

## Inkjet printing of polyvinyl alcohol multilayers for additive manufacturing applications

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**ABSTRACT:** Here we demonstrate that inkjet printing technology is capable of producing polyvinyl alcohol (PVOH) multilayer structures. PVOH water-based inks were formulated with the addition of additives such as humectant and pigments. The intrinsic properties of the inks, such as surface tension, rheological behavior, pH, wetting, and time stability were investigated. The ink's surface tension was in the range 30–40 mN/m. All formulated inks displayed a pseudoplastic (non-Newtonian shear thinning and thixotropic) behavior at low-shear rates and a Newtonian behavior at high-shear rates; were neutral solutions (pH7) and demonstrated a good time stability. A proprietary 3D inkjet printing system was utilized to print polymer multilayer structures. The morphology, surface profile, and the thickness uniformity of inkjet printed multilayers were evaluated by optical microscopy and FT-IR microscopy. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43572.

**KEYWORDS:** manufacturing; morphology; rheology; viscosity and viscoelasticity

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### INTRODUCTION

Additive manufacturing<sup>1</sup> based on inkjet printing technology has gained a large interest in the recent years. The factors driving this continuous interest are mainly attributed to its efficiency in material use, digital and additive patterning, large area capability, compatibility with rigid/flexible substrates, and low cost. Inkjet printing is a non-contact method and works by ejecting ink through very fine nozzles. This technology involves three basic elements: ink; cartridge, and substrate. The physical properties of the ink such as surface tension and rheological properties (shear viscosity) play a crucial role, both on jetting behavior and on the quality of the printed film. From the cartridge (piezoelectric) perspective, the driving waveform actually defines the directionality, uniformity, and the drop formation, and hence the image quality. Therefore, to ensure a good adhesion of the ink to the substrate the surface tension of the ink has to be lower, at least 10 points in mN/m, than the surface energy of the substrate surface.<sup>2</sup>

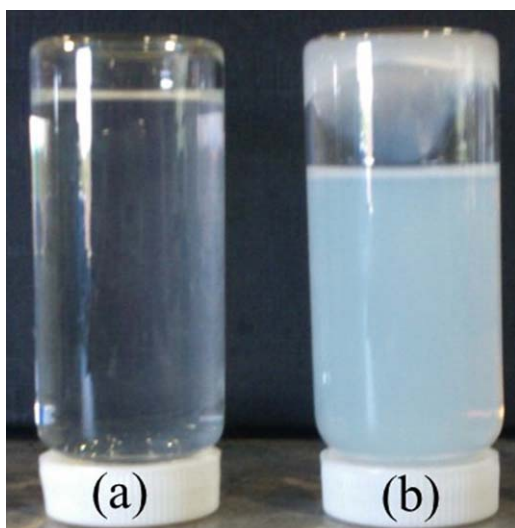
To date, functional polymers,<sup>3,4</sup> metals,<sup>5,6</sup> ceramics,<sup>7,8</sup> and even pharmaceuticals<sup>9</sup> have been successfully deposited using the inkjet printing technique. The direct-writing of polymers and metal particles without requiring any auxiliary steps or equipment has had a strong impact on the development of “plastic” flexible and lightweight electronic devices such as organic solar cells, transistors, and light emitting devices, which are highlighted in a review article by Singh.<sup>10</sup>

Polyvinyl alcohol (PVOH) is a non-toxic, water soluble, and biodegradable polymer that is widely used in a large number of applications. Currently, PVOH is used in the food packaging industry, water treatment, textile, agriculture, cleaning and detergent products, additives in construction and in medical devices.<sup>11</sup> From the manufacturing perspective, PVOH films were produced via solution by either spin coating or electrospinning. However, these methods have a number of limitations in terms of waste of unwanted material, quite restrictive process as being subtractive techniques and overall high process cost. In order to overcome the limitation of the conventional solution processing, here we explore the potential of inkjet printing technology to provide a novel platform for producing PVOH multilayer structures that will have a strong impact on both material and applications perspectives. This article also reports on the formulation of the ink suitable for inkjet printing of PVOH multilayers. The main physical properties, such as rheological behavior, surface tension, stability, and wettability, of the PVOH water-based ink were investigated. The surface profile, structural, and chemical analysis of inkjet printed multilayers were evaluated by optical microscopy and FT-IR microscopy.

