

Thermal Properties of Ceramic Injection Moulding Suspensions in the Liquid and Solid States

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Abstract

Thermal diffusivity and specific heat of ceramic suspensions containing up to 60 vol.% Al_2O_3 were measured in the temperature range relevant to injection moulding. The ceramic mass or volume fraction dependence of these properties was related to relevant models and the measured properties of the organic vehicle were compared with values predicted from group contribution theory. Procedures are thus described for the acquisition of thermal property data for ceramic injection moulding suspensions with minimal experimentation. Such information facilitates the computer modelling of the solidification stage of ceramic injection moulding.

Die Temperaturleitfähigkeit und die spezifische Wärme von keramischen Suspensionen, die bis zu 60 Vol.% Al_2O_3 enthielten, wurden in dem für das Spritzgießen relevanten Temperaturbereich gemessen. Die Abhängigkeit der keramischen Massen- bzw. Volumenverhältnisse wurde zu entsprechenden Modellen in Beziehung gesetzt und die gemessenen Eigenschaften der organischen Trägermaterialien wurden mit den Werten, die von der Gruppenbeitrags-theorie vorhergesagt wurden, verglichen. Es werden Methoden beschrieben, die Daten für die thermischen Eigenschaften der keramischen Spritzgußmasse mit möglichst wenigen Experimenten zu gewinnen. Diese Informationen erleichtern die Computermodellrechnung des Verfestigungsstadiums der keramischen Spritzgußmasse.

La diffusivité thermique et la chaleur spécifique de suspensions de céramiques contenant jusqu'à 60% volumiques d' Al_2O_3 ont été mesurées dans le domaine de températures intéressant pour le moulage par injection. La variation de ces propriétés en fonction de

la fraction massique ou volumique de céramique est reliée aux modèles convenables, et on a comparé les propriétés du milieu organique aux valeurs prévues par la théorie de contribution des groupes. Ainsi, on décrit des techniques d'acquisition de données sur les propriétés thermiques de suspensions pour le moulage par injection de céramiques qui nécessitent très peu d'expériences. De telles données facilitent une modélisation informatique de l'étape de solidification des céramiques lors du moulage par injection.

1 Introduction

The fabrication of technical ceramic bodies by injection moulding continues to attract considerable attention as a mass production procedure. The initial empirical developments^{1,2} have given way to a more determined attempt to come to terms with the very complex processes involved.³ For this reason efforts have been made to quantify the process of solidification in the cavity,^{4,5} in order to understand how the many material and machine parameters influence the formation of voids and the build up of residual stresses which may cause cracks.^{6,7} Such computer models permit a large number of simulated experiments to be executed in order to investigate the influence of a large number of parameters on the incidence of defects.

However, there is no value in computer models which are not validated by reference to experiment. Neither do such models have value if the material parameters which they use are inaccessible or difficult to measure without specialised equipment. The present work is part of an attempt to acquire thermal and material property data for ceramic injection moulding suspensions by laboratory procedures which are generally available, and to use

the collected data to validate computer models of the solidification process. Furthermore, the extent to which such properties of particle filled composites can be predicted from mass or volume fraction dependence models is of great interest because it further reduces experimentation. In this context, the present work examines the thermal diffusivity and specific heat of alumina suspensions as a function of temperature and volume loading of ceramic. It also investigates the accuracy with which properties of the organic vehicle can be calculated from group contribution theory which also reduces experimentation. Extensive computer modelling of a wide range of powders, organic vehicles and volume fractions then becomes possible without resort to experiment, so that the computer can be used to narrow down the large number of combinations and ranges of parameters before an optimisation programme enters the laboratory.

2 Experimental Details

2.1 Preparation of suspensions

RA6 alumina was donated by Alcan Chemicals Ltd (Gerrards Cross, UK). The isotactic and atactic polypropylenes were grade GY545M from ICI (Welwyn Garden, UK) and grade MF5 from APP Chemicals (Salop, UK) respectively. Stearic acid was purchased from BDH Chemicals (Poole, UK).

