

## Dispersant selection for aqueous medium pressure injection moulding of anhydrous dicalcium phosphate

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### Abstract

Injection moulding is an extremely versatile method for producing ceramic parts with complex shapes. However, there are many disadvantages associated with conventional injection moulding methods, which may include the requirement of high viscosity polymers, toxic solvents, high temperatures and pressures. In recent years, considerable attention has been directed towards the development of low/medium pressure injection moulding which is an alternative low-cost forming method using water and low melting point gelling food binders. The basic requirement for injection moulding is the preparation of a stable, well-dispersed slip, which is achieved by the selection of an effective dispersant. This paper details an investigation into the dispersing abilities of sodium citrate, sodium pyrophosphate and sodium carbonate in different concentrations (0.01, 0.1, 0.3, 0.5, 1 and 1.5 wt.%) in anhydrous dicalcium phosphate (DCPA) slips by studying the two main interlinking properties: electrophoretic mobility and rheology. Furthermore, the effects of temperature on the behaviour of the dispersants are also investigated. The results obtained showed that the optimum dispersant was sodium citrate at a concentration of 0.3 wt.% which yielded the greatest viscosity decrease (95.6%) relative to the slip without dispersant and showed the best stability over the injection temperature range.

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### 1. Introduction

The earliest patent for ceramic moulding was granted as early as 1929.<sup>1</sup> The need to manufacture complex ceramic shapes grew with the manufacture of automobiles and the need for large numbers of spark plugs. New shape-forming techniques had to be developed to accommodate the demand which led to the AC Spark Plug Division of General Motors using injection moulding

to produce spark plugs in 1937. In the space of 60 years, the metal and ceramic injection moulding technology have come a long way and there are now hundreds of powder injection moulding (PIM) firms worldwide specialising in making parts for watches, medical applications, orthodontics appliances, computer disk drives and parts for the automotive industry.<sup>2</sup>

Powder injection molding (PIM) is a method for manufacturing complex metal and ceramic parts. In this method, very small particles of powder are mixed with a bonding agent (mainly a thermoplastic material). This mixture is processed in a way analogous to plastic injection moulding. During the next step, the bonding additives are removed without damaging the form of the component and the last step is sintering. The advantages of PIM Technologies include providing net, or near net-shape metal and ceramic components with complex geometries, high precision, superior mechanical properties, in large production quantities at very economical costs.

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The conventional ceramic injection moulding process has several drawbacks, associated with the use of large concentrations of polymeric binders. Typical formulations include concentrations of thermoplastic or thermosetting polymers as large as 15–50 vol.% which dramatically increase the viscosity of the slurry, requiring high temperatures and pressures to injection mould.<sup>3</sup> This will, in effect increase, the mould tooling costs, and require long debinding times. Furthermore, the solvents employed are not environmentally friendly.

Low/medium pressure injection moulding is an alternative process being developed to obtain complex-shaped parts with better properties whereby the solvent and high viscosity polymers are substituted by water and low melting point gelling binders such as agarose,<sup>4–6</sup> agar,<sup>7,8</sup> carrageenan,<sup>3,9,10,11</sup> maltodextrins,<sup>12</sup> cellulose derivatives,<sup>13</sup> egg white (ovalbumin),<sup>14</sup> and gelatine.<sup>15,16</sup> The advantages of this system are the use of low viscosity binders requiring low temperatures and pressures to inject as well as clean and rapid debinding and the ability to mould into soft tooling due to the relatively low moulding pressure and temperature, therefore reducing tooling costs. The main ceramic material which has been studied and reported extensively in literature with regards to aqueous low/medium pressure injection moulding is alumina.<sup>11,16–23</sup> There is a lack of information in the literature on the aqueous low/medium pressure injection moulding of calcium phosphate which is extensively used in biomaterials and pharmaceutical applications.

A basic requirement for aqueous medium pressure injection moulding is the preparation of a stable, well-dispersed ceramic slurry and therefore obtaining the optimum dispersion is vital.

