, F. F. and Metcalf, F., Processing-related fracture origins II. Agglomerate motion and cracklike internal surfaces, *J. Am. Ceram. Soc.*, **66** (1983) 398–406.
9. Lange, F. F., Davis, B. E. and Aksay, I. A., Processing-related fracture origins III. Differential sintering of ZrO_2 agglomerates, *J. Am. Ceram. Soc.*, **66** (1983) 407–8.
10. Lange, F. F., Sinterability of agglomerated powders, *J. Am. Ceram. Soc.*, **67** (1984) 83–9.
11. Hornsby, P. R., Design and application of a laboratory twin-screw compounding extruder, *Plastics Compounding*, **6** (1983) 65–70.
12. Edirisinghe, M. J. and Evans, J. R. G., *Proc. Brit. Ceram. Soc.*, to be published.
13. Tadmor, Z. and Gogos, C. G., *Principles of Polymer Processing*, Wiley, New York, 1979, p. 434 et seq.
14. Barringer, E. A. and Bowen, H. K., Formation, packing and sintering of monodisperse TiO_2 powders, *J. Am. Ceram. Soc.*, **65** (1982) C199–201.

15. Milne, S. J., *Proc. Brit. Ceram. Soc.*, to be published.
16. Fan, L. T., Chen, S. J. and Watson, C. A., Solids mixing, *Ind. Eng. Chem.*, **62** (1970) 53–69.
17. Fan, L. T. and Wang, R. H., On mixing indices, *Powder Technology*, **11** (1975) 27–32.
18. Lacey, P. M. C., Developments in the theory of particle mixing, *J. Appl. Chem.*, **4** (1954) 257–68.
19. Weidenbaum, S. S., Mixing of solids, in *Advances in Chemical Engineering II*, Eds T. B. Drew and J. W. Hooper, Academic Press, New York, 1958, 211–321.
20. Irving, H. F. and Saxton, R. L., Mixing of high viscosity materials, in *Mixing Theory and Practice II*, Eds V. W. Uhl and J. B. Gray, Academic Press, New York, 1967, Chapter 8.
21. Tadmor, Z. and Gogos, C. G., *Principles of Polymer Processing*, Wiley, New York, 1979, Chapter 8.
22. Schwartzwalder, K., Injection moulding of ceramic materials, *Am. Ceram. Soc. Bull.*, **28** (1949) 459–61.
23. Taylor, H. D., Injection moulding intricate ceramic shapes, *Am. Ceram. Soc. Bull.*, **45** (1966) 768–70.
24. Mann, D. L., *Injection Moulding of Sinterable Silicon-Base Non-Oxide Ceramics*, Technical Report AFML-TR-78-200, Dec. 1978.
25. Quackenbush, C. L., French, K. and Neil, J. T., Fabrication of sinterable silicon nitride by injection moulding, *Ceram. Eng. Sci. Proc.*, **3** (1982) 20–34.
26. Birchall, J. D., Howard, A. J. and Kendall, K., Imperial Chemical Industries Ltd, UK, *Cementitious product*, Eur. Patent 0021682, 7 Jan. 1981. Date of filing: 6 Jun. 1980.
27. Fenner, R. T., *Principles of Polymer Processing*. Macmillan, London, 1979, Chapter 6.
28. Fisher, E. G., *Extrusion of Plastics*, Butterworths, London, 1976.
29. Tadmor, Z. and Klein, I., *Engineering Principles of Plasticating Extrusion*, R. E. Krieger Publ. Co., New York, 1978.
30. Janssen, L. P. B. M., *Twin-Screw Extrusion*, Elsevier, Amsterdam, 1978.
31. SpA Plastic Materials Laboratory, *Improvements in or relating to moulding thermoplastic synthetic resins by extrusion*, UK Patent 629 109, 13 Sept. 1949. Date of filing: 2 May 1946.
