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Properties of ceramic injection-moulding formulations

Part 2 *Integrity of Mouldings*

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Five ceramic injection-moulding formulations with 65 vol % powder and polypropylene as the main organic component were injection-moulded under identical conditions. The extent of mould filling and the production of moulding defects in thick sections were examined in the light of rheological and shrinkage properties of the formulations.

1. Introduction

The fabrication of technical ceramics by injection moulding is being developed for manufacture of complex shapes, in particular for advanced heat engine components. The selection of materials for moulding compositions has recently been reviewed [1], as have moulding techniques [2]. The main criteria for the selection of polymer components are that they should confer fluidity for mould filling, that they should allow defect-free solidification in the mould cavity and be amenable to removal from the prefired body without disruption to the assembly of particles. The present work is an attempt to quantify the former two criteria.

A number of workers have drawn attention to the suitability of polypropylene as a major binder component [3–6] and finished components have produced a Weibull Modulus of 20 after processing with polypropylene [6]. Previous work [7] has described the development of nine ceramic injection-moulding blends with a fixed volume fraction of powder and with polypropylene as the main component of the polymer blend. Three rheological parameters were examined for each formulation. In the first place, fluidity at the moulding temperature and at a shear rate characteristic of flow in the sprue and gate was measured. The pseudoplastic nature of the fluid was characterized and the temperature dependence of viscosity in the region of the nozzle temperature was recorded.

The present work examines the quality of mouldings produced from five of these formulations with identical ceramic powder loading, moulded under identical machine conditions. The properties of the polymer blends determine the incidence and type of defects in ceramic mouldings and hence the likely scrap rates.

The defects which appear in injection-moulded ceramic articles in the moulding operation fall into two categories depending on the stage in the process at which they originate. There are those defects which occur at the mould filling stage and include incomplete cavity filling and the incidence of weld or knit lines. Secondly, there are defects which originate at the solidification stage as a consequence of residual stresses, and consist typically of cracking, microcracking or the formation of voids or microvoids.

The higher thermal conductivity and lower specific heat of ceramic–polymer blends compared with unfilled polymers means that incomplete mould filling, especially of thin sections may result from low material fluidity, low mould temperatures or low injection speeds. Filled polymers do not exhibit the die swell [8] typical of high polymers and show a greater tendency to jet into the cavity producing a coil and resulting in knit lines in the product [9]. Weld lines are known to decrease the toughness of unfilled polymers [10] and their effect on ceramics which have much greater sensitivity to flaw size is severe. In general, weld lines can be avoided by side gating the cavity to generate plug flow [9].

The development of cracking or voiding in ceramic injection mouldings originates from the thermomechanical response of the material during solidification in the mould cavity while fluid hold pressures are applied. After injection the solid layer thickness adjacent to the mould wall increases during non-steady state heat transfer to the mould. During the early stages of solidification, the applied fluid pressure continues to inject liquid into the central region of the moulding and compensates for volume shrinkage. At some point the material in the sprue or runner solidifies and thereafter the disconnected pocket of liquid in the centre of the moulding undergoes a shrinkage associated with the difference in specific volume between amorphous and crystalline phases and with thermal contraction.

In unfilled polymers the resulting internal tensile stresses can cause "sink" marks in the surface of mouldings [11], but in heavy filled polymers the lower mechanical strength may encourage cracking or voiding. Void nucleation in a particle-filled material is particle-size dependent [12] with the dependence taking a Griffith form [13]. The competition between void nucleation and crack propagation as a means of relieving internal stresses is influenced by the crack arrest temperature for the material [13].