The purpose of the present work is to investigate dispersing capabilities of three dispersants (sodium pyrophosphate, sodium citrate and sodium carbonate) on anhydrous dicalcium phosphate (DCPA) slips and to select the most effective dispersant as the starting point for an effective aqueous injection mouldable DCPA slurry for pharmaceutical applications. Sodium citrate and sodium carbonate are both pharmaceutical excipients.<sup>24</sup> Other sources point to the use of sodium pyrophosphate as a dispersant for DCPA.<sup>25</sup> Sodium pyrophosphate is extensively used in the food industry,<sup>26</sup> therefore, it is safe to be ingested.

For effective dispersion, the two main interlinking properties which had to be investigated were: (i) electrophoretic mobility (particle surface charge) and (ii) viscosity (rheological characterisation). Furthermore, the temperature effects on dispersion abilities were also investigated. The best dispersant was selected on the basis of electrophoretic measurements and rheological characterisation as well as the stability over the injection moulding temperature range.

## 2. Experimental procedure

Commercially available DCPA powder (Rhodia, UK) with average density of 2.83 g/cm<sup>3</sup> (measured by AccuPyc 1330 pycnometer, DCPA degassed @250 °C for 24 h) and average particle size of 14 µm (measured by laser diffraction, Malvern Mastersizer 2000, UK) was used in the present study. The dispersants

studied were sodium pyrophosphate (Aldrich, UK), sodium citrate (Aldrich, UK) and sodium carbonate (Aldrich, UK), which are all soluble in water.

### 2.1. Slip preparation

The dispersant was added to 20 ml distilled water and sonicated for 15 min. DCPA powder was then added (0.3 wt.% for electrophoretic measurements and 60 wt.% for rheological characterisation) and sonicated for a further 15 min and tumble mixed for 6 h. The pH of the slurry was measured using a digital pH meter (HI 98230 Microprocessor Logging pH Meter, Hana Instruments).

### 2.2. Electrophoretic mobility measurements

For electrophoretic mobility measurements, aqueous slips of DCPA were prepared in 20 ml distilled water to solid loadings of 0.3 wt.% for measurements with different concentrations (0.01, 0.1, 0.3, 0.5, 1 and 1.5 wt.%) of the three different dispersants added in powder form. The addition of 0.3 wt.% dispersant was found to be the optimum loading content to obtain a valid zeta potential reading since higher solid loadings tended to fall outside the sample count rate indicative of a good signal due to the opaqueness of the suspension.

Electrophoretic mobility measurements were conducted using a Malvern Zetasizer 3000 HaS (Malvern Instruments, UK) at 25 °C. The sample chamber cell was flushed with distilled water prior to loading with the slip as well as between each measurement. The injection of the sample into the chamber was performed in a slow manner to prevent the generation of small bubbles in the capillary cell, which would interfere with the reading. The  $f(\kappa\alpha)$  selection parameter in the Zetasizer was set to the Smoluchowski assumption, since the particles are larger than 0.2 µm and dispersed in aqueous media. The instrument was instructed to repeat each zeta potential value measurement five times and calculate an average.

### 2.3. Rheological characterisation

Rheological characterisation of the slips was performed using a parallel-plate rheometer (Rheometrics S2000, UK) with plates of diameter 40 mm. The rheometer was driven by the Rhios Orchestrator software package (Rheometrics, UK). The load cell on the rheometer had a torque range of 10<sup>-6</sup> to 2 × 10<sup>-1</sup> Nm. The separation of the parallel plates was maintained between 0.7 mm and 0.8 mm for all measurements. The test used was a steady rate sweep test to characterise the behaviour of the slips with increasing shear rate over a temperature range from 25 to 65 °C. The covering plate was lowered at temperatures above 25 °C to prevent evaporation and maintain the temperature of the slip. Prior to each measurement, the slip was left between the plates for 30 min to stabilise. The shear rates used were in the range 10–1000 s<sup>-1</sup> since these covered the calculated shear range that would act on the slip during injection moulding. Measurements were repeated five times and an average was taken.