32. Martelli, F., *Twin Screw Extruders*, Van Nostrand, New York, 1983.
33. UK laboratory compounding extruder sets high standards, *European Plastics News*, June (1982) 9.
34. Abram, J., Bowman, J., Behiri, J. C. and Bonfield, W., The influence of compounding route on the mechanical properties of highly loaded particulate filled polyethylene composites, *Plast. and Rubb. Proc. and Appl.*, **4** (1984) 261–9.
35. Hornsby, P. R. and Sothern, G. R., Polymer degradation during twin screw extrusion compounding, *Plast. and Rubb. Proc. and Appl.*, **4** (1984) 165–71.
36. Donald, I. W. and McMillan, P. W., Review: ceramic–matrix composites, *J. Mat. Sci.*, **11** (1976) 949–72.
37. Schioler, L. J. and Stiglich, J. J., Ceramic matrix composites: a literature review, *Am. Ceram. Soc. Bull.*, **65** (1986) 289–92.

38. Folkes, M. J., *Short Fibre Reinforced Thermoplastics*, Wiley, New York, 1982.
39. Delmonte, J., *Technology of Carbon and Graphite Fibre Composites*, Van Nostrand Reinhold, New York, 1981.
40. Bevis, M. J., Gaspar, E., Allan, P. and Hornsby, P. R., Brunel University, UK, *Forming articles from composite materials*, UK Patent Application 8511152. Date of filing: 2 May 1984.
41. Willis, R. R., Markle, R. A. and Mukherjee, S. P., Siloxanes, silanes and silazanes in the preparation of ceramics and glasses, *Am. Ceram. Soc. Bull.*, **62** (1983) 904–11.
42. Sturges, R. F., *Manufacture of candlesticks and lamp pillars*, UK Patent 12480, 14 Aug. 1849. Date of filing: 14 Feb. 1849.
43. Hyatt, I. S. and Hyatt, J. W., Celluloid Manufacturing Co., USA, *Improvements in processes and apparatus for manufacturing pyroxyline*, US Patent 133 229, 19 Nov. 1872.
44. Hyatt, J. W., Celluloid Manufacturing Co., USA, *Improvements in coating articles with celluloid and carbon*, US Patent 202 441, 16 Apr. 1878. Date of filing: 25 Mar. 1878.
45. Rubin, I. I., *Injection Moulding Theory and Practice*, Wiley, New York, 1972, 1.
46. Richards, F. H., *Apparatus for moulding playing balls*, US Patent 791 649, 6 Jun. 1905. Date of filing: 10 Feb. 1903.
47. Eichengrun, A., Cellon Works, Germany, *Process for the production of moulded articles from cellulose acetate*, UK Patent 147 904, 9 Nov. 1921. Date of filing: 9 Jul. 1920.
48. Eichengrun, A., Cellon Works, Germany, *Process for the production of moulded articles from cellulose acetate and the like cellulose derivatives*, UK Patent 171 432, 9 Nov. 1921. Date of filing: 9 Jul. 1920.
49. Buchholz, H., *Process of making moulded articles*, US Patent 1 810 126, 16 Jun. 1931. Date of filing: 14 Nov. 1923.
50. Thomas, I., *Injection Moulding of Plastics*, Reinhold, New York, 1947, Chapters 1 and 2.
51. Gaspar, E., Polymer history: the injection moulding process, *Shell Polymers*, **5** (1981) 40–2.
52. Walker, J. S. and Martin, E. R., *Injection Moulding of Plastics*, Iliffe, London, 1966, 2.
53. Jeffrey, H. L., Grotelite Co., USA, *Moulding machine*, US Patent 2 111 857, 22 Mar. 1938. Date of filing: 5 Apr. 1932.
54. Piperoux, R. P. and Radburn, N. J., Celluloid Corp., USA, *Extruded article and device for making same*, US Patent 2 161 588, 6 Jun. 1939. Date of filing: 22 Mar. 1935.
55. Gastrow, H., *Improvements in and relating to apparatus for moulding plastic material*, UK Patent 424 369, 20 Feb. 1935. Date of filing: 11 Dec. 1933.
