Defence Science Journal, Vol. 56, No. 2, April 2006 pp. 279-288

Rheological Behaviour of Ceramic Inks for Direct Ceramic Inkjet Printing

P. Ponnambalam, N. Ramakrishnan, P.K. Rajesh, and K. Prakasan

PSG College of Technology, Coimbatore–641 004

ABSTRACT

In this paper, studies were made on the preparation of ceramic inks with: (i) alumina powder in ethyl alcohol and (ii) zirconia powder in ethyl alcohol at different volume fractions of ceramic. Different amounts (0.75-3.00 vol %) of an organic dispersant (oleic acid) were added to ceramic ink containing 5 per cent of ceramic by volume in ethyl alcohol. The viscosities of the suspensions were determined with Brookefield viscometer (model: DV-E), which is suitable for measuring the viscosities of suspensions accurately. These inks were deposited on a substrate to see their spread. The sediment packing densities (ϕ_m) of the resulting suspensions were calculated using theoretical models which can be related to the density that can be achieved in the final product. The highest sediment packing density was arrived at low viscosity values of the ink and occurred when 1 per cent of dispersant by volume was used for 5 per cent alumina content. For 5 per cent zirconia content, 2 per cent of dispersant by volume gave a similar result. Experiments were also conducted to find the value of ϕ_m for different solid loadings (5-25 vol %) of ceramic with 1 per cent dispersant. It was observed that the sediment packing density and the apparent viscosities were increasing when solid loading concentrations were increased for both alumina and zirconia-based inks. The optimum value of ϕ_m and viscosity have been determined from this study. The results of this preliminary study will be useful for further investigations on the rheological behaviour of ceramic inks for direct ceramic inkjet printing.

Keywords: Direct ceramic inkjet printing, sediment packing density, dispersant, solid loading

1. INTRODUCTION

Direct ceramic inkjet printing (DCIJP) uses ceramic powder contained in a carrier medium which is deposited using a delivery system actuated by a piezoelectric device. Since the diameter of nozzles[1] used in the DCIJP is in the range 20-75 µm, the typical droplet diameter is 60 µm. Successful DCIJP depends on the preparation of suitable ceramic ink which is essentially a well-dispersed suspension of a fine powder. The dispersion must be stable and free from agglomerates. The DCIJP technique, for assembling ceramic particles into a complex shape layer by layer ready for sintering, is suited for the manufacture of components of advanced materials.

Microfabrication of ceramic parts at the submillimeter scale is a time-consuming and expensive process. Lithographic techniques used for ceramic microfabrication, which are also used to fabricate the integrated circuits and microelectromechanical systems (MEMSs), take several weeks to go from CAD drawings to completed chips and require very expensive facilities and extreme processing conditions.

Revised 04 January 2005

An alternate approach in which multiple small volumes of ceramic material is deposited at computer-defined positions, could enable tool-less all-additive fabrication of such devices on a much faster and economical basis. The droplet shape, its spread, and quantity of ink delivered, are to be controlled for making the process economical. In the modified drop-on-demand jet printer, a droplet of ink is formed by a pressure pulse generated by a piezoelectric actuator adjacent to the orifice.

In such a process, increasing the volume fraction of the ceramic is desirable to increase the deposition rate. However, the volume fraction of ceramic in the ink is limited, because the ink must flow through small (micro) nozzles, to form fine droplets. The study reveals that an active research is taking place in the area of DCIJP.

Thus, an attempt has been made to carry out a systematic study in the preparation of ceramic inks, and determination of their properties for DCIJP. These studies are aimed at providing actual data relevant to the preparation of ceramic inks and their rheolological behaviour so that researchers can use these as initial values and further refine these.

2. PREPARATION OF CERAMIC INK

The success of DCIJP is dependent on the rheological behaviour of ceramic ink, which is essentially a well-dispersed dilute suspension of a powder in a liquid.

The important requirements of ceramic ink are:

- The ink should have appropriate viscosity and surface tension for consistent droplet formation.
- The ink should possess good dispersion and stability of ceramic powders to prevent blockage at the nozzles and to avoid sedimentation in the valves and pipelines of the printer.
- The ink should have sufficiently high drying rate to increase the printing speed while avoiding sagging and obtaining good edge quality.
- The ink should have sufficient strength and flexibility for subsequent handling.

The sedimentation behaviour of a ceramic suspension is often used as an indication of the degree of deflocculation. The rate of sedimentation can be used to assess the state of flocculation. Viscosity of a ceramic suspension is influenced by the degree of dispersion.

