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Properties of ceramic injection moulding formulations

Part 1 *Melt rheology*

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The rheological properties of nine ceramic injection moulding compositions based on polypropylene with a fixed silicon powder loading were measured. Minor components of the polymer–ceramic blend were shown to have a considerable effect on the properties of the melt. An attempt was made to derive, from capillary rheometer flow curves, the parameters which are thought to influence moulding quality. In particular, the shear rate dependence of viscosity at the nozzle temperature, fluidity at a shear rate of $100\,\text{sec}^{-1}$, the temperature dependence of viscosity in the region of the nozzle temperature and at a shear rate of $100\,\text{sec}^{-1}$ and the yield stress are discussed. In Part 2 the influence of these variables and other properties of the formulations, on quality of moulding will be considered.

1. Introduction

Injection moulding is receiving attention as a method of shaping engineering artefacts from non-clay ceramic powders [1] because it offers near net shape production by automated processes. In order to take advantage of the injection moulding fabrication route the powder is blended with an organic vehicle. This should confer both fluidity and the ability to change state in the mould cavity in order to resist shear stresses associated with ejection and handling. To this end, both thermosetting [2, 3] and low [4, 5] and high [6–8] molecular weight thermoplastics have been investigated but much attention has focused on the high molecular weight thermoplastics which are themselves fabricated routinely by injection moulding, and in particular on polypropylene [9–11].

The selection process for organic vehicle compositions has been reviewed recently [12]. The two dominant criteria are (a) that it should provide a rheology that permits defect-free moulding, and (b) that it should pyrolyse in a non-catastrophic manner to permit defect-free removal from the ceramic body. The parameters which define both criteria have not been established beyond dispute and the present work investigates flow properties of molten ceramic injection moulding blends.

Usable moulding compositions generally include, in addition to the ceramic powder, several organic components [13]: a major binder component which determines the general range of properties, minor components such as plasticizers for the main polymer which are intended as flow modifiers, oils that are claimed to modify pyrolysis and processing aids which are supposed to act as surfactants to the ceramic and improve particle wetting.

The interaction of the two criteria for choice of organic vehicle compositions described above makes the selection process a complex and time consuming operation. In both cases there is a need for simple tests which give guidance on the likely performance of the final composition in moulding trials. In terms of characterizing the rheological properties which are relevant to moulding behaviour, three approaches are available [14]: (i) measurement of viscosity in a rheometer over a range of temperature and shear rate, (ii) spiral flow moulding trials, (iii) pressure, time and temperature adjustment during the moulding of a relevant artefact. Both (ii) and (iii) involve considerable machine time and large quantities of material, and therefore the present work chooses to characterize nine prospective ceramic injection moulding blends by capillary rheometry.

2. Predicting the mouldability of filled systems

For unfilled thermoplastics it has been shown that capillary flow tests give a good measure of material behaviour during flow through the nozzle and into the mould [14]. Furthermore, viscosity at a relevant shear rate corresponding to nozzle conditions correlates well with spiral flow length using a standard mould [14]. It has also been found that the temperature dependence of viscosity correlates with the temperature dependence of mould filling, indicating that relaxation effects in the polymer during non-steady state conditions are of secondary importance [15]. Yet despite empirical correlations of this type the complexity of the injection moulding process makes it difficult to state a universal relationship between laboratory viscosity measurements and mouldability and this is particularly so in the case of injection moulding of ceramic powder/binder systems that contain a high volume fraction of filler [1]. Indeed the goal of relating capillary viscosity measurements directly to moulding behaviour is considered a major issue in solving reproducibility and control during injection moulding [16].

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Interpreting capillary viscometer results in order to predict mouldability in terms of molecular structure of the polymeric binders is complex [14]. Refined and accurate techniques with long capillaries are required for truly significant results in this direction [14]. For the case of unfilled polymers, Weir [17] has proposed a model based on viscosity measurements in a rheometer to arrive at a parameter α_{STV} which correlates with spiral flow length, allows prediction of the moulding temperature to give minimum cycle time, the short shot temperature and the temperature at which flashing will occur [18]. In this parameter, STV represents shear–temperature–viscosity and

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{d \log \eta / d \log \dot{\gamma}}{d \log \eta / d(1/T)}$$

where η_0 is the viscosity at a reference shear rate (chosen by Weir at $10\,sec^{-1}$), $\dot{\gamma}$ is shear rate and T temperature. The first factor, reciprocal viscosity or fluidity, is influenced most strongly by molecular weight. The other factors are influenced by molecular weight distribution and a number of structural properties. The interaction of viscosity, shear rate, temperature and molecular structure is reviewed extensively by Kumar [19]. The corresponding relationships for polymer blends are yet more complex [20, 21].

The Weir model makes no mention of melt compressibility, melt elasticity, specific heats, thermal conductivities or the host of other properties which can be shown to affect moulding. The results of these omissions are that whilst α_{STV} reflects the mouldability of a polymer of a given chemical type, a general criterion has not thereby been established.

Mutsuddy and Kahn [16] have questioned whether the Weir model analysis fits ceramic powder/binder systems. They concluded that due to filler particle interactions the Weir model failed to predict the mouldability of such systems. Simple fluidity ($1/\eta$) at the relevant temperature was found to bear a better relationship to the actual mouldability of the formulations. Recently, Holman *et al.* [22] have attempted to use computer flow modelling of fluid flow to arrive at a convenient solution in order to predict mouldability. Yet several of the computer techniques used had marked disadvantages.