56. Burroughs, C. F., *Injection moulding apparatus*, US Patent 2 202 140, 28 May 1940. Date of filing: 4 Aug. 1936.
57. Rapid, continuous injection of thermosetting materials, *Modern Plastics*, **21** (1944) 90–1.
58. Stanley, F. B. (Ed.), Three newcomers, *Modern Plastics*, **21** (1944) 121–3 and 188.

59. Injection–compression moulding of acrylic feeder heads, *Modern Plastics*, **23** (1945) 146–50.
60. Rakas, N. J. and Cousino, W. B., A multi-purpose moulding machine, *Modern Plastics*, **22** (1944) 133–41 and 196.
61. Crawford, R. J., *Progress in Plastics Engineering*, Pergamon Press, London, 1981, 169–70.
62. Fisher, E. G. and Maslen, W. A., Preplasticising in injection moulding. Part I. The principles of preplasticising and the history of its development, *British Plastics*, **32** (1959) 417–22.
63. Wood, R., Preplasticising in injection moulding. Part II. A classification of plunger and screw type machines and equipment in use, *British Plastics*, **32** (1959) 468–74.
64. Fisher, E. G. and Maslen, W. A., Preplasticising in injection moulding. Part III. Comparison of extruding systems and suggested requirements of an ideal system, *British Plastics*, **32** (1959) 516–20.
65. Simonds, H. R. (Ed.), *The Encyclopedia of Plastics Equipment*, Reinhold, New York, 1964, 306.
66. Kriner, W. G., Graphic comparison of screw and plunger machine performance, *Modern Plastics*, **39** (1962) 121–32 and 214.
67. Weir, C. L. and Zimmerman, P. T., Facts and figures on ram versus screw injection, *Modern Plastics*, **40** (1962) 122–5 and 220.
68. Weir, C. L. and Zimmerman, P. T., Ram versus screw injection Part II, *Modern Plastics*, **40** (1962) 123–8, 133 and 190.
69. Peshek, J. R., Machinery for injection moulding of ceramic shapes, in *Advances in Ceramics*, Vol. 9, Ed. J. Mangels, 1984, 234–8.
70. *Special Purpose Machines*, Mercia Machinery Sales Ltd, UK, Trade literature, 1986.
71. *Injection Moulding Machine for New Ceramics*, Japan Steel Works (Hiroshima Plant), Trade literature, 1984.
72. Peltsman, I. and Peltsman, M., Low pressure moulding of ceramic materials, *Interceram*, **4** (1984) 56.
73. Rottenkolber, P., Langer, M., Storm, R. S. and Frechette, F., *Design, Fabrication and Testing of an Experimental Alpha Silicon Carbide Turbocharger Rotor*, Society of Automotive Engineers, USA, Publication No. 810523, 1981.
74. Uchida, I. and Inami, T., The control system and the program of 'μPACS-2000' for injection moulding machine, *Nihon Seihojo Giho*, **41** (1982) 21–35.
75. Mangels, J. A., Injection moulding ceramics, *Ceram. Eng. and Sci. Proc.*, **3** (1982) 529–37.
76. Crossley, I. A., Kirk, G. E., Anthony, N. H. and Bamber, D. R., Rolls-Royce Ltd, London, UK, *Injection of a ceramic into a mould cavity*, US Patent 3 882 210, 6 May 1975, Date of filing: 17 Nov. 1972.
77. Ohnsorg, R. W., The Carborundum Co., USA, *Composition and process for injection moulding ceramic materials*, US Patent 4 144 207, 13 Mar. 1979. Date of filing: 27 Dec. 1977.
78. Ohnsorg, R. W., The Carborundum Co., USA, *Process for injection moulding sinterable carbide ceramic materials*, US Patent 4 233 256, 11 Nov. 1980. Date of filing: 18 Dec. 1978.
79. Cox, H. W., Mentzer, C. C. and Custer, R. C., The flow of thermoplastic melts—Experimental and predicted, *SPE Antec*, **29** (1983) 694–7.