Attempts have been made to prepare ceramic inks in the form of zirconia suspension and suspension of alumina powder in paraffin wax with viscosity values sufficiently low to allow inkjet printing using a commercially available printer[3-5]. In these studies, viscosity, surface tension, and dispersion achieved in the inks, drying rate, and green strength of the deposit were considered.

Zirconia has been doped with 5.4 wt per cent yttria having density of 5954 kg/m^3 in 99.5 wt per cent butyl acetate of 881 kg/m^3 density with the hypermer KDI dispersant. The average particle size and specific surface area of the powder[5] has been 100 nm and 7 m^2/g, respectively. Alumina powder with a particle size of 400 nm and specific surface area[1] of 8.2 m^2/g has been dispersed in a low melting paraffin wax having viscosity of 2.8 mPa.s at 100 ^{o} C, to produce stable suspensions of alumina with hypermer FPI or hypermer LPI as dispersant. Efforts have been made to optimise the dispersion and viscosity of inks and it has been found that addition of 1-2 wt per cent of dispersant corresponds to the highest adsorption level of the powder, the maximum sediment-packing efficiency, and the minimum ink viscosity[4]. Attention has also been focused on binders that will result in good surface finish, dimensional accuracy, and high resolution.

3. INK DEPOSITION TECHNIQUES

Various techniques attempted on ceramic inkjet printing are piezoelectric drop-on-demand, continuous inkjet printing, and thermal techniques. Studies have been carried out on the deposition of ceramic inks through piezoelectric continuous inkjet printing[6,7]. It has been identified that with the appropriate binders and dispersants, the ceramic ink containing zirconia can be printed to produce 2.5 mm thick bars. Deposition of ceramic ink has also been carried out using piezoelectric drop-on-demand inkjet printing[8].

4. THEORETICAL STUDIES ON VARIOUS EMPIRICAL MODELS FOR PREDICTING VISCOSITY OF CERAMIC SUSPENSIONS

Mooney[9] derived an empirical relation between the relative viscosity and the effective dispersed volume as

$$\mu = \mu_v \left[\frac{\sqrt{1+0.5\phi_s}}{1-\phi_s} e^{\left(\frac{1.25\phi_s}{1-\phi_s}\right)} \right] \quad (1)$$

where, μ is the viscosity of suspension (apparent viscosity), μ_v is the viscosity of the organic carrier, and ϕ_s is the solids loading volume fraction.

Later, studies conducted by Krieger and Dougherty[9] led to an approximate model for concentrated solutions given by the following equation:

$$\mu = \mu_v \left[1 - \frac{\phi_s}{\phi_m} \right]^{-K_H \phi_m} \quad (2)$$

where ϕ_m is the apparent maximum solids concentration (depends on the additives used and the concentration of the additives), and K_H is the apparent hydrodynamic shape factor of particles.

Krieger-Dougherty validated this equation with experimental setup consisting of an aqueous suspension of latex spheres.

In the latest study made by Liu[10], all the above models were considered and several equations were used to correlate viscosity of suspension with solid concentration, and an equation that can produce a rather satisfactory prediction for highly concentrated suspensions was developed. The model has been proven experimentally to be applicable to several concentrated suspensions, and it has the following form:

$$\mu = \mu_v \left[1 - \frac{\phi_s}{\phi_m} \right]^{-2} \quad (3)$$

After a critical literature survey, it was understood that there is enough scope to carry out research in the area of preparation of ceramic inks, their rheological behaviour, and spread of these inks on a substrate. These results can provide the researchers with valuable information on the properties of ceramic ink and the characteristics of actuation mechanism to eject the droplet, and spread of droplets for different substrate conditions. Therefore, a systematic study was carried out with the objectives as described below:

4.1 Objectives

With the above background, a preliminary study was carried out to prepare ceramic inks based on the previous experiments conducted by other researchers and study their properties for the DCIJP. The objectives of this study were to prepare ceramic inks with alumina as the solid in ethyl alcohol (carrier) with different levels of alumina content with a suitable dispersant, measure their viscosities over a range of shear rates, determine the maximum packing densities using theoretical models, repeat the above for zirconia-based ink, highlight the salient points inferred from these studies, and suggest suitable levels of ceramic and dispersant in the ink for the best performance.