Residual stresses in unfilled polymer mouldings have been measured by a number of methods including the application of stress-cracking agents [14], measurement of curvature after layer removal [15–17] and stress relaxation measurements [16]. Calculation of stresses from first principles is possible for simple shapes [18]. In general, residual stresses are compressive in the surface of mouldings and tensile in the centre of thick sections. Under ideal conditions, if the equation of state of the polymer and coefficient of expansion are known, moulding temperatures and pressures can be selected to produce a desired shrinkage, positive or negative ([11] p. 270 *et seq.*). Thus Kubat and Rigdahl [19], using static injection pressures of up to 450 MPa, were able to produce low-density polyethylene mouldings with tensile surface stresses and compressive internal stresses. Unfortunately, the very high pressures used are beyond the capability of most moulding machinery and tooling.

In the present work, mouldings of variable cross section were prepared under identical conditions using five polypropylene-based polymer blends. An attempt was made to relate the incidence of defects in mouldings to the rheological properties previously reported [7] and to material properties of the formulations. The following properties were considered to be relevant; softening point, thermal expansion coefficient and crystallinity. The room-temperature mechanical properties of the blends were also investigated.

2. Experimental details

2.1. Compositions

The compositions of the injection-moulding blends are given in Table I and the rationale for their development has been previously described [7]. All mouldings contained 65 vol % silicon powder suitable for the fabrication of reaction-bonded silicon nitride. The minor binders were microcrystalline wax (F3), polyethylene wax (F5), low-density polyethylene (F6) and silicone oil (F7).

2.2. Injection moulding

A Bone Cravens Daniels 350-120 injection moulding machine was used to mould seventy samples of each formulation F1, F3 and F5–7 as step-wedge mouldings under identical processing conditions. The moulding conditions are shown in Table II and a moulding complete with sprue and runner is shown in Fig. 1. It contains steps of 2, 5, 7.5, 10, 15 and 20 mm. Each moulding weighed approximately 40 g.

TABLE II Injection-moulding machine conditions

Screw diameter (mm)	45
Screw *L*/*D* ratio	18 : 1
Screw speed (r.p.m.)	45
Barrel temperature profile (feed-nozzle (° C)	160–225–230–230–225
Mould temperature (° C)	30
Injection pressure (MPa)	150
Hold pressure (MPa)	140
Hold time (sec)	120
Cycle time (sec)	150
Feed	Granules dried under vacuum at 90° C for 24 h

2.3. Dilatometry

Dilatrometric thermal expansion curves were obtained for 5 mm sections cut from the 10 mm steps of mouldings. A Perkin Elmer TMS1 thermomechanical analyser was used to record coefficient of linear expansion in the range 40 to 100° C. The dilatometric softening point and the total linear expansion between room temperature and the dilatometric softening point were also determined. A load of 3 g was used on a flat-ended silica glass rod of diameter 4 mm.

TABLE I Compositions of injection-moulding formulations (wt %)

Formulation	Silicon	Polypropylene	Minor binder	Stearic acid
F1	82.46	15.59	–	1.95
F3	82.44	11.71	3.90	1.95
F5	82.40	11.73	3.91	1.96
F6	82.38	11.75	3.91	1.96
F7	82.22	11.85	3.95	1.98

2.4. Softening point

In addition to the dilatometric softening point, a Davenport Vicat softening point apparatus was used to determine the Vicat softening point of mouldings [20]. The rate of heating was $50^\circ\mathrm{C\,h^{-1}}$ and the penetration was 1 mm.

2.5. Differential scanning calorimetry

A Perkin Elmer DSC 2 differential scanning calorimeter was used to measure crystalline melting enthalpies of each moulding composition. A scan speed of $10\,\mathrm{K\,min^{-1}}$ was used during heating and cooling between room temperature and 475 K. For formulation F7 a Perkin Elmer DSC 1B was used with a scan speed of $8\,\mathrm{K\,min^{-1}}$.

2.6. Mechanical testing

It was not possible to obtain the material in suitable form for tensile or bending tests, therefore cylinders 32 mm diameter were compression moulded in a metallurgical mounting press and tested in compression using an Instron testing machine between fixed plattens. The machine deflection was subtracted from the compression curves.