It has been stated that during ceramic injection moulding shear rates vary between 100 and $1000\,sec^{-1}$ and that flow during moulding requires a viscosity of less than 1000 Pa sec [23]. Thus a binder system which produces a viscosity of less than 1000 Pa sec within the shear rate range 100 to $1000\,sec^{-1}$ when the ceramic powder is added can be regarded as a usable formulation [23]. There is considerable interest in employing mixtures with the maximum volume fraction of powder to achieve high green density and reduce shrinkage on subsequent sintering. The viscosity increases considerably with increase in filler loading [24], therefore it is necessary to reduce the viscosity by adding suitable minor components. Weir [17] has drawn attention to the fact that the flow properties are most critical at the mould filling stage where a low shear rate prevails.

It has been reported [23] that ceramic binder formulations with either Bingham or pseudoplastic flow characteristics were most successful. The pseudoplasticity criterion requires that the slope of log viscosity–shear rate curve be negative, i.e. since

$$\tau = k\dot{\gamma}^n$$

where τ is shear stress, $\dot{\gamma}$ is shear rate, n is the flow behaviour index and k is a constant, thus viscosity

$$\eta = k'\dot{\gamma}^{n-1}$$

and $n < 1$ for pseudoplasticity.

One important criterion in predicting mouldability of a ceramic injection moulding formulation is the temperature dependence of viscosity. A plot of log viscosity against temperature at a shear rate of $100\,sec^{-1}$, which approximated injection moulding conditions at the nozzle/mould has been found to provide useful information [8]. The graph fitted a straight line relationship within a narrow temperature range of about 40° C and it was suggested that the slope of this graph should be as small as possible to avoid sudden viscosity changes that can cause undue stress concentrations in the moulded parts, cracking and distortion.

Clearly since polymer viscosity is an activated process involving polymer chain segment mobility within the melt, the viscosity–temperature relationship is best represented by an Arrhenius equation from which the appropriate activation energy can be deduced. The justification for the log viscosity–temperature plot, which is linear over a narrow range of temperature, is purely its empirical usefulness [8]. However, it is pertinent to note that in practice the Arrhenius representation of the temperature dependence of viscosity of polymers is not linear, since activation energy at constant shear rate varies with temperature [25].

The yield point of the ceramic powder/binder formulation has also been listed as a property that will affect successful injection moulding [23]. It is claimed that if the formulation has a high yield point, it injects into the mould cavity like a thread of ribbon that coils upon itself, tending to trap air that can induce mechanical stresses [23]. However, yield stress determinations do not accompany this thesis. Moore [26] has described a method by which the yield stress can be estimated from capillary viscometer data.

These facts show that it is reasonable to analyse capillary rheometer data for ceramic injection moulding formulations in the following manner:

1. Assess $n - 1$ from a viscosity against shear rate graph at the nozzle temperature.
2. Assess the fluidity $1/\eta$ at the nozzle temperature and $\dot{\gamma} = 100\,sec^{-1}$.
3. Assess $d \log \eta/dT$ and the activation energy for viscous flow for the relevant temperature range and $\dot{\gamma} = 100\,sec^{-1}$.
4. Assess the yield stress from a shear rate against shear stress graph.

The present work considers a range of polypropylene systems with a fixed volume loading of silicon powder. Where possible, rheological parameters summarized above were deduced from flow curves obtained by

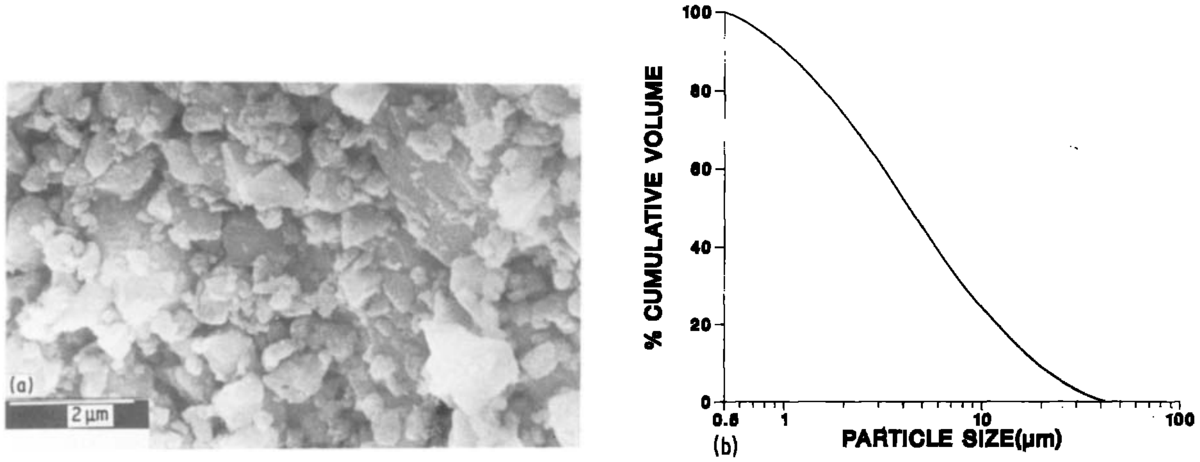

Figure 1 (a) Scanning electron micrograph of the vibratory milled silicon powder. (b) Particle size distribution for the as-received vibratory milled silicon powder.

capillary rheometry. The relevance of these and related parameters have been verified by examining defects in the as-moulded bodies and this will be discussed in Part 2.