5. METHODOLOGY/EXPERIMENTAL PROCEDURE

5.1 Preparation of Ceramic Ink

An electronic balance from Shimadzu Corporation, Japan, having capacity: 220 g, readability: 0.001 g, type BL: 220H was used for accurately weighing the ceramic particles. Ceramic inks were prepared using ultrasonicator (Sonics Vibra Cell, USA). The frequency was set at 20 kHz. The viscosity of suspension (with different vol % of ceramic and dispersant) was measured using Brookfield digital viscometer (model: DV-E). Zirconia (ZrO_2) having density of 5.5 kg/m^3, molecular weight of 123.22, and assay 98.5 % and alumina having density of 3.96 kg/m^3, molecular weight of 101.96, were used. Ethyl alcohol of 99.9 % purity was used as a carrier medium and oleic acid as a dispersant.

5.2 Determination of Packing Density

After studying various viscosity models, Equation (3) given by Liu[9] was used to calculate the apparent maximum solid concentration (ϕ_m) and to determine its value, the procedure was followed as found in literature[10]. The values of logarithmic viscosity (log μ) have been plotted against $\gamma^{1/2}$, where γ is shear rate (s^{-1}) and the value of viscosity corresponding to $\gamma^{1/2}$ approaching zero is obtained (infinite shear). The shear rate, that is used to achieve the extrapolation, are typically 1000-15000 s^{-1} for all the suspensions[11]. Using Eqn (3) the value of ϕ_m was found. This procedure was applied to determine the value of ϕ_m for: (a) ceramic ink containing 5 per cent alumina by volume and ethyl alcohol with different vol per cent of dispersant and (b) ceramic ink containing 5 per cent zirconia by volume and ethyl alcohol with different vol per cent of dispersant. This was to study the effect of dispersant content in achieving the desired levels of packing density. The value of ϕ_m was determined for ceramic inks containing: (a) different vol per cent of alumina with dispersant content of 1 per cent by volume and (b) different vol per cent of zirconia with dispersant content of 1 per cent by volume, as in the previous procedure. This was to study the effect of solid content in achieving the desired levels of packing density. After carrying out these studies, the results have been plotted graphically.

6. RESULTS & DISCUSSION

6.1 Discussion on Measurement of Viscosity and Calculation of ϕ_m

In this study, ceramic inks with different compositions: (a) 5 per cent alumina by volume and ethyl alcohol with different dispersant contents, (b) 5 per cent zirconia by volume and ethyl alcohol with different dispersant contents, (c) different vol per cent of alumina contents and ethyl alcohol with 1 per cent of dispersant, and (d) different vol per cent of zirconia contents and ethyl alcohol with 1 per cent of dispersant, were prepared and viscosity measurements were carried out at different shear rates. The observations are graphically represented in Figs 1-4.

Figure 1 represents the variation of viscosities with shear rate for the ceramic ink containing different vol per cent of alumina and ethyl alcohol with 1 per cent of dispersant. It is evident that with increase of shear rate, viscosity is reduced, typical shear thinning (pseudo plastic) behaviour represented by several ceramic inks. With ceramic content increasing also the same trend is observed. The same is observed for zirconia-based ink as shown in Fig. 2. At higher volume content of ceramic, the viscosity values significantly differ for these two inks. The increased density of zirconia (5.5 kg/m^3) compared to alumina (3.96 kg/m^3) results in faster settling of particles, thereby increase in viscosity.

Figures 3 and 4 represent the variation of viscosity with dispersant content at several shear rates for ceramic inks containing 5 per cent alumina by volume and ethyl alcohol, and 5 per cent zirconia by volume and ethyl alcohol, respectively. The addition of