80. Farris, R. J., Prediction of the viscosity of multimodal suspensions from unimodal viscosity data, *Trans. Soc. Rheol.*, **12** (1968) 281–301.
81. Rubin, I. I., *Injection Moulding Theory and Practice*, Wiley, New York, 1972, 270–317.
82. Kubat, I. and Rigdahl, M., Influence of high injection pressures on the internal stress level in injection moulded specimens, *Polymer*, **16** (1975) 925–9.
83. Rubin, I. I., *Injection Moulding Theory and Practice*, Wiley, New York, 1972, 104.
84. Morrison, R. V., Discovision Assoc., USA, *Hot sprue assembly for an injection moulding machine*, US Patent 4 412 805, 1 Nov. 1983. Date of filing: 23 Sept. 1981.
85. Menges, G., Koenig, D., Luettgens, R., Sarholz, R. and Schuermann, E., Follow up pressure pulsation in the manufacture of thick walled high strength thermoplastic components, *Plastverarbeiter*, **31** (1980) 185–93.
86. Demag Kunststofftechnik, Federal Republic of Germany, *Method of apparatus for moulding plastic ceramic materials*, UK Patent 1 553 924, 10 Oct. 1979. Date of filing: 23 Dec. 1976.
87. Allan, P. S. and Bevis, M., The production of void-free thick-section injection-flow mouldings I. Shot-weight and dimensional reproducibility, *Plast. and Rubb. Proc. and Appl.*, **3** (1983) 85–91.
88. Allan, P. S. and Bevis, M., The production of void-free thick-section injection-flow mouldings II. Preferred orientation and residual stress measurements, *Plast. and Rubb. Proc. and Appl.*, **3** (1983) 331–6.
89. Allan, P. S. and Bevis, M., Producing void-free thick-section thermoplastic and fibre reinforced thermoplastic mouldings, *Plas. Rubb. Int.*, **9** (1984) 32–6.
90. Edirisinghe, M. J. and Evans, J. R. G., *J. Mater. Sci. Lett.* (1986), in press.
91. Huther, W., Motor and Turbine Union, Federal Republic of Germany, *Injection moulding apparatus*, UK Patent 2 086 796, 19 May 1982. Date of filing: 27 Oct. 1981.
92. Huther, W., Motor and Turbine Union, Federal Republic of Germany, *Apparatus for injection moulding of precision parts*, US Patent 4 412 804, 1 Nov. 1983. Date of filing: 4 Nov. 1981.
93. Stanciu, V. V., Tooling for ceramic injection moulding, in *Advances in Ceramics*, Vol. 9, Ed. J. Mangels, 1984, 239–40.
94. IFO AB, Sweden, *Improvements in or relating to injection moulding machines*, UK Patent 1 433 638, 28 Apr. 1976. Date of filing: 20 Jul. 1973.
95. Johnson, C. F. and Mohr, T. G., Injection moulding 2·7 g/cc silicon nitride turbine rotor blade rings utilising automatic control, in *Ceramics for High Performance Applications II*, Eds J. J. Burke, E. N. Lenoe and R. N. Katz, Brook Hill Publishing Co., Chestnut Hill, MA, 1978, 193–206.
96. Honstrater, R. A., A practical approach to screw and barrel wear and repair, *Plastics Engineering*, **37** (1981) 35–8.
97. Bowden, F. P. and Tabor, D., *The Friction and Lubrication of Solids*, Clarendon Press, Oxford, 1950, 294.
98. Edirisinghe, M. J. and Evans, J. R. G., to be published.
99. Reinhard, M., Ways of wear reduction in plastics processing, *SPE Antec*, **30** (1984) 798–802.
100. Dawson, D., A.E. Turbine Components Ltd, UK, private communication.

101. Mutsuddy, B. C., Injection moulding research paves way to ceramic engine parts, *J. Ind. Res. and Dev.*, **25** (1983) 76–80.
