# Predicting the Viscosity of Ceramic Injection Moulding Suspensions

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# Abstract

The value of semi-empirical equations relating relative viscosity to the volume fraction of ceramic powder was explored for ceramic injection moulding suspensions containing up to 64 vol% alumina. The errors associated with the determination of volume fraction and viscosity were evaluated. An extension of the Chong equation was used for relative viscosity so that the effect of an unknown powder on viscosity could be established from a minimum of two viscosity measurements in a characterised organic vehicle. This simplifies decisions on composition to achieve a specified viscosity.

Das Ziel dieser Untersuchung war die Bewertung halbempirischer Gleichungen, die das Verhältnis der relativen Viskosität zum Volumenanteil von Keramikpulvern in Beziehung setzen. Es wurden Spritzgußsuspensionen verwendet. die bis zu 64 vol% Aluminiumoxid enthielten. Die Fehler, die mit der Bestimmung von Volumenanteilen und Viskositäten verbunden sind, wurden ausgewertet. Es wurde eine erweiterte Form der Gleichung von Chong für die relative Viskosität angewendet, so daß der Effekt eines unbekannten Pulvers auf die Viskosität mit einem Minimum von 2 Viskositätsmessungen in einem charakterisierten organischen Trägermedium bestimmt werden konnte. Das erleichtert die Entscheidung für eine Zusammensetzung, um eine spezifizierte Viskosität zu erhalten.

La validité des équations semi-empiriques reliant la viscosité relative à la fraction volumique d'une poudre céramique a été étudiée pour le cas de suspensions de moulage par injection contenant jusqu'à 64% en volume d'alumine. Les erreurs liées à la détermination de la fraction volumique et de la viscosité ont été évaluées. Une extension de l'équation de Chong a été utililisée pour la viscosité relative, de sorte que l'effet d'une poudre inconnue sur la viscosité puisse être établi pour un minimum de 2 mesures de viscosité dans un milieu organique connu. Cela simplifie le choix de compositions nécessaires à atteindre une viscosité spécifique.

# **1** Introduction

The emergence of high-performance ceramics as materials for engineering components relies on the perfection of methods for the creation of shape from assemblies of fine particles. From a mass production viewpoint, one of the most attractive routes to this end is injection moulding.<sup>1,2</sup> The ceramic powder is incorporated in an organic vehicle which is caused to solidify inside a cavity. The vehicle is then extracted, frequently by pyrolysis, before firing the ceramic. Control over flow properties of the moulding suspension is needed for this process and capillary rheometry offers a simple procedure for quantitative assessment.<sup>3,4</sup> The problem for the ceramist is to know the volume loading of powder in suspension to give a specified viscosity for injection moulding when presented with a new powder.

The viscosity of suspensions is very sensitive to ceramic loading at the high volume fractions needed for injection moulding, and also to the type of powder. Even for a given powder, inter-batch variation can cause a significant alteration of flow properties. The critical powder volume concentration (CPVC) has been used as an approximation to the optimum powder loading<sup>5</sup> and the test for this quantity has been simplified as the spatula rub-out test.<sup>6</sup> Unfortunately, this gives no quantitative indication of viscosity. At present, there is no accurate analytical route to the prediction of maximum packing fraction and hence viscosity from a knowledge of particle size distribution, particle shape and specific surface area, although attempts to solve this problem have attracted interest in the past<sup>7</sup> and continue to do so.<sup>8,9</sup>

If the viscosity,  $\eta$ , of a suspension is expressed as relative viscosity  $\eta_r$  such that

$$\eta_r = \eta/\eta_0 \tag{1}$$

where  $\eta_0$  is the viscosity of the unfilled organic vehicle measured under identical conditions, then a range of functions of ceramic volume fraction can be used to model the viscosity of suspensions.<sup>1</sup> Of these, only a few offer a good fit to experimental data at high ceramic loadings. Mooney<sup>10</sup> presents

$$\eta_r = \exp\left(\frac{2 \cdot 5V}{1 - kV}\right) \tag{2}$$

where k is  $1/V_m$  and  $V_m$  is the maximum packing fraction. Eilers<sup>11</sup> proposed the following function:

