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Thermal Expansion and Equation of State for Ceramic Injection Moulding Suspensions

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Abstract

In order to model the solidification of ceramic suspensions in the injection moulding operation, linear and cubical thermal expansion coefficients for the suspensions were obtained, and the equation of state was derived. The relevance of the law of mixtures to the prediction of these properties was investigated. The accuracy with which group contribution theory can predict the thermal properties of the organic vehicle was evaluated. Such predictions permit the numerical modelling of solidification to be executed with the minimal experimentation for diverse suspensions.

Zur Modellbeschreibung der Verfestigung keramischer Suspensionen während des Spritzgießens wurde anhand gemessener linearer und kubischer Wärmeausdehnungskoeffizienten eine Zustandsgleichung hergeleitet. Die Relevanz des Mischungsgesetzes auf die Vorhersagbarkeit der Eigenschaften und die Genauigkeit, mit der die Gruppenverteilungstheorie die thermischen Eigenschaften des organischen Bindemittels beschreibt, wurde untersucht. Mit Hilfe solcher Methoden können mit wenigen durchgeführten Experimenten numerische Berechnungen zur Voraussage der Verfestigung keramischer Spritzgußsuspensionen gemacht werden.

Afin de modéliser la solidification de suspensions de céramiques lors du moulage par injection, on a obtenu les coefficients de dilatation thermique linéaires et cubiques des suspensions, et on en a déduit leur équation d'état. On a examiné la validité de la loi des mélanges quant à la prévision de ces propriétés. On a évalué la précision avec laquelle la théorie de contribution des groupes peut prédire les propriétés thermiques du milieu organique. De telles prévisions permettent une modélisation de la solidification avec un minimum d'expériences pour différentes suspensions.

1 Introduction

The injection moulding of ceramics as a means of generating complex shapes from assemblies of fine particles is one of the most attractive routes for mass production of ceramic artefacts.[1,2] As ceramic manufacturers confront the total number of experiments needed to explore the numerous material and machine parameters in an effort to produce quality products, greater interest focuses on the value of mathematical modelling in preference to trial and error by experiment.

It has been emphasised that two major problems, each associated with the manufacture of large sections, remain to be solved.[2] One is the removal of organic vehicle after moulding[3] and the other the avoidance of defects that tend to occur in large sections during solidification.[4,5] Previous work has described experimental procedures for the computer modelling of the solidification stage for a zirconia–polystyrene system.[6,7] This allowed both voids and residual stresses to be predicted. Once such a model is on computer and has been validated by appeal to experiment, a large number of explorations of material and machine parameters become possible without entering the laboratory. In order to validate these procedures, a well-defined injection moulding suspension is needed. Thermal expansion in the liquid and solid states, thermal diffusivity and mechanical properties are required. Furthermore, the equation of state for the fluid suspension is

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needed. In previous work, the analysis was performed for a suspension based on an amorphous polymer.[7] The work of which this forms a part extends this analysis to semi-crystalline materials. It is also intended to facilitate the prediction of physical properties as a function of the ceramic volume fraction for the high fractions encountered in ceramic injection moulding. It is further of considerable interest to see how accurately the properties of diverse organic vehicles can be predicted from group contribution theory[8] in order to minimise experimental work.

2 Experimental Details

The alumina powder used throughout was RA6, donated by Alcan Chemicals Ltd. The organic vehicle was made up of isotactic polypropylene (GY545M ex ICI), atactic polypropylene (MF5 ex APP Chemicals) and stearic acid in the weight ratio 4:4:1. Mixing was effected by using a twin-screw extruder in a procedure previously described.[9] The exact volume fractions of dry alumina were calculated from the results of seven or eight ashing experiments and are shown in Table 1.

The samples were prepared by compression moulding at 170°C. Samples for dilatometry were in the form of cylinders, 8 mm in diameter and between 5 and 7 mm long, with flat parallel ends. Samples for cubical thermal expansion were rectangular bars 12 mm × 12 mm × 45 mm with rounded edges.

Thermal expansion in the solid state was measured by using a Perkin–Elmer TMS-1 thermomechanical analyser with a flat ended silica rod at a loading of 4 g and a heating rate of 4°C/min. The dilatometer was calibrated by measuring the thermal expansion of a pure aluminium standard. All samples were first annealed at 120°C for 1 h to relieve residual stresses from the pressing operation.

