The Use of Modulated Pressure in Ceramic Injection Moulding

J. G. Zhang, M. J. Edirisinghe & J. R. G. Evans

Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

Abstract

Ceramic rotors consisting of either 57 vol. % silicon nitride or 65 vol. % silicon powders in a polypropylene and wax vehicle were injection-moulded with oscillating hold pressure. At low pressure amplitudes, moulding defects resulting from residual stresses were detected by X-ray radiography. At high amplitudes, defects were detected after a low-temperature heat treatment. At intermediate amplitudes the components were free from macroscopic defects prior to polymer extraction.

Keramische Rotoren, bestehend aus 57 Vol.% Siliziumnitrid oder 65 Vol.% Siliziumpulver in Polypropylen und einem Wachsbindemittel, wurden mit oszillierenden Haltedrücken spritzgegossen. Bei niedrigen Druckamplituden wurden Gußdefekte, hervorgerufen durch Restspannungen, mit röntgenographischen Untersuchungen gefunden. Bei hohen Druckamplituden konnten Defekte nach Temperaturbehandlungen bei niedrigen Temperaturen festgestellt werden. Amplituden bei mittleren Drücken führten zu Bauteilen ohne makroskopische Defekten vor der Polymerextraktion.

Des rotors en céramique constitués soit de 57% volumiques de poudre de nitrure de silicium, soit de 65% volumiques de poudre de silicium dans un véhicule de cire et de polypropylène ont été moulés par injection sous pression oscillante. A basse amplitude, les défauts de moulage résultant des contraintes résiduelles ont été détectés par radiographie de rayons X. Pour de hautes amplitudes, les défauts ont été détectés après un traitement thermique à basse température. Les éléments soumis seulement à des amplitudes intermédiaires ne présentaient pas de défauts macroscopiques avant l'extraction du polymère.

1 Introduction

The rapid development of technical ceramics for heat engine applications has placed emphasis on the mass production of ceramic components of complex shape from fine particles. Provided the powder can be incorporated in an organic vehicle, a range of plastic-forming processes becomes available to ceramic technology, among them extrusion,[1] blow moulding[2] and, most importantly, injection moulding.[3,4] There is therefore considerable scope for the appropriate application of reinforced polymer manufacturing techniques in ceramics fabrication. The forming process must, in each case, be followed by a polymer removal stage in which the organic vehicle is extracted, generally by pyrolysis,[4] prior to sintering the ceramic to near full density.

The initial operation is the dispersive mixing of fine ceramic powder in a polymer blend. It has been shown that intensive shear mixing in a laboratory twin screw extruder[5,6] is more effective in dispersing agglomerates than other mixing methods[7] and thus twin-screw extrusion was used as the compounding method in this work. On the basis of a study of the rheology of ceramic suspensions,[8,9] a polypropylene and wax blend was selected as the organic vehicle.

There is a tendency for moulded ceramic bodies, especially those containing large sections, to contain macroscopic internal defects arising from shrinkage in the mould.[10] These take the form of voids or cracks and, in concentrated suspensions which have higher rigidity and lower toughness than unfilled polymers, take preference over plastic deformation as a means of relieving residual stresses. Their effect on the mechanical properties of the fired ceramic is catastrophic. This problem has been alleviated in the case of unfilled polymers either by using very high static pressures[11] to produce residual compressive stresses in the centre of the mouldings or by using

hot runner moulds[12,13] to allow the applied pressure to compensate for volume shrinkage. The former technique demands very high machine pressures and the latter requires a small gate which introduces mould-filling problems with concentrated suspensions.

An attractive solution is the introduction of oscillating, rather than static, post-injection pressure to the material in the cavity.[14] This allows greater control over solidification of the moulding.

Allan and Bevis[15,16] have used this method to produce defect-free, thick-section thermoplastic mouldings. The method uses an oscillating pressure device which can be fitted to a standard injection-moulding machine as shown in Fig. 1. The technique. causes pressure in the sprue to oscillate at a preset frequency between pre-determined limits. The oscillating pressure prolongs solidification of the sprue and compensates for shrinkage in the moulded part. More recently, short fibre reinforced thermoplastics have been moulded in this way.[17] Preliminary work[18] has shown that the technique is also capable of reducing the incidence of defects in technical ceramic mouldings, and the oscillating valve has been redesigned to take account of the severe abrasive wear encountered with ceramic suspensions.[19] In this respect the oscillating pressure valve was modified to receive interchangeable and rapidly replaceable piston and liner inserts. A number of wear-resistant materials have been investigated for this purpose.[20]