$$\eta_r = \left(1 + \frac{1 \cdot 25V}{1 - V/V_m}\right)^2$$
(3)

and Chong, et al.<sup>12</sup> present:

$$\eta_r = \left[1 + 0.75 \frac{V/V_m}{(1 - V/V_m)}\right]^2 \tag{4}$$

In previous work<sup>13,14</sup> Chong's equation has been proved to offer a reasonable fit for ceramic injection moulding suspensions measured at a shear rate of  $100 \,\mathrm{s}^{-1}$ , which represents the low end of the shear rate range encountered in injection moulding. Equation (4) can be arranged to show a function of  $(V_m - V)$  as denominator:

$$\eta_r = \left(\frac{V_m - 0.25V}{V_m - V}\right)^2 \tag{5}$$

This factor represents the extra volume fraction of organic vehicle over and above that needed to fill the interstices between contacting ceramic particles. The latter quantity is  $(1 - V_m)$ , and the equation shows that where the volume loading of ceramic rises to  $V_m$ , viscosity approaches infinity.

Equation (4) is thus a semi-empirical relationship, but approximates to Einstein's well known equation at very low volume loadings if  $V_m = 0.605$ , which is valid for monosized spheres.<sup>12</sup>

Chong's equation shows close agreement with the relative viscosity of silicon nitride suspensions, and also for silicon nitride suspensions with added silicon carbide whiskers.<sup>15</sup> Provided that the suspensions fit such a semi-empirical equation, a single viscosity measurement in the high volume loading regime can be used to predict the required organic vehicle content for a given ceramic powder, or for a new batch of powder, in order to obtain a desired viscosity without the tedious procedure of preparing a large number of trial compositions. If analytical relationships between powder characteristics and  $V_m$ become available, the relative viscosity – powder volume loading curve may allow determination of the composition of ceramic injection moulding blends with minimal experiment.

The present work investigates the errors in this procedure, notably where the powder does not present an ideal fit to eqn (4). The sensitivity of viscosity to volume loading means that attention must be given to the errors associated with determination of volume loading, viscosity and with inherent deviations from the model curve.

#### 2 Experimental Procedure

#### 2.1 Materials

The alumina was grade RA6 and was kindly donated by Alcan Chemicals Ltd (Gerrards Cross, Buckinghamshire, UK). All the powder used was taken from a single batch. The isotactic polypropylene was grade GY545M, supplied by ICI plc, and the atactic polypropylene was grade MF5 from APP Chemicals Ltd, UK. The stearic acid was obtained from BDH Chemicals Ltd (Poole, Dorset, UK).

## 2.2 Density determinations

The alumina powder density was found by density bottle determination, using two batches of five measurements each. In the first, a powder volume fraction of approximately 0.2 was used with distilled water. In the second, a volume fraction of approximately 0.4 was used with distilled water incorporating Decon 90 (supplied by Decon Laboratories Ltd) as a wetting agent. In both cases the bottles were held under partial vacuum for 1 h to displace air but to prevent boiling, before final filling. The bottles were weighed on a Sartorius R300S balance accurate to  $0.1 \text{ mg at a room temperature of } 19^{\circ}\text{C}.$ 

The density of the organic blend was measured by Archimedes' method with an attached weight. The upthrust on the weight and supporting assembly was determined separately. A Perkin–Elmer TGS-2 thermogravimetric balance was used to observe the water loss from the ceramic powder during heating at 5°C/min.

#### 2.3 Preparation of suspensions

The materials were weighed out to give approximately 0, 25, 40, 50, 55, 60 and 65 vol% powder. The organic vehicle was composed of isotactic polypropylene, atactic polypropylene and stearic acid in the weight ratios 4:4:1 throughout the work. The components were preblended in a Henschel highspeed non-refluxing mixer at 3000 rpm before being starve fed into a TS40 twin-screw extruder operating at 60 rpm with barrel temperatures of 190, 200, 220, 220 and 210°C feed to die. The method has been described previously.<sup>4</sup> The extrudate was watercooled and, after drying in a vacuum oven at 90°C, was granulated. A minimum of seven samples of approximately 3 g were ashed to 600°C to obtain the exact weight fraction of alumina.