3. Results and discussion

The dispersive mixing achieved by the twin screw

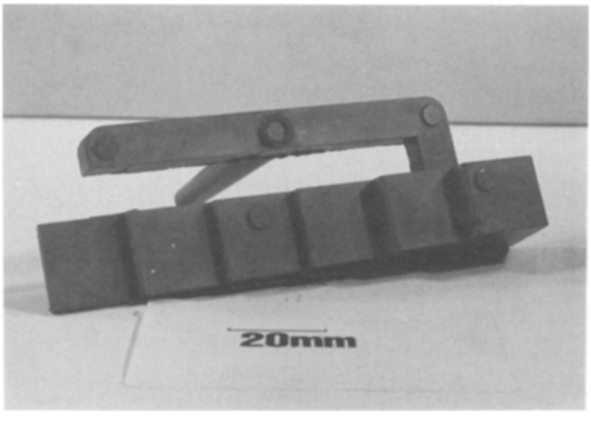

Figure 1 The complete step-wedge moulding.

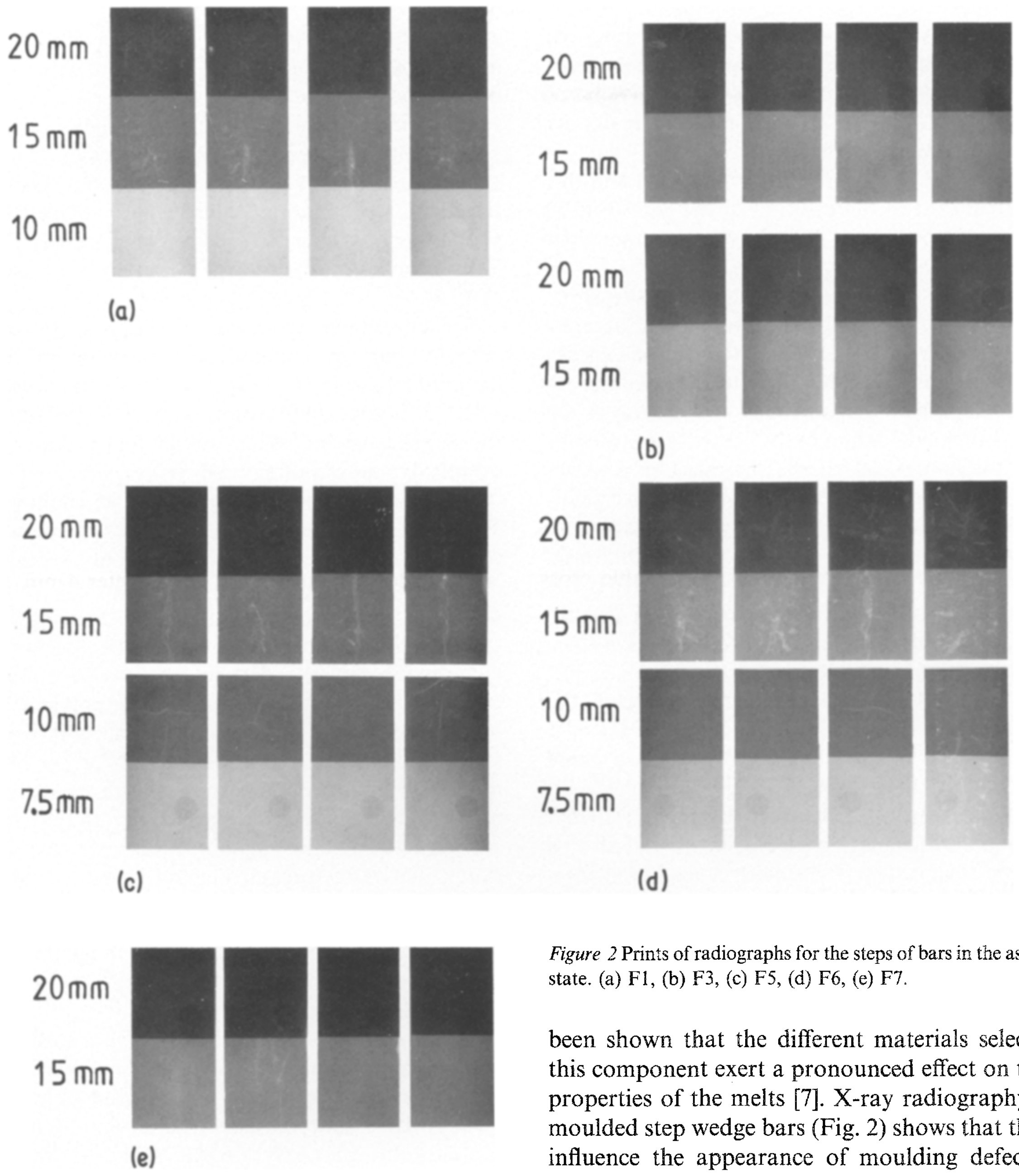

Figure 2 Prints of radiographs for the steps of bars in the as-moulded state. (a) F1, (b) F3, (c) F5, (d) F6, (e) F7.

compounder–extruder ensured that the property measurements were characteristic of well dispersed powder composites [21]. Dispersion was assisted by the relatively coarse particle size which resulted in a powder almost free of agglomeration.

The injection-moulding temperatures were chosen to be the lowest compatible with material viscosities of less than 1000 Pa sec [7]. The mould temperature was kept constant at 30° C throughout, and the moulding conditions were identical for each moulding composition. The injection pressures and hold pressures represent the maximum capacity for the machine and the hold time was chosen to be sufficiently long to ensure that it exceeded the gate freeze-off time. In practice, optimization of the machine conditions would lead to lower pressures and hold times and this would make the overall cycle time more attractive commercially.

The moulding compositions differ only in the nature of the material used for the minor binder component or "plasticizer" which amounts to 22 wt % of the organic component of the blends. It has already been shown that the different materials selected for this component exert a pronounced effect on the flow properties of the melts [7]. X-ray radiography of the moulded step wedge bars (Fig. 2) shows that they also influence the appearance of moulding defects. The radiographs of mouldings shown in Fig. 2 were representative of all the mouldings made. In general, with the exception of formulation F3, employing a wax plasticizer, moulded bodies contained gross internal defects of dimensions comparable with the width of the body. Very few mouldings made with formulation F3 contained moulding defects and those detected were considerably