In the present work the technique was applied to the moulding of a straight bladed rotor (Fig. 2) which was used to simulate the problems of moulding a gas turbine engine rotor or a turbocharger rotor without incurring the tooling costs of profiled blades. Two ceramic powders with widely
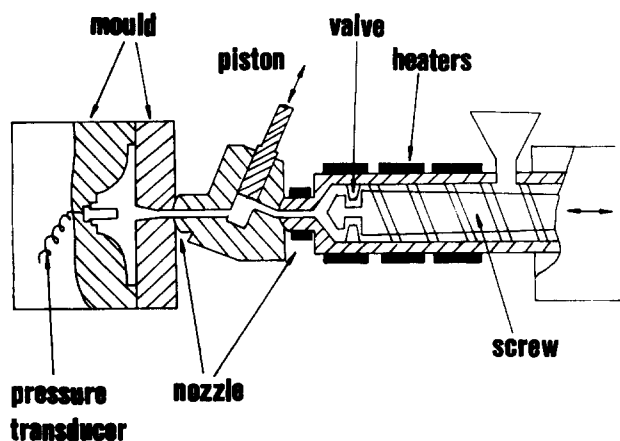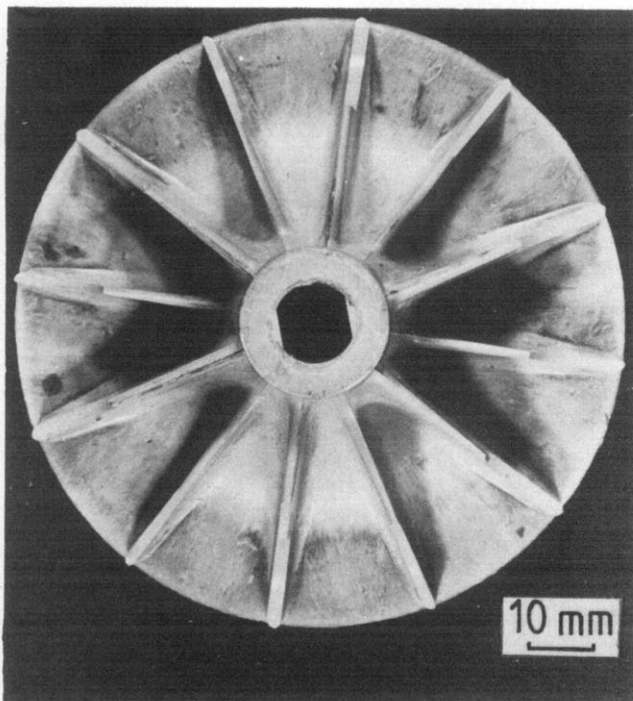

Fig. 2. The straight-bladed rotor used throughout this work.

different thermal properties were selected to show the effect of different cooling rates on the moulding operation. Furthermore, a composition which included a silane coupling agent was included to investigate the effect of viscosity, independent of thermal property changes. Such coupling agents, added in small amounts, are known to reduce the viscosity of highly filled polymer–ceramic suspensions.[21]

2 Experimental Details

2.1 Materials

The particle size distribution of the vibratory-milled silicon powder (Elkem Pilamec-milled; density 2300 kg m^{-3}; specific surface area 5·7 m^2 g^{-1}; irregular particle shape) suitable for the fabrication of reaction-bonded silicon nitride is shown in Fig. 3.

Table 1. Composition of the sinterable silane-treated silicon nitride powder

Constituent	wt %
Silicon nitride	83·64
Y$_2$O$_3$	6·35
Al$_2$O$_3$	4·23
SiO$_2$	4·68
PCIA silane coupling agent[a]	1·10

[a] ex Union Carbide, UK.

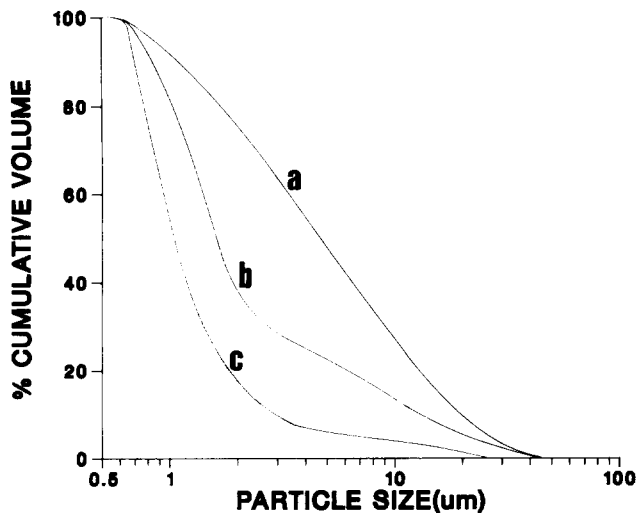Fig. 1. Schematic diagram of the oscillating pressure equipment.

Fig. 3. Particle size distribution for (a) silicon, (b) silicon nitride, (c) silicon nitride + sintering aids (after milling).

Silicon nitride powder (Anzon; density $3190\,kg\,m^{-3}$; specific surface area, before milling $11\cdot6\,m^2\,g^{-1}$, after milling $15\cdot6\,m^2\,g^{-1}$; irregular particle shape) was also used after milling for 48 h with sintering aids and a silane coupling agent (Table 1). The particle size distribution of as-received and milled silicon nitride are also shown in Fig. 3.

2.2 Compositions

The compositions of the injection moulding blends are given in Table 2. The silicon mouldings (formulation F3) contained 65 vol. % powder, a loading which was preferred in previous work.[7,8] The silicon nitride rotors contained 57 vol. % powder (formulations F16 and F17), comparable with the volume loadings of silicon nitride achieved by others.[22,23]

The organic vehicle contained polypropylene (grade GY545M, ICI Ltd, Welwyn Garden City, UK, density $905\,kg\,m^{-3}$; $\overline{M}_n = 31\,850$, $\overline{M}_w/\overline{M}_n = 8\cdot9$) as the major binder, micro-crystalline wax (grade 1865Q, Astor Chemicals Ltd, West Drayton,

Middlesex, UK, density $910\,kg\,m^{-3}$; $\overline{M}_n = 300$, $\overline{M}_w/\overline{M}_n = 1\cdot5$) as the minor binder and stearic acid (grade 302 69 4Q, BDH Chemicals Ltd, Essex, UK; density $941\,kg\,m^{-3}$) as the processing aid.

