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Preparation of PZT suspensions for direct ink jet printing

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Abstract

The present paper contains an experimental study of two different kinds of PZT suspensions for direct ink jet printing at 25 and 120 °C, respectively. The effect of processing parameters such as mixing time, the amount of dispersant, solid loading and milling method was investigated for the optimisation of viscosity for feasible jetting. The viscosity of PZT suspensions was within 5–15 mPa·s range for room temperature suspensions with MEK/EtOH medium and 10–20 mPa·s for high temperature suspensions with wax medium. FTIR analysis is also presented to explain the rheological behaviour of PZT suspensions. Finally, a demonstration of room temperature jetting of PZT suspension is shown.

Keywords: PZT; Spectroscopy; Suspensions

1. Introduction

Drop-on-demand 3D printing technology has been developed as a means of fabricating complex shapes of ceramic materials alongside other solid freeform fabrication (SFF) techniques such as stereolithography, selective laser sintering, and laminated object manufacture.[1] Like other SFF techniques, 3D printing technique is a net or near net shape, tool-less manufacturing technique. Its major advantage is that sub-nanolitre voxel resolution can be achieved by a comparatively simple and inexpensive way. Therefore, it is suitable for fabricating complicated ceramic structures.

There are two types of 3D ink jet printers; continuous and drop-on-demand. Although continuous ink jet printing offers faster building speed, there is a condition that the ink should be conductive. Therefore, it is not suitable for most ceramic suspensions. On the other hand, the only two requirements of ceramic slurry used in drop-on-demand printing are viscosity and surface tension. Moreover, this technique offers better resolution. As demonstrated by other SFF techniques, there are now several novel structures of PZT which are easily obtained, but are very difficult to achieve using conventional manufacturing techniques. Therefore, it is our intention to investigate PZT suspensions suitable for direct drop-on-demand ink jet printing in order to fabricate novel PZT structures.

There are two ways of achieving direct drop-on-demand ink jet printing; jetting can be done at high temperature or at room temperature. From the viewpoint of ceramic processing and slurry stability, the room temperature printing technique seems to offer an easier and better way because, at high temperature, there is a possibility of the degradation of dispersant. However, productivity seems to favour the high temperature jetting technique, because rapid solidification usually takes place on a surface which has a temperature much lower than that of the droplets. Moreover, some high temperature medium can act as a binder. Therefore, it is meaningful to use two different printing methods.

2. Experimental

For the room temperature printing, methyl ethyl ketone and absolute ethanol (MEK/EtOH) azeotropic mixture (67/33 wt.%) was used as a medium.[2] Wax was used for the high temperature medium.[3] For both cases, a phosphate ester based dispersant (Phospholan PE182 from Akros Chemicals Ltd., Manchester, UK) was used. The PZT powders were supplied with binders already mixed, therefore, they were heat-treated at 750 °C for 24 h to remove them. To reduce particle size and break up agglomerates, ball milling or attrition milling was used. In case of the ball milling, milling time was up to 72 h, whereas for the attrition milling it was 6 h.

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The dried powders were mixed with the appropriate medium and dispersant at 10–20 rpm. The mixing/milling process was conducted at room temperature in the case of the room temperature system. The temperature of mixing for the wax-based suspension was 120 °C, which is the operating temperature of the high temperature ink jet head.

For the study of rheological properties of the suspensions a concentric cylinder rheometer was used. For the wax system, viscosity was measured at 120 °C. To investigate the interaction between the dispersant and the powder, Fourier transform infrared spectroscopy (FTIR) was used in normal transmittance mode and diffuse reflectance infra-red Fourier transform (DRIFT) mode.

For the purpose of a printing demonstration, a room temperature jetting machine was used. It consisted of a glass tube with a 30 μm diameter nozzle surrounded by a PZT tube. A 20% PZT suspension was used for printing; the values of operation parameters were the driving voltage of 50 V, the frequency of 13 kHz, the rise/fall time of 3 μs and the pulse width of 20 μs.

3. Results and discussion

Viscosity should be less than 30 mPa·s in order to print ceramic suspensions. Therefore, we studied various processing parameters to achieve maximum solid loading with less than 30 mPa·s viscosity.

After initial ball milling to reduce particle size, dried powders were mixed with a medium and the dispersant and ball milled for various durations. Determining the optimum ball milling time is important because local heating during ball milling can cause the degradation of dispersant.