### EXPERIMENTAL

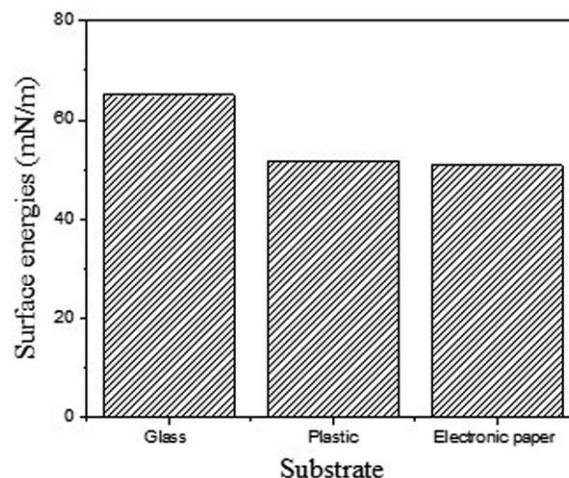
#### Ink Formulation

The solution for inkjet printing was prepared by dissolving the PVOH (PVOH Polymers Ltd, UK) in purified water at 60 °C. In



**Figure 1.** Stability test results for solutions based on (a) PVOH\_A and (b) PVOH\_B after storage for 6 months after formulation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

order to achieve optimum viscoelastic properties and to prevent blocking of the printhead, a humectant [glycerine or mono propylene glycol] was added to the solution. Also, inks with Dya-syn Acid Violet pigment were formulated. All solutions were stirred for several hours to ensure homogeneity and then filtered through a 5  $\mu\text{m}$  filter to remove any particulates that might block the printhead nozzles. In this work, PVOH with two different grades were used, having different average molecular weights and degrees of hydrolysis. Gel permeation chromatography (Agilent 1260 Infinity multidetector GPC system) was performed to determine the molecular weight of the PVOH grades used. PVOH\_A had a mass average molecular weight  $M_w = 23.810$  g/mol and 80% degree of hydrolysis, while PVOH\_B is of low molecular weight PVOH grade with  $M_w = 14.484$  g/mol and 40% degree of hydrolysis. Hoath *et al.*<sup>12</sup> demonstrated that the polymer molecular weight affects the ink-jet printability through control of ink viscosity. Our work demonstrated that for PVOH\_A grade, 4 wt % aqueous solution was suitable for printing and for polymer PVOH\_B grade, 8 wt % was suitable. Furthermore, the homogeneity, sedimentation,



**Figure 2.** The surface free energies of three potential substrates. Then, prior to deposition the wettability was investigated by measuring the contact angle on the glass substrates via the sessile drop analysis method (Optical Tensiometer, Biolin Scientific, Sweden).

and skinning (immediately and after 6 months from preparation) were visually assessed. Note that all fluids were stored in sealed beakers at room temperature. After formulation, all solutions were clearly free from visible large particles, with PVOH\_A being transparent and PVOH\_B having a milky appearance. The PVOH\_A ink was transparent and stable for more than 6 months [Figure 1(a)]. It is worthy to note that a gel [Figure 1(b)] is formed in the case of PVOH\_B (more pronounced when glycerine is used as humectant) ink after a 6-month storage period.

The viscosity, surface tension, and pH of the resulting inks were measured, and the results are summarized in Table I. The surface tension of the inks was measured at room temperature using the pendant drop method via an Attension Theta Optical Tensiometer (Biolin Scientific, Sweden). The viscosity of the solutions at low-shear rates was measured using a Brookfield DV2T viscometer with a cylindrical spindle geometry (Brookfield, UK). However, the high shear rate viscosities were tested using a 55mm diameter parallel plate and with a 300 micron gap using Bohlin C-VOR (Malvern Instruments, UK). The pH