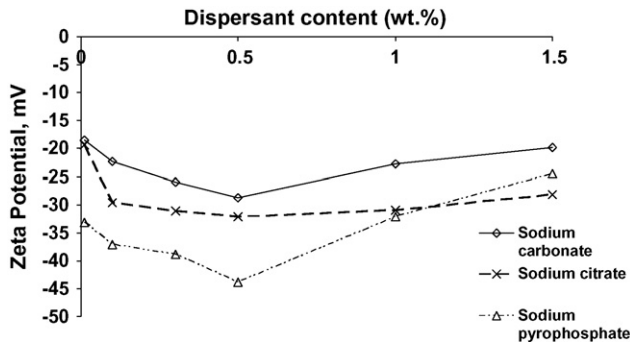


Fig. 1. Effect of adding different concentrations of sodium carbonate, sodium citrate and sodium pyrophosphate on the zeta potential of 0.3 wt.% DCPA at 25 °C.

### 3. Results

#### 3.1. Electrophoretic mobility

The slip without dispersant had a zeta potential value of 0 mV. Fig. 1 shows the effects of dispersant addition on the zeta potential values of 0.3 wt.% DCPA slips.

#### 3.2. Rheological characterisation

Aqueous DCPA slips were prepared with solids content of 60 wt.% and different dispersant concentrations between 0.01 and 1.5 wt.% with respect to solids. Slips were rheologically characterised using shear rates  $\dot{\gamma}$  ranging from 10 to 1000  $\text{s}^{-1}$  at different temperatures. The shear rates used were the estimated shear rates operating on the slip during injection. The calculation was based on the force required to push the sample through an orifice according to Eq. (1):

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (1)$$

where  $Q$  is the slip flow which is the volume of slip passing to the cavity as a function of the injection time ( $\text{mm}^3 \text{s}^{-1}$ ) and  $R$  is the radius of the orifice (mm). Considering the actual mould dimensions of 13 mm diameter, 2.33 mm thickness, and orifice radius of 1.5 mm and injection times between 1 and 6 s, the resulting calculated shear rates were between 116 and 700  $\text{s}^{-1}$ , and therefore the shear rates used in this study covered this range.

#### 3.3. Sodium pyrophosphate

The pH values of the ceramic slips containing 60 wt.% DCPA and different concentrations of sodium pyrophosphate are shown in Table 1.

Fig. 2 shows the viscosity for 60 wt.% DCPA slips as a function of sodium pyrophosphate content at shear rates of 100  $\text{s}^{-1}$  and a temperature of 25 °C.

Fig. 3 shows the viscosity flow profiles for 60 wt.% DCPA slips containing different concentrations of sodium pyrophosphate dispersant as a function of increasing shear rates at a constant temperature of 25 °C.

Table 1

pH values of 60 wt.% DCPA slurries with different dispersant concentrations

Dispersant content (wt.%)	Sodium pyrophosphate (pH)	Sodium citrate (pH)	Sodium carbonate (pH)
0.01	5.6	5.6	6.6
0.1	6.5	6.2	7.2
0.3	7.1	6.6	7.6
0.5	7.8	6.6	7.6
1	8.2	6.8	7.8
1.5	8.1	6.9	7.9

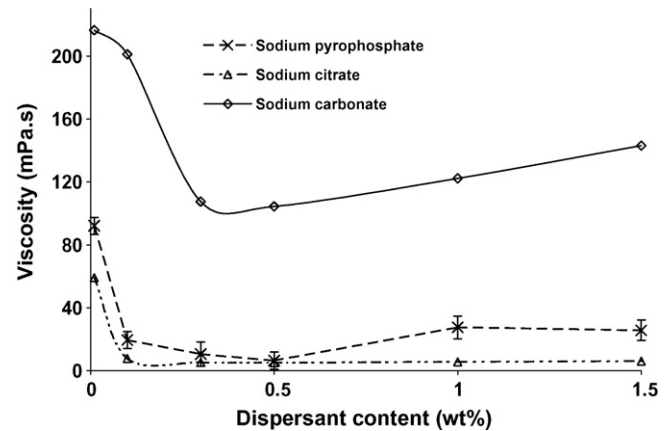


Fig. 2. Effect of adding different concentrations of sodium carbonate, sodium citrate and sodium pyrophosphate on the viscosity of 60 wt.% DCPA slip at shear rate of 100  $\text{s}^{-1}$  and temperature of 25 °C.