2.3 Compounding

The ceramic powder, preheated to 160°C, and the stearic acid were preblended in a Henschel mixer at 3000 rpm for 2 min. After cooling to room temperature polypropylene and wax were added and mixing continued for a further 2 min. The preblends were then compounded using a laboratory co-rotating intermeshing twin-screw extruder (model TS40 DV-L, Betol Machinery, Luton, UK). Details of the machine conditions are given in Table 3.

2.4 Injection moulding

A Bone Cravens Daniels 350-120 injection moulding machine was used and the operating conditions for the three formulations are given in Table 4 together with the oscillating hold pressure conditions.

The mouldings were contact-radiographed in order to detect moulding defects using a Hewlett Packard Faxitron X-ray system, operating at 50 kV and 3 mA with an exposure time of 30 min.

Some rotors were subjected to a post-moulding heat treatment in which the temperature was increased at a rate of $5°C\,h^{-1}$ to 120°C and held at 120°C for 1 h. This temperature is approximately 35°C below the softening point of the suspension.[10]

Table 3. Compounding machine conditions

Screw diameter (mm)	40
Screw L/D ratio	17
Screw speed (rpm)	60
Barrel temperatures (°C)	220 (feed)-225-235-225 (nozzle)

Table 2. Compositions of injection moulding blends

Composition (wt %)	Formulation number		
	F3	F16	F17
Si₃N₄	—	—	82·1
Si₃N₄ + silane	—	83·2	—
Silicon	82·4	—	—
Polypropylene	11·7	11·2	11·9
Wax	3·9	3·7	4·0
Stearic acid	2·0	1·9	2·0

Table 4. Injection-moulding machine conditions and oscillating pressure unit settings

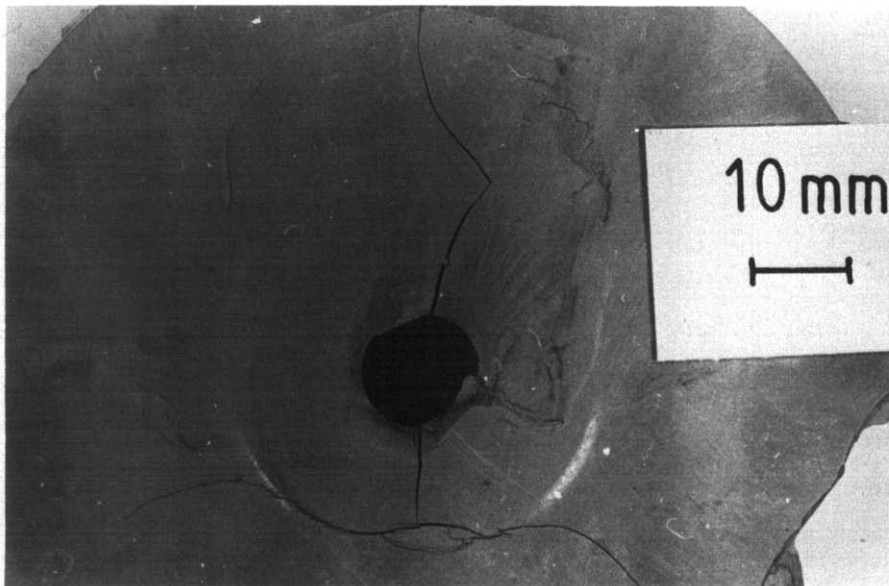|	
Screw diameter (mm)	45
Screw L/D ratio	18
Screw speed (rpm)	45
Barrel temperature profile (°C)	160 (feed)-225-230-230-225 (nozzle)
Oscillating pressure	
Compress time (s)	0·5
Relax time (s)	0·5
Compress pressure (MPa)	52-139
Relax pressure (MPa)	52
Background pressure (MPa)	30

Fig. 4. Central region of a silicon nitride rotor moulding (F17) made with a static pressure of 152 MPa.

3 Results and Discussion

3.1 Oscillating pressure duration

Figure 4 shows the central region of a silicon nitride rotor moulding (F17) fabricated with a static hold pressure of 152 MPa held for 200 s. Cracks appeared in thick sections of the hub of such mouldings rendering them scrap.

A series of silicon nitride mouldings (F17) were prepared with an oscillating hold pressure of frequency 1 Hz and amplitude varying from 52 to 122 MPa. The pressure modulation commenced shortly after the injection-stage cavity pressure of 152 MPa had been reached.

Figure 5 is the pressure–time trace for such a moulding with a set pressure amplitude of 87 MPa. The trace shows the initial cavity pressure of 152 MPa, followed by a modulated pressure region of amplitude approximately 87 MPa, and a fall in pressure to point C, which was taken to be the time at which the bulk of the moulding had solidified. Thereafter, the cavity pressure transducer continued to register the pressure oscillations mainly because of its position directly opposite the sprue.
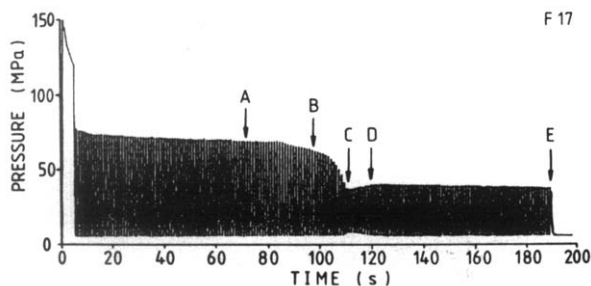

Fig. 5. Pressure–time trace for a silicon nitride moulding (F17) made with a set pressure amplitude of 87 MPa.