smaller. A small population of mouldings made with formulation F7, containing silicone oil were also free of gross defects. Of considerable interest, therefore, are the properties of the blends which influence the origin of defects and these are the subject of the present investigation. All the compositions tested showed complete mould filling and this agrees with the observation [22] that viscosity of less than 1000 Pa sec is preferred for ceramic injection-moulding blends. Indeed formulation F1 with a viscosity of 1430 Pa sec at 225° C and 100 $\sec^{-1}$ has also filled the mould [7], suggesting that high machine pressures can accommodate fluids with viscosities slightly in excess of 1000 Pa sec for some cavities. This restriction sets an upper limit on the powder volume fraction and suggests that in this case several of the formulations used could tolerate a slight increase in powder loading without diminishing the mould-filling properties [7]. However, the increase in viscosity at high filler loadings is very sensitive to volume fraction of filler [23] and thus increases of only a few per cent would be possible.

Weld lines are absent from the mouldings and this can be attributed to the position of the gate (Fig. 1) which allowed plug flow into the cavity rather than jetting [9].

A wide range of defects associated with shrinkage during cooling in the cavity can be seen in radiographs for formulations F1 and F5–7. These include cracks and voids and their location in the thickest sections of the step-wedge bars suggests that they occur at the final stage of solidification in the centre of the moulding after the runner has frozen. They are thus a consequence of the change in specific volume due to crystalline phase transitions in the polymer blends and to thermal contraction during cooling to room temperature. Of particular interest, therefore, is the contribution to overall shrinkage offered by crystallization of the polymer and thermal contraction since this influences polymer selection.