3. Experimental detail

3.1. Materials

Silicon powder suitable for the fabrication of reaction-bonded silicon nitride was used as the ceramic powder. Fig. 1a shows a scanning electron micrograph and Fig. 1b shows a typical particle size distribution of the silicon powder. Polypropylene was selected as the major binder because previous work [27] has suggested advantages compared with other major binders such as low density polyethylene and ethylene vinyl acetate. Data on the ceramic powder and major binder are contained in Table I.

3.2. Compounding

Details of the equipment used for compounding are summarized in Table II, together with typical operating temperatures.

Preblends of the silicon powder and stearic acid (used as the processing aid) were prepared in a Henschel high speed mixer at 3000 r.p.m. for 2 min in 1.5 kg batches. Subsequently the binders were added and mixing continued for a further 2 min. The preblends were then compounded using a laboratory co-rotating intermeshing twin-screw extruder developed at Brunel University. This extruder is available commercially and extensive information on its capabilities have been published [28, 29]. The compounded formulations were dried and granulated before being used in the rheological testing programme. A sample of each formulation was ashed at 600° C in order to estimate the actual filler loading. Rule of mixtures was used to obtain the polymer blend volume fraction and since the polymer densities are similar, the error in volume fraction of ceramic introduced by the influence of any polymer–polymer solubility will be small.

TABLE I Materials

Major binder: Polypropylene	
Density (kg m^{-3})*	905
Melt index (g/10 min)*†	15.0
Molecular weight ($\bar{M}_n$)‡	31850
Molecular weight distribution $\left(\frac{\bar{M}_w}{\bar{M}_n}\right)$‡	8.9
Filler: Vibratory milled silicon powder	
Density (kg m^{-3})	2300
Specific surface area (m^2 g^{-1})	5.7
Particle shape§	irregular

*ICI Ltd., published data.

†190° C, 10 kg load.

‡By GPC at RAPRA, Polymer Supply and Characterization Centre.

§By scanning electron microscopy.

Silicone oil used in formulation F7 left a residue when ashed. Therefore a correction was made to the ashing results of formulation F7. Silicone oil was ashed on its own for this purpose.

3.3. Rheology

An attempt was made to characterize the formulations by estimating the melt flow index using a Davenport standard Melt Flow Rate Apparatus Model 3/80. Some formulations could not be extruded at the standard test conditions of 2.16 kg load and 230° C [30]. Therefore, a 5 kg load and a temperature of 230° C was used. The weight extruded during a period of 15 sec was measured.

Viscosities of the formulations were measured in a Davenport capillary rheometer, using the standard procedure with temperature control of ± 1° C and allowing 10 min to reach thermal equilibrium after charging the barrel.

The pressure drop across the length of the die was measured using a pressure transducer situated adjacent to the die entrance. The piston velocity was

TABLE II Compounding machine conditions

Machine used: Gays co-rotating twin screw extruder, TS40-DVL	
Screw diameter (m)	40
Screw L/D ratio	17
Barrel temperature profile (feed-die) (° C)	220-225-240-235-225
Screw speed (r.p.m.)	60
Extrudate coming out of rod die (diameter = 6 mm) was water cooled and broken up into small lengths	

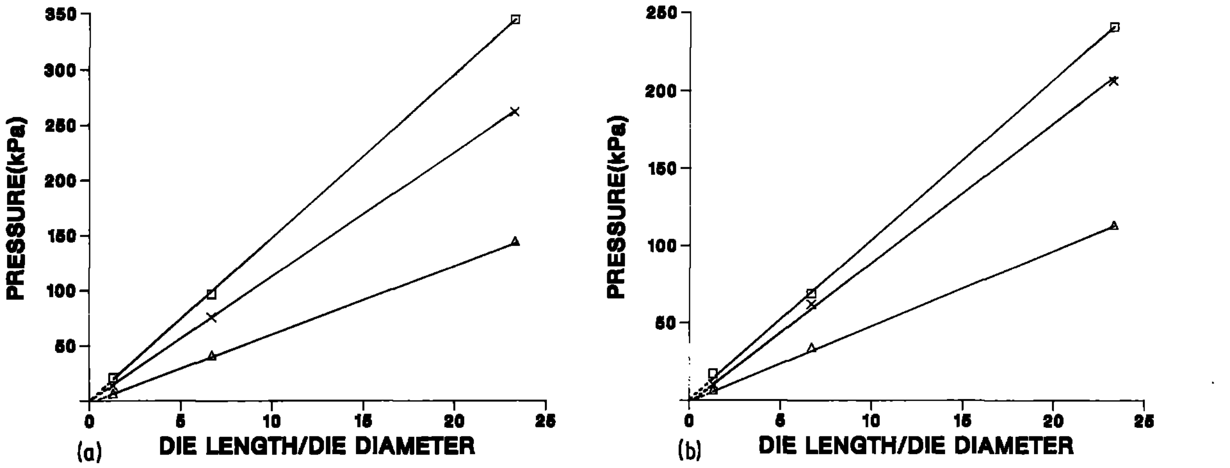

Figure 2 Variation of pressure drop with capillary length-to-diameter ratio for formulation F1. (a) At 195° C, (b) at 225° C. Die diameter = 1.5 mm; shear rate: (△) 108 sec^{-1}, (x) 538 sec^{-1}, (□) 1075 sec^{-1}.