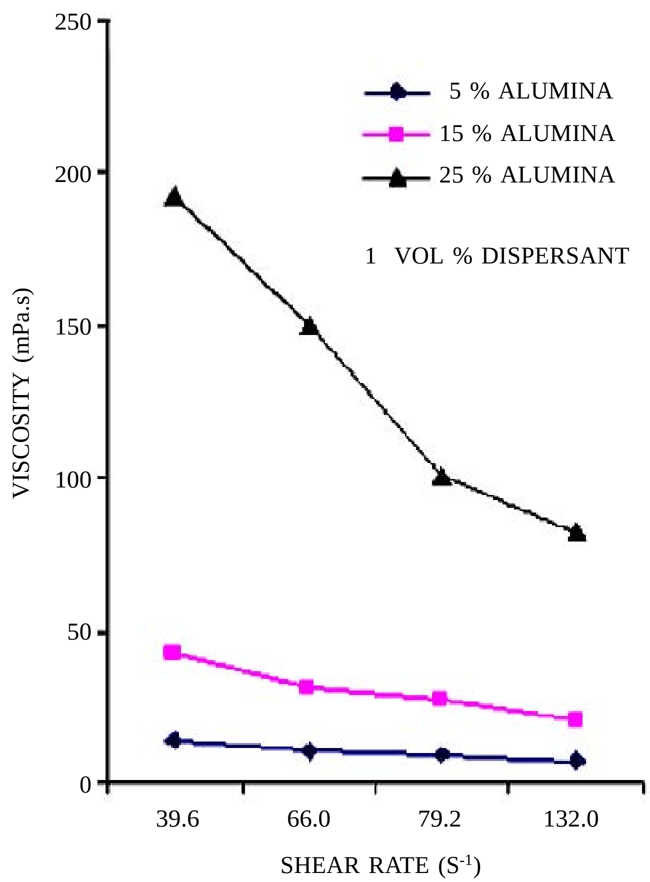


Figure 1. Variation of viscosity with shear rates

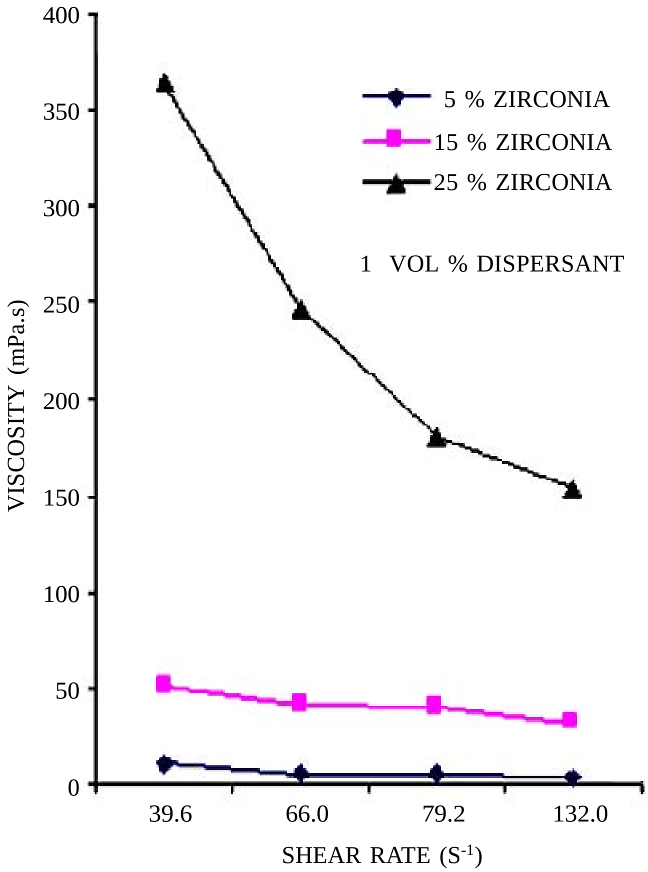


Figure 2. Variation of viscosity with shear rates

dispersant influences (increases) the viscosities of the ceramic inks significantly at lower shear rates when the dispersant content is 1.5-2.0 per cent for alumina-based ink and at 1.5 per ent (approximately) for zirconia-based ink[3]. The influence of dispersant is felt only for a particular level because the interaction between the ceramic particles depends upon p*H* values and the net electric field created. It may be noted that oleic acid is a viscous liquid (180 mPa.s).

The packing densities were calculated using Eqn (3) as mentioned in methodology. To determine the viscosity at infinite shear rate as required by Eqn (3), Fig. 5 is used in which logarithm of viscosity values are plotted against square root of shear rates. Fig. 5 represents this variation for the ceramic ink containing 5 per cent alumina by volume, ethyl alcohol and 0.75 per cent dispersant. This is repeated for inks with different ceramic (alumina and zirconia) contents keeping dispersant level constant and for inks with varying dispersant content maintaining