The flow behaviour of the slips can be divided into groups with similar flow profiles: (i) the “no additive” and 0.01 wt.% slips, (ii) the 1 and 1.5 wt.% slips and (iii) the 0.1, 0.3 and 0.5 wt.% slips.

#### 3.4. Sodium citrate

The pH values of the ceramic slips containing 60 wt.% DCPA and different concentrations of sodium citrate are shown in Table 1.

Fig. 2 shows the viscosity for 60 wt.% DCPA slips as a function of sodium citrate content at shear rates of 100  $\text{s}^{-1}$  and a temperature of 25 °C.

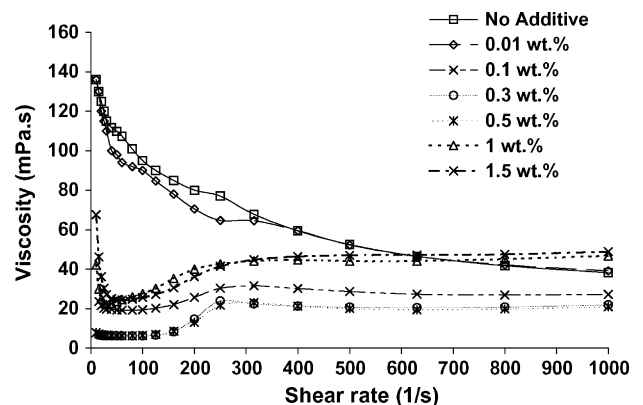


Fig. 3. Effect of adding sodium pyrophosphate on the viscosity of 60 wt.% DCPA slurry at 25 °C.

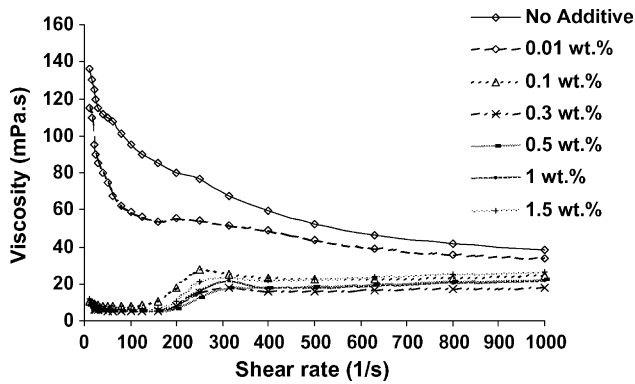


Fig. 4. Effect of adding sodium citrate on the viscosity of 60 wt.% DCPA slurry at 25 °C.

Fig. 4 shows the viscosity flow profiles for 60 wt.% DCPA slips containing different concentrations of sodium citrate dispersant as a function of increasing shear rates at a constant temperature of 25 °C.

The flow profiles are similar to the ones observed with sodium pyrophosphate dispersant, although two groups can be seen rather than three: (i) the no additive and 0.01 wt.% slips and (ii) the remaining slips (0.1, 0.3, 0.5, 1 and 1.5 wt.%).

### 3.5. Sodium carbonate

The pH values of the ceramic slips containing 60 wt.% DCPA and different concentrations of sodium carbonate are shown in Table 1.

Fig. 2 shows the viscosity for 60 wt.% DCPA slips as a function of sodium carbonate content at shear rates of  $100 \text{ s}^{-1}$  and a temperature of 25 °C.

Fig. 5 shows the viscosity flow profiles for 60 wt.% DCPA slips containing different concentrations of sodium carbonate dispersant as a function of increasing shear rates at a constant temperature of 25 °C.