changed to obtain different shear rates and the corresponding pressure drop measurements were used to calculate the shear stresses. A 1.5 mm diameter, 35 mm length die was used. The end correction to be applied was estimated by using a graph of pressure against die length/die diameter as described by Fenner [31]. Die length was varied using a further two dies, 10 and 2 mm in length, both having a die diameter of 1.5 mm. The end correction is proportional to the intercept on the die length/die diameter axis [31]. The end correction was negligible for all the formulations (Figs 2a and b) and therefore because of the difficulty in measuring low pressures the bulk of the results were quoted for the single 35 mm die with end correction ignored. The results were corrected for non-Newtonian flow effects using the Rabinowitsch correction [32]. Rheology of the formulations were studied at 195 and 225° C, to cover the temperature range discussed above (Fig. 2). Samples of rheometer extrudates at both temperatures were ashed at 600° C to verify the filler loading in order to ensure that the same formulation was being tested throughout.

3.4. Development of formulations

In ceramic injection moulding, 50 to 70% volume loading of ceramic powder is desired [9]. The research described in this paper deals with formulations containing nominally 65% by volume ceramic powder. In all the formulations studied the remaining 35% by volume, being the organic component, was made up of 11.1 wt % processing aid (stearic acid) and 88.9 wt % binder. The binder was divided into a major and minor component as described below.

The first formulation (F1) contained, in addition to stearic acid, only the major binder polypropylene as the organic component. The major binder remained unchanged in all the formulations.

Minor components considered in this investigation were selected on the basis that they should show some compatibility with the major binder polypropylene. Compatibility is used here to imply ability to mix on a molecular scale [33]. Some intermolecular entanglement in the melt is to be expected in the compositions chosen but the present work does not attempt to characterize the dispersion of molten polymer blends.

The minor components were also required to have a low volatility [34]. Formulations F2, F3 and F4 contained different proportions of microcrystalline wax (Grade 1865Q, density 910 kg m^{-3}, Astor Chemical Ltd, West Drayton, Middlesex, UK) as a minor binder. The proportions by weight were as follows:

F2 polypropylene : microcrystalline wax = 7 : 1
F3 polypropylene : microcrystalline wax = 3 : 1
F4 polypropylene : microcrystalline wax = 1 : 1

As discussed below, formulation F3, where the major binder : minor binder ratio was 3 : 1, was a usable blend. Therefore, in order to compare results, formulations F5, F6, F7, F8 and F9 were preblended such that the major binder : minor binder ratio was maintained at 3 : 1 by weight. The minor binders used in these formulations were as follows:

F5 polyethylene wax (Grade AC6, density 920 kg m^{-3}, Allied Chemical Corporation, Birmingham, UK)

F6 low-density polyethylene (Grade LD657, density 926 kg m^{-3}, ESSO, Southampton, UK)

F7 Silicone oil (Grade 200, density 975 kg m^{-3}, Dow Corning, Glamorgan, UK)

F8 polypropylene glycol (Grade Pluriol P4000, density 1000 kg m^{-3}, BASF UK Ltd, Cheshire, UK)

F9 dioctyl phthalate (Grade D20-115-4, density 981 kg m^{-3}, Aldrich Chemical Co, Dorset, UK)

The exact compositions are given in Table III.

TABLE III Exact compositions of F1–9

Formulation	% by weight			
	Silicon	Major binder (polypropylene)	Minor binder	Stearic acid
F1	82.46	15.59	–	1.95
F2	82.44	13.66	1.95	1.95
F3	82.44	11.71	3.90	1.95
F4	82.44	7.81	7.80	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
F8	82.14	11.91	3.97	1.98
F9	82.20	11.87	3.95	1.98

TABLE IV Ashing results of the formulations indicating the actual filler loadings obtained

Formulation	As-compounded (% by volume)	Rheometer extrudate	
		195° C (% by volume)	225° C (% by volume)
F1	64.66	64.82	65.13
F2	64.97	64.97	65.13
F3	64.82	64.82	64.82
F4	65.13	65.13	65.29
F5	64.97	64.66	64.66
F6	64.66	65.13	65.29
F7*	65.29	65.29	64.97
F8	65.13	64.66	64.82
F9	64.97	64.97	65.29

*Ashing correction made.

TABLE V MFI values of the formulations

Formulation	MFI (g/10 min)
Polypropylene	65
F1	6–7
F2	46–55
F3	47–51
F4	46–58
F5	11
F6	14–18
F7	10–11
F8	16–20
F9	16–18

4. Results and discussion

4.1. Filler loading

Ashing results are contained in Table IV. They indicated that all the formulations compounded contained 65% by volume silicon powder with a maximum variability of 0.44%. Ashing results of the rheometer extrudates, also shown in Table IV, indicated that there was no appreciable change in the volume fraction of the filler loading, hence justifying comparisons of rheological results.

