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Rheological characterization of liquid electrolytes for drop-on-demand inkjet printing

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ABSTRACT

Physico-chemical properties of inkjet printing liquids significantly affect the quality of print-out, thus being the key parameter in the performance of printed electronic device (PEDs). Complex hydrodynamic interactions that inks are subjected to in an inkjet printing device has an influence on their rheological response, thus final drop formation, jetting, and drying kinetics. This paper provides a systematic comparison of three PED electrolytes based on different solvents i.e. Sulfolane, 3-Methoxypropionitrile and Acetonitrile that gave them different physico-chemical properties. Rheological properties of printed electrolytes were found to strongly influence the quality of print-outs, which is investigated both optically and morphologically. Best printing results were obtained with the sulfolane-based electrolyte that has the most uniform temperature and shear rate dependent rheological behavior as well as the lowest evaporation rate. By carefully controlling the printing temperature window, it is possible to subject PED electrolytes to higher shearing viscosity profiles while avoiding undesirable dilatant behavior which results in clogged printing nozzles and disrupted droplet trajectory.

1. Introduction

As the most mature practice of direct writing (DW) technology [1], inkjet printing offers mask-free material deposition with micrometer accuracy and cost saving of the materials [2]. For the last decades drop-on-demand (DoD) inkjet printing has been extensively used in lab-scale research and it has been one of the most promising technique for massive production of printed electronic devices (PEDs), in particular integrated circuits, small antennas, solar cells, batteries, thin-film transistors and light-emitting diodes [3–8]. Development of PED sets an on-going demand for improved resolution and printability on different substrates. Such a target can be achieved only by optimal, reliable, and sustainable droplet formation, jetting and substrate-drop interaction which depend on the physical characteristics of the inks such as surface tension and viscosity [9].

Upon applying a sufficient voltage to the piezoelectric actuator in the microchannel of the printer nozzle, the ink flows through the channel depending on its viscosity [10]. Once kinetic energy and surface energy of the ink overcomes the energy required for ejection of a spherical droplet, with the help of contraction within the chamber, a droplet is formed and gets ejected from the nozzle [9,11]. Printing inks are semi-diluted suspensions consisting of the complex mix of particles which are segregated due to the mutual immiscibility and cross-material repulsive forces in the stationary state, such that the system remains de-mixed [12–14]. After strain and shear are applied, ink may first exhibit an induced elasticity as the resistance to mixing reaches a maximum, which induces dilatancy [15,16]. Dilatancy induced in high shear rate jetting conditions accompanied with rapid evaporation upon ejection leads to undesirable clogging of nozzles [17,18]. By determining the viscosity dependence over a broad shear rate range that affect droplet formation, ink recovery rate and trajectory formation that affect droplet setting, it is possible to correlate the flow parameters with print-out performance [19–21].

In this paper we provide investigation of different rheological and printing performance of three dye-sensitized solar cell inks based on three different solvents (sulfolane, 3-

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methoxypropionitrile and acetonitrile). Using the same inks for different printing temperature conditions using the paper as printing substrate, we correlate the change of rheological parameters with the printing performance. Rheological behavior of ink accompanied with the evaporation rate of electrolyte has an important effect on the printing results, and for suboptimal electrolytes it can be tuned by changing the temperature conditions, to improve the complex set of parameters that affect the end up performance.

2. Experimental

2.1. Materials

The electrolytes were prepared in the similar way as reported in the literature, with sulfolane, 3-methoxypropionitrile and acetonitrile as liquid ink vehicles and labeled as SFN, MPN and ACN respectively [22–24]. Table 1 lists the components of the electrolytes used in this study along with their molar ratios and the corresponding abbreviations can be found at the end of Table 1.

DMII, PMII (>98% purity), EMII (>98% purity) were purchased from Io-Li-Tec and EMITCB and anhydrous LiI was obtained from Merck. GuSCN (purity > 99%), NMBI (purity 99%), TBP (purity 96%), I_2, NBB and all the solvents (Sulfolane 99% purity, Acetonitrile 99.8% anhydrous, 3-Methoxypropionitrile 98% purity) were supplied by Sigma Aldrich.