**Table I.** Ink Compositions and the Measured Parameters

	PVOH	H <sub>2</sub> O	MPG	Glycerine	Pigment	Surface tension (mN/m)	Viscosity, cP (25 rpm/min)
Ink_1	HV	x	x			38.5	5.4
Ink_2	HV	x	x		x	45.6	4.4
Ink_3	HV	x		x		42.6	4.9
Ink_4	HV	x		x	x	43.1	4.4
Ink_5	LV	x		x		40.5	7.5
Ink_6	LV	x	x			39.3	7.5

HV refers to high molecular weight PVOH\_A and LV to low molecular weight PVOH\_B. X indicates that the additive was present. Actual values used are proprietary. PVOH, polyvinyl alcohol; MPG, mono propylene glycol.

**Table II.** Waveform Parameters for All Investigated Inks

Ink	Draw voltage (V)/ pulse width ( $\mu$ s)	Release voltage (V)/ pulse width ( $\mu$ s)
Ink_1	13/5	6.5/10
Ink_2	12/5	6/10
Ink_3	14/5	7/10
Ink_4	13/5	6.5/10
Ink_5	16/5	8/10
Ink_6	15.4/5	7.7/10

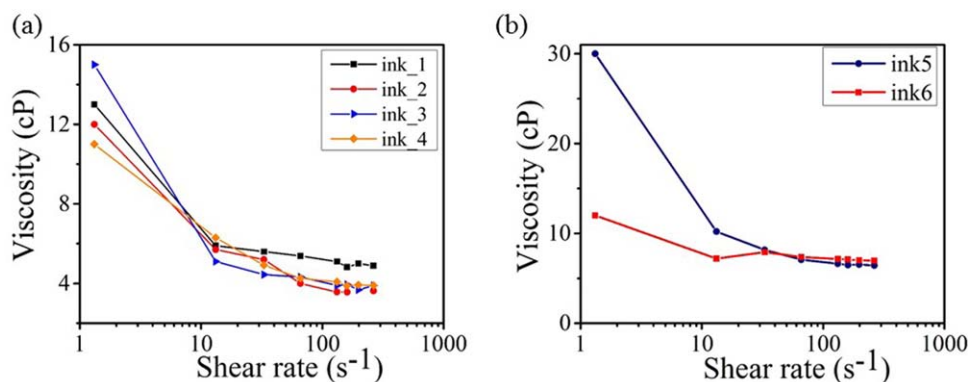
All inkjet printing depositions were carried out at room temperature.

was tested using a HANNA pH meter (HANNA Instruments, UK)

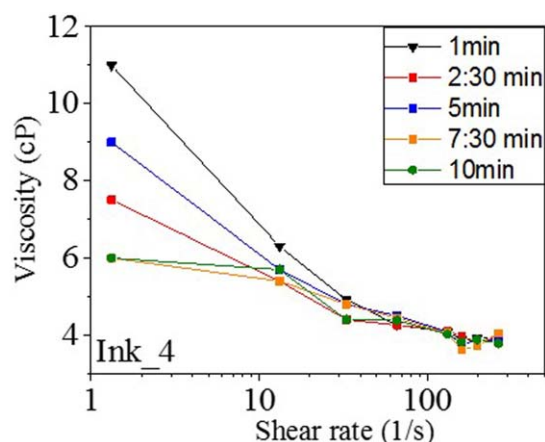
To ensure a good adhesion of the ink to the substrate, the surface energy of standard glass microscope slides, plastic and electronic grade paper was tested via the sessile drop analysis method (Optical Tensiometer, Biolin Scientific, Sweden), with the results presented in Figure 2. The interactions between the drop and substrate play a key role on the printing quality; and for good wetting of the surface by the drop, the surface energy of the substrate should exceed the surface tension of the ink by 10–15 mN/m. For this reason, the glass slides were utilized as substrates in our work.