In complete contrast to the results observed with sodium pyrophosphate and sodium citrate, where the addition of either dispersant caused a decrease in viscosity, the addition of sodium carbonate dispersant resulted in an increase in viscosity relative to the slip without dispersant. Furthermore, the flow profiles

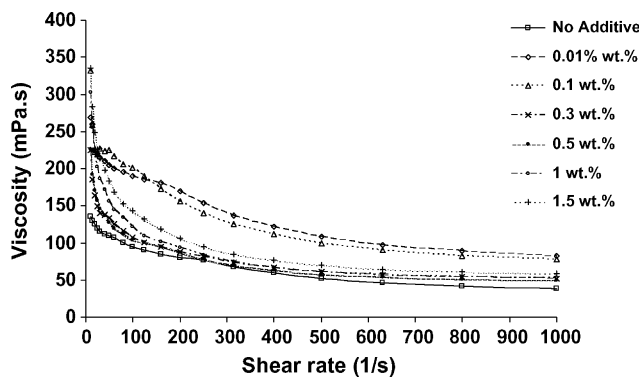


Fig. 5. Effect of adding sodium carbonate on the viscosity of 60 wt.% DCPA slurry at 25 °C. The addition in sodium carbonate caused the viscosity to increase for all concentrations.

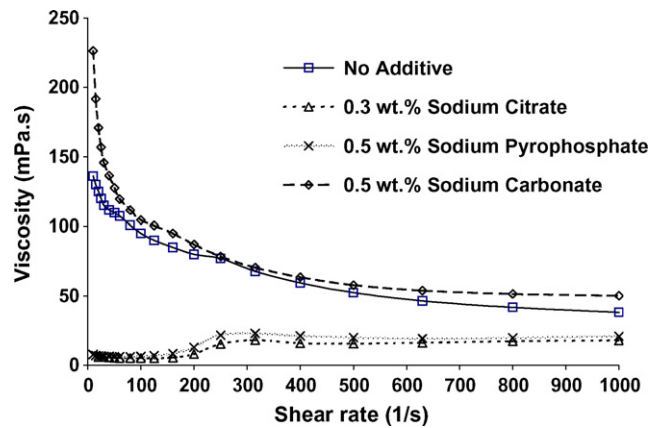


Fig. 6. Comparison of adding the three different dispersants on the viscosity of 60 wt.% DCPA slip at 25 °C. The 0.3 wt.% sodium citrate slurry yielded the lowest viscosity at all shear rates.

of all the slips exhibited shear thinning behaviour, unlike the case with the previous dispersants whereby some of the slips exhibited both shear thinning and shear thickening.

### 3.6. Comparisons between sodium pyrophosphate, sodium citrate and sodium carbonate

Fig. 6 shows a plot of viscosity as a function of shear rate for the three different dispersants (0.5 wt.% sodium pyrophosphate, 0.3 wt.% sodium citrate and 0.5 wt.% sodium carbonate). These concentrations were chosen because, in the case of sodium pyrophosphate and sodium citrate, they yielded the greatest viscosity decrease relative to the slip without dispersant. The 0.5 wt.% sodium carbonate was chosen because this concentration produced the greatest viscosity decrease relative to the other concentrations, but it was higher than the virgin slip (no additive).

Fig. 7 shows a plot of viscosity of the three dispersant slips as a function of increasing temperature at a shear rate of  $100 \text{ s}^{-1}$ . The viscosity of sodium pyrophosphate and sodium carbonate slips both increased with increasing temperature while sodium citrate slip showed a slight decrease in viscosity with increasing temperature.

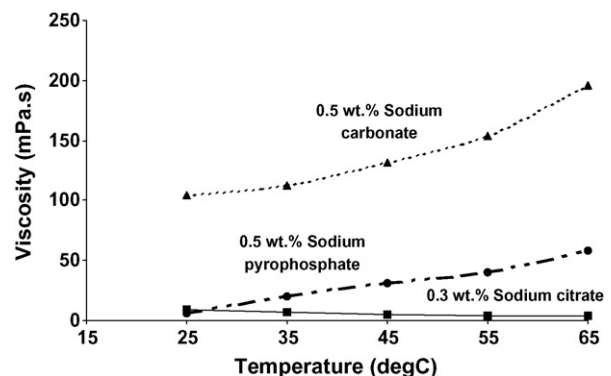


Fig. 7. Effect of increasing the temperature on the viscosity of 60 wt.% DCPA slips with different dispersants at shear rates of  $100 \text{ s}^{-1}$ .