#### 2.4 Rheometry

Viscosity measurements were carried out using a Davenport Capillary Rheometer fitted with 1500 psi (10.4 mPa) and 5000 psi (34.5 mPa) full scale deflection Dynisco transducers as appropriate. The transducers were calibrated using an oil-filled chamber fitted with a Bourdon gauge, and the transducer calibration lines were used in preference to the manufacturer's nominal specification. The die diameter was checked with mandrels and found to be 1.50 mm. Two dies of 20 and 35 mm length were used to obtain an end correction. Shear stress was measured in the shear rate range  $72-1075 \text{ s}^{-1}$ . End corrections were averaged over the narrow shear rate range explored for each composition, and shear stress was calculated from the corrected pressure for the larger die.

Ten minutes were allowed for temperature equilibration in the 19.05 mm diameter barrel after charging the machine. Flow was continued until a steady pressure was observed on a chart recorder. Where unsteady flow was observed, runs were repeated until sufficient data was obtained to take an average pressure from successive readings.

# **3 Results and Discussion**

#### 3.1 Exact volume loadings

The steep dependence of viscosity on volume fraction of ceramic powder in the high volume loading regime demands that careful attention be given to the calculation of exact volume loadings. Theoretical densities may be taken for the powder, but real powder densities may be reduced by internal porosity, and the presence of grain boundaries and unfilled surface fissures. The density bottle deter-

minations using 0.2 volume fraction of powder and no wetting agent gave a powder density of  $3890 \pm 3 \text{ kg m}^{-3}$ , and the determinations using 0.4 volume fraction of powder and a wetting agent gave  $3891 \pm 7$  kg m<sup>-3</sup>. However, the fine ceramic powder possesses significant adsorbed water. Drying prior to weighing is an inadequate method of allowing for this error, since rapid adsorption takes place during reweighing. The powder was therefore heated in a thermogravimetric balance to 600°C in dry oxygen and the corresponding loss was 0.82 wt%. The weighing of powder during density bottle determination was therefore corrected for water content and this gave a density of  $3986 \text{ kg m}^{-3}$ , being similar to the theoretical density of  $3987 \text{ kg m}^{-3}$ . The density of water was taken as  $998.6 \text{ kg m}^{-3}$  at  $19^{\circ}$ C.

Since errors are introduced during the preparation of ceramic-polymer suspensions, the exact volume loading of fillers must be obtained from the results of ashing experiments.<sup>3,4</sup> The final weighings were made after equilibration with ambient humidity and the weight of dry alumina was obtained by accounting for the 0.82 wt% water content. The volume fraction of dry alumina in the suspension was obtained by noting that, after heating to the temperature used in processing, the alumina retained 0.29 wt% adsorbed matter.

The results are presented in Table 1, along with 95% confidence limits calculated from a 't' distribution for low populations.

The density of the organic vehicle was obtained from the mean of four experiments by Archimedes' method to be  $907 \pm 6 \text{ kg m}^{-3}$ . This is slightly higher than the density based on law of mixtures, using the manufacturer's data, which was  $893 \text{ kg m}^{-3}$ .

In Table 1 it is indicated that the error in the calculated volume loading associated with retained adsorbed water can account for up to 0.75 vol% at the upper volume loadings. This is the region in which viscosity becomes steeply dependent on volume loading, and this error is quantified below.

