Chemical Engineering Science 149 (2016) 1–13

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Inkjet printing of ceramic colloidal suspensions: Filament growth and breakup

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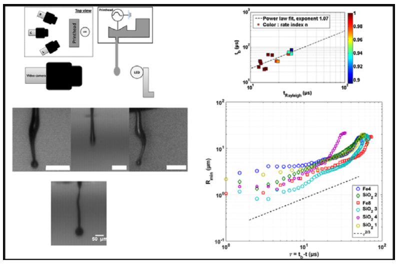
HIGHLIGHTS

- Ceramic colloidal suspensions were formulated for drop-on-demand inkjet deposition.
- Filament formation, growth rate, thinning and breakup were investigated.
- The breakup time and the minimum radius evolution both scale with the Rayleigh time.
- The actuation voltage and dwell time have the strongest effect on thread growth.
- Rheological viscoelastic parameters and their influence on drop formation were also obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form
5 April 2016
Accepted 7 April 2016
Available online 9 April 2016

Keywords:
Inkjet printing
Drop-on-demand
Colloidal suspensions
Ceramics
Fluid mechanics
Filament breakup

ABSTRACT

Filament growth and breakup are investigated in the context of ceramic inkjet printing. Several inks were formulated and ejected on a printer dedicated to ceramic materials. They consisted of six colloidal inks, four simple fluids and two graphic inks. For each, stroboscopic snapshots were acquired and the filament shape was extracted and analysed, for different nozzle actuation pulses. The filament length and the thread minimum radius were measured during the ejection process. A scaling of the breakup time with the Rayleigh number was obtained, as well as a general behaviour for the filament growth rate during the ejection process.

1. Introduction

Inkjet printing (IJP) is a shaping process allowing us to generate three-dimensional objects in a fast, precise and versatile way. First, some amount of fluid is pressed through each nozzle of the

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http://dx.doi.org/10.1016/j.ces.2016.04.015

printhead. A filament appears, undergoing thinning and eventually breakup into droplets. The generated droplet impacts a substrate and dries. In order to create a three-dimensional object, several layers of droplets of fluid are deposited, according to a design defined by a Computer-Aided Design (CAD) file. Thus, complex architectures can be achieved, with a resolution of the order of 50–100 microns. Recently, this technique has been successfully extended to ceramic materials (Noguera et al., 2005; Blazdell et al., 1995; Xiang et al., 1997; Bhatti et al., 2001; Mohebi and Evans, 2002; Zhao et al., 2002). In contrast to pure polymer printing, the specificity is to eject a colloidal suspension, *i.e.* a two-phase fluid consisting of small particles dispersed in an organic medium (solvent and organic additives). The inkjet printing technology offers new possibilities for 3D architectures of ceramic electronic devices including metallic layers (tracks, electrodes or vias) and functional ceramic materials (capacitive, dielectric, magnetic, etc.). In fact, compared to standard routes such as screen-printing or tape-casting, the IJP process could improve productivity by decreasing the number of manufacturing steps through multimaterial deposition: ceramic and metallic layers would be deposited in one single step, by using two printheads. In addition, the use of CAD fabrication files offers the possibility to achieve complex 3D architectures improving the performances of microelectronic devices such as multi-layer ceramic capacitors (MLCC), high and low temperature ceramic capacitor (HTCC and LTCC) (Dossou-Yovo et al., 2012; Beaudrouet et al., 2014; Singlard et al., 2014). Finally, IJP is a fully additive technology and can also reduce material consumption. Some authors focus on ceramic ink formulation adjustment for this process for their specific system (Dossou-Yovo et al., 2012; Gratton and Witelski, 2008; Noguera et al., 2005). A major interest for fabrication is to maximize particle loading (Ainsley et al., 2002; Bhatti et al., 2001; Seerden et al., 1999; Reis et al., 1999; Seerden et al., 2001), where inks up to 40 vol% solid content were achieved in paraffine dispersions, with an acceptable viscosity for the resulting ink thanks to additives such as dispersants. The waveform actuation has also to be adjusted depending on the physical properties of the ejected material (Seerden et al., 1999; Reis et al., 1999; Singlard et al., 2014; Seerden et al., 2001).