The composition of the organic vehicle was atactic polypropylene, isotactic polypropylene and stearic acid in the ratios 4:4:1 throughout. The volume loadings of alumina corrected for adsorbed species were obtained from 7 or 8 ashing experiments.

The method of compounding involved preliminary mixing of the powders at room temperature in a Henschel high speed mixer at 3000 rpm followed by twin screw extrusion using a Betol TS40 with barrel temperatures 190, 200, 220, 220, 210°C feed to die. The procedure has been described previously.⁸

2.2 Measurement of thermal diffusivity

The apparatus was a modified version of that used by Hands & Horsfall⁹ and consisted of two cylindrical bronze cavities clamped by six bolts, equally spaced (Fig. 1). Heaters were clamped to both faces of the cavities and 36 swg type K thermocouples were arranged as shown in Fig. 1. The heaters were controlled by a Eurotherm 818P programmable temperature controller and were balanced with a wire wound dropping resistor to equalise surface temperatures. The disc-shaped

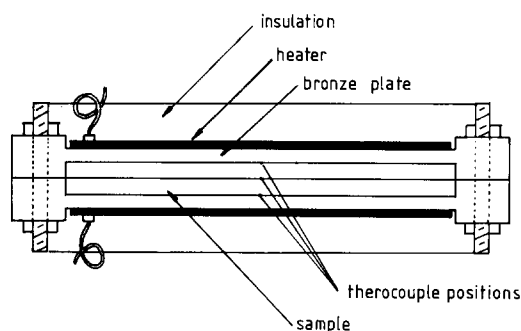


Fig. 1. The apparatus used for thermal diffusivity measurement.

samples measuring 180 mm in diameter by 6 mm in thickness were compression moulded. Since the sensitivity of the method is mainly dependent on the temperature difference between surface and centre, the relevant thermocouples were connected so as to amplify the difference in e.m.f. The size of the apparatus was greater than that used by Hands and Horsfall⁹ in order to permit larger thermal diffusivities to be measured without resort to fast heating rates. The method of calculating the size of the apparatus has been described.⁴ For typical ceramic compositions the radial heat flow in the modified apparatus produces an error of less than 0.2%. Constant heating rates in the range 3–5°C/min were used and a small hole was provided for the overflow of material in the liquid state. The thermocouple wire was calibrated against a thermometer with a BSI certificate but individual thermocouples were not calibrated because a new set was used for each run.

2.3 Measurement of specific heat

A DSC-2 Perkin Elmer differential scanning calorimeter was used for specific heat measurement using samples of 10–15 mg and a heating rate of 5°C/min in dry nitrogen. The instrument was calibrated with a sapphire standard and the deviation from the accepted value for the specific heat of sapphire¹⁰ was 2.1% at 370 K and 1.1% at 400 K.

3 Results and Discussion

3.1 Volume fraction of ceramic

The volume fractions of alumina calculated from the mean of 7 or 8 ashing experiments are given in Table 1 together with 95% confidence limits. The procedure used for obtaining the densities of components has been described previously.¹¹

Table 1. Volume fraction of alumina

Composition no.	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)

95% confidence limits are given. The number of ashing experiments is given in brackets.

3.2 Specific heat of ceramic suspensions

The DSC traces from which specific heat was calculated are shown in Fig. 2. During initial heating, accurate values are not obtained below 310 K, and so the specific heats at room temperature were found by short extrapolation.

The mass specific heat can be expressed as a function of temperature by:

$$C_p = a + bT \quad (1)$$

over the temperature range of interest and the constants a and b are given in Table 2 for the individual constituents of the blend as well as for the suspensions. This allows investigation of the ceramic weight fraction dependence of specific heat as well as the usefulness of methods for predicting the specific heat of polymer blends.