The volume fraction of ceramic in a two-phase mixture is given by:

$$V = \frac{m\rho_p}{m(\rho_p - \rho_c) + \rho_c} \tag{6}$$

where *m* is the weight fraction of ceramic, and  $\rho_c$  and  $\rho_p$  are the densities of ceramic and polymer respectively. Differentiating *V* with respect to *m* shows how an individual error in weight fraction is reflected in volume fraction. It should be remembered that this procedure is valid as an assessment of the amplification of error in weight fraction for a

Composition no.ª	$ \begin{array}{c} Dry \ Al_2O_3 \\ (wt\%) + 95\% \ CL^b(n) \end{array} $	$\begin{array}{c} Dry \ Al_2O_3\\ (vol\%) + 95\% CL(n) \end{array}$	$Al_2O_3 + H_2O$ (vol%) + 95% CL(n)	Dry $Al_2O_3$ (vol%) at 200°C
2	$58.38 \pm 0.20$ (7)	24.30 + 0.15 (7)	24.48 + 0.15 (7)	21.50
3	74.84 + 0.64 (7)	40.40 + 0.81 (7)	$40.87 \pm 0.83$ (7)	36.66
4	$81.27 \pm 0.09$ (8)	$49.72 \pm 0.17$ (8)	50.30 + 0.17 (8)	45.78
5	82.19 + 0.07 (7)	51.25 + 0.12 (7)	$51.84 \pm 0.12$ (7)	47.30
6	85.02 + 0.35 (8)	56.41 + 0.69 (8)	57.06 + 0.69 (8)	52.50
7	86.43 + 0.02 (8)	59.20 + 0.04 (8)	59.90 + 0.04 (8)	55.34
8	87.30 + 0.02 (8)	61.05 + 0.04 (8)	61.76 + 0.04 (8)	57.23
9	$88.59 \pm 0.03$ (8)	$63.90 \pm 0.07$ (8)	64.65 + 0.07 (8)	60.19

 Table 1. Corrected ashing results and exact volume loading for dry alumina and alumina with an adsorbed water layer (n is the number of experiments)

<sup>a</sup> The organic vehicle, free from ceramic, was designated as composition 1.

<sup>b</sup> Confidence limits.

limited range of error and is invalid for error expressed as a percentage:

$$\frac{\mathrm{d}V}{\mathrm{d}m} = \frac{\rho_c \rho_p}{\left[m(p_p - \rho_c) + \rho_c\right]^2} \tag{7}$$

Thus, at 60 vol% ceramic of density 4000 kg m<sup>-3</sup>, an error in volume fraction is roughly twice an error in weight fraction. Clearly, this error is magnified as *m* increases since 0 < m < 1 and  $\rho_c > \rho_p$ . For a fixed volume loading it also increases as the density of the ceramic increases.

#### 3.2 Rheometry

The end corrections, expressed as an effective increase in die length, were generally less than 5 mm and decreased with increasing volume loading of ceramic. When only two dies are used to obtain the end correction, an error in pressure measurement enhances the error in end correction for several reasons. If a large and small die length are used, the pressure drop across the short die is very small and error is considerable. If, as in the present case, two relatively large dies are used, the graphical lever increases the end correction error. With the present arrangement an error in pressure measurement of 1% on both dies in an opposing sense creates an error in end correction of 1 mm and this relationship holds up to about 5% error. Insufficient material prevented the acquisition of end corrections for compositions 4, 6 and 7, and therefore values for the nearest volume fraction were used.

Of particular interest is the viscosity at the lower end of the shear rate range encountered in injection moulding, and previous work has used the viscosity as  $100 \, \text{s}^{-1}$  as one of several criteria for assessing the mouldability of ceramic suspensions: a maximum of about 1000 Pas at the moulding temperature is preferred.<sup>3</sup>

In Fig. 1 is shown the viscosity – shear rate data on

logarithmic axes for the suspensions studied, indicating that the flow behaviour index is little affected by volume loading. Only one data point was obtainable for the 64 vol% suspension using the 20 mm die at  $108 \,\mathrm{s}^{-1}$ ; other measurements overloaded the equipment. The observation that the flow behaviour index is not significantly influenced by filler loading has been made by a number of authors.<sup>16,17</sup> Flow behaviour indices obtained by least squares regression analysis are listed in Table 2. The average of all compositions is 0.55 with 95% confidence limits of  $\pm 0.03$ . Table 2 also shows the viscosity characteristics including relative viscosity at  $108 \,\mathrm{s}^{-1}$ . The viscosity for composition 9 was obtained by assuming that this composition showed the average flow behaviour index, and by extrapolating from a shear rate of  $72 \text{ s}^{-1}$  to  $108 \text{ s}^{-1}$ . The relative viscosity at constant shear rate of  $108 \, \text{s}^{-1}$  is plotted as a function of dry volume loading of alumina in Fig. 2. The error bars on relative viscosity were deduced



Fig. 1. Viscosity – shear rate data plotted on logarithmic axes for the nine suspensions studied.