### PRINTING AND ANALYSIS OF PVOH MULTILAYERS

The surface topology and thickness profile of the inkjet printed multilayers were evaluated using a Contour GT-K 3D optical microscope (Bruker Corp.). The morphology and the chemical map were carried out using the Cary 620 Imaging Microscope coupled with a Cary 670 FT-IR spectrometer (Agilent Technologies, UK). The Cary 620 was used in a standard configuration, with x15 magnification IR objective and a  $64 \times 64$  element Focal Plane Array (FPA) detector. The samples were measured in both reflectance and micro-ATR modes. In the case of reflectance mode, the pixel resolution was  $5.5 \times 5.5 \mu\text{m}$ ; and the field of view (FOV) was  $350 \times 350 \mu\text{m}$ . Micro-ATR (Ge crystal) mode gave an achievable pixel resolution of  $1.1 \times 1.1$  and  $70 \times 70 \mu\text{m}$  FOV.



**Figure 3.** Viscosity as a function of shear rate for (a) PVOH\_A and (b) PVOH\_B. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

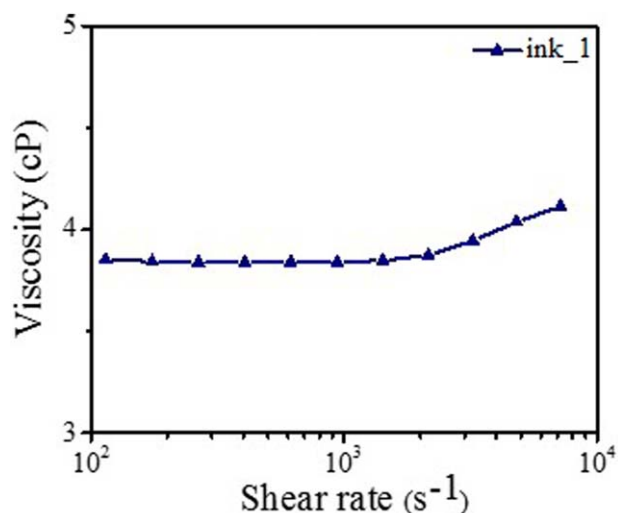


**Figure 4.** Time-dependent viscosity for PVOH\_A-based ink (Ink\_4). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Inkjet Printing of PVOH Ink. The PVOH multilayers were deposited using a piezoelectric XYPrint100Z Hybrid inkjet printing machine (Industrial Inkjet Ltd, UK) using a Konica Minolta KM512 high-resolution print head with 512 nozzles ( $256 \times 2$  rows),  $30 \mu\text{m}$  nozzle diameter, jetting 42pL drops at 7.6 kHz. The jetting process for this particular printer is controlled through a unipolar waveform. In fact, the driving waveform controls both steps: pull ink into the chamber and eject ink out through the nozzles—via Draw voltage pulse— $V_D$  and Release pulse ( $V_R$ ), respectively. Then every ink was tested to determine the optimum magnitude and width of voltages ( $V_D$  and  $V_R$ ) in order to achieve a stable printing condition. The waveform parameters for all investigated inks were included in Table II.

### RESULTS AND DISCUSSION

The rheological behavior of the ink plays a crucial role on the jetting performance and hence on the printed quality and for this reason this was investigated first. The rheology of all inks was evaluated by measuring the viscosities as a function of the shear rate. For all tested fluids, the viscosities, at low-shear rates, decreased with increasing shear rate, defining the non-