Silcione oil when ashed left a residue of 47.19% by weight. Since 3.95% by weight silicone oil was used in formulation F7 this gives rise to a correction of −1.86% by weight.

In the present work the volume fraction of powder was kept constant and since the powder has a wide particle size distribution, high volume loadings are possible. In fact the distribution is close to the optimum distribution for injection moulding achieved by Mangels [35].

4.2. Melt flow index

A zero result was obtained at the standard test conditions for filled polypropylene and therefore results could only be obtained under arbitrary conditions. The values obtained showed very high errors, 23% in some cases (Table V). The melt flow index test was therefore considered to be inapplicable to the characterization of injection moulding blends.

4.3. Yield stress

An attempt was made to deduce the yield stresses from the shear stress–shear rate curves in Fig. 3a by the tangent construction used by Moore [26]. The continuous curvatures shown in Fig. 3a, meant that the yield stresses would have arbitrary values. For the same reason the Buckingham–Reiner equation [36, 37] cannot be applied to the results to give yield stress [38]. If, however, the fluid shows quasi-plastic behaviour with a yield stress τ_y, it should obey the expression [39]:

$$\tau - \tau_y = k\dot{\gamma}^n$$

when τ_y is the yield stress and n is obtained from the slope of the $\log \eta$–$\log \dot{\gamma}$ plot. Thus if τ is plotted as a function of $\dot{\gamma}^n$ a straight line should result, with intercept τ_f. The results of Fig. 3a are replotted in this form in Fig. 3b and it is interesting to note that all the lines intercept the origin within the limits of experimental error. The method cannot, therefore, measure the yield stress and the implication of the results is that, for the fluids studied, yield stress is low. Experiments at much lower shear stresses would be needed to obtain this value.

4.4. Fluidity

In analysing the rheology data obtained in this work the materials have been treated as uniform in composition within the capillary. The justification for this lies in the objective of the work, which is to

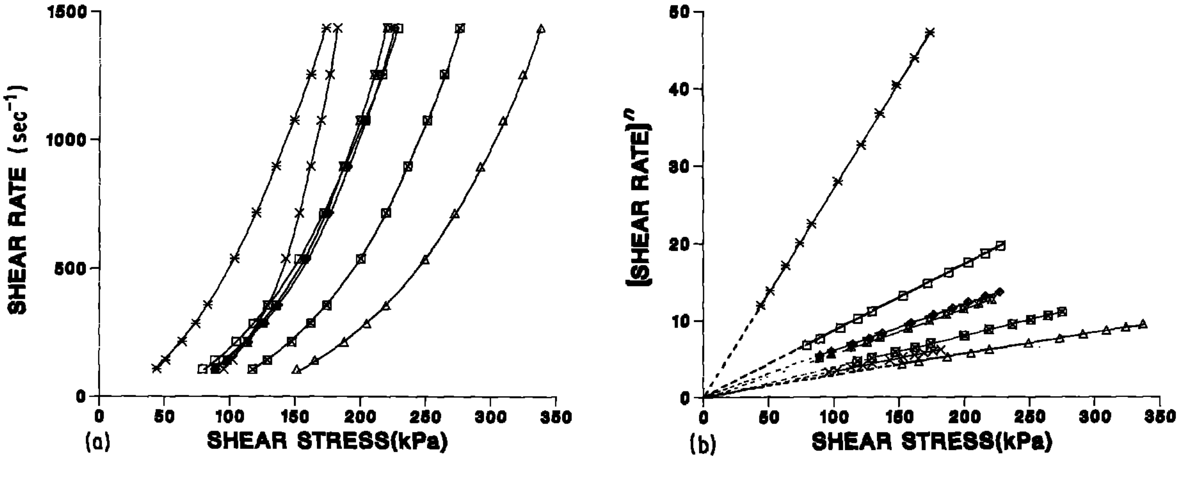

Figure 3 (a) Graphs of shear rate against shear stress of formulations, (△) F1, (x) F3, (□) F5, (☒) F6, (XX) F7, (∗) F8, (◈) F9. (b) Graphs of (shear rate)^n against shear stress of formulations (△) F1, (x) F3, (□) F5, (☒) F6, (XX) F8, (∗) F8, (◈) F9. Temperature = 225° C.

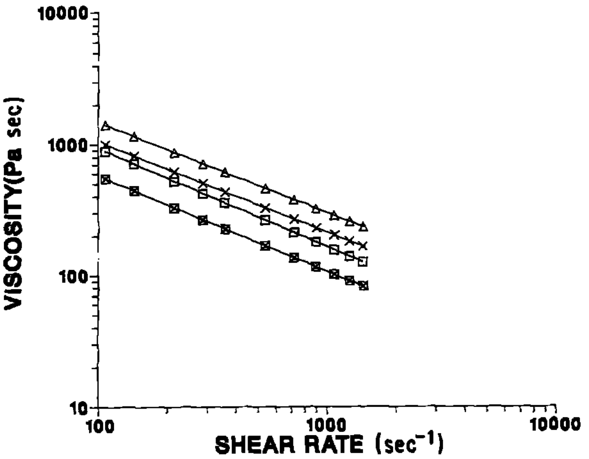

Figure 4 Viscosity against shear rate graphs of formulations (△) F1, (x) F2, (□) F3 and (☒) F4. Temperature = 225° C.

define relevant parameters for the characterization of ceramic injection moulding blends. It is possible that precise compositional analysis of the capillary boundary layer for some materials would reveal a fluid slightly depleted in filler or rich in a minor component. If so, an identical situation would occur in the boundary layer in the injection moulding machine.