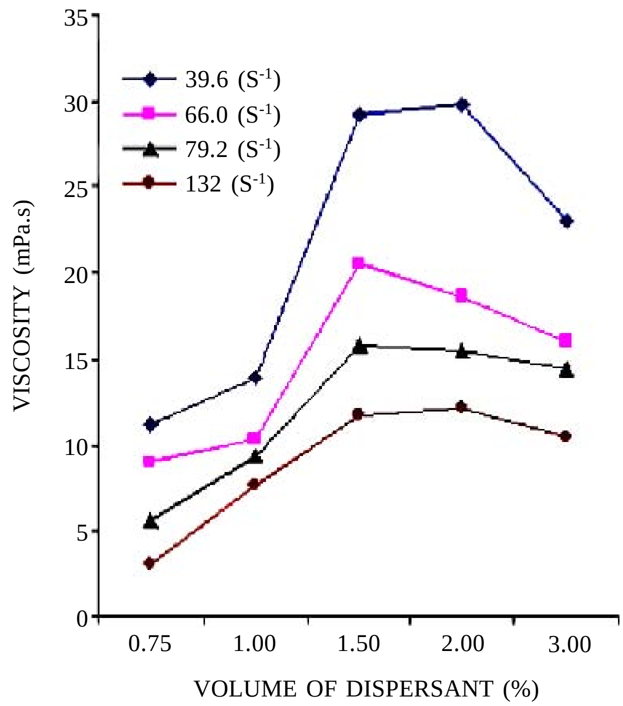


Figure 3. Variation of viscosity with dispersant content (5 % alumina).

constant ceramic content. Thus, ϕ_m is determined for a large set of experiments.

Figure 6 represents the variation of packing densities with dispersant content for 5 per cent

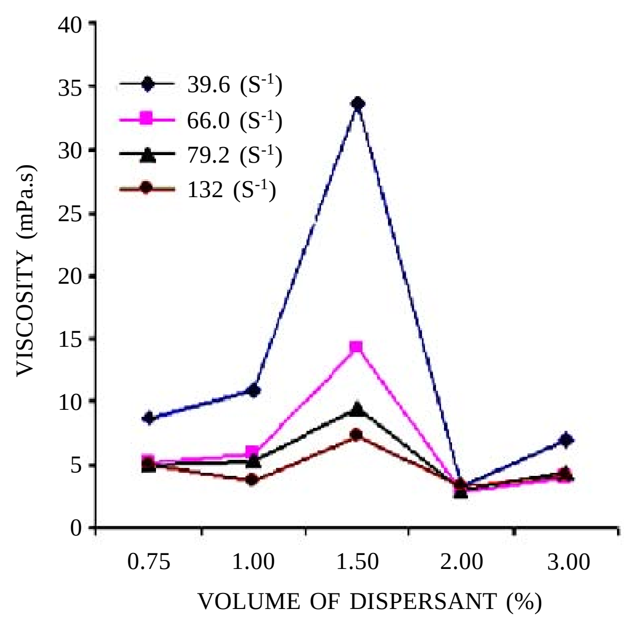


Figure 4. Variation of viscosity with dispersant content (5% zirconia).

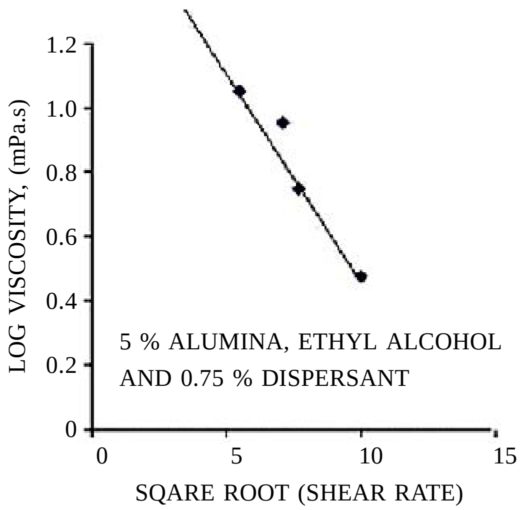


Figure 5. Determination of μ at infinite shear rate

alumina ink. The maximum packing density is achieved at 1 per cent dispersant content. As dispersant content is increased, there is reduction in packing density at 1.5 per cent dispersant content and there is a marginal increase beyond this.

For zirconia-based ink (5 % volume), the maximum packing density is achieved at 2 per cent dispersant content. Beyond this there is a drop. This is shown in Fig 7. The behaviour of packing density with dispersant vol per cent is found to be non-monotonic.

As discussed earlier, the role of dispersant is to alter the interparticle forces (electrostatic in nature) and control several rheological properties. Thus, there will be an optimum level for a dispersant for a given ceramic suspension so that more ceramic particles are bonded together, leading to a maximum concentration in an ink droplet. For other ranges of dispersant content, interparticle forces developed may not lead to the same particle content.

When ceramic content is increased, keeping dispersant content constant as expected, there is an increase in packing density for both the types of inks. This is due to the increased concentration of particles Figs 8 and 9.

These observations are useful to relate the frequency of actuating membrane with viscosity-shear rate relations, dispersant content-viscosity relations and dispersant content-packing density relations of these inks. The preparation of inks and design of nozzle can benefit from these studies.