## 4. Discussion

### 4.1. Electrophoretic mobility

The general dividing line between stable and unstable suspensions is generally taken at either +30 or –30 mV.<sup>27</sup> Most of the sodium pyrophosphate slips except the one containing 1.5 wt.% (–24.5 mV) showed zeta potential values more negative than –30 mV. The 0.3, 0.5 and 1 wt.% sodium citrate slips had zeta potential values below –30 mV while 0.01, 0.1 and 1.5 wt.% were above (–19.3, –29.6 and –28.1 mV, respectively). All the sodium carbonate slips had zeta potential values above –30 mV, indicating unstable slips which could be an explanation to why the viscosity increased on addition of sodium carbonate relative to the slip without dispersant (see Fig. 5).

From Fig. 6, it can be seen that the optimum dispersant and concentration which causes the greatest decrease in viscosity is 0.3 wt.% sodium citrate.

### 4.2. Rheological characterisation

The reason for the viscosity decrease on addition of dispersant is due to formation of repulsive like charges on DCPA particles preventing them from approaching each other. The viscosity is essentially determined by how close particles approach each other and by the degree of attraction or repulsion between the particles. Therefore, as sodium pyrophosphate or sodium citrate dispersant is added, the DCPA particles become charged and repel each other until a maximum is reached. Further addition compresses the double layer, allowing the DCPA particles to approach each other and therefore increasing the viscosity.

The “no additive slip”, 0.01 wt.% sodium citrate, 0.01 wt.% pyrophosphate slips and all sodium carbonate slips displayed shear thinning flow profiles (see Figs. 3–5) whereby viscosity decreased with increasing shear rates. Shear thinning occurs due to the ordering of particles into layers. These existing layered structures break down with increasing shear rate and particles align in such a way that they exhibit minimal resistance against movement with respect to each other resulting in a decrease in viscosity.<sup>28</sup>

The remaining sodium pyrophosphate and citrate slips displayed initial shear thinning flow profiles at low shear rates, followed by shear thickening flow profiles at higher shear rates. The microstructural origins of why thickening takes place are not resolved,<sup>29</sup> although two explanations have been proposed: Hoffman’s order–disorder transition (ODT)<sup>30,31</sup> and the “cluster formation” mechanism.<sup>32–36</sup>

From the observed results, the ODT theory was favoured to explain the reasons for shear thickening taking place since the phenomenon was only observed in ordered, stable slips. Sodium carbonate slips had zeta potential values above –30 mV indicating instability and hence disorder. The flow profiles of sodium carbonate slips were all shear thinning and did not demonstrate shear thickening. Hoffman argued that for shear thickening to occur, the slip must undergo a change from an ordered state to a disordered one and cannot take place in the absence of an ordered state. This also applies to the slips without disper-

sant since these slips did not contain the dispersant to impart repulsion, stability and order to the slip. Therefore, these slips exhibited shear-thinning behaviour without any shear thickening taking place since their starting point was that of disorder.

The addition of sodium citrate and pyrophosphate caused a decrease in viscosity and stability as was indicated by the negative zeta potential values below –30 mV. The stable, ordered DCPA slips containing these two dispersants possessed shear thinning behaviour initially at low shear rates but as the shear rate was increased, a critical shear thickening rate, which in most cases was  $125 \text{ s}^{-1}$ , was reached whereby lubrication forces between neighbouring particles in the highly organised, layered flow induced the particles to rotate out of alignment destabilising the flow to cause disorder. Hence, the viscosity of the slip increased due to an increase in DCPA interparticle interactions in the flowing disordered state.