The log viscosity against log shear rate graphs of all the formulations fitted a straight line relationship with correlation coefficients greater than 0.9 (Figs 4 and 5). Fig. 4 shows a graph of log viscosity against log shear rate for formulation F1 that contains only the major binding polypropylene. At a low shear rate (e.g. 108 sec^{-1}) the viscosity was 1406 Pa sec and was thus well above the previously suggested [23] limit of 1000 Pa sec. Therefore, minor components were incorporated to reduce the viscosity of this formulation. Shear rate and viscosity values of compositions which include a microcrystalline wax are plotted in Fig. 4 (F2, F3, F4) which indicates that the substitution of microcrystalline wax for polyproylene at a 1 : 7 ratio by weight reduced the viscosity by approximately 29% to 995 Pa sec at a shear rate of 108 sec^{-1}. According to the fluidity criteria [23] this composition must be regarded as marginal.

However, substitution at the 1 : 3 and 1 : 1 ratios by weight (compositions F3 and F4, respectively) effected reductions in viscosity of approximately 37% and 61% at a shear rate of 108 sec^{-1}. Both these compositions have viscosities below 1000 Pa sec at all shear rates studied and thus from a fluidity criterion were suitable blends. Unfortunately, formulation F4 containing a polypropylene : microcrystalline wax ratio 1 : 1 was very brittle and extruded in very fragile short lengths, probably due to macroscopic segregation of the low molecular weight wax. Low mechanical strength in an injection moulded ceramic component after solidification in the mould may influence the tendency to crack during thermal contraction and to fracture during ejection. Hence formulation F3 with a polypropylene : microcrystalline wax ratio of 3 : 1 was considered to be the most suitable.

The polypropylene substitution at the 1 : 3 by weight ratio provides a marked alteration of flow properties and therefore a range of other flow modifiers were substituted in this level, the silicon volume fraction remaining constant. Figs 5a and b show the viscosity against shear rate graphs for formulations F5 to F9. According to the fluidity criteria, all formulations other than F6 which contained a low density, high-melt flow index polyethylene were suitable for injection moulding. Fig. 5b illustrates the striking increase in fluidity afforded by polypropylene glycol.

The fluidity ($1/\eta$) at a shear rate of 108 sec^{-1}, that is, at the lower end of the shear rate range and at the nozzle temperature of 225° C was recorded from the graph and the values of this parameter along with other relevant flow parameters are given in Table VI for comparison. The exact values of viscosity at two temperatures, 195 and 225° C, are displayed in Tables VII and VIII and allow the calculation of these parameters. It is noteworthy that in the measurement of fluidity the error in pressure, and thus shear stress, is greatest at low shear rates and therefore the viscosity values at 108 sec^{-1} were determined from the complete flow curve and not from a single point measurement. It is also pertinent that at low shear rates differences between polymers are accentuated, thus the procedure chosen is an effective comparative technique.

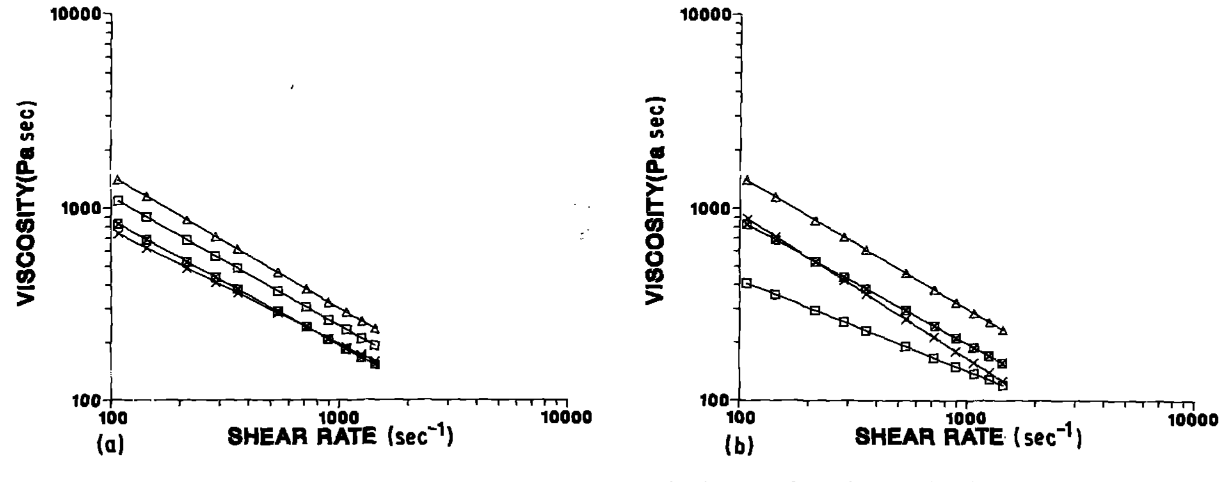

Figure 5 Viscosity against shear rate graphs of formulations having a major binder : minor binder ratio of 3 : 1 by weight. The graph of formulation F1 (△) which contains only the major binder polypropylene is reproduced for reference. (a): (x) F5, (□) F6 and (☒) F7, (b): (x) F3, (□) F8 and (☒) F9. Temperature = 225° C.