The heat capacity per unit volume of a composite at constant pressure is given by:¹²

$$C = \bar{C} + 9T \left(\frac{\alpha_2 - \alpha_1}{1/K_2 - 1/K_1} \right)^2 \left[\frac{1}{K^*} - \left(\frac{1}{K} \right) \right] \quad (2)$$

where \bar{C} is the specific heat of the composite based on the rule of mixtures, α is the thermal expansion, and K is the bulk modulus and K^* is the bulk modulus of the composite. Subscripts 1 and 2 refer to ceramic and matrix respectively and $\bar{1}/K$ is the

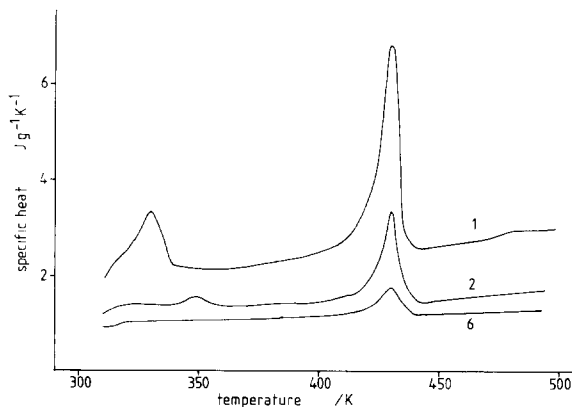

Fig. 2. DSC traces for specific heat measurement.

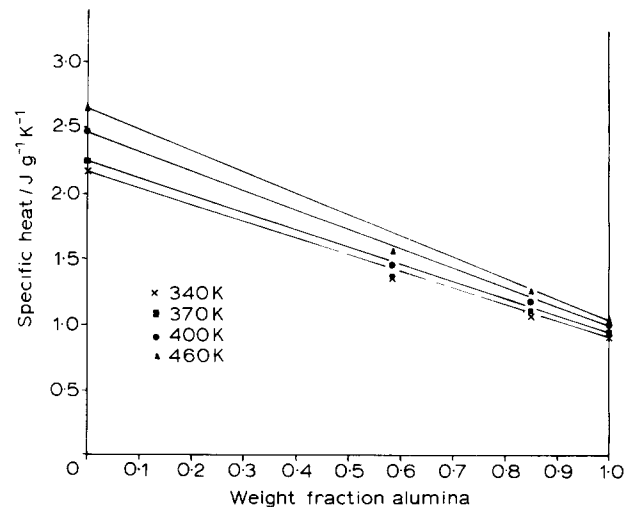
Table 2. The dependence of specific heat on temperature ($C_p = a + bT$ (J/kg K))

Material	C_p (298)	a	b	Temperature range (K)
IPP	1829	93	5.8	298 ~ 375, 442 ~ 500
APP	2146	1008	3.5	298 ~ 400, 440 ~ 500
SA	2161	1043	3.8	298 ~ 323, 347 ~ 430
Al_2O_3	865	513	1.2	298 ~ 520
1	2180	2180	0	348 ~ 360
		-367	7.1	360 ~ 400
		-711	7.3	450 ~ 500
2	1335	1335	0	298 ~ 340, 360 ~ 380
		871	5.8	380 ~ 410
		173	3.8	450 ~ 500
6	1012	552	1.5	298 ~ 410, 430 ~ 500

average inverse bulk modulus. If the bulk modulus of the continuous phase is very low by comparison with that of the ceramic, the rule of mixtures is an adequate estimate of C . Figure 3 shows specific heat at 340, 370, 400, 460 K as a function of weight fraction of ceramic. The straight line represents the law of mixtures. The experimental results deviate from the rule of mixtures by 2.5–9% for a volume loading of 25 vol.% ceramic and 2–4% for a volume loading of 56 vol.%. For suspensions of composition relevant to ceramic injection moulding therefore, the rule of mixtures is an acceptable procedure for the calculation of C_p , if the specific heats of the organic and ceramic constituents are known.

3.3 Thermal diffusivity

The modified Hands and Horsfall⁹ method for one directional heat flow allows thermal diffusivity to be measured as a function of temperature throughout the solid and liquid states over a temperature range


Fig. 3. Specific heat as a function of ceramic weight fraction at a range of temperatures.