Cubical thermal expansion was performed by mercury displacement by using the apparatus shown in Fig. 1 and following the standard procedure.[10] Figure 1(a) shows the glass bulb that was used for compositions 3 and 5. The modified bulb (Fig. 1(b)) was used for composition 1. The sample size, however, deviated from the standard specification for ease of manufacture. The inversion of the bulb was needed to prevent the ceramic-free sample from melting and blocking the mercury stem. The whole assembly was heated in a well-lagged oil bath, and for each temperature increment the height of the mercury column was measured once it was stable.

Table 1. Volume fraction of alumina

Composition number	*Vol% Al_2O_3*
1	0
2	24·3 ± 0·1 (7)
3	40·4 ± 0·8 (7)
4	49·7 ± 0·2 (8)
5	51·3 ± 0·1 (7)
6	56·4 ± 0·7 (8)
7	61·8 ± 0·2 (8)

Confidence limits (95%) are given. The number of ashing experiments is given in parentheses.

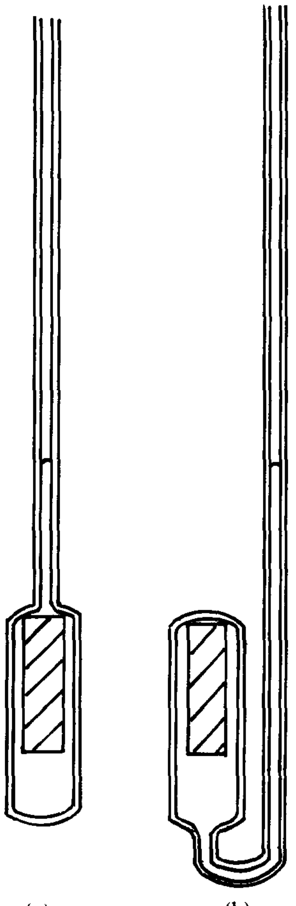

Fig. 1. Arrangement of the glass capillary and bulb.

Differential scanning calorimetry was used to obtain the enthalpy of melting for the organic species. A Perkin–Elmer DSC-2 was used with a heating rate of 10 K/min, and calibration was provided by using an indium standard.

3 Results and Discussion

3.1 Linear thermal expansion

In order to measure the coefficient of linear expansion by dilatometry, all the samples were first annealed. This process removes anomalies introduced by the method of fabrication, which are

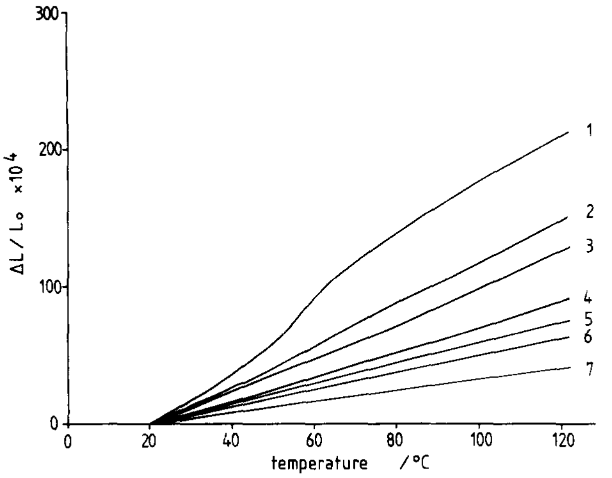

Fig. 2. Dilatometric expansion curves for ceramic moulding suspensions. For composition, see Table 1.

discussed elsewhere.[11] Figure 2 shows the thermal expansion curves from room temperature to 120°C. The unfilled organic vehicle presents a dilation in the region of 60°C, which may be associated with the independent melting of the stearic acid component. This dilation is also present in the filled material but is undetectable at high loadings of ceramic. Above approximately 130°C, the curves deviate from linearity as melting of the crystalline polypropylene fraction commences and the dilatometric softening point is approached. This deviation is measured more precisely by the cubical expansion method described below, in which effects of push-rod loading and slight variation in sample size do not influence the curve. The deviation is related to the melting expansion calculated from DSC melting enthalpies discussed below.