TABLE VI Comparison of formulations

Formulation	$n-1$ ($\mathrm{Pa\,sec^2}$) Temp. = 225° C	Fluidity, $1/\eta$ 10^{-3} ($\mathrm{Pa^{-1}\,sec^{-1}}$) Temp. = 225° C $\bar{\gamma} = 108\,\mathrm{sec^{-1}}$	Temperature dependence of viscosity	
			$\mathrm{d}\log\eta/\mathrm{d}T$ 10^{-3} ($\mathrm{Pa\,sec\,°C^{-1}}$) $\dot{\gamma} = 108\,\mathrm{sec^{-1}}$	Activation energy for viscous flow, E ($\mathrm{kJ\,mol^{-1}}$) $\dot{\gamma} = 108\,\mathrm{sec^{-1}}$
F1	−0.69	0.7	−1.7	7.4
F3	−0.75	1.1	−0.3	1.4
F5	−0.59	1.4	−6.3	28.2
F6	−0.67	0.9	−2.6	11.6
F7	−0.65	1.2	−2.9	13.1
F8	−0.47	2.5	−5.0	22.2
F9	−0.64	1.2	−2.3	10.4

4.5. Shear rate dependence of viscosity

The negative values of $(n - 1)$ in Table VI indicate that all the formulations show pseudoplastic flow characteristics and indeed the value of the parameter $(n - 1)$ is generally in the range of -0.6 to $-0.7\,\mathrm{Pa\,sec^2}$. One exception is the formulation which employs polypropylene glycol as a minor binder which has an exceptionally low pseudoplasticity but the highest fluidity value. The other striking exception is the formulation which uses microcrystalline wax. This has a strong pseudoplasticity ($-0.75\,\mathrm{Pa\,sec^2}$) but only intermediate fluidity. It is the complex interplay between these parameters and the parameters which influence solidification in the mould which determine moulding quality. Clearly according to Mutsuddy [23] as all the formulations satisfy the condition for pseudoplasticity they deserve full investigation as potentially usable moulding compositions. A positive value of $(n - 1)$ indicates a dilatant material in which separation of vehicle and powder could occur under high pressures. It is also quite possible for an apparently pseudoplastic system to become dilatant at high shear rates and thus η should be measured over a wide shear rate range.

4.6. Temperature dependence of viscosity

In addition to influencing the ability to control viscosity within a moulding machine by controlling the temperature of barrel, nozzle and mould, the temperature dependence of viscosity may have an effect on the response of the material to the sudden non-uniform cooling within the cavity. It is at this stage that high temperature gradients are set up and shrinkage of the polymer may introduce cracking or porosity in the moulded part. In particular the ability of the static post-injection hold pressure to compensate for shrinkage in the moulded part will be influenced by the rate of change of viscosity with temperature over the range of temperature between the injection temperature and the softening point, together with the actual value of the softening point [14].

Of the flow parameters discussed in this work, the value of $\mathrm{d}\log\eta/\mathrm{d}T$ and the activation energy for viscous flow showed the greatest composition sensitivity (Table VI). Formulation F5 with a polyethylene wax plasticizer had the highest temperature dependence of viscosity expressed as $\mathrm{d}\log\eta/\mathrm{d}T$ and activation energy for viscous flow. It is interesting to note that all mouldings produced with this formulation showed macroscopic moulding defects despite a relatively high fluidity. Conversely, composition F3 with a microcrystalline wax plasticizer which shows the lowest value of $\mathrm{d}\log\eta/\mathrm{d}T$ and activation energy for viscous flow allowed macroscopic defect-free mouldings to be obtained. Formulation F7 with dioctyl phthalate as plasticizer should, according to this superficial interpretation of results, produce sound mouldings. In fact, recent Japanese research [10] has

TABLE VII Shear rate and viscosity results for formulation F1 where only polypropylene was present as a binder and for formulations F1, F2 and F3 which contained the proportions of polypropylene (major binder) and microcrystalline wax (minor binder) mentioned below

Shear rate ($\mathrm{sec^{-1}}$)	Viscosity (Pa sec)							
	Polypropylene only (F1)		Polypropylene : wax = 7 : 1 (F2)		Polypropylene : wax = 3 : 1 (F3)		Polypropylene : wax = 1 : 1 (F4)	
	195° C	225° C	195° C	225° C	195° C	225° C	195° C	225° C
108	1576	1406	1110	995	906	886	560	547
143	1307	1152	944	816	756	713	456	443
215	1004	871	753	617	585	526	342	329
287	833	714	641	506	488	424	279	267
358	721	612	565	434	424	359	238	227
538	554	463	451	328	329	265	179	169
717	459	380	384	269	274	213	146	137
896	397	325	338	230	238	181	124	116
1075	353	287	306	203	212	157	109	102
1255	319	258	280	183	193	140	98	91
1434	293	235	260	167	177	127	89	83