A series of mouldings were then made with the oscillating hold pressure interrupted at points A to E (Fig. 5) and the mouldings were allowed to cool in the cavity for the remaining time up to 200 s.

Radiographs of rotor mouldings interrupted at points A to E clearly showed that mouldings A and B contained macroscopic cracks in the thick hub and were scrap. However, the rotors for which the modulated pressure was continued to point C and beyond were free of these macroscopic defects.

These results suggest that in order to avoid residual stress cracking, the modulated hold pressure should be continued at least up to the position on the cavity pressure–time trace corresponding to point C on Fig. 5 and that this probably corresponds to the solidification of the sprue. It is not known whether the sprue remains partially molten under the influence of oscillating pressure beyond point C, because the transducer may be capable of sensing pressure through the solidified material. In subsequent work therefore, the oscillating hold pressure duration was adjusted to exceed the solidification time by 8–25 s.

3.2 Oscillating pressure amplitude

Table 5 gives details of silicon nitride mouldings made with formulation F17 with a mould temperature of 40°C and with the pressure amplitude varied between 52 and 122 MPa. Figure 6 shows that the solidification time increases monotonically with pressure amplitude. On initial inspection therefore, it appears that the oscillating pressure device allowed considerable extension of solidification time and hence control over residual stress. However, to

Table 5. Details of mouldings made from silicon nitride formulation F17 with a mould temperature of 40°C

Pressure amplitude (MPa)	Solidification time (s)	Modulated pressure duration (s)	X-Ray radiography As-moulded	X-Ray radiography Heat-treated	Number of mouldings
52	38	50	Cracks	—	3
70	64	75	Cracks	—	2
87	100	120	No defects	No defects	3
104	115	125	No defects	No defects	2
122	115	125	No defects	Cracks	1
122	115	125	No defects	[a]	1

[a] Component was not heat-treated but cracked after storage for 5 months.

achieve this, it is essential that the device is capable of applying high pressures, and wear of the piston may prevent this.[19] At amplitudes of 70 MPa and below, the mouldings contained cracks in the hub comparable with those observed in static pressure mouldings. At amplitudes of 87 MPa and above the rotors were free of cracks in the as-moulded state. Thus for a given cavity, mould temperature and moulding composition, there is likely to be a lower limit of modulated pressure amplitude above which defective mouldings are avoided.

These highly-filled polymers tend to have very low mechanical strength, typically in the region of 12–15 MPa in flexure,[21] and the possibility of time-dependent failure under the influence of residual stresses cannot be ruled out. In particular, the process of polymer removal by pyrolysis involves a slow reheating of the moulded components to a temperature of 200–500°C. The early stage of reheating is effectively an accelerated stress-rupture test and cracks generated at this stage are unacceptable. All the moulded rotors were therefore sub-

Fig. 6. Dependence of solidification time on pressure amplitude for silicon nitride formulation F17 with mould temperature 40°C.

jected to reheating at a rate of 5°C h⁻¹ to 120°C followed by slow cooling. They were then re-examined by radiography. In the case of formulation F17, Table 5 shows that, of the components made with a pressure amplitude of 122 MPa, one developed cracks on reheating which were not present after moulding and another cracked on storage for 5 months. In the latter case the cracking was enhanced by heating to 120°C. When the cracking on storage was first observed the defect-free mouldings were all re-examined by radiography and found to be sound. The significance of the stress-rupture phenomenon is discussed below. The results in Table 5 suggest that there is an upper limit for pressure amplitude above which the component contains residual stresses insufficient to cause cracking after cooling to room temperature, but capable of generating time-dependent failure either during storage or during an accelerated test by reheating.

A similar series of experiments were performed with silicon nitride formulation F16 which differed from F17 in that it contained a silane coupling agent, which reduced the viscosity of the fluid from 942 Pa s to 546 Pa s at 225°C and had a shear rate of 108 s⁻¹. The use of such coupling agents in silicon-based ceramic moulding compositions has been shown to have several advantages.[21] Table 6 shows the results of moulding trials using F16 at a mould temperature of 50°C. The pattern of results was broadly similar to that for F17. At a pressure amplitude of 70 MPa and below, cracks appeared in the as-moulded component. There followed a wide range of pressure up to 122 MPa where the components did not show failure after slow reheating to 120°C. At an amplitude of 139 MPa cracks were observed after reheating. Unfortunately only one sample was available for this test but the similarity with the behaviour of F17 suggests consistency with the trend.