For the room temperature suspensions, viscosity decreases with increasing ball milling time as shown in Fig. 1. The powder ball milled for 18 h showed less than 5 mPa·s viscosity. Viscosity increased when the milling time was extended. This can be attributed to the degradation of dispersant by the local heating effect caused by excessive ball milling.

The same trend is shown in Fig. 2 when the high temperature wax media and the measurement temperature of 120 °C were used. The optimum ball milling time is 4 h in contrast with 18 h in the case of the room temperature system. The increased temperature adversely affects the degradation of the dispersant, which explains the much shorter optimum milling time.

Figs. 3 and 4 show the effect of the amount of dispersant on viscosity for the room temperature and the high temperature system. For both cases, 1 wt.% dispersant shows the optimum viscosity. Initially, the viscosity decreases with increasing amount of dispersant, but it increases when the amount of dispersant exceeds the optimum value. Excess molecules of the dispersant are mixed with the media, therefore, they contribute to the

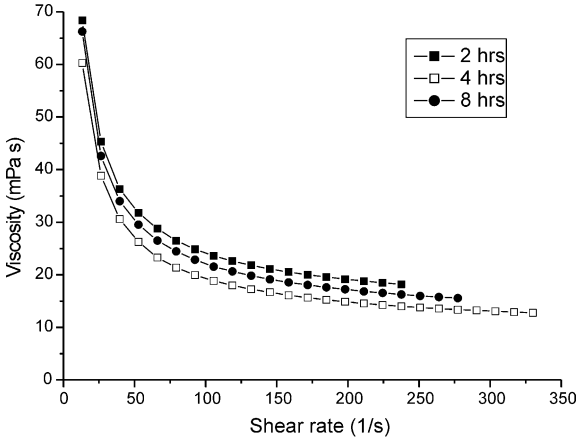

Fig. 2. Effect of ball milling time on viscosity for the high temperature PZT-Wax suspension (20 vol.% PZT, 1 wt.% PE182).

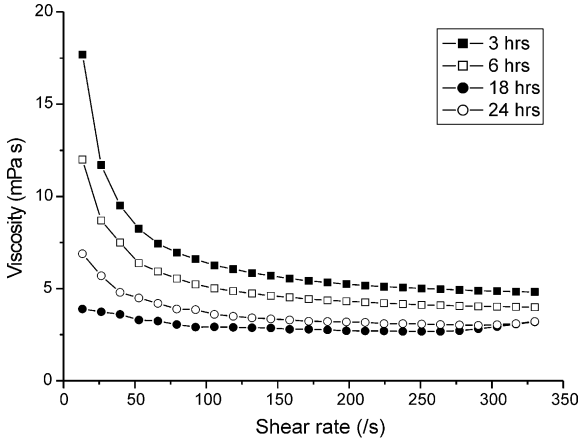

Fig. 1. The effect of ball milling time on viscosity for the room temperature PZT-MEK/EtOH suspension (20 vol.% PZT, 1 wt.% PE812).

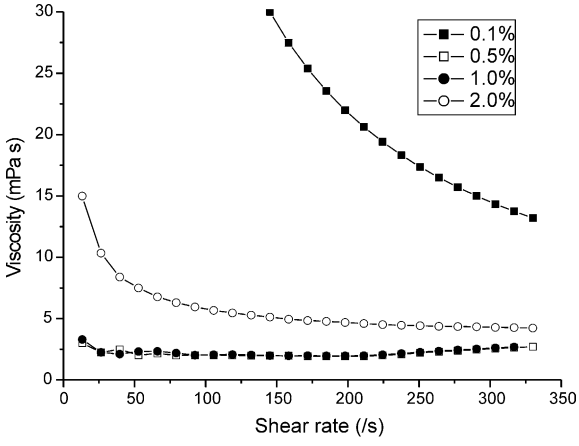

Fig. 3. Effect of the amount of dispersant on viscosity for the room temperature PZT-MEK/EtOH suspension (20 vol.% PZT, ball milled for 18 h).

overall increased viscosity because the viscosity of the dispersant is usually very high.

The room temperature system shows a very low viscosity value even when the solid loading is 30 vol.%. As shown in Fig. 5 the viscosity is less than 10 mPa·s at shear rates beyond 100/s. In the case of the wax media shown in Fig. 6, the viscosity of 30 vol.% suspension is not suitable for jetting because it exceeds 80 mPa·s at the shear rate of 80/s. In all cases, the room temperature system shows much lower viscosity than the high temperature system.