The "herring bone" pattern of voids seen in the radiographs for formulations F1, F5 and F6 is a projection of a defect which is dendritic in three dimensions and this can be seen in fracture surfaces. The main defects were found in the 15 and 20 mm sections but in formulation F5 cracking could also be seen in the 10 mm step. The smaller steps were generally free of these defects and this is consistent with the dimensions of the runner and gate which were 6 mm × 10 mm. It is thought that the sections comparable with these dimensions solidified at the same time as the runner and were thus free from shrinkage defects. Clearly the sections smaller than the runner would have solidified while the runner was still fluid.

Identification of the material properties which have the greatest influence on the generation of defect-free moulding was considered to be a major objective.

In the first place the softening point of the blend can be used to give an indication of the temperature at which the gate freezes and ceases to transmit fluid to the centre of the moulding. The Vicat method, being intended for unfilled thermoplastics, was subject to greater variability when used on highly filled polymers. The results in Table III are average readings and the specification that successive readings differ by no more than 2° C could not be used [20], differences of 3 or 4° C being typical. The dilatometric softening points, in which the material is subject to a much lower indentation stress are slightly higher than the Vicat results. The results show that the difference in softening point between formulations is unlikely to be adequate in explaining the appearance of defects in all compositions except F3.

TABLE III Softening point determinations

Formulation	Softening point (° C)	
	Vicat	Dilatometric
F1	148	154
F3	151	158
F5	155	155
F6	154	155
F7	160	167

Assuming equal mould packing, a higher softening point would be expected to generate greater shrinkage stresses and hence more severe defects but this is not the case for formulation F7 which has a slightly higher softening point than the others. The defects in F7 are less pronounced than those in other formulations (Fig. 2).

Semicrystalline polymers generally show undercooling, but the solidification point is not easily deduced by mechanical experiment as is the softening point. It is the solidification point which determines the temperature at which mould filling ceases. The extent of undercooling can be expected to vary throughout the moulding depending on cooling rate. The order of magnitude of the polypropylene undercooling can be deduced from differential scanning calorimetry described below. For cooling rates of 10° C min^{-1} undercooling of up to 42° C was observed.

The point at which solidification occurs still remains incompletely determined because the application of pressure to a semicrystalline polymer has a pronounced effect on melting point [24] and an increase in melting point of up to 0.37° C per MPa is reported for polypropylene. Although cavity pressures could not be recorded, a pressure on material of 150 MPa was used throughout these experiments indicating that cavity pressures could be up to 150 MPa and an increase of up to 55° C in the crystalline melting point was possible. This increase in melting point would tend to counteract the reduction effected by undercooling.

Measurements of thermal expansion also revealed only minor differences between compositions (Table IV). The average coefficient in the region 40 to 100° C was 83 MK^{-1} and the standard deviation between compositions was only 4.6 MK^{-1}. These small differences are unlikely to account for the incidence of defects in all mouldings other than those made with formulation F3. When the total shrinkage between softening point and room temperature was considered (Table IV) the average value was 1.07% and the standard deviation between the five blends was 0.1%. Therefore, this property determination does not account for the different moulding behaviour of the formulations.