The displacement of the dependence of solidification time on pressure amplitude for F16 (Fig. 7) is partly caused by the higher mould temperature and
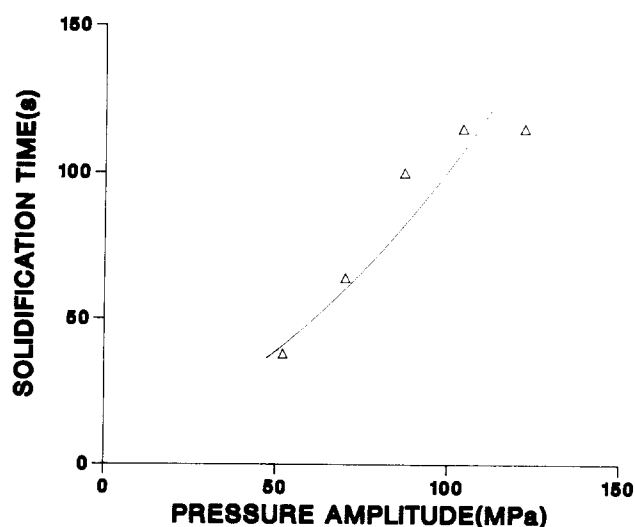
Table 6. Details of mouldings made from silicon nitride formulation F16 with a mould temperature of 50°C

Pressure amplitude (MPa)	Solidification time (s)	Modulated pressure duration (s)	X-Ray radiography		Number of mouldings
			As-moulded	Heat-treated	
70	40	48	Cracks	—	1
87	68	79	No defects	No defects	2
104	83	93	No defects	No defects	1
122	115	128	No defects	No defects	1
139	165	170	No defects	Cracks	1

Table 7. Details of mouldings made from silicon formulation F3 with a mould temperature of 40°C

Pressure amplitude (MPa)	Solidification time (s)	Modulated pressure duration (s)	X-Ray radiography		Number of mouldings
			As-moulded	Heat-treated	
52	11	25	Cracks	—	2
70	15	40	Cracks	—	2
87	20	45	Cracks	—	2
104	33	45	Cracks	—	2
122	40	53	No defects	No defects	2
139	50	60	No defects	No defects	3

partly by the difference in properties of the formulation caused by silane addition.

The influence of pressure amplitude on the solidification time and on the incidence of cracking revealed by radiography for the silicon powder formulation F3 is shown in Table 7. In this case, because of the different thermal properties of the composition, the solidification times were very short and were less influenced by pressure amplitude (Fig. 8). Nevertheless the trend was the same as that observed for the silicon nitride formulations with cracks in the as-moulded rotors appearing at

pressure amplitudes below 104 MPa but absent above 122 MPa. This means that for the silicon composition, much higher pressures are needed to avoid defective components, although it may be that elevated mould temperature may compensate for higher pressures to an extent.

Mouldings of both F17 and F16 made under the optimum conditions of 50°C mould temperature and 87 MPa pressure amplitude as described above were free from macroscopic defects after heat treatment and 23 mouldings of F17 were therefore prepared for subsequent polymer removal and sintering.
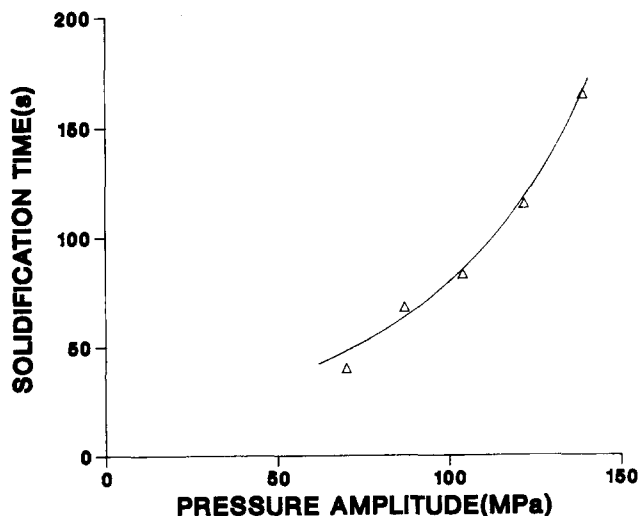

Fig. 7. Dependence of solidification time on pressure amplitude for silicon nitride formulation F16 with mould temperature 50°C.
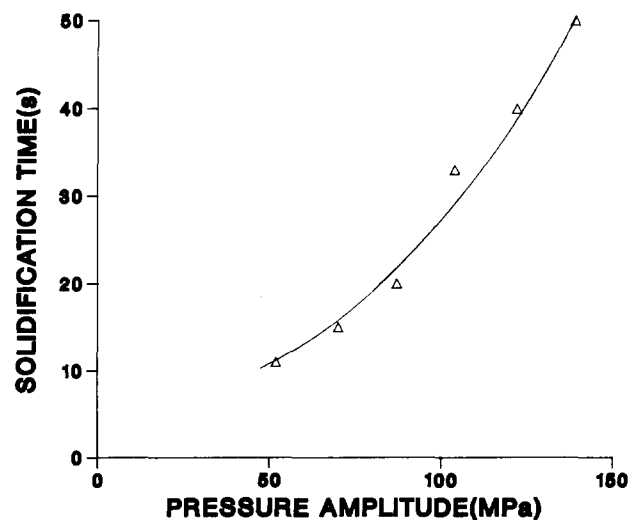

Fig. 8. Dependence of solidification time on pressure amplitude for silicon formulation F3 with mould temperature 40°C.