102. Gribovsky, P. O., *Hot Moulding of Ceramic Parts*, G.E.I., Moscow-Leningrad, 1961, 400.
103. Peltsman, I. and Peltsman, M., Improvements in machinery for hot moulding of ceramics under low pressure, *Ceram. Eng. and Sci. Proc.*, **3** (1982) 865–8.
104. Wunderlick, B. (Ed.), *Macromolecular Physics III*, Academic Press, New York, 1980, 91.
105. Sugano, T., Materials for injection moulding silicon carbide, in *Proceedings of the 1st Symposium on Research and Development of Basic Technology for Future Industry*, Fine Ceramics Project, Japan Tech. Assoc., Tokyo, 1983, 67–84.
106. Mangels, J. A. and Trela, W., Ceramic components by injection moulding, in *Advances in Ceramics*, Vol. 9, Ed. J. Mangels, 1984, 220–3.
107. Criens, R. M. and Moste, H. G., On the influence of knit lines on the mechanical behaviour of injection moulded structural elements, *SPE Antec*, **28** (1982) 22–4.
108. Crawford, R. J., *Progress in Plastics Engineering*, Pergamon Press, London, 1981, 189–97.
109. Su, K. B. and Suh, N. P., Void nucleation of particulate filled polymeric materials, *SPE Antec*, **27** (1981) 46–9.
110. Gent, A. N. and Park, B., Failure processes in elastomers at or near a rigid spherical inclusion, *J. Mat. Sci.*, **19** (1984) 1947–56.
111. Grassie, N., Degradation, in *Polymer Science*, Vol. II, Ed. A. D. Jenkins, North Holland, Amsterdam, 1972.
112. Reich, L. and Stivala, S. S., *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971.
113. Conley, R. T. (Ed.), *Thermal Stability of Polymers*, Marcel Dekker, New York, 1970.
114. Johnsson, A., Carlstrom, E., Hermansson, L. and Carlsson, R., Minimization of the extraction time for injection moulded ceramics, *Proc. Brit. Ceram. Soc.*, **33** (1983) 139–7.
115. Mutsuddy, B. C., Oxidative removal of organic binders from injection moulded ceramics, *International Conference on Non-Oxide Technical and Engineering Ceramics*, National Institute of Higher Education, Limerick, Ireland, 10–12 July 1985.
116. Wiech, R. E., *Method and means for removing binder from a green body*, US Patent 4 305 756, 15 Dec. 1981. Date of filing: 14 Jan. 1980.
117. Strivens, M. A., Standard Telephones and Cables Ltd, UK, *Improvement in or relating to the formation of moulded articles from sinterable materials*, UK Patent 808 583, 4 Feb. 1959. Date of filing: 13 Jul. 1956.
118. Wiech, R. E., Parmatech Corp., USA, *Manufacture of parts from particulate material*, UK Patent 1 516 079, 28 Jun. 1978. Date of filing: 30 Mar. 1977.
119. Litman, A. M., Schott, N. R. and Tozlowski, S. W., Rheological properties of highly filled polyolefin/ceramic systems suited for injection moulding, *Soc. Plas. Eng. Tech.*, **22** (1976) 549–51.
120. Strivens, M. A., Standard Telephones and Cables, UK, *Improvements in or relating to the formation of moulded articles from sinterable materials*, UK Patent 779 242, 17 Jul. 1957. Date of filing: 7 Aug. 1953.

121. Watanabe, K., Special Ceramics Co., Japan, *Ceramic binder removal method*, Japanese Patent 100973, 23 Jun. 1982. Date of filing: 10 Dec. 1980.
122. Curry, J. D., Leco Corp., USA, *Apparatus and method of manufacture of article containing controlled amounts of binder*, US Patent 4011291, 8 Mar. 1977. Date of filing: 2 Sept. 1975.
123. Sedlazek, B., Verberger, C. G., Mark, H. F. and Fox, T. G. (Eds), Degradation and stabilization of polyolefins, *J. Polym. Sci. Polymer Symposium No. 57*, Wiley, New York, 1976.