Qualitative studies were made on spread of droplets made of inks as discussed. These inks were deposited from a burette on wetting substrate (black colour thick conventional paper) and photographs are presented in Figs 10(a) to 10(j). The pattern of spread of droplets of inks (alumina, zirconia) are found to be distinctly different. This difference

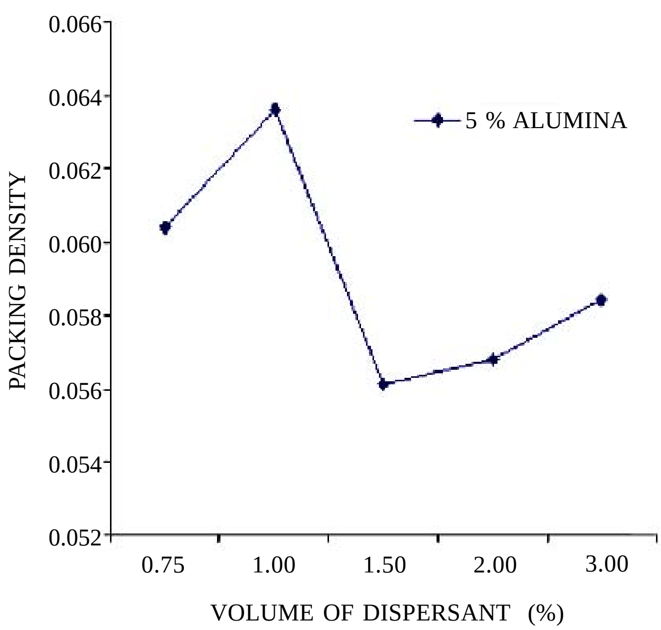


Figure 6. Variation of packing density with dispersant content

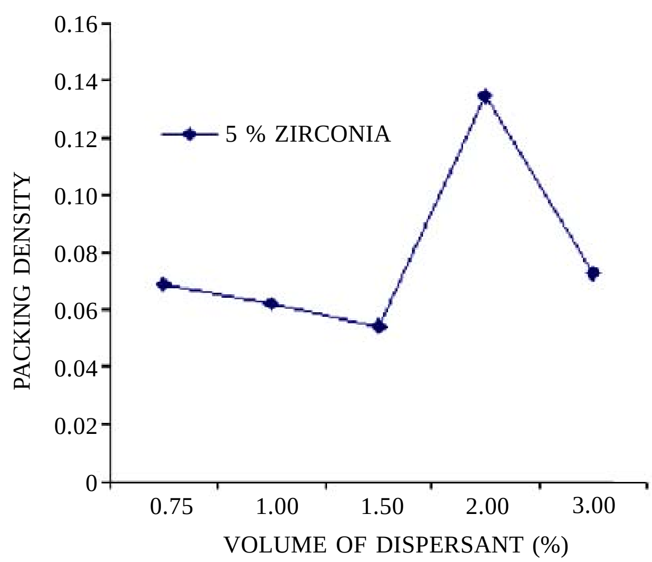


Figure 7. Variation of packing density with dispersant content

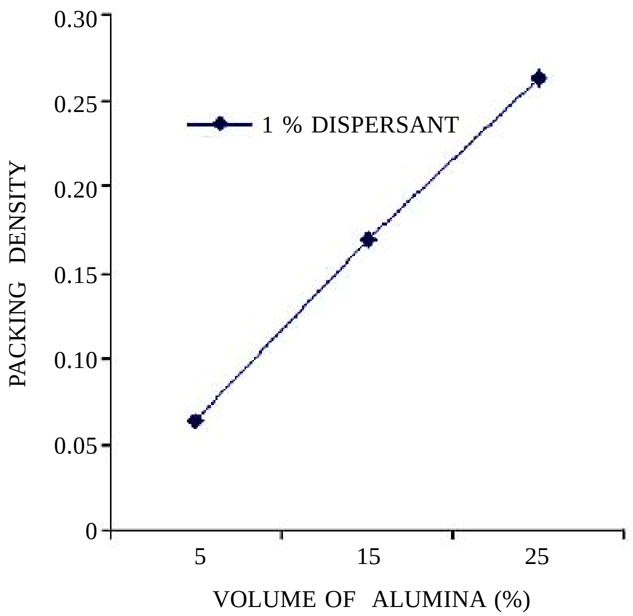


Figure 8. Variation of packing density with alumina content

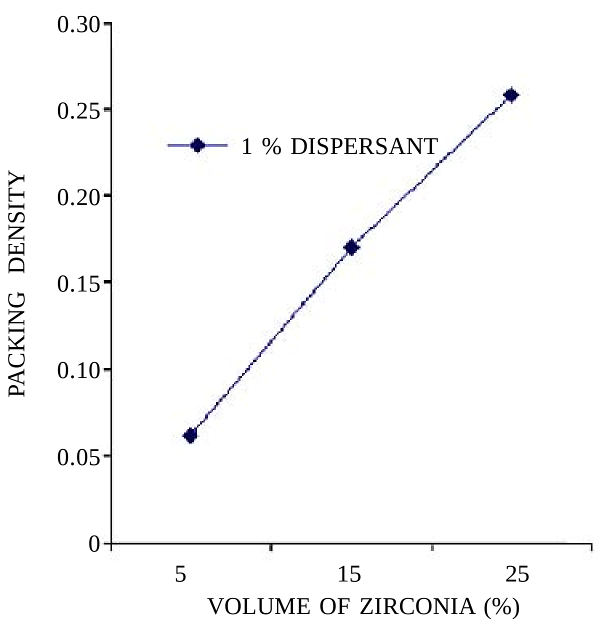


Figure 9. Variation of packing density with zirconia content

can be attributed to the force system existing on the drop-substrate interface, which is governed by the forces developed due to the particle interactions in the drop. As zirconia is heavier compared to alumina, the settling of zirconia particles is significant and it is indicated by the higher viscosity values. As the viscous forces oppose the capillary forces, spread is reduced in the case of zirconia-based ink droplet.

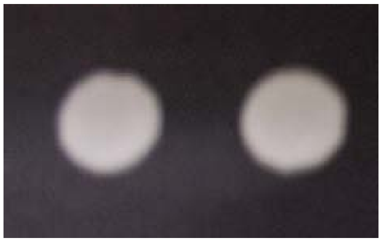
7. CONCLUSIONS

Ceramic inks were prepared with different ceramics with varying contents of ceramics and dispersant using ultrasonic equipment. Viscosities of these inks were measured with Brookfield viscometer. The packing density was calculated using theoretical models proposed by the researchers. The addition of dispersant influences the viscosities of the inks for a specific range of dispersant content. Beyond this range, this effect is not very significant. Basically, the