The framework of the present study was a project which aimed to build microtransformers by ejecting selectively all the different materials involved. To do so, several inks containing insulating, conductive and magnetic materials have been formulated. To obtain good results, ink formulation plays a key role, in order to have repeatable and stable drop ejection. In the case of particulate inks, specific additives are required, such as surfactants, plasticizers, binders and humectants (Wang et al., 2012). Until now, ceramic ink formulations have been adjusted according to required specifications in terms of viscosity, surface tension and stability. However, despite being within the required operating ranges, some particulate inks cannot lead to successful ejection, or require additional adjustments. In order to improve this crucial step in the fabrication process, a closer insight in the filament breakup and drop formation for this specific case is necessary.

The investigation of inkjet behaviour has to deal with several aspects. The first are the general dynamics of filament growth and breakup leading to drop formation. Filament breakup can occur in several geometries: for example, liquid bridging where the fluid is sandwiched between parallel plates, or gravity dripping (Eggers, 1997). In the case of jetting, an external force is applied in order to generate a high speed filament, and can be obtained using a printhead. The second aspect is thus related to printhead operation, and on the impact of the actuation parameters on the ejection process.

The phenomena involved with the use of a printhead have been thoroughly investigated, both experimentally (Pierron et al., 2001; Wijshoff, 2010; Meinhart and Zhang, 2000) and numerically (Liou et al., 2009; Yildirim and Basaran, 2006). Drop-on-demand shaping by three-dimensional printing implies a very precise deposition method. Thus, the ejection parameters need to be adjusted in order to result in a single drop travelling straight to the substrate. Inkjet printing nozzles are piezo-electric pumps, usually tens of microns in diameter. Since the size of the printing nozzle is very small, inkjet occurs at micronic time and lengthscales, which makes the observation quite difficult given the limitations of the observation techniques. The fast timescale requires a stroboscopic setup.

As stated before, the ejectability criteria have been expressed considering Newtonian systems, *i.e.* with a single value of viscosity. Filament thinning and breakup of non-Newtonian or viscoelastic polymeric fluids have been investigated by several authors (Cooper-White et al., 2002; Christanti and Walker, 2001; German and Bertola, 2010), where the behaviour for the minimum radius versus time was characterized, as well as extensional properties. In these studies, inertial effects were negligible, as opposed to the current work. The case of ceramic inks is more complex. Ceramic inks are colloidal suspensions, where the rheological behaviour is often non-Newtonian. The presence of particles and of other additives influencing their interaction potential often lead to shear thinning or shear thickening effects (Larson, 1998; Seerden et al., 2001). The shear stress applied by the nozzle induces a "destructuration" of the equilibrium state of the ink resulting from these interactions. Even in minute amount, polymeric additives may also confer some viscoelastic properties (Basaran et al., 2013). As two-phase fluids, the presence of particles can play a role, especially at the high shear rates involved in inkjet printing. An example of a setup allowing a good characterization at higher shear rates is described in Wang et al. (2010), using the capillary rheometer technique. The authors compared the behaviour at low and high shear rates and showed that the latter may be significantly different from the former one, an effect which increases with particle loading. Another major interest from this approach for ink characterization is that the flow configuration is similar to what happens in the nozzle. A fundamental study of filament breakup in high shear rate generation regime for particulate fluids is scarce. As an example, nozzle clogging has been investigated by Lee et al. (2012) for nanometric ZnO suspensions, where they found printing parameters allowing us to reduce this phenomenon by reducing the elongational contribution to the flow, and by increasing flow velocity, thanks to a novel nozzle design. Other works considered micron sized particles (van Deen et al., 2013; Bonnoit et al., 2012; Mathues et al., 2015) and showed that the particles accelerated the breakup compared with a simple fluid with similar viscosity. Below a critical neck radius, the continuum medium approach fails, particles rearrange themselves in the pinch-off region and the interstitial fluid has to be considered. Lastly, the wetting properties have to be considered. Simulations of particulate inks in Connington et al. (2015) focused on the wetting properties of the particles in the surrounding medium. The authors found that neutrally wetting particles (*i.e.* particles with a 90° angle with the solvent) increased the rupture length. The shape and orientation of the adsorbed particles can also have a stabilizing or destabilizing effect on thin films, as discussed in Morris et al. (2015). This effects depend on the equilibrium configuration of the particles at the fluid/air interface and the resulting meniscus shape.

The aim of this study is to give further insight into the filament breakup and thinning behaviour for the specific case of particulate ceramic suspensions in the context of inkjet printing. Filament thinning and breakup is the first stage of drop formation, and a thorough characterization is still missing for this specific context. The major objectives are to extend filament thinning studies