The average coefficients of linear expansion obtained from Fig. 2 between room temperature and 120°C are plotted in Fig. 3 as a function of the dry ceramic volume fraction calculated from ashing results. Included in Fig. 3 is the coefficient of expansion for >99·5% alumina taken from Ref. 12.

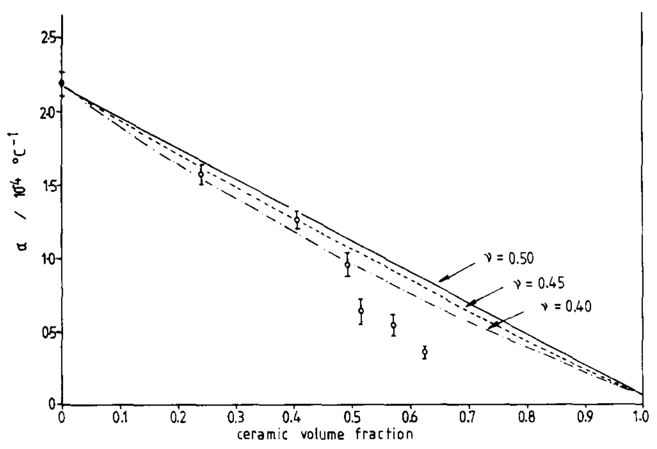

Fig. 3. Coefficient of linear expansion as a function of ceramic volume loading.

For a particle-filled composite material in the solid state, the linear expansion deviates slightly from the volumetric law of mixtures. The deviation depends on the difference in bulk moduli of the two phases, and the effective expansion coefficient is given by[13]

$$\alpha^* = \alpha_2 - \frac{(\alpha_2 - \alpha_1)K_1(3K_2 + 4\mu_2)V_1}{K_2(3K_1 + 4\mu_2) + 4(K_1 - K_2)\mu_2 V_1} \tag{1}$$

where α^* is the thermal expansion coefficient of the composite; α, K and μ are the expansion coefficients, bulk moduli and shear moduli, respectively; and subscripts 1 and 2 refer to the dispersed phase and the continuous phase, respectively.

Both K and μ can be found from Young's modulus E for each material:

$$K = \frac{E}{3(1-2v)} \qquad \mu = \frac{E}{2(1+v)} \tag{2}$$

where v is Poisson's ratio. Taking $E = 360$ GPa (Ref. 12) and $v = 0{\cdot}25$ (Ref. 12) for alumina gives $K_1 = 240$ GPa and $\mu_1 = 144$ GPa.

The room temperature elastic modulus of composition 1 was found by the method described in an ASTM standard[14] to be 0·32 GPa at 21°C. Poisson's ratio for isotactic polypropylene is 0·4 and, for atactic polypropylene,[15] $v = 0{\cdot}49$. Taking Poisson's ratio as 0·45 for the polymer blend gives $K_2 = 1{\cdot}07$ GPa and $\mu_2 = 0{\cdot}11$ GPa. Since $K_1 \gg K_2$ and $K_1 \gg \mu_2$, eqn (1) simplifies to

$$\alpha^* \approx \alpha_2 - \frac{(\alpha_2 - \alpha_1)(3K_2 + 4\mu_2)V_1}{3K_2 + 4\mu_2 V_1} \tag{3a}$$

$$= \alpha_2 - \frac{(\alpha_2 - \alpha_1)CV_1}{3 + (C-3)V_1} \tag{3b}$$

where

$$C = \left[3 + \frac{6(1-2v_2)}{1+v_2}\right]$$

and is a function of Poisson's ratio of the unfilled polymer only. Figure 3 therefore includes theoretical curves for various values of v_2. This figure appears to show that the effective Poisson ratio of the organic vehicle decreases with increasing ceramic volume fraction, but a decrease in expansion coefficient may simply be related directly to the change in relative volume fraction of the ceramic. At this stage, the composite is effectively a ternary system with an adsorbed polymer volume fraction, which is dependent on the powder surface area and hence the ceramic volume fraction and the polymer chain end-to-end distance.[16]

The important observation from Fig. 3 is that the volumetric law of mixtures may significantly overestimate the expansion coefficient for fine ceramic powders at high volume loadings in the solid state.