TABLE VIII Shear rate and viscosity results for formulations F5, F6, F8 and F9 where polypropylene was the major binder in combination with different minor binders mentioned below at a weight of ratio 3 : 1

Shear rate (sec^{-1})	Viscosity (Pa sec)									
	Polypropylene, polyethylene wax (F5)		Polypropylene, low-density polyethylene (F6)		Polypropylene, silicone oil (F7)		Polypropylene, polypropylene glycol (F8)		Polypropylene, dioctyl phthalate (F9)	
	195° C	225° C	195° C	225° C	195° C	225° C	195° C	225° C	195° C	225° C
108	1138	735	1306	1091	1013	827	577	409	972	827
143	960	620	1105	899	860	686	504	357	802	688
215	756	488	873	685	682	527	417	295	611	530
287	638	412	739	565	579	437	364	258	504	441
358	559	361	650	487	510	378	328	232	434	383
538	440	284	513	371	405	291	271	192	331	295
717	372	240	434	306	343	241	237	168	273	246
896	326	210	382	264	302	208	213	151	235	213
1075	293	189	343	233	273	185	196	138	208	189
1255	267	172	314	210	250	168	182	129	187	172
1434	247	159	291	192	231	154	171	121	171	158

confirmed that a combination of polypropylene and phthalates were found to be very successful in ceramic injection moulding.

The activation energies in Table VI could cast some light on the nature of polymer blends. The value of $7.4\,\text{kJ mol}^{-1}$ for composition F1 between 195 and 225° C should be compared with literature values of $15\,\text{kJ mol}^{-1}$ for an isotactic polypropylene between 190 and 210° C [40].

The low value of $7.4\,\text{kJ mol}^{-1}$ probably arises because the polymer fraction F1 contains 11.1% by weight stearic acid which may be sufficiently compatible to act as a flow modifier rather than confining itself to adsorption on the ceramic surface as a surfactant.

The effect of microcrystalline wax ($\bar{M}_n = 300$) in composition F3 is probably similar; perhaps the molecular weight is sufficiently low to allow some solubility in the melt. Some indications of the behaviour of the polyethylene wax F5 and the low-density polyethylene F6 can be obtained by considering the work of Noel and Carley [40]. They used blends of high molecular weight polyethylene (M.F.I. 5; density $964\,\text{kg m}^{-3}$) and a polypropylene (M.F.I. 15) and found behaviour characteristic of two-phase mixtures which was confirmed by microscopy. The polyethylene wax ($\bar{M}_n = 2610$) F5 and the low-density polyethylene ($\bar{M}_n = 14\,500$) F6 are probably intermediate in compatibility with polypropylene between the microcrystalline wax and the high molecular weight polyethylene used by Noel and Carley [40]. Their influence on flow is complicated by the effects of chain branching and molecular weight distribution. The polypropylene glycol ($\bar{M}_n = 8600$) F8, silicone oil ($\bar{M}_n = 22\,800$) F7 and dioctyl phthalate effect only a marginal increase in activation energy and their state of dispersion or of segregation to the capillary wall is not known at present.

5. Conclusions

The results of this work clearly show that a single point test such as the melt flow index was unsuccessful in characterizing ceramic injection moulding formulations. It also showed that flow curves obtained from capillary rheometer data at shear rates above $100\,\text{sec}^{-1}$ cannot be used to deduce the yield stress of formulations. On the other hand, the values of $n - 1$, fluidity, $\text{d} \log \eta/\text{d}T$ or activation energy for viscous flow obtained from capillary rheometer data were reliably deduced. These parameters are considered to be important characteristics of ceramic injection moulding formulations.

It is clear that minor components of the polymer–ceramic blend have a considerable influence on these flow parameters and this provides a rational basis for tailoring the composition of ceramic injection moulding blends to meet the criteria for defect-free cavity filling. Understanding of injection moulding and development or refinement of such criteria continue to evolve in current research worldwide.

The literature survey suggests that, in general, fluidity at $100\,\text{sec}^{-1}$ should be greater than $1 \times 10^{-3}\,\text{Pa}^{-1}\,\text{sec}^{-1}$ and all but one of the formulations prepared meet that criterion. Indeed several formulations could tolerate an increase in filler loading without exceeding that viscosity. However, the arbitrary value of 1000 Pa sec must depend on available machine pressures as well as sprue, gate and mould design and it is likely that in some cases lower fluidities could be tolerated.

Fluidity alone is thought to be a necessary but insufficient criterion for mouldability. The formulation should be pseudoplastic in nature and there is an implication, though not tested, that the lower the value of n the better. All formulations showed pseudoplastic behaviour over the range of shear rate 100 to $1000\,\text{sec}^{-1}$.

The temperature dependence of viscosity was the most composition sensitive parameter tested and the choice of minor organic vehicle components produced values of $\text{d} \log \eta/\text{d}T$ from 0.3 to $6.3\,\text{Pa sec}°\,\text{C}^{-1}$ and activation energies of 1.4 to $24.8\,\text{kJ mol}^{-1}$. As a general rule, the values of these parameters should be as low as possible over the range of temperature close to the nozzle temperature.

On this basis the formulations using microcrystalline wax (F3), silicone oil (F7) and dioctyl phthalate (F9) show most promise as moulding blends.

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