No.	Viscosity (Pas) at 108 s <sup>-1</sup>	Flow behaviour index at 200°C	Relative viscosity at 108 s <sup>-1</sup>
1	59	0.51	1
2	84	0.51	1.42
3	124	0.54	2.10
4	171	0.56	2.90
5	230	0.59	3.90
6	353	0.57	5.98
7	636	0.60	10.8
8	931	0.51	15.8
9	2 481		42.1

 Table 2. Viscosity characteristics of the ceramic-polymer compositions

from multiple readings of pressure for individual viscosity measurements and combined as root mean squares. For composition 9 the percentage error is that measured at  $72 \,\text{s}^{-1}$ . Since flow behaviour indices are very similar for each composition, the relative viscosity curve is virtually independent of shear rate within the decade investigated.

Superimposed on the data points in Fig. 2 are the curves for Mooney's (M), Eiler's (E) and Chong's (C) equations. These are plotted for a value of  $V_m$  which gives the best fit to the data at a relative viscosity of 17. This corresponds to a viscosity of 1000 Pa s for the system explored, and it is in this region that the



Fig. 2. Relative viscosity at  $108 \text{ s}^{-1}$  and  $200^{\circ}\text{C}$  as a function of volume loading. M, Mooney's equation with  $V_m = 1.34$ ; E, Eiler's equation with  $V_m = 0.81$ ; C, Chong's equation with  $V_m = 0.76$ .

predictive capability of theory is most desirable for ceramic injection moulding.

In order to achieve this fit,  $V_m$  for Mooney's equation is 1.34, which is clearly unrealistic. This problem with Mooney's equation at high volume loadings has been noticed by others.<sup>18</sup>  $V_m$  in Eiler's equation is 0.81, which is a reasonable value, but  $V_m$  for Chong's equation is 0.76. Chong's equation clearly provides the best available fit to the data points, but leaves some precision to be desired.

If Chong's equation is written in the form

$$\eta_r = \left(\frac{V_m - CV}{V_m - V}\right)^2 \tag{8}$$

with the constant 0.25 now treated as a disposable constant, it quickly becomes apparent that the constant C influences the curvature. A similar procedure was used by Ghosh *et al.*<sup>19</sup> to model the flow of coal oil suspensions: however, they treated the exponent as a disposable constant, as well as C and  $V_m$ . Chong's equation is a modification of the earlier Eilers' equation, and in the present work a simple procedure is obtained if the exponent is retained and C is treated as a disposable constant. The equation can then be rewritten in the form of a straight-line relationship:

$$\frac{1}{\sqrt{\eta_r} - 1} = \frac{V_m}{1 - C} \frac{1}{V} - \frac{1}{1 - C}$$
(9)

allowing the intercept to yield the value of C and the slope to give  $V_m$  for the best fit to the data. Least-squares regression analysis of the data produced a value of C = 0.70 and  $V_m = 0.68$ , and the resulting line is shown in Fig. 3 with the original data points. This considerably extends the predictive value of a semi-empirical equation of this form. If two volume fractions of ceramic are available in a known vehicle, then C and  $V_m$  are obtainable and the full curve can be plotted for that system. In this way, composition can quickly be arrived at to give a desired viscosity.