role of dispersant is to alter the electric field surrounding each particle when it is suspended in a carrier. As this is controlled by p*H* values, it is possible to have an optimum range for the dispersant content to influence the particle interactions. Increased shear rate reduces the viscosity of the inks significantly. This is in agreement with the observation that ceramic inks are shear thinning.

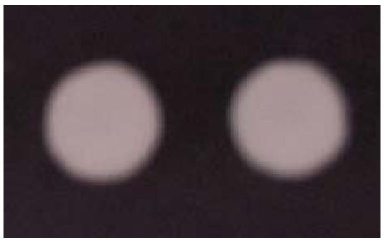
The dispersant content influences packing density also. This is again attributed to the dispersion achieved in the ceramic ink. When particles are well separated, a drop can contain less number of ceramic particles. But when these are less dispersed, the deposit will have an increased content of ceramics. Thus, an optimum can be determined from these studies. As dispersant content is increased, there is reduction in packing density at 1.5 per cent dispersant content and there is a marginal increase beyond this.

Spread of the droplet of these inks, as seen in the photographs, indicates the variation in diameter and drop shape for these two inks. The interfacial energy of the ink-substrate system controls the droplet spread. Alumina-based ink is seen to have good spread compared to the zirconia-based ink. Zirconia-based ink is found to settle faster, which can be attributed to the higher density of zirconia. Thus, it is more viscous and resists the capillary forces, leading to reduced spread.

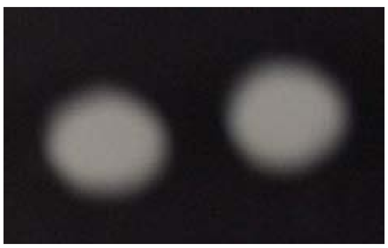
This preliminary study can help researchers in the preparation of inks with suitable rheological properties and simulation studies can provide them with directions to the design of the equipment for ink delivery.