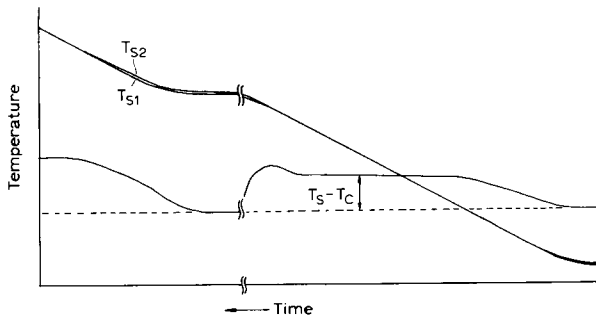


Fig. 4. Typical thermocouple traces from the thermal diffusivity apparatus. T_{s1} and T_{s2} represent the surface temperatures while $T_s - T_c$ is the differential e.m.f. between the centre and surface thermocouples.

relevant to ceramic injection moulding. The results obtained at temperatures below 80°C were not included because in this range all three temperatures had not attained a constant rate of rise.

Figure 4 shows a typical temperature trace obtained by this apparatus. The organic vehicle contains a significant crystalline fraction and therefore enthalpy of melting distorts the heating curves in the melting region. Thermal diffusivity cannot be measured by this method in the melting region even if the enthalpy is known, because the method is only valid for a constant heating rate. Thermal diffusivity can be calculated at any temperature from:

$$\alpha = \frac{a^2(T_1' + 5T_0')}{12(T_1 - T_0)} \quad (3)$$

where a is the half thickness of the complete disc, T_1 is the average of the two surface temperatures, T_0 is the centre temperature and the prime indicates rate of temperature increase.

Figure 5 shows α as a function of temperature for the compositions studied. The procedure is subject to the following errors.

- (i) Temperature difference between the two surfaces. Power to the heaters was balanced with a variable dropping resistor but temperature differences of $1\text{--}3^\circ\text{C}$ were encountered. This difference tended to be more pronounced for low ceramic volume loadings but for such samples the temperature difference ($T_1 - T_0$) is also larger. The resulting error in thermal diffusivity was less than 15%.
- (ii) Sample expansion or change in thermocouple position. The method is sensitive to the value of a and therefore a change in thermocouple position of 0.2 mm may induce a 7% error in α .

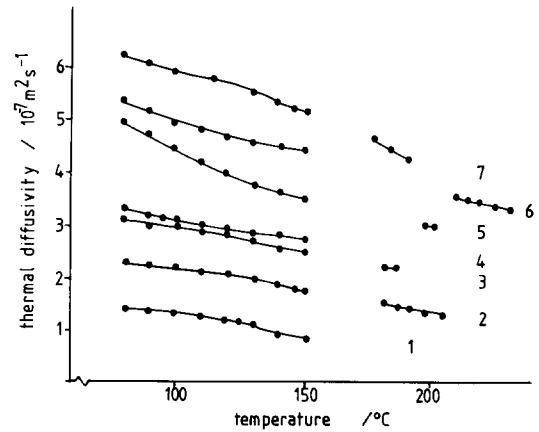


Fig. 5. Thermal diffusivity as a function of temperature for the compositions studied.

- (iii) Variation in heating rate. Using a low heating rate and a programmable controller with adaptive tuning of the PID parameters, heating rate error was less than $0.2^\circ\text{C}/\text{min}$ which would induce a 4% error in α .

From Fig. 5 it can be seen that for the purpose of computer modelling, thermal diffusivity can be approximated as a linear function of temperature by the expression

$$\alpha = mT + \alpha_v \quad (4)$$

with the constant α_v being a function of volume fraction. The slope m also varies slightly with volume fraction. This is because within the temperature range studied, the conductivity of alumina decreases by $\sim 20\%$ (Ref. 13) whereas that of common polymers decreases by $\sim 8\%$ (Ref. 14). Values of α_v and m are given in Table 3.