One of the reasons for the lower viscosity of the room temperature system is the low viscosity of the media used in the room temperature system. The viscosity of EtOH and MEK is 1.074 mPa·s at 25 °C and 0.428 mPa·s at 20 °C, respectively.[4] The viscosity of the wax used is 5 mPa·s at 100 °C. The apparent viscosity of non-aqueous, concentrated colloidal suspensions can be described by a modified Krieger–Dougherty expression[5]

$$\mu = \mu_0 \left(1 - \frac{\phi}{\phi_m}\right)^{-n},$$

where μ is the apparent viscosity, μ_0 is the viscosity of the medium, ϕ is the volume concentration of particles, ϕ_m is the maximum packing, and n is the experimental fitting coefficient. According to this equation, the viscosity of the medium has a dominant effect on the viscosity of the suspension. This is one of the reasons the room temperature system has much lower viscosity values. Other reasons are the reduced dispersant degradation, the effective adsorption of the dispersant, acidity of the medium, etc.

Fig. 7 shows the effect of the amount of dispersant for the attrition milled powder as well as the different milling method used. As with the ball milled powder, the optimum amount of dispersant seems to be around 1 wt.%. The viscosity of the attrition milled powder is two times less than that of the ball milled powder. Even though it is 30 vol.%, the viscosity is less than 5 mPa·s.

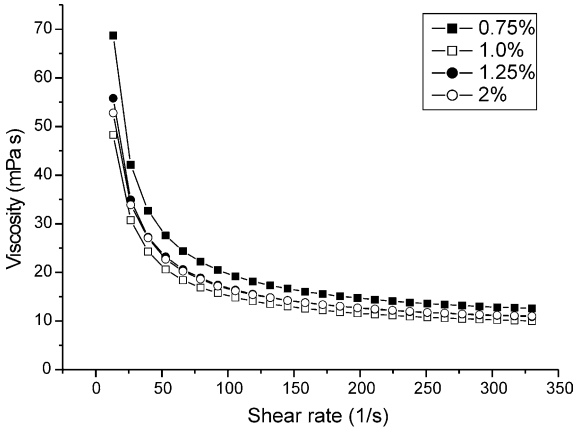

Fig. 4. Effect of the amount of dispersant on viscosity for the high temperature PZT-wax suspension (20 vol.% PZT, ball milled for 4 h).

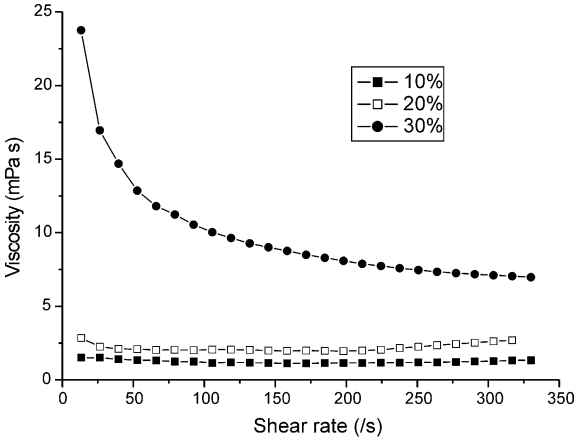

Fig. 5. Effect of solid loading on viscosity for the room temperature PZT-MEK/EtOH suspension (1 wt.% PE182, ball milled for 18 h).

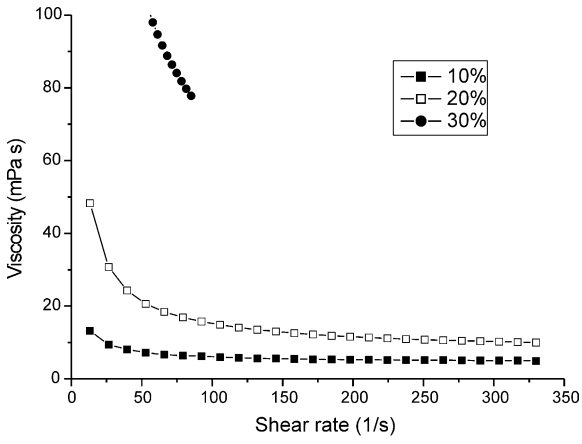

Fig. 6. Effect of sold loading on viscosity for the high temperature PZT-wax suspension (1 wt.% PE182, ball milled for 4 h).