It has been argued that relative viscosity should be calculated for constant shear stress  $[\eta_r]_{\tau}$  rather than constant shear rate  $[\eta_r]_{\tau}$  when fluids with pseudoplastic characteristics are used as the medium.<sup>20</sup> This demands extra experimentation because viscosity must be investigated over a wide shear rate range in order to gather data at a common shear stress for each filler loading without extrapolation. In contrast, the method described above demands only a single viscosity measurement on each suspension. However, within the linear region of the logarithmic flow curve, provided that the flow behaviour index is



Fig. 3. Relative viscosity data from Fig. 2 plotted against a modified Chong equation with  $V_m = 0.68$  and C = 0.7 (solid line) and for volume fractions corrected to 200°C with  $V_m = 0.65$  and C = 0.68 (dashed line).

constant for each suspension, it can be shown that

$$[\eta_r]_{\tau} = [\eta_r]_{j}^{1/n} \tag{10}$$

Thus with the present fluids ( $\bar{n} = 0.55$ ) the relative viscosity at constant shear stress can be found from the relative viscosity at a constant shear rate, but only for shear stresses which fall within the linear range of the flow curve for all compositions. In the present case this is not possible, but at a shear stress of 50 kPa minimum extrapolation of the flow curves for compositions 1, 2, 7 and 8 allows an estimate of  $[\eta_r]_r$  to be made if composition 9 is omitted. This quantity, calculated from eqn (10), is plotted in Fig. 4 along with eqn (5) with  $V_m = 0.66$ . Clearly,  $[\eta_r]_{\tau}$  shows a better fit to Chong's original equation, as suggested by Poslinski et al.<sup>21</sup> The estimate of  $V_m$ obtained from curve fitting is slightly lower than the 0.68 predicted by eqn (9). Obviously, if shear stresses are selected in a region of the flow curves where the power law does not apply,  $V_m$  prediction will deviate significantly.

The only access to  $V_m$  is through semi-empirical equations such as eqns (2), (3) and (4); yet  $V_m$  does have the physical significance of a maximum



Fig. 4. Relative viscosity at constant shear stress deduced from the data in Fig. 2. The line represents the best fit for Chong's original equation.

packing efficiency for a given powder and should, in principle, be discernable from powder characteristics. It is well known that the prediction of  $V_m$  from such equations depends on the flow conditions and the method of calculating  $\eta_r$ .<sup>18</sup> Capillary rheometry at wall shear rates comparable to the injection moulding situation gives quantitative information which is relevant to the prediction of material behaviour in the machine, but it must be recognised that  $V_m$  prediction may vary by a few percent depending on the method of calculation. It is doubtful whether the prediction of packing efficiencies for commercial ceramic powders from particle characteristics will achieve greater accuracy.

The experimental data shows a steep dependence of relative viscosity on volume loading at the high loadings of interest in ceramic injection moulding and a consequence is that error in viscosity is sensitive to error in volume fraction.

If Chong's original equation is differentiated;

$$\frac{\mathrm{d}\eta_r}{\mathrm{d}v} = \frac{1.5}{(V_m - V)^3} \frac{V_m(V_m - 0.25 \, V)}{(V_m - V)^3} \tag{11}$$

Thus if  $V_m = 0.75$  and V = 0.6, an error of 1 vol% results in a change in relative viscosity of 2 on a value of 16. As discussed above, an error of 1 vol% may arise from an error in 0.5 wt% for alumina ceramic, so that the viscosity of ceramic injection moulding blends is extremely sensitive to weighing errors in mixing; notably to metering errors if continuous feed is used in a compounding extruder. Again it should be remembered that this procedure is valid for a limited range of error, and is invalid for errors expressed as a percentage.

The same procedure applied to the more general form of Chong's equation yields:

$$\frac{\mathrm{d}\eta_r}{\mathrm{d}v} = \frac{2(1-C)V_m(V_m - CV)}{(V_m - V)^3} \tag{12}$$

and this function is shown in Fig. 5, plotted against the volume fraction of ceramic for the data in Fig. 3, with C = 0.70. This reveals how the error in viscosity prediction is amplified at high volume loadings.

An advantage claimed for Chong's equation is that if  $V_m$  is taken as 0.605 for monosized spheres it reduces to Einstein's equation at low volume fraction. In fact at V = 0.1, generally considered to be the limit of applicability of Einstein's equation, Chong overestimates relative viscosity by 5.5%, but with C = 0.70 the equation underestimates by 10% for the same conditions.