Shrinkage associated with polymer phase changes is not revealed by dilatometry and therefore differential scanning calorimetry was used to record enthalpies of

TABLE IV Thermal expansion data for formulations

Formulation	Coefficient of expansion 40 to 100° C (MK^{-1})	Linear shrinkage between softening point and room temperature
F1	81	0.92
F3	79	1.02
F5	88	1.07
F6	87	1.18
F7	78	1.15
Mean	83	1.07
S.D.	4.6	0.09

TABLE V Specific enthalpies for polypropylene in each formulation

Formulation	ΔH(J g^{-1})	Crystallinity* (%)
As-received polypropylene	83	50
F1	88	53
F3	92	56
F5	90	55
F6	88	53
F7	95	58

*Using $\Delta H = 165\,\mathrm{J\,g^{-1}}$ from [25].

melting and resolidification. The crystalline fraction and hence specific volume change during solidification could then be deduced. In each case the individual components of binder displayed peaks corresponding to the position of peaks in the as-received materials. The exception was silicone oil which obviously showed no melting endotherm. Table V shows the specific enthalpy for polypropylene in the as-received state and after blending. It is interesting to note that despite intensive mixing the polypropylene showed the same degree of crystallinity in each blend. This suggests that at least in the solid state, phase separation had occurred.

The peaks associated with minor components were too small to allow accurate characterization of the enthalpy changes in blended material because of the low concentration. The only way in which their contribution of shrinkage could be assessed was to assume that they too crystallized to the same extent as in the as-received material.

Taking the value of the enthalpy of fusion for a 100% crystalline polypropylene as $165\,\mathrm{J\,g^{-1}}$ [25], the average value from Table V is $89.3\,\mathrm{J\,g^{-1}}$ giving a crystallinity of 54%. The volume shrinkage associated with crystallinity of each component of the blend could be calculated as:

$$\text{specific volume change} \times \text{density} \times \text{fraction crystallinity} \times \text{volume fraction in the blend}$$

As the volume shrinkage calculated in this way is based on total volume, the shrinkages of individual components are additive.

The crystalline fraction of the ethylene polymers was calculated from DSC enthalpy changes divided by crystal enthalpies calculated from [25]:

$$\Delta H_f = 227.14 + 0.786t - 1.060 \times 10^{-3}t^2 - 8.51 \times 10^{-6}t^3$$

where t is the melting point in °C from DSC melting peaks. The specific volume change for polypropylene was taken as $0.116\,\mathrm{m^3\,Mg^{-1}}$ [25] and was calculated for ethylene polymers using [25]:

$$\Delta V = 0.162 + 5.57 \times 10^{-4}t - 1.0 \times 10^{-7}t^2$$

The melting points of the microcrystalline wax, polyethylene wax and low density polyethylene were 57, 108 and 115°C, respectively. This allows the compilation of crystalline shrinkage contributions for the formulations (Table VI).

It is instructive to compare crystalline shrinkage with that associated with thermal contraction. The average linear shrinkage from softening point to room temperature for all compositions was 1.07% (Table IV). This provides a volume shrinkage of 3.18% which is nearly twice the shrinkage due to crystallinity shown in Table VI. These results have implications for the selection of polymer blends for injection moulding. Rigidity in the moulded body is important for precision engineering ceramics where subsequent machining cannot correct distortion during ejection and handling. Rigidity can be obtained either by employing a semicrystalline polymer or an amorphous polymer with the glass transition temperature above ambient temperature. Clearly a minimum of crystalline shrinkage compatible with rigidity in the solid state is desirable. The results also show that a very high volume shrinkage arising from thermal contraction is undesirable and in this sense the blends prepared suffer from a rather high softening point.

TABLE VI Volume shrinkage of moulding material caused by crystallization of polymer blends (vol %)

Formulation	Polypropylene	Minor binder	Total
F1	1.77	–	1.77
F3	1.33	0.33	1.66
F5	1.33	0.49	1.82
F6	1.34	0.54	1.88
F7	1.34	–	1.34

Radiography of mouldings showed that the most severe defects occurred in formulations F5 and F6 with cracks extending into the 7.5 mm step (Fig. 2). These blends have unfavourable viscosity characteristics [7] in that the temperature dependence of viscosity of F5 is high and the fluidity of F6 at the moulding temperature is low. These blends are also distinguished by a marginally higher crystalline shrinkage contribution (Table VI) which exceeds that of formulation F3 by 0.2%. Since the shrinkage due to thermal contraction provides the greatest contribution, the significance of this small difference is difficult to assess. Thus it is not possible unequivocally to allocate causes to the origin of defects. However, the formulation F3 which is free of gross defects does not have the lowest shrinkage and its crystalline shrinkage contribution differs from the polypropylene-only formulation F1 by only 0.1%. The latter shows severe defects. Thus shrinkage considerations alone do not explain the origin of moulding defects.