There are a number of models for the volume fraction dependence of mass, heat, magnetic or electrical flux in composite materials. These are reviewed by Hale,¹⁵ Christensen¹² and Barrer.¹⁶ The most widely used flux-volume fraction equations reduce to Maxwell's equation.¹⁷ These include the spherical inclusion model of Brailsford and Major¹⁸ in which particles of ceramic are surrounded by a continuous second phase and

$$\frac{\lambda^*}{\lambda_2} = \frac{1 - 2V_1 \left(\frac{\lambda_2 - \lambda_1}{2\lambda_2 + \lambda_1} \right)}{1 + V_1 \left(\frac{\lambda_2 - \lambda_1}{2\lambda_2 + \lambda_1} \right)} \quad (5)$$

where λ^* is the thermal conductivity of the composite and subscripts 1 and 2 refer to the ceramic and organic vehicle respectively. The model is valid for low concentrations. Possibly of more general

Table 3. The dependence of thermal diffusivity on temperature (353–423 K) ($\alpha = \alpha_v + mT$ ($m^2/s \times 10^{-7}$))

Composition	α_v	$m \times 10^3$
1	4.48	-8.57
2	5.38	-8.57
3	6.38	-9.29
4	6.58	-9.29
5	11.66	-19.30
6	10.65	-15.00
7	11.80	-15.71

relevance are the upper and lower bounds defined by the theory of Hashin and Shtrikman.¹⁹

$$\lambda^* = \lambda_1 + \frac{V_2}{\frac{1}{\lambda_2 - \lambda_1} + \frac{V_1}{3\lambda_1}} \quad (6a)$$

$$\lambda^* = \lambda_2 + \frac{V_1}{\frac{1}{\lambda_1 - \lambda_2} + \frac{V_2}{3\lambda_2}} \quad (6b)$$

Rearrangement shows that eqns (5) and (6b), together with the model described by Christensen (Ref. 12, p. 319), reduce to Maxwell's equation.¹⁷

If eqn (5) is rewritten as

$$\lambda^* = \lambda_2 \frac{(1 + 2V_1)\lambda_1 + 2(1 - V_1)\lambda_2}{(1 - V_1)\lambda_1 + (2 + V_1)\lambda_2} \quad (7)$$

then it can be seen that if $\lambda_1 \gg \lambda_2$, thermal conductivity is controlled almost entirely by the continuous phase and

$$\lambda^* \approx \lambda_2 \frac{(1 + 2V_1)}{(1 - V_1)} \quad (8)$$

In principle, Brailsford and Major's model is valid for dilute suspensions and it is therefore interesting to explore its limitations.

The derivation of the spherical inclusion models assumes that a particle of phase 1 is surrounded by a region of phase 2 which is in turn surrounded by material having an average conductivity equal to that which is to be calculated. This scheme is reasonable for a well dispersed ceramic suspension in which, during mixing, each particle has become surrounded by a layer of organic vehicle.

It sometimes helps in modelling the behaviour of concentrated suspensions, to propose that the surrounding region of phase 2 is absent and that each particle is surrounded by a matrix of average conductivity. This self-consistent scheme (SCS) approximation was originally intended for polycrystalline materials but has been applied to two-phase media (Ref. 12, p. 59). Brailsford & Major¹⁸ suggested the application of an SCS-type equation

(eqn (9)) which was derived by Landauer²⁰ for electrical conductivity of two phase materials:

$$V_1 \left(\frac{\lambda_1 - \lambda^*}{\lambda_1 + 2\lambda^*} \right) + (1 - V_1) \left(\frac{\lambda_2 - \lambda^*}{\lambda_2 + 2\lambda^*} \right) = 0 \quad (9)$$

from which λ^* can be obtained.

Nielsen²¹ suggests that the thermal conductivity of particle-filled polymers can be obtained from:

$$\frac{\lambda^*}{\lambda_2} = \frac{1 + ABV_1}{1 - B\psi V_1} \quad (10)$$

where $A = K_e - 1$ and $B = (\lambda_2\lambda_1 - 1)/(\lambda_2\lambda_1 + A)$. Here K_e is the volume fraction coefficient in Einstein's viscosity equation and is 2.5 for spherical inclusions in a liquid. ψ is a function given by:

$$\psi = 1 + [(1 - V_m)/V_m^2]V$$

where V_m is the maximum packing fraction and V_1 is the volume fraction of filler in suspension.