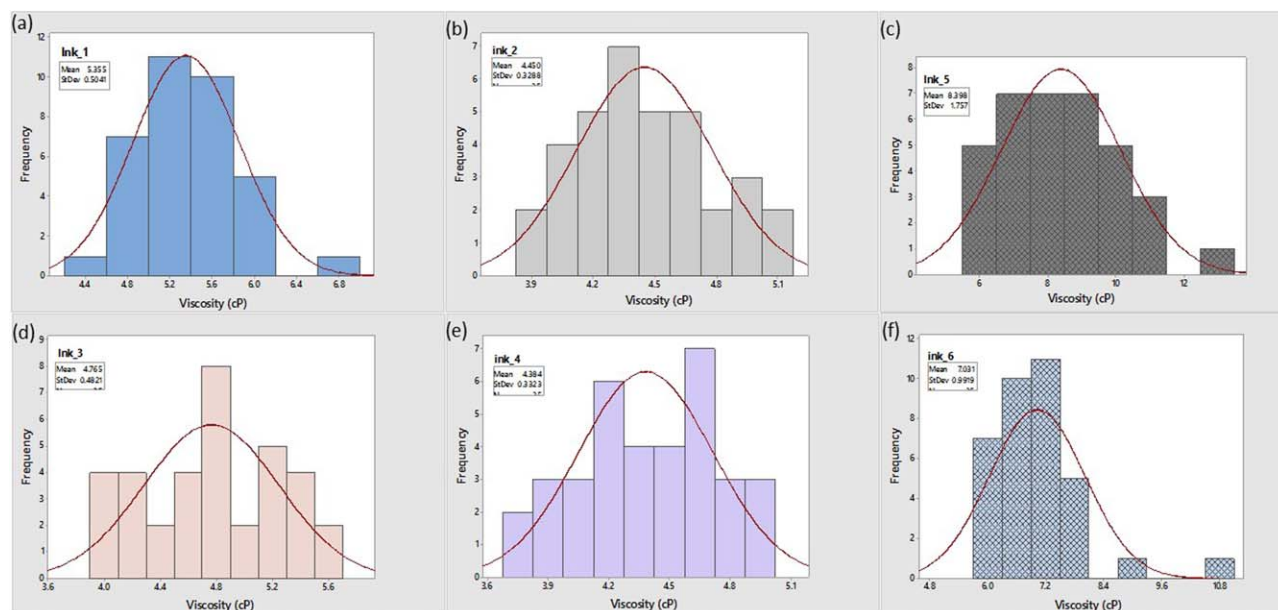
**Figure 5.** Shear viscosity of Ink\_1 as a function of the shear rate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Newtonian—shear thinning behavior as shown in Figure 3, and we can conclude that formulated solutions based on both PVOH grades display a pseudoplastic behavior over the range of shear rates from 1 to 100/s.

Moreover, it has been also observed that the inks display a time-dependent viscosity in the low shear rate range, as demonstrated in Figure 4.

The change in viscosity with testing time, that is a decreasing viscosity with increasing time, defines a thixotropic behavior for the formulated fluids, and has been observed that this effect is more pronounced at shear rates from 1.32 to 33/s.

The viscosity measured at high shear rate conditions, as would be observed in inkjet printing. In order to have a complete picture over the rheological behavior, the viscosities of the formulated inks were also measured at high-shear rates. As can be seen in the Figure 5, the PVOH Ink\_1 exhibits Newtonian behavior over the range of high-shear rates studied (100–10,000/s).