3.2 Cubical thermal expansion

Samples of compositions 3 and 5 were tested by using the standard procedure[10] and a glass bulb as shown in Fig. 1(a) but with modified sample dimensions. When composition 1 was tested by this method, it melted and proceeded to enter the capillary. The modified bulb shown in Fig. 1(b) was therefore constructed. The expansion curves are shown in Fig. 4.

The relative expansion of the sample is given by

$$\frac{V}{V_0}=\frac{A\,\Delta X}{V_0}-\frac{\beta_m V_m \Delta T}{V_0}+\frac{(V_m+V_s)\beta_g \Delta T}{V_0} \qquad (4)$$

where A is the cross-sectional area of the capillary; ΔX is the displacement of the column; β_m and β_g are the coefficients of cubical thermal expansion of the mercury[10] and glass, taken as $18{\cdot}2\times10^{-5}$/°C and $9{\cdot}9\times10^{-6}$/°C (borosilicate glass, J. Bibby Science Products Ltd, UK), respectively; V_0 is the volume of the test piece at room temperature measured by the Archimedes method; and V_s is the volume of the test piece after a temperature change ΔT.

Figure 4 shows the volume dilation associated with melting of the crystalline fraction of composition 1, which is 5·0 vol% and corresponds to expansion calculated from the enthalpy of melting described below. In the liquid state, the shear modulus of the organic vehicle is effectively zero, and the coefficients of expansion of the ceramic suspensions can be estimated from the volumetric law of mixtures,[13] which for the present constituents gives

$$\beta^*=2{\cdot}0\times10^{-5}V_1+7{\cdot}7\times10^{-4}(1-V_1) \qquad (5)$$

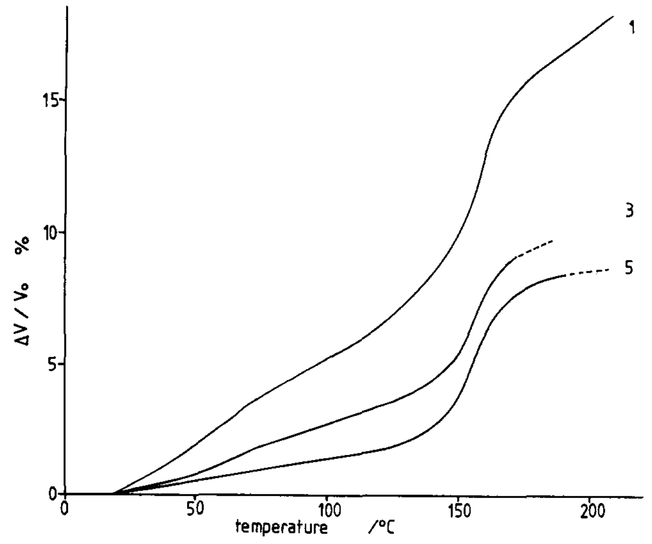

Fig. 4. Volumetric expansion curves for compositions 1, 3 and 5.

Table 2. Comparison of coefficient of linear expansion ($\alpha\times10^{-4}$/°C) measured by dilatometry and from cubical expansion measurement

Sample	*Dilatometry*	*Mercury displacement*
1	2·10	2·13
3	1·20	1·10
5	0·64	0·62

Table 2 compares the linear expansion coefficients measured by the two methods for compositions 1, 3 and 5. The measurements agree to within 9%.

3.3 Estimation of thermal expansion of organic vehicle

The thermal expansion of polymers in both the crystalline and amorphous state based on the Simha–Boyer model and Bondi theory as surveyed by van Krevelen[8] is given by

$$\varepsilon_l\approx10^{-9}V_W \qquad \varepsilon_c\approx\varepsilon_g\approx4\times10^{-10}V_W$$

where ε is the molar thermal expansion in units of m³/mol K; l, c and g refer to organic liquid and crystalline and amorphous polymer, respectively, and V_W is the van der Waals volume. The parameter V_W can be calculated from group contributions, and most organic group contributions are given by van Krevelen.[8]

The values for the organic binder used in this experiment were calculated by using this method. In order to simplify the calculation, the expansion of stearic acid was taken as being the same as APP. Above 60°C, the stearic acid, which is a minor component, is in the molten amorphous state. The law of mixtures, $\alpha^*=\sum\alpha_i V_i$, was used for the compositions.