One possible explanation as to why the addition of sodium carbonate caused an increase in viscosity was due to partial adsorption of sodium carbonate on the ceramic particle. Partial adsorption will result in the remaining carbonate becoming excess in the fluid leading to an increase in viscosity.

### 4.3. Temperature effects

In general, the viscosity of a slip is expected to decrease with increasing temperature. However, Guo et al.<sup>37</sup> have shown that the temperature can exert dramatic effects on the stability of a slip dispersed with polyelectrolytes by affecting the viscosity and the adsorption state. This will have knock-on effects on the structure and density of the compact prepared from such unstable slip. Therefore, it was imperative to conduct rheological tests on the slips at the injection temperature to assess their behaviour. The results observed in Fig. 7 clearly demonstrate that temperature exerts a significant effect on the stability of 0.5 wt.% sodium pyrophosphate and 0.5 wt.% sodium carbonate slips where a strong increase in viscosity with increasing temperature was observed. This indicates that the concentration of both dispersants which is effective at 25 °C is no longer useful at higher temperatures, causing destabilisation of the slip and decreasing the dispersive state. This is due to the fact that adsorption of the dispersant on the surfaces of DCPA increases with increasing temperature resulting in compression and thinning of the electrical double layer and therefore more dispersant is required to reach a new double layer equilibrium. Furthermore, the degree of flocculation is enhanced with increasing temperature as a result of double layer compression, i.e. the double layer thickness is reduced allowing ceramic particle to approach each other with greater ease and flocculating. This temperature effect implies that the temperature plays an important role in the interactions between these two particular dispersants and the DCPA particles. These results are in agreement with the results obtained by Guo et al.<sup>37</sup> and Millán et al.<sup>38</sup> showing an increase in viscosity with increasing temperature for dispersed alumina slips with low concentrations of dispersant.

The reason as to why adsorption increases with increasing temperature is not yet clear, however a study using alumina particles Guo et al.<sup>37</sup> found the presence of an additional attractive

interaction between the alumina particles and the polyelectrolyte molecules apart from electrostatic interaction and van der Waals forces which they referred to as the hydrophobic interaction.

The reverse was observed with 0.3 wt.% sodium citrate whereby the viscosity slightly decreased with increasing temperature. Even though the concentration of sodium citrate was lower by 0.2 wt.% than sodium carbonate and sodium pyrophosphate concentrations, the results showed that this concentration was effective at both 25 °C and higher temperatures, maintaining the stability and dispersive state of the slip at low and higher temperatures (the injection moulding temperature range) which is a favourable result. This implies that sodium citrate adsorption does not change with increasing temperature and therefore the double layer equilibrium is maintained for the temperature range investigated. The reason why the adsorption state does not increase with increasing temperature in such a system is not yet clear.

## 5. Conclusions

Three dispersants, sodium pyrophosphate, sodium citrate, and sodium carbonate were investigated to assess which had the best dispersing effects on DCPA slips, as well as finding the optimum concentration of the most effective dispersant.

All three dispersants charged the DCPA particles as was indicated by the electrophoretic mobility results, although the slips containing sodium carbonate all had zeta potential values above the stability dividing line of –30 mV indicating unstable slips.

Of the three different dispersants, the greatest initial viscosity reduction (95.6%) was obtained with 0.3 wt.% sodium citrate. Furthermore, the sodium citrate slips displayed the greatest stability over the injection moulding temperatures ranges between 25 °C to 65 °C. With increasing temperature, the viscosity of the slip containing 0.3 wt.% sodium citrate decreased slightly, while both sodium pyrophosphate and carbonate slips increased drastically showing instability at higher temperatures. The addition of sodium carbonate had a deleterious effect on the viscosity by increasing it.

In conclusion, the addition of 0.3 wt.% sodium citrate yielded the greatest decrease in viscosity as well as showing stability with increasing temperature. Therefore, sodium citrate was chosen as the most suitable dispersant for DCPA out of the three dispersants investigated and 0.3 wt.% is the optimum content to achieve desirable results for aqueous medium pressure injection moulding.

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