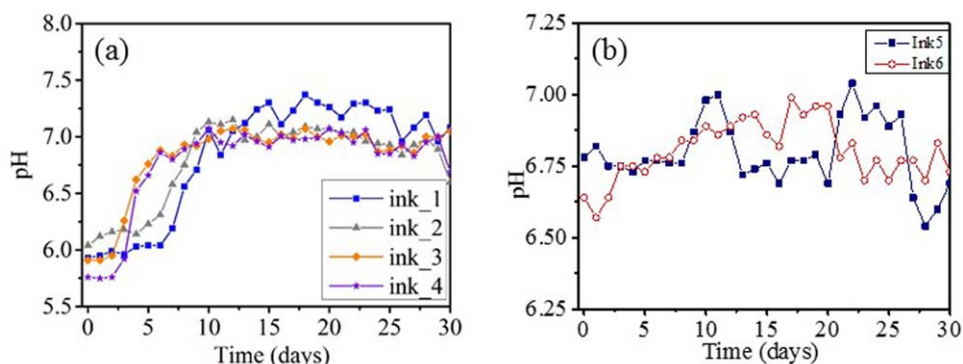


**Figure 6.** Histogram of all PVOH-based inks under investigation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

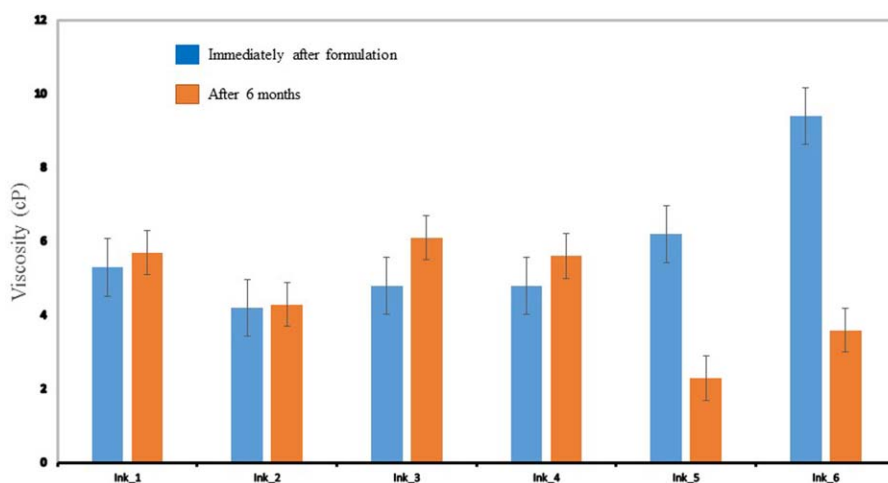
**Table III.** Measured Viscosities of Inks Based on Both PVOH Grades

Ink	Viscosity minimum value (cP)	Viscosity maximum value (cP)	Viscosity maximum/minimum	Mean viscosity (cP)	Standard deviation (cP)
Ink_1	4.64	6.08	1.31	5.4	0.4
Ink_2	3.88	5.16	1.32	4.4	0.3
Ink_3	3.96	5.64	1.42	4.9	0.4
Ink_4	3.8	4.96	1.30	4.4	0.3
Ink_5	5.52	11.24	2.03	8	2
Ink_6	6.84	8.76	1.28	7.6	0.5





**Figure 7.** pH aging of (a) PVOH\_A and (b) PVOH\_B-based inks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



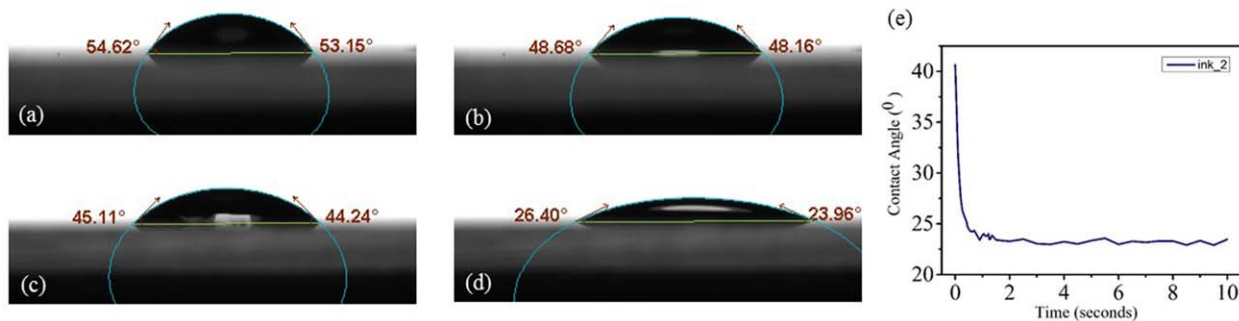
**Figure 8.** Viscosities of PVOH-based inks immediately (blue) and at 6 months (orange) after formulation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Overall, the rheological tests demonstrated that PVOH-based inks exhibited a combination of non-Newtonian—shear thinning behavior at low-shear rates with a Newtonian behavior at high-shear rates.