2.2. Characterization of inks

For an ideal print outcome, a high-performance jetting ink should meet certain demands regarding its physical properties (28–42 mN/m surface tension; 10–12 mPa s viscosity; <100 °C boiling point; >1 g/cm^{3}density; <0.2 μm particle size; 4–9 pH) [25]. Being the key parameter for the volatility of the ink at the nozzle orifice, solvent boiling temperatures are 285 °C, 164 °C and 82 °C for SFN, MPN and ACN electrolytes, respectively. Surface tension values of 24.5 ± 0.6, 33.9 ± 0.14, 42.7 ± 0.09 mN/m, respectively, were measured using an optical tensiometer (CAM 200 from KSV instruments) in pendant drop mode at room temperature and the inks were more characterized at elevated temperatures as mentioned in the results part. In order to characterize substrate-ink interaction, contact angle measurements were conducted in sessile drop mode at room temperature in 65% relative humidity with optical tensiometer.

A sub-optimal ink might cause clogging of the nozzles or drops deviating from the expected flying direction due to ambient interaction while spherical are anticipated [26]. Drop formation and performance characteristics of inkjet printing inks have been benchmarked using a set of non-dimensional parameters consisting of inverse Ohnesorge number ($Oh^{-1} = Z$), Reynolds number (Re) and Weber number (We) given by Equations (1)–(4) [27,28].

$$Z = \sqrt{(d\rho\gamma)} \Big/ \eta \tag{1}$$

$$Re = \rho v d / \eta \tag{2}$$

$$We = \rho d v^2 \Big/ \gamma \tag{3}$$

$$Z = Oh^{-1} = Re \Big/ \sqrt{We} \tag{4}$$

Where d, ρ, γ, η and ν refer to nozzle radius, density, surface tension, dynamic viscosity measured at low shear and drop velocity, respectively. By virtue of being mostly experimental, the correlation of non-dimensional parameters with printing results has been determined within different limits. Defined as the equilibrium indicator of viscous forces to surface tension forces of the ink Z was experimentally demonstrated to be $1 < Z < 10$ for jettable fluids [29]. On the other hand many researchers challenged this defined range as presented in Ref. [30] as $2 < Z < 40$ or in Ref. [31] as $0.67 < Z < 50$. Re and We, being indicators of drop formation, impact and spreading, represent the ratio of inertial forces to viscous and surface tension forces, respectively and they are characteristically fall into 1–100 for inkjet printers [32].

2.3. Inkjet printing process

In this study, we carried out a proof-of-concept study using a lab scale, DoD and piezoelectric based materials printer (DMP-2831, Fujifilm Dimatix, Inc., CA, USA) [25]. In order to obtain uniformity of factors affecting printability, droplet jetting frequency of 1 kHz was used for all inks, whilst paper substrate was kept the same. Jetting temperature was chosen as to correlate with temperature set up for rheological tests, and apart from room temperature (23 °C), it was increased to 40 °C and 60 °C, by adjusting the heating system in the printer.

Jetting trajectories and velocity of the ejected drops were determined by embedded stroboscopic drop watcher camera. Deviation of the drop trajectory and a drop travelling velocity different than optimal value (7–9 m/sec for this printer geometry) are highly detrimental for the printing results and might give rise to shorter cartridge life cycle by clogging the nozzles due to possible agglomeration on the orifice [33]. In many studies the complicated response of the non-Newtonian fluids during the dispensing process was highlighted [34] and the drop velocity adjustment was proposed in order to improve the printing results [35].

In this study an in-house algorithm written in Mathematica technical computing software was applied to the captured images by embedded stroboscopic drop watcher camera in order to obtain detailed data to identify the tail and filament structures along with the final drop formation process of medium dilatant MPN electrolyte as an example [36]. The algorithm had two main functions: image processing and regression analysis. The image processing function was designed to binarize and categorize the pixels based on their color functions. For binarization threshold, Otsu method

Table 1
Electrolytes used in this study.

Electrolyte	Components	Molar ratio	Reference
SFN	DMII:EMII:EMITCB:I_2:NBB:GuSCN	12:12:16:1.67:3.33:0.67	[22]
MPN	I_2:GuSCN:NMBI:PMII	0.06:0.1:0.5:0.5	[23]
ACN	DMII:I_2:LiI:TBP:GuSCN	1:0.03:0.05:0.5:0.1	[24]

DMII: 1, 3-dimethylimidazolium iodide, EMII: 1-ethyl-3-methylimidazolium iodide, EMITCB: 1-ethyl-3-methylimidazolium tetracyanoborate, I_2: Iodine, NBB: N-butylbenzoimidazole, GuSCN: Guanidine Thiocyanate, PMII: 1-methyl-3 propylimidazolium iodide, LiI: lithium iodide, TBP: 4-tertbutylpyridine.