With this procedure the estimated linear thermal expansion coefficients for the liquid state and solid state were $2{\cdot}14\times10^{-4}$/°C and $1{\cdot}91\times10^{-4}$/°C, respectively. The corresponding experimental results were $2{\cdot}57\times10^{-4}$/°C and $2{\cdot}10\times10^{-4}$/°C, respectively. The errors of 9 ~ 16% should be set against the powerful predictive capability that this technique confers on ceramic injection moulding, where the combination of organic species that are available for exploration is vast.

3.4 Volume changes on melting

The enthalpy change associated with melting of the crystalline fraction of the polymer was 49·5 J/g. This

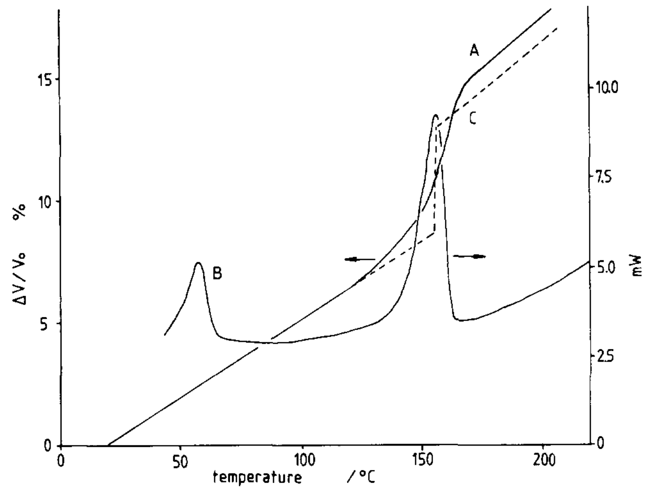

Fig. 5. The volumetric expansion of composition 1 (curve A) compared with the DSC trace for composition 1 (curve B); curve C is the simplified expansion to be used for subsequent computer modelling.

corresponds to 30% crystallinity based on data provided by Wunderlick.[17] This is made up of 50% crystallinity from the isotactic polypropylene and 9% for the atactic polypropylene, which includes a residue of isotactic material extracted during the manufacture of isotactic polypropylene. By using the specific volumes for the crystalline and amorphous regions at the melting point, which are $1{\cdot}095 \times 10^{-3}\,m^3/kg$ and $1{\cdot}286 \times 10^{-3}\,m^3/kg$, respectively,[8] the volume dilation associated with melting is 4·7 vol%, which should be compared with 5·0% observed by mercury displacement during melting of the crystalline polypropylene fraction. Figure 5 superimposes the DSC curve for composition 1 on the expansion curve, showing how the endotherms for melting of both the stearic acid and polypropylene correspond with the dilations. It is noteworthy that the addition of large quantities of alumina slightly reduces the crystalline fraction of polypropylene (Table 3). Two effects of added filler on crystallinity can be expected. On the one hand, the ceramic particles act as nucleating agents and may marginally increase the crystalline fraction. On the other hand, large amounts of ceramic of high specific surface area may introduce an adsorbed polymer fraction in which crystalline morphology may be restricted. Hence, in preparing a simplified version of the dilatometric expansion curve for the organic binder for use in computer modelling, the lower crystallinity of 25% was used. The formalised curve is shown in Fig. 5.

3.5 Equation of state

In order to derive the equation of state, the volume expansion curve for composition 1 from Fig. 4 was used for the organic phase, and the method of Spencer and Gilmore[18] was adopted. This has found wide acceptance for polymers.[20,21] The equation of state was considered to be made up of two separate contributions due to the ceramic and polymer. Since the bulk compressibility of the ceramic is $4{\cdot}1 \times 10^{-12}/Pa$ compared with $3{\cdot}2 \times 10^{-9}/Pa$ for the polymer, the error in specific volume introduced in treating the ceramic as incompressible was 0·036% at 150 MPa and room temperature for a ceramic volume fraction of 0·6. The corresponding error in the change in specific volume was 0·66%.

Table 3. Enthalpy of melting and crystallinity of the polypropylene fraction

Composition number	*Enthalpy (J/g)*	*Crystallinity (%)*[a]
1	49·5	30
2	49·3	30
3	49·0	30
4	45·5	28
5	41·3	25
6	42·7	26
7	40·7	25
APP	14·2	9
IPP	82·9	50

[a] For the crystalline fraction $\Delta H = 165\,J/g$ (from Wunderlich[17]).