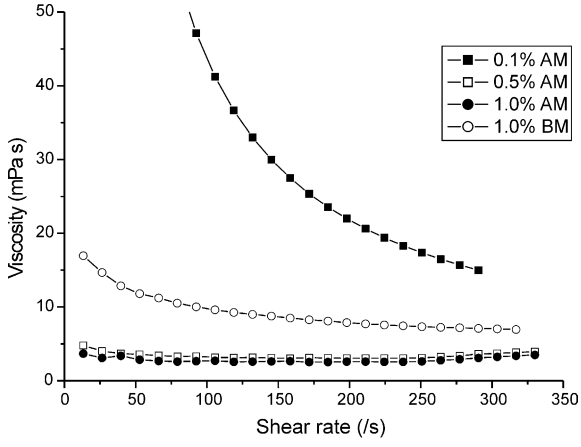

Fig. 7. Effect of milling method on viscosity for the room temperature PZT-MEK/EtOH suspension (30 vol.% PZT, ball milled for 18 h or attrition milled for 6 h).

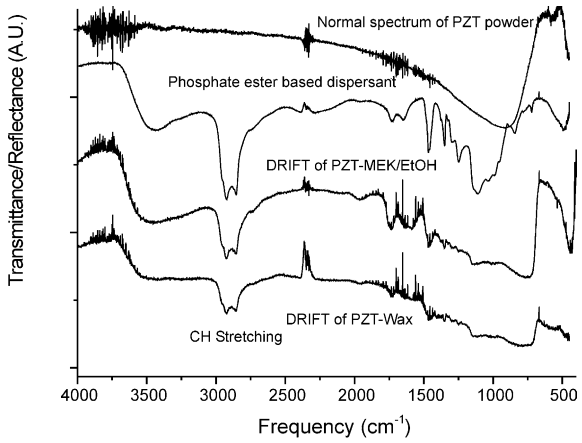

Fig. 8. Transmittance and diffuse reflectance FTIR spectra of the starting PZT powder, the dispersant used, the room temperature PZT suspension and the high temperature PZT suspension.

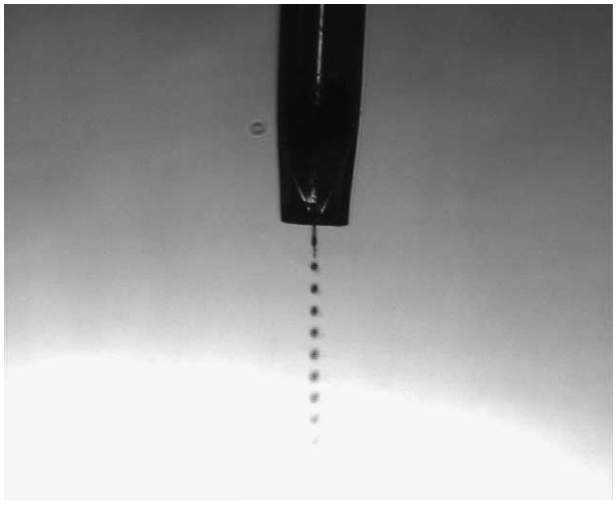

Fig.9. Photograph of 20 vol.% PZT suspension droplets jetted from the room temperature jet head. (voltage = 50 V, frequency = 13 kHz, rise/fall time = 3 μs, pulse width = 20 μs).

Further study is required such as the surface area and particle size distribution.

Transmittance and DRIFT FTIR spectra of PZT suspensions are shown in Fig. 8. Both the high temperature and room temperature suspensions show C–H stretching at frequencies near 2850 and 2930 cm^{-1}. These two peaks indicate that the dispersant molecules are attached to the particle surfaces; otherwise they are not detected. From the DRIFT data alone, it is not clear whether the particle-dispersant-medium interaction mechanism of the room temperature suspension is different from that of the high temperature suspension.

Fig. 9 shows 20 vol.% PZT suspension droplets jetted from the room temperature jet head. The diameter of the droplets is 15 μm, and the jetting is repeatable demonstrating MEK/EtOH media is very effective for the direct printing of PZT suspensions.

4. Conclusions

PZT suspensions for room temperature jetting was prepared using MEK/EtOH medium. The viscosity of the 30 vol.% PZT suspension prepared from ball milling was under 10 mPa·s. For the attrition milled 30 vol.% PZT suspension, the viscosity was less than 5 mPa·s. A repeatable and reliable jetting behaviour was observed for the 20 vol.% PZT suspension.

For high temperature printing, wax medium with the melting point of 60 °C was used. A viscosity near 10 mPa·s was achieved for the ball milled 20% suspension. For the present wax-based system, the maximum solid loading for printing seems to be 20–25 vol.%. Further investigation is required for attrition milled powders for better particle size distribution.

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