The total volume shrinkage of 5% was not, of course, observed when comparing the dimensions of the moulded body with that of the mould. The linear shrinkage observed from length measurements of mould and moulded body was 0.24% giving an equivalent volume shrinkage of 0.72%. The remainder is accounted for as follows; compensation by post-injection hold pressure during moulding, the incidence of voids, residual stresses or "sinking" deformation of the moulding during cooling. Of these the former makes the main contribution.

Of interest is the extent of undercooling displayed by the main binder as this impinges on the softening point and hence the thermal contraction during cooling to room temperature. Table VII shows that, as is typical for polypropylene, the

TABLE VII Polypropylene melting and solidification peak temperatures

Formulation	Temperature (° C)		
	Heating	Cooling	ΔT
As-received polypropylene	162	112	50
F1	163	115	48
F3	157	111	46
F5	163	115	48
F6	162	114	48
F7	154	108	46

undercooling is significant and moreover, consistent in each blend.

An indication of differences in mechanical properties was also sought. A full analysis of the modulus–temperature characteristics of the blends was beyond the scope of the present work. Initially elastic constants were obtained by a pulse-echo ultrasonic technique on the step-wedge mouldings but the elastic constants so determined bear little resemblance to the quasi-static mechanical situation in the mould. Unfortunately, the material could not be obtained in a suitable form for tensile or flexure testing and finally compression testing was used to identify gross differences in mechanical response. The stress–strain curves for each formulation are shown in Fig. 3. It was difficult to determine strains at low stresses without an extensometer but at low strains the compression modulus of each formulation is identical within the limits of experimental error. Thereafter, formulation F3 shows premature yielding at a stress of 43 MPa compared to yield stresses of 50 to 60 MPa for the other blends. Although it bears little resemblance to the moulding situation the test reveals differences in mechanical properties which suggest that in formulation F3, with a low yield stress, voiding or cracking would be facilitated. Fig. 2 does not reveal such defects suggesting that viscosity and shrinkage properties exert a stronger influence on the origin of defects than mechanical properties.

The preparation of discs by uniaxial compression moulding allowed precise density determinations which were prevented by defects in the injection-moulded bodies. In Table VIII the measured densities are compared with those calculated from the weight fractions in Table I. The density values confirm the assumption about the effect of polymer blending on density, made in Part 1 [7], in order to calculate the volume fraction of powder.

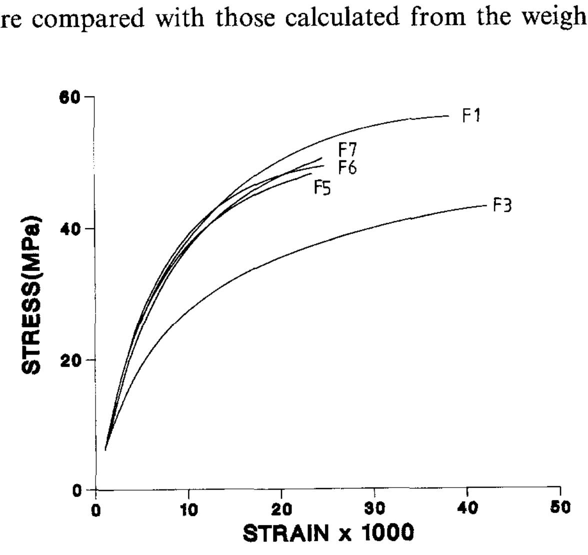

Figure 3 Room-temperature compression test results for the formulations, (corrected for machine deflection and initial slack).