The Spencer and Gilmore modification of the van der Waals equation gives[18,19]

$$(P + \pi)(V - W) = (R/M)T \qquad (6)$$

where M is the molecular weight of the repeat unit, T is the absolute temperature, and π and W are constants to be determined experimentally. The parameter W can be found by extrapolation of the thermal expansion data in the liquid state to 0 K, whereupon $V(0) = W$. The slope of the expansion curve, $\partial V/\partial T$, at zero pressure gives the value for π:

$$\pi = \frac{R}{M}\left(\frac{\partial V}{\partial T}\right)^{-1}_{p=0} \qquad (7)$$

The curve at 0·1 MPa is used to approximate to the situation at zero pressure. Since the stearic acid content of the organic fraction is small, M was taken as 42, the molecular weight of the repeat unit for polypropylene. From the data plotted in Fig. 4 by using the curve for the liquid state for the unfilled material, $\pi = 257\,MPa$ and $W = 9{\cdot}3 \times 10^{-4}\,m^3/kg$.

For comparison, these constants can also be estimated from group contributions:[8]

$$\pi = R/\varepsilon_1 \qquad W = 1{\cdot}3 V_W/M \qquad (8)$$

For isotactic polypropylene in the liquid state, $\pi = 211\,MPa$ and $W = 9{\cdot}5 \times 10^{-4}\,m^3/kg$. These estimates agree to within 18% and 2%, respectively.

Table 4. Specific volume (10^{-3} m^3/kg) at 200°C for isotactic polypropylene (columns 2 and 3) and the polymer blend used in the present work (column 4)

Pressure (MPa)	*Foster* et al.	*van Krevelen*	*Present work*
1	1·34	1·39	1·29
62·6	1·28	1·29	1·22

Without high-pressure equipment, the resulting equation of state cannot be validated. Foster and co-workers[21] measured the specific volume of isotactic polypropylene at temperatures up to 250°C and pressures up to 63 MPa. The blend used in the present work differs in composition from their material, particularly in respect of the 11 wt% stearic acid, but in the molten state the differences in polypropylene crystallinity are removed, and it is interesting to compare calculated specific volumes from eqn (6) with their experimental data. Table 4 makes this comparison at 200°C and also includes the calculated specific volumes for isotactic polypropylene from van Krevelen.[22]

The specific volume of ceramic is given by its temperature dependence:

$$V_c = \frac{1}{3986} + \{1 + 2{\cdot}0 \times 10^{-5}(T - 298)\} \qquad (9)$$

The specific volume of the polymer phase is given by the Spencer and Gilmore equation of state:[18]

$$V_p = \frac{197{\cdot}8T}{(P + 2{\cdot}57 \times 10^8)} + 9{\cdot}3 \times 10^{-4} \qquad (10)$$

The specific volume of suspensions is then obtained by combining eqns (9) and (10) as

$$V^* = V_c M_c + V_p M_p \qquad (11)$$

where M_c and M_p are mass fractions. The *P–V–T* behaviour of composition 6 in the injection moulding temperature range 170–220°C and for pressures of 0–150 MPa is plotted in Fig. 6.

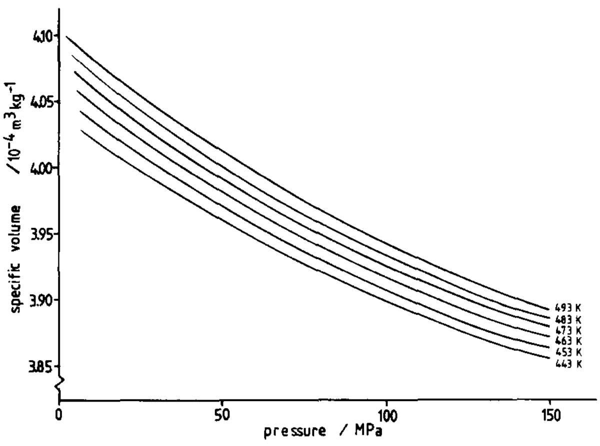

Fig. 6. *P–V–T* behaviour of a suspension containing 56 vol% alumina in the temperature and pressure range relevant to injection moulding.