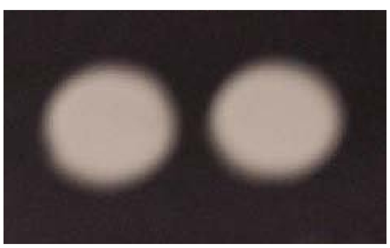
(a) 1 vol % dispersant + 5 vol % Al_2O_3 + ethyl alcohol



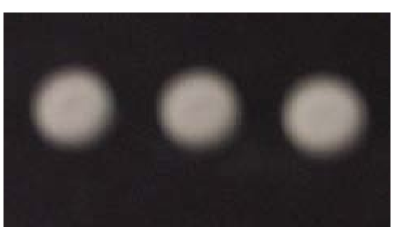
(b) 2 vol % dispersant + 5 vol % Al_2O_3 + ethyl alcohol



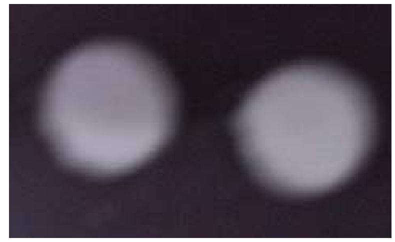
(c) 3 vol % dispersant + 5 vol % Al_2O_3 + ethyl alcohol



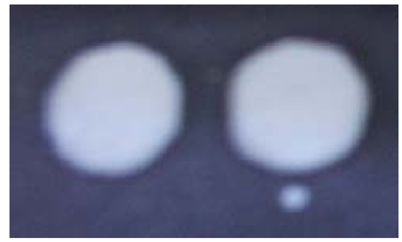
(d) 15 vol % Al_2O_3 + 1 vol % dispersant + ethyl alcohol



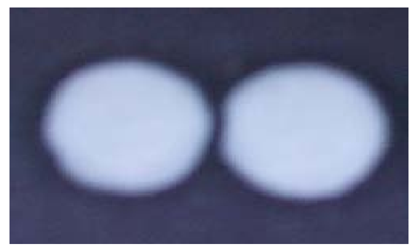
(e) 25 vol % Al_2O_3 + 1 vol % dispersant + ethyl alcohol



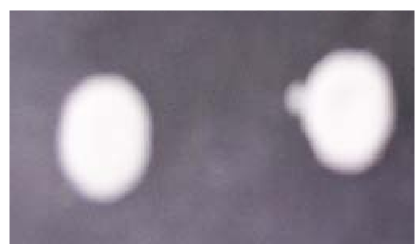
(f) 1 vol % dispersant + 5 vol % ZrO_2 + ethyl alcohol



(g) 2 vol % dispersant + 5 vol % ZrO_2 + ethyl alcohol



(h) 3 vol % dispersant + 5 vol % ZrO_2 + ethyl alcohol



(i) 15 vol % ZrO_2 + 1 vol % dispersant + ethyl alcohol

(j) 25 vol % ZrO_2 + 1 vol % dispersant + ethyl alcohol

Figure 10. Droplet spread for varying volume per cent of dispersants and ceramic particles

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Science and Technology, Govt of India for funding the project on direct ceramic inkjet printing. They also thank the Management and the Principal of PSG College of Technology, Coimbatore, for extending all infrastructural facilities to carry out the above studies.

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Contributors

Mr P. Ponnambalam obtained his BE (Mech Engg) from the PSNA College of Engineering, Madurai Kamaraj University and ME (Computer-aided Design) from the Govt College of Engineering, Periyar University. He is working as Project Engineer, CAD/CAM Centre, PSG College of Technology, Bharathiar University, Coimbatore. His interests are: CAD/CAM, direct ceramic inkjet printing.

Mr N. Ramakrishnan obtained his BE (Mech Engg) from the J.J. College of Engineering & Technology, Tiruchirapalli, Bharathidasan University and ME (Product Design & Commerce) from the PSG College of Technology, Bharathiar University, Coimbatore.

Mr P.K. Rajesh obtained his BE (Mech Engg) from the Sri Siddhartha Institute of Technology, Bangalore University and ME (Production Engg) from the PSG College of Technology, Bharathiar University, Coimbatore. He is working as Senior Project Engineer, TIFAC-CORE in Product Design and Optimisation and Collaborative Product Commerce. His interests are: CAD/CAM, direct ceramic inkjet printing (DCIJP).

Dr K. Prakasan obtained his BTech (Aero) from the Madras Institute of Technology, Anna University, Chennai, in 1988 and MTech (Aircraft Production Engg) from the Indian Institute of Technology Madras, Chennai. He worked at the Hindustan Aeronautics Ltd as Engineer and Dy Manager associated with flight-testing of MiG-21 and MiG-27 aircraft and mechanical system checks. Later, he joined Indian Institute of Science, Bangalore, for his PhD as a regular student and worked with metal-matrix composites. After completion of his PhD in 1997, he joined the PSG College of Technology, Bharathiar Uniersity, Coimbatore. Currently, he is working as Assistant Professor, coordinating the activities of CAD/CAM Centre. His interests are: Mathematical modelling and solving of multi-physics problems.