The effective thermal conductivities at 100°C were calculated from eqns (5)–(10) and the results are shown in Fig. 6. The thermal conductivity of alumina was taken as 24 W/m K.¹³ The densities were calculated using thermal expansion data previously obtained²² and the specific heat was obtained from the law of mixtures using data from this work for the two phases. The experimental thermal conductivities are shown in Fig. 6 alongside the theoretical curves. It is noted that the Maxwell equation in the form of the Hashin and Shtrikman lower bound or as Brailsford and Major's model gives a reasonable fit to the data points and can be used to predict the thermal conductivity of ceramic moulding suspensions as a function of ceramic volume fraction.

The simplification given by eqn (8) actually provides a slightly better fit to the data, the error at

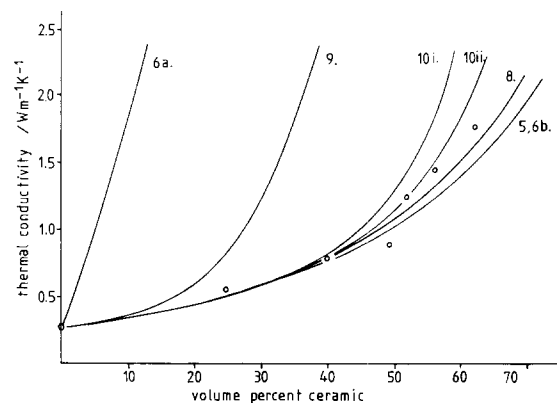


Fig. 6. Experimental thermal conductivities at 100°C compared with values predicted by eqns (5), (6), (8), (9) and (10).

56 vol.% being 7%. The self-consistent scheme given by eqn (9) deviates seriously from the data and is inappropriate. This, together with the approximation of eqn (8), shows that thermal transport in the suspension is strongly influenced by the organic layer surrounding each particle.

The Nielsen equation, which is claimed to fit the thermal conductivity of filled polymers over a wide volume fraction range requires a knowledge of V_m . A value of $V_m = 0.68$ was inserted using viscosity data for this powder¹¹ to obtain curve 10i in Fig. 6. The fit is rather poor and substitution of $V_m = 0.74$ for the packing of monodisperse spheres improves the situation (10ii in Fig. 6). There is really very little justification for taking this value of V_m and Nielsen's equation seems to offer a less predictive value on this occasion as well as demanding additional powder data.

3.4 Predicting the specific heat of polymer blends

Since the computer simulation of the solidification stage of injection moulding demands so many material properties and since practitioners wish to explore a wide range of polymers and waxes, it is of great interest to examine procedures for reducing the extensive experimentation the acquisition of such data entails. The specific heat of a ceramic suspension may be obtained from a knowledge of specific heats of the ceramic and organic components by application of the law of mixtures, but more can be done to reduce experimentation. The accuracy with which the specific heat of a blend of organic species can be estimated from group contribution theory will therefore be explored.

Group contributions for specific heat obtained by Satoh and by Shaw are surveyed by van Krevelen.²³ Melting enthalpy data have shown the crystallinity of the atactic and isotactic polypropylenes to be 9% and 50% respectively.²² Combining values for group contributions for polypropylene, for the amorphous and crystalline states from Ref. 22, the specific heat at 25°C, $C_p(298)$, is predicted to be 2070 and 1903 J/kg K for atactic and isotactic polypropylene respectively. These predictions agree with experimental results to within 5%. The procedure can be extended to predict the specific heat of the injection moulding binder used in the present work. The approximation is made that the specific heat of stearic acid is the same as atactic polypropylene, since its specific heat in the solid state and liquid state obey the same function, and its fraction is small. For this composition, $C_p(298) = 1996$ J/kg K which deviates from the measured value obtained by short extrapolation in Fig. 2 by less than 8.4%.

The prediction of the temperature dependence of specific heat is also possible but with diminished accuracy. Van Krevelen gives empirical functions for the crystalline and amorphous states which are intended to be general for a wide range of polymers.

$$\frac{C_{p(T)}^s}{C_{p(298)}^s} = 0.106 + 0.003T \quad (11a)$$

$$\frac{C_{p(T)}^l}{C_{p(298)}^l} = 0.64 + 0.0012T \quad (11b)$$

Van Krevelen accepts that the mean deviations for a wide range of polymers are 5% for eqn (11a) and 30% for eqn (11b).