Table 8. Comparison of thermal properties of silicon and silicon nitride formulations

	Silicon nitride	*Silicon*	*Polypropylene*
Volume fraction	0·57	0·65	—
Thermal conductivity (Wm^{-1} K^{-1})	17·2[24]	108[26]	0·12[28]
Specific heat (J kg^{-1} K^{-1})	710[25]	702[27]	1923[28]
Density of composite (kg m^{-3})^a	2198	1812	—
Specific heat of composite (J kg^{-1} K^{-1})^a	1232	1129	—
Thermal conductivity of composite (Wm^{-1} K^{-1})^b	4·3	30·3	—
Thermal diffusivity of composite × 10^{-7} (m^2 s^{-1})	16	148	—

^{a} Rule of Mixtures used.
^{b} Hashin and Shtrikman[29] bounds used, i.e. (*upper bound + lower bound*)/2.

3.3 Influence of rheology

Figure 9 shows typical pressure–time traces for rotors made from silicon nitride formulations F17 and F16 with a mould temperature of 50°C and a pressure amplitude of 87 MPa and all other moulding conditions identical. The difference between these formulations is the addition of a silane coupling agent to F16. The thermal diffusivity of both blends is likely to be very similar. The difference in solidification time under oscillating pressure conditions is therefore thought to be associated with the absorption of mechanical energy in the sprue. This is likely to be influenced by a number of properties, notably the viscosity and the variation of viscosity with pressure. The viscosity at constant shear rate (108 s^{-1}) and 225°C was reduced by 42% due to the presence of the coupling agent, indicating that the difference in rheological properties is likely to be responsible for the differing abilities of these formulations to absorb mechanical energy under identical moulding conditions.

3.4 Influence of thermal properties on solidification

The influence of thermal properties of ceramic suspensions on solidification in the mould is well illustrated by comparing the pressure–time traces for silicon nitride formulation F17 and silicon
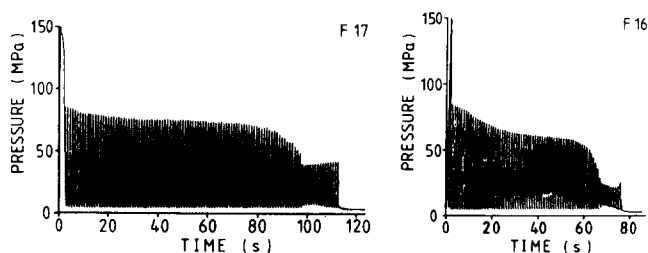
formulation F3 under identical moulding conditions with a mould temperature of 40°C and a pressure amplitude of 87 MPa (Fig. 10). The polymer blend was made up from components in the same weight ratio in both formulations but the silicon nitride formulation contained 57 vol. % powder and the silicon formulation 65 vol. %. The differences in thermal properties are a consequence of both the filler loading and the different thermal properties of each filler[24–28] as shown in Table 8. In this table, the thermal conductivity of silicon nitride–polypropylene and silicon–polypropylene composites were estimated using the equations of Hashin and Shtrikman.[29] Their equations for upper and lower bounds were used to calculate the average of the upper and lower bound for thermal conductivity at the relevant volume loadings.

Upper bound

$$K = K_c + \frac{V_p}{\dfrac{1}{(K_p - K_c)} + \dfrac{V_c}{3K_c}}$$

Lower bound

$$K = K_p + \frac{V_c}{\dfrac{1}{(K_c - K_p)} + \dfrac{V_p}{3K_p}}$$

Fig. 9. Pressure–time traces for silicon nitride formulations F17 and F16 with pressure amplitude 87 MPa and mould temperature 50°C.
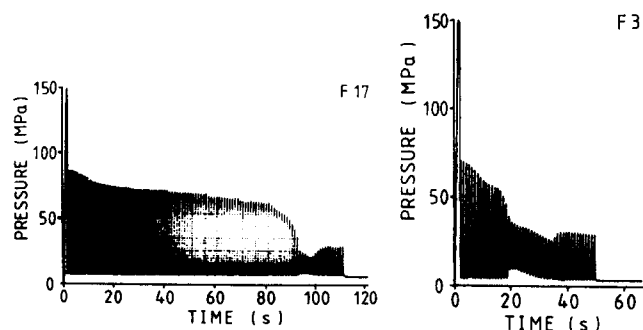

Fig. 10. Pressure–time traces for silicon nitride formulation F17 and silicon formulation F3 with pressure amplitude 87 MPa and mould temperature 40°C.

where

V_c = volume fraction of the ceramic
V_p = volume fraction of the polymer
K_c = thermal conductivity of the ceramic
K_p = thermal conductivity of the polymer

Such relationships have recently been reviewed by Hale[30] and most other equations are only valid for dilute suspensions. More recent equations by Nielsen[31] to model thermal conductivity for particle-filled two-phase systems have not been experimentally validated for high filler levels used in the present research.

The experimental determination of thermal conductivities was beyond the scope of the present work and in the absence of other structural information apart from volume fractions, Hashin and Shtrikman bounds are the most appropriate methods of estimation.[30] Nevertheless, in situations where component thermal conductivities are appreciably different, the bounds are widely separated, and actual experimental values are in the central region between bounds,[30] thus justifying the adoption of the average value of upper and lower bounds for estimating the thermal conductivity of the composites used in the present work.