TABLE VIII Calculated and measured densities of moulding blends

Formulation	Density ($kg\,m^{-3}$)	
	Calculated	Measured
F1	1813	1804
F3	1814	1813
F5	1814	1801
F6	1815	1820
F7	1818	1806

The filling of a mould cavity with a heavily filled particle composite and its subsequent solidification is an extremely complicated phenomenon. Hitherto the selection of polymer blends for ceramic injection moulding has been largely empirical [1]. Although models for the flow into a cavity are currently being developed, the incidence of defects in ceramic injection mouldings, particularly in components containing large sections, demands urgent attention. In the present work ceramic injection mouldings have been made and studied radiographically. Thermo-mechanical property measurements have been made in order to distinguish the behaviour of polymer blends and these, together with the rheological data previously reported [7] enable the following conclusions to be drawn.

4. Conclusions

Ceramic moulding blends with 65 vol % silicon powder and with polypropylene as the main binder component were injection moulded into a mould with varying sections without mould-filling defects. The blends differed only in the material used as the minor component which made up 22 wt % of the organic fraction. A viscosity of less than 1000 Pa sec was preferred for mould filling but a blend with a viscosity of 1430 Pa sec at 100 sec^{-1} at the nozzle temperature was also moulded with a pressure on material of 150 MPa.

The sections, which were of similar thickness or thinner than the runner, were free from solidification defects. Gross moulding defects were detected in radiographs of thick sections of all the mouldings with the exception of the mouldings made with a blend of polypropylene and microcrystalline wax.

Previous work has shown that this blend is characterized by a very low temperature dependence of viscosity which would allow packing of the moulded body to compensate for shrinkage. Approximately 4 vol % of expected shrinkage was accommodated in this way.

Other differences between the formulations which might account for the absence of large moulding defects were sought. The softening point measured by the Vicat method and by dilatometry did not differ greatly and in each case were in the region of 154° C.

The coefficient of thermal expansion between 40 and 100° C was identical for each formulation, being 83 MK^{-1}. The overall shrinkage between softening point and room temperature was also the same for each formulation at 1.1% linear.

Differential scanning calorimetry revealed undercooling of the polypropylene melting peaks and this may have reduced the softening points. However, the effect of pressure on melting point may compensate for this displacement.

The volume shrinkage of moulding compositions associated with thermal contraction on cooling was therefore 3.2%. Although polymers tend to have high expansion coefficients this large shrinkage suggests that the selection of a blend with a lower softening point is desirable.

The initial polypropylene crystallinity was preserved in each formulation at 54% indicating that crystallinity was not affected by intensive mixing with other polymers and that phase separation occurred on solidification. The volume shrinkage associated with polymer crystallinity was between 1.3% for the blend with silicone oil and 1.8% for the blend with polypropylene only. The most severe defects were found in mouldings with a large crystalline shrinkage but the composition which had the lowest incidence of moulding defects did not have the lowest shrinkage. This indicates that the minimum proportion of semicrystalline polymer in order to achieve rigidity of mouldings is desirable, but that other factors which influence mould packing may override the tendency for shrinkage to induce defects.

A difference in room-temperature mechanical properties in compression testing was observed between the polypropylene-microcrystalline wax formulation and those formulations which produced shrinkage defects in mouldings. The former exhibits a lower yield stress which would tend to suggest that voiding would be facilitated. The absence of gross defects suggests that in this case the origin of defects was influenced more by viscosity and shrinkage characteristics than by mechanical properties.

The largest difference in rheological properties was revealed in previous work which showed that the polypropylene-microcrystalline wax formulation had a very low temperature dependence of viscosity, allowing the post-injection hold pressure to pack the moulding efficiently during solidification and to compensate for shrinkage defects.

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