By combining the coefficients according to the law of mixtures based on mass fraction for the organic binder used in the present work, the following expressions for specific heat are obtained:

$$C_{p(T)} = 1027 + 3.218T \quad 298 < T < 423 \quad (12a)$$

$$C_{p(T)} = 1341 + 2.515T \quad T > 443 \quad (12b)$$

Comparing this prediction with the measured specific heat shown in Table 2, the error is 0.8% at 353 K, 5.1% at 393 K and 8.0% at 473 K.

3.5 Predicting the thermal conductivity of polymers

Equipped with suitable thermal transport–volume fraction relationships the next stage is to explore how accurately the thermal conductivity of diverse organic binders can be obtained from theory without experiment. Van Krevelen¹⁴ discusses procedures for the prediction of the thermal conductivity of polymers. For amorphous polymers the thermal diffusivity can be estimated from

$$\alpha = \frac{\lambda}{\rho C_p} = C \left(\frac{U}{V} \right)^3 \left[\frac{3(1-\nu)}{1+\nu} \right]^{1/2} \quad (13)$$

where C is a constant and for most polymers is in the region $0.6 \times 10^{-8} \pm 0.08 \times 10^{-8}$ and U is the Rao function which is almost independent of temperature and behaves as an additive molar quantity and can therefore be calculated from group contributions. V is the molar volume and ν is Poisson's ratio.

This allows calculation of thermal diffusivity for the amorphous atactic content of the organic binder used in this work. The Sakiadis and Coutes²⁴ group contribution to the Rao function gives $U = 2716$. The density is 859 kg/m³ for the atactic fraction²⁵ and the specific heat for atactic polypropylene is 2150 J/kg K. This predicts a thermal diffusivity of 1.06×10^{-7} m²/s. The thermal conductivity of the

crystalline fraction can now be estimated from the general rule:¹⁴

$$\frac{\lambda_c}{\lambda_a} - 1 = 5.8 \left(\frac{\rho_c}{\rho_a} - 1 \right) \quad (14)$$

From the above prediction, $\lambda_a = 0.195 \text{ W/m K}$ and the density of crystalline polypropylene is 950 kg/m^3 (Ref. 25), thus using eqn (14), $\lambda_c = 0.328 \text{ W/m K}$. For the estimation of the thermal diffusivity of the blend, stearic acid is taken as an amorphous liquid as discussed in Section 3.3 and a graphical procedure is used to obtain λ as a function of weight percent crystallinity for a value of $\lambda_c/\lambda_a = 1.68$ at $X_c = 0.27$. This predicts a room temperature thermal conductivity of 0.224 W/m K and a thermal diffusivity of $1.12 \times 10^{-7} \text{ m}^2/\text{s}$. Van Krevelen gives a master curve for reduced conductivity $\lambda(T)/\lambda(T_g)$ as a function of reduced temperature T/T_g for a wide range of polymers which allows the temperature dependence of thermal conductivity to be estimated. Using this master curve, the thermal conductivity of the blend at 100°C is predicted to be 0.218 W/m K and the thermal diffusivity $1.12 \times 10^{-7} \text{ m}^2/\text{s}$. This prediction, which has used no new experimental data, lies within 13% of the measured value of $1.28 \times 10^{-7} \text{ m}^2/\text{s}$.

4 Conclusions

Laboratory procedures are described for the acquisition of thermal property data for ceramic injection moulding suspensions. Specific heat can safely be predicted from law of mixtures and a number of functions of volume fraction are described for the estimation of thermal diffusivity. Procedures are described for estimating the thermal properties of polymers from group contribution theory so that the properties of suspensions may be estimated with minimal resort to experiment.

These procedures allow the estimation of the thermal properties of diverse ceramic injection moulding suspensions so that computation methods can be used to simulate the ceramic injection moulding process without prior experimentation.

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