4 Conclusions

Conventional laboratory procedures can be used to measure the volume dilations of ceramic injection moulding suspensions associated with thermal expansion in the liquid and solid states, and to measure the volume dilation caused by crystalline fractions. From the data, the equation of state can be derived. Such information, coupled with heat transfer and mechanical properties, permits the numerical modelling of the solidification of ceramic mouldings. The effect of large additions of fine ceramic powder causes thermal expansion in the solid state to deviate from theoretical curves and reduces the crystallinity of polypropylene. The law of mixtures allows estimation of the expansion properties in the liquid state and hence derivation of the equation of state. Furthermore, group contribution theory can be used to estimate these properties to within approximately 10%, and this allows calculations to be performed on a wide range of organic species for use in ceramic injection moulding.

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References

1. 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.
2. Edirisinghe, M. J. & Evans, J. R. G., Review: fabrication of engineering ceramics by injection moulding. II: Techniques. *Int. J. High Tech. Ceram.*, **2** (1986) 249–78.
3. Woodthorpe, J., Edirisinghe, M. J. & Evans, J. R. G., Properties of ceramic injection moulding formulations. III: Polymer removal. *J. Mater. Sci.*, **24** (1989) 1038–48.
4. Edirisinghe, M. J. & Evans, J. R. G., Properties of ceramic injection moulding formulations. II: Integrity of mouldings. *J. Mater. Sci.*, **22** (1987) 2267–73.
5. Thomas, M. S. & Evans, J. R. G., Non-uniform shrinking in ceramic injection moulding. *Br. Ceram. Trans. J.*, **87** (1988) 22–6.
6. Hunt, K. N., Evans, J. R. G. & Woodthorpe, J., Computer modelling of the origin of defects in ceramic injection moulding. I. *J. Mater. Sci.* (in press).

7. Hunt, K. N., Evans, J. R. G. & Woodthorpe, J., Computer modelling of the origin of defects in ceramic injection moulding. II. *J. Mater. Sci.* (in press).
8. van Krevelen, D. W., *Properties of Polymers*. Elsevier, Amsterdam, The Netherlands, 1972, pp. 55–65.
9. Edirisinghe, M. J. & Evans, J. R. G., The rheology of ceramic injection moulding blends. *Br. Ceram. Trans. J.*, **86** (1987) 18–22.
10. ASTM D864-52 (1981), Standard Test Method for the Coefficient of Cubical Thermal Expansion of Plastics.
11. Zhang, T. & Evans, J. R. G., Anomalies in the thermal expansion of injection-moulded ceramics. *J. Mater. Sci. Lett.* (in press).
12. Morrell, R., *Handbook of Properties of Technical and Engineering Ceramics, Part 2*. HMSO, London, 1987, pp. 95–7, 123–8.
13. Hale, D. K., The physical properties of composite materials. *J. Mater. Sci.*, **11** (1976) 2105–41.
14. ASTM D638-80 (1981), Standard Test Method for Tensile Properties of Plastics, pp. 228–44.
15. van Krevelen, D. W., *Properties of Polymers*. Elsevier, Amsterdam, The Netherlands, 1972, pp. 157–8.
16. Zhang, T. & Evans, J. R. G., Predicting the viscosity of ceramic injection moulding suspensions. *J. Eur. Ceram. Soc.*, **5** (1989) 165–72.
17. Wunderlich, B., *Macromolecular Physics*, Vol. 3. Academic Press, London, 1980, p. 95.
18. Spencer, R. S. & Gilmore, G. D., Equation of state for polystyrene. *J. Appl. Phys.*, **20** (1949) 502–6.
19. Throne, J. L., *Plastics Process Engineering*. Marcel Dekker, New York, 1979, p. 706.
20. Rubin, I. I., *Injection Moulding Theory and Practice*. Wiley, New York, 1972, p. 270.
21. Foster, G. N., Waldman, N. & Griskey, R. G., Pressure–volume–temperature behaviour of polypropylene. *Polym. Engng Sci.*, **6** (1966) 131–4.
22. van Krevelen, D. W., *Properties of Polymers*. Elsevier, Amsterdam, The Netherlands, 1972, p. 93.