# 3.3 Effect of temperature

Volume loadings of ceramic were calculated from room temperature densities; yet viscosity was measured at 200 C. The polypropylene has, in addition to a higher cubical coefficient of expansion than the alumina, a dilation associated with melting of the crystalline fraction. Thus the volume fraction of ceramic changes slightly with temperature. The volume fraction of alumina at 200°C was calculated



**Fig. 5.** Gradient of the curve in Fig. 3 given by eqn (12). showing the error amplification at high volume loadings of ceramic.

taking the linear coefficient of expansion of >99% alumina<sup>22</sup> as  $6.7 \times 10^{-6}$ °C<sup>-1</sup> and the total volumetric dilation of the compounded organic vehicle as 0.175 between room temperature and 200°C.<sup>23</sup> These volume fractions are also shown in Fig. 3 on the dashed curve. Using the method described above, C = 0.68 and  $V_m = 0.65$  for the suspension at 200°C. Thus the predicted maximum packing fraction is significantly reduced by taking into account the effect of temperature.

### 3.4 Effect of adsorption

These procedures facilitate the empirical use of the relative viscosity – ceramic volume loading relationship for the purpose of prediction, but neglect the influence on viscosity of organic adsorbates. With fine ceramic powders the formation of an immobile adsorbed layer can be considered to increase the effective volume fraction of ceramic to a far greater extent than adsorbed moisture which was discussed above.

Priel and Silberberg<sup>24</sup> studied the adsorption of a range of polystyrenes from solution on the glass walls of a capillary viscometer. The effective hydrodynamic layer thickness of the adsorbate was found to lie in the region 5–100 nm, and to correspond to the random coil dimensions for the range of molecular weights employed. The dimensions of the random coil may be found from the chain end to end distance, *h*, given by

$$h^2 = n\beta^2 \tag{13}$$

where *n* is the number of links in the polymer chain, found from molecular weight, and  $\beta$  is the effective bond length allowing for restrictions on mobility, and may be found from light scattering experiments.<sup>25</sup> For many polymers  $\beta \approx 3L$ , where *L* is the bond length.

The effective volume fraction of ceramic,  $V_e$ , which incorporates the organic adsorbate may then be expressed as

$$V_e = V(1 + k\rho_c Sh) \tag{14}$$

where V is the volume fraction of pure ceramic,  $\rho_c$  is the density of ceramic, S is the specific surface area of the powder and k is a constant (0 < k < 1) which defines the fraction of adsorbate that is sufficiently immobile to be considered as a solid phase.

Since the hydrodynamic layer thickness measured in Priel and Silberberg's experiment may be greater than the effective layer thickness applicable to particles which closely interact in shear flow, the difficulty in applying eqn (14) lies in finding a value for k. Viscosity-volume loading curves for an identical powder using organic vehicles of differing molecular weights would be needed to confirm the procedure, and this is beyond the scope of the present work.

If  $a = k\rho_c Sh$  the effective volume fraction of ceramic can be substituted into Chong's eqn (5) to give:

$$\eta_r = \left[\frac{V_m - 0.25 V(1+a)}{V_m - V(1+a)}\right]^2$$
(15)

Dividing the numerator and denominator within the brackets by (1 + a) shows that the constant  $V_m$  becomes  $V_m/(1 + a)$  and therefore an independent value for a cannot be found from the relative viscosity – volume loading curve unless  $V_m$  is known from some other experiment.

## 4 Conclusions

Of the semi-empirical equations linking relative viscosity to ceramic volume fraction, that due to Chong and coworkers offers the best fit to data for ceramic suspensions measured under conditions relevant to the injection moulding operation. It can be further extended to allow viscosity prediction at all volume fractions of ceramic by making viscosity measurements on a minimum of two suspensions in a well characterised organic vehicle. It can be used to assess the error introduced into predicted viscosity by errors in mixing or in the determination of volume fraction. It cannot independently account for the effect of adsorbed layers on viscosity.

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