The values in Table 8 show how the thermal diffusivity of the composite is dominated by the properties of the ceramic powder. The short solidification time for the silicon moulding is thus a consequence of the rapid heat loss to the mould competing with heat input from the centre of the sprue as energy is absorbed. At present it is not possible to quantify the energy input, but using a standard non-steady state graphical heat transfer analysis[32] it is possible to use the diffusivity data to calculate the solidification time for an infinitely long cylinder of radius r simulating the sprue. This gives the time at which the centre of a sprue of known dimensions reaches the softening point of the formulation (150°C) after injection at 225°C into a mould at 40°C, and this is plotted in Fig. 11. This shows that the solidification time for the silicon composition is always considerably shorter than that for the silicon nitride mixture, and this is commensurate with the solidification time under oscillating pressure deduced from Fig. 10, where the solidification time for silicon nitride was approximately five times that of silicon. This has important implications for the moulding of high conductivity powders at high loadings, such as the practice of injection moulding powder metallurgy components of large sections. High mould temperatures and pressure amplitudes would be needed.
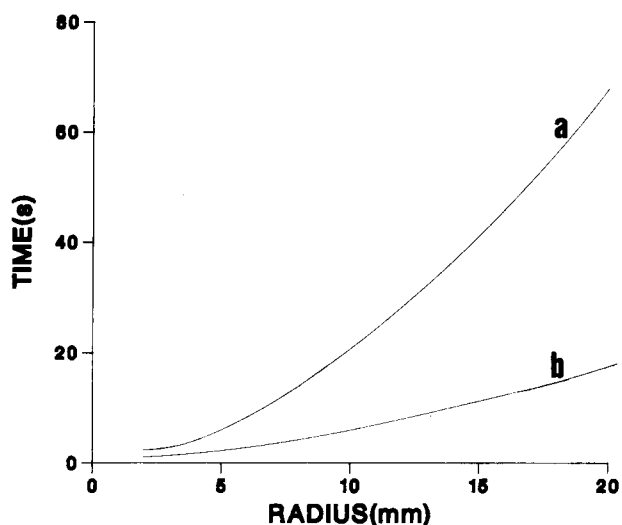

Fig. 11. Time for solidification of the centre of sprue of radius r after injection at 225°C into a mould at 40°C for (a) 57 vol. % silicon nitride–polypropylene, (b) 65 vol.% silicon–polypropylene. A surface heat-transfer coefficient of 1000 Wm^{-2} K^{-1} was used in calculating solidification times.

3.5 Stress rupture during storage and reheating

An interesting feature of ceramic injection moulded components is that because they have low mechanical strength, typically 12 MPa,[21] they are subject to time-dependent failure during reheating or storage under the influence of residual stresses. It is known that stress-rupture lifetimes are strongly influenced by the melt flow index[33] and this is clearly unfavourable for a moulding vehicle where lower molecular weight polymers are desirable to enhance fluidity. The stress-rupture lifetime is also strongly temperature dependent at temperatures up to 100°C.[34] Stress-relaxation becomes significant at temperatures above 120°C,[35] and therefore the reheating schedule for polymer removal from injection moulded ceramic bodies must take account of several processes as the temperature is raised. At low temperatures < 100°C, the reheating process is effectively an accelerated stress-rupture test, in which residual stresses may initiate failure in an otherwise macro defect-free moulding. At higher temperatures, stress-relaxation mechanisms operate and are liable to cause deformation if significant residual stress levels are present. At temperatures approaching 200°C and beyond, degradation of the polymer blend may commence. Thus in order to remove the polymer by pyrolysis it is necessary to traverse these lower temperature regions where residual stresses may render scrap mouldings which in the as-moulded state were free from macroscopic defects.

4 Conclusions

A method of controlling residual stresses in large injection-moulded bodies by employing an oscillating hold pressure to prolong sprue solidification has been successfully applied to ceramic suspensions containing either 57 vol.% silicon nitride or 65 vol.% silicon powder. Solidification time increased monotonically with pressure amplitude, but the correlation took a different form for different compositions and mould temperatures. Below a critical pressure amplitude the thick section of moulded parts contained defects, probably resulting from residual stresses generated during non-uniform cooling. The critical amplitude was found to be different for each formulation and at present can only be inferred by experiment.

The addition of a silane coupling agent enhanced fluidity without altering thermal diffusivity and this resulted in quite different solidification times under oscillating pressure conditions, indicating that the absorption of energy was influenced by rheological properties. The thermal diffusivity of the suspensions had a dramatic effect on solidification time and was influenced largely by the thermal properties of the powder as well as its volume fraction.

Some mouldings which were free from defects after moulding had a tendency to crack on storage or reheating. This is thought to be a stress-rupture effect under the influence of residual stresses. It was noted in components moulded with a high pressure amplitude.