124. Luongo, J. P., Infra-red study of oxygenated groups formed in polyethylene during oxidation, *J. Polym. Sci.*, **42** (1960) 139–50.
125. Canterino, P. J., Ethylene polymers, in *Encyclopedia of Polymer Science and Technology*, Vol. 6, Eds H. F. Mark and N. G. Gaylord, Wiley, New York, 1967, 275–454.
126. Adams, J. H., Analysis of non-volatile oxidation products of polyethylene, *J. Polym. Sci.*, **8** (1970), 1077–90.
127. Tsuchiya, Y. and Sumi, K., Thermal decomposition products of polypropylene, *J. Polym. Sci.*, **7** (1969), 1599–1607.
128. Tsuchiya, Y. and Sumi, K., Thermal decomposition products of polyethylene, *J. Polym. Sci.*, **6** (1968) 415–24.
129. Chaudhri, S. A., The metal salt catalysed antioxidation of atactic polypropylene in solution II. Behaviour of Co, Ni, Fe and Cu salts as catalysts, *Polymer*, **9** (1968) 604–8.
130. Hansen, R. H., Thermal and oxidative degradation of polyethylene, polypropylene and related olefin polymers, in *Thermal Stability of Polymers*, Ed. R. T. Conley, Marcel Dekker, New York, 1970, 153–88.
131. Hansen, R. H., Thermal and oxidative degradation of polyethylene, polypropylene and related olefin polymers, in *Thermal Stability of Polymers*, Ed. R. T. Conley, Marcel Dekker, New York, 1970, 162.
132. Hansen, R. H., Thermal and oxidative degradation of polyethylene, polypropylene and related olefin polymers, in *Thermal Stability of Polymers*, Ed. R. T. Conley, Marcel Dekker, New York, 1970, 158–60.
133. Reich, L. and Stivala, S. S., *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971, 10.
134. Rice, R. W., Ceramics from polymer pyrolysis. Opportunities and needs, *Am. Ceram. Soc. Bull.*, **62** (1983) 889–92.
135. Burroughs, J. E. and Thornton, H. R., Refractory aerospace structural components by plastic moulding process, *Am. Ceram. Soc. Bull.*, **45** (1966) 187–92.
136. Matkin, D. I., Denton, I. E., Valentine, T. M. and Warrington, P., The fabrication of silicon nitride by ceramic/plastic technology, *Proc. Brit. Ceram. Soc.*, **22** (1973) 291–304.
137. Chantrell, P. G. and Popper, P., Inorganic polymers and ceramics, in *Special Ceramics*, Ed. P. Popper, Academic Press, New York, 1965, 87–103.
138. Hasegawa, Y., Limura, M. and Yajima, S., Synthesis of continuous silicon carbide fibre, *J. Mat. Sci.*, **15** (1980) 720–8.
139. Yajima, S., Hasegawa, Y., Ohamura, K. and Matsuzawa, T., Development of high tensile strength silicon carbide fibre using an organosilicon polymer precursor, *Nature*, **273** (1978) 525–7.
140. Walker, B. E., Rice, R. W., Becker, P. F., Bender, B. A. and Coblenz, W. S.,

Preparation and properties of monolithic and composite ceramics produced by polymer pyrolysis, *Am. Ceram. Soc. Bull.*, **62** (1983) 916–23.
141. Seyferth, D. and Wiseman, G. H., High yield synthesis of Si_3N_4/SiC ceramic materials by pyrolysis of a novel polyorganosilane, *J. Am. Ceram. Soc.*, **67** (1984) C132–7.
142. Yajima, S., Special heat resisting materials from organometallic polymers, *Am. Ceram. Soc. Bull.*, **62** (1983) 893–915.
143. Schilling, C. L., Wesson, J. P. and Williams, T. C., Polycarbosilane precursors for silicon carbide, *Am. Ceram. Soc. Bull.*, **62** (1983) 912–15.

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