References

1. Schuetz, J. E., Methylcellulose binders for extrusion of ceramics. *Amer. Ceram. Soc. Bull.*, **65** (1986) 1556-9.
2. Kazuo, K., Furuta, M. & Maeno, Y., N.G.K. Insulators Ltd, Japan, A ceramic arc tube of a metal vapour discharge lamp and a method of producing the same. European Patent 0034056, 6 Feb. 1981.
3. Edirisinghe, M. J. & Evans, J. R. G., Review: Fabrication of engineering ceramics by injection moulding. I—Materials selection. *Int. J. High Tech. Ceram.*, **2** (1986) 1-31.
4. Edirisinghe, M. J. & Evans, J. R. G., Review: Fabrication of engineering ceramics by injection moulding. II—Techniques. *Int. J. High. Tech. Ceram.*, **2** (1986) 249-8.
5. Hornsby, P. R., Design and application of a laboratory twin-screw compounding extruder. *Plastics Compounding*, **6** (1983) 65-71.
6. Anon., UK laboratory compound extruder sets high standards. *European Plastics News*, June 1982, p. 9.
7. Edirisinghe, M. J. & Evans, J. R. G., Compounding ceramic powder prior to injection moulding. *Proc. Brit. Ceram. Soc.*, **38** (1986) 67-80.
8. Edirisinghe, M. J. & Evans, J. R. G., Rheology of ceramic injection moulding formulations. *Brit. Ceram. Trans. J.*, **86** (1987) 18-22.
9. Edirisinghe, M. J. & Evans, J. R. G., Properties of ceramic injection moulding formulations: Part I—Melt rheology. *J. Mat. Sci.*, **22** (1987) 269-77.
10. Edirisinghe, M. J. & Evans, J. R. G., Properties of ceramic injection moulding formulations: Part II—Integrity of mouldings. *J. Mat. Sci.*, **22** (1987) 2267-73.
11. Kubat, I. & Rigdhal, M., Influence of high pressures on the internal stress level in injection moulded specimens. *Polymer*, **16** (1975) 925-9.
12. Rubin, I. I., *Injection Moulding Theory and Practice*. Wiley, London, 1972, p. 104.
13. Morrison, R. V., Discovision Assoc., USA, Hot sprue assembly for an injection moulding machine. US Patent, 4412805, 1 Nov. 1983.
14. Menges, G., Koenig, D., Luettgens, R., Sarholz, R. & Schuermann, E., Follow-up pressure pulsation in the manufacture of thick-walled high strength thermoplastic components. *Plastverarbeiter*, **31** (1980) 185-93.
15. Allan, P. S. & Bevis, M. J., The production of void-free thick-section injection-flow mouldings. I—Shot-weight and dimensional reproducibility. *Plas. Rubb. Proc. Appl.*, **3** (1983) 85-91.
16. Allan, P. S. & Bevis, M. J., The production of void-free thick-section injection-flow mouldings. II—Preferred orientation and residual stress measurements. *Plas. Rubb. Proc. Appl.*, **3** (1983) 331-6.
17. Allan, P. S. & Bevis, M. J., Producing void-free thick-section thermoplastic and fibre-reinforced thermoplastic mouldings. *Plas. Rubb. Int.*, **9** (1984) 32-6.
18. Allan, P. S., Bevis, M. J., Edirisinghe, M. J., Evans, J. R. G. & Hornsby, P. R., Avoidance of defects in injection-moulded technical ceramics. *J. Mat. Sci. Lett.*, **6** (1987) 165-6.
19. Edirisinghe, M. J. & Evans, J. R. G., An oscillating pressure unit for ceramic injection moulding. Part A. Materials and design. *Materials and Design*, **VIII** (1987) 284-8.
20. Edirisinghe, M. J., Zhang, J. G. & Evans, J. R. G., An oscillating pressure unit for ceramic injection moulding. Part B. Performance. *Materials and Design*, **9** (1988) 85-93.
21. Zhang, J. G., Edirisinghe, M. J. & Evans, J. R. G., The use of coupling agents in ceramic injection moulding. *J. Mat. Sci.*, **23** (1988) 2115-20.
22. Johnson, A., Carlstrom, E., Hermansson, L. & Carlsson, R., Minimisation of the extraction time for injection-moulded ceramics. *Proc. Brit. Ceram. Soc.*, **33** (1983) 139-47.
23. Markoff, C. J., Mutsuddy, B. C. & Lennon, J. W., Method of determining critical ceramic powder volume concentration in the plastic forming of ceramic mixes. In *Advances in Ceramics*, **9**, ed. J. Mangels. American Ceramic Society, Columbus, OH, 1984, pp. 246-50.
24. Samsonov, G. V., *High Temperature Materials No. 2.* Plenum Press, NY, 1964, p. 127.
25. Shaffer, T. B., *High Temperature Materials No. 1.* Plenum Press, NY, 1964, p. 285.
26. Weast, R. C., *Handbook of Chemistry and Physics.* CRC Press, FL, 1974, p. E13.

27. Shaffer, T. B., *High Temperature Materials, No. 1.* Plenum Press, NY, 1964, p. 235.
28. *Encyclopedia of Polymer Science and Technology*, **13**, ed. H. F. Mark & N. G. Gaylord. Wiley, NY, 1970, p. 780.
29. Hashin, Z. & Shtrikman, S., A variational approach to the theory of the effective magnetic permeability of multiphase materials. *J. Appl. Phys.*, **33** (1962) 3125–31.
30. Hale, D. K., Review: The physical properties of composite materials. *J. Mat. Sci.*, **11** (1976) 2105–41.
31. Nielsen, L. E., The thermal and electrical conductivity of two-phase systems. *Ind. Eng. Chem. Fundam.*, **13** (1974) 17–20.
32. Holman, J. P., *Heat Transfer.* McGraw-Hill, London, 1981, pp. 118–27.
33. Gebler, H., The influence of processing on the quality of HDPE pressure pipes. *Kunststoffe*, **73** (1983) 2.
34. Kresser, T. O. J., *Polypropylene.* Reinhold, London, 1960, p. 64.
35. Faucher, J. A., Viscoelastic behaviour of polyethylene and polypropylene. *Trans. Soc. Rheo.*, **3** (1959) 81–93.