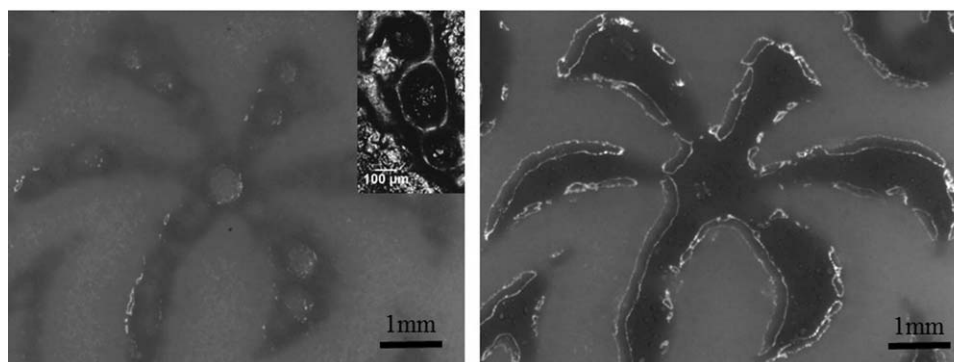
As the stability of the ink is a very important issue in maintaining quality during inkjet printing, the solutions' stability at ambient condition was further tested. To facilitate a

comprehensive study, short term as well as a storage-long-term stability tests were performed. The first short-term study was performed by measuring the viscosity and pH of the same ink as a function of time via daily measurements over 30 tested days.

The histograms of the collected data were generated and are given in Figure 6. The mean value and the standard deviation of viscosity for each individual ink are included in Table III.



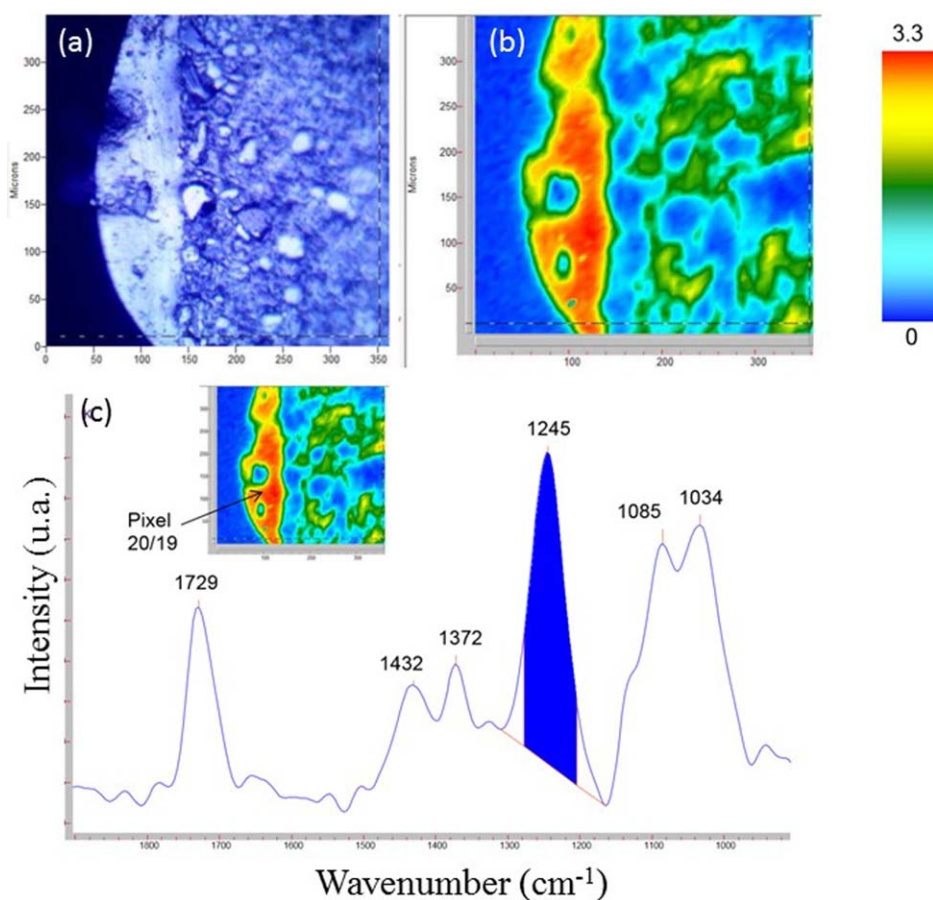
**Figure 9.** Images of the ink droplets on glass substrate (a) Ink\_1 first contact (b) Ink\_2 after 30 s; (c) Ink\_2 first contact; (d) Ink\_2 after 30 s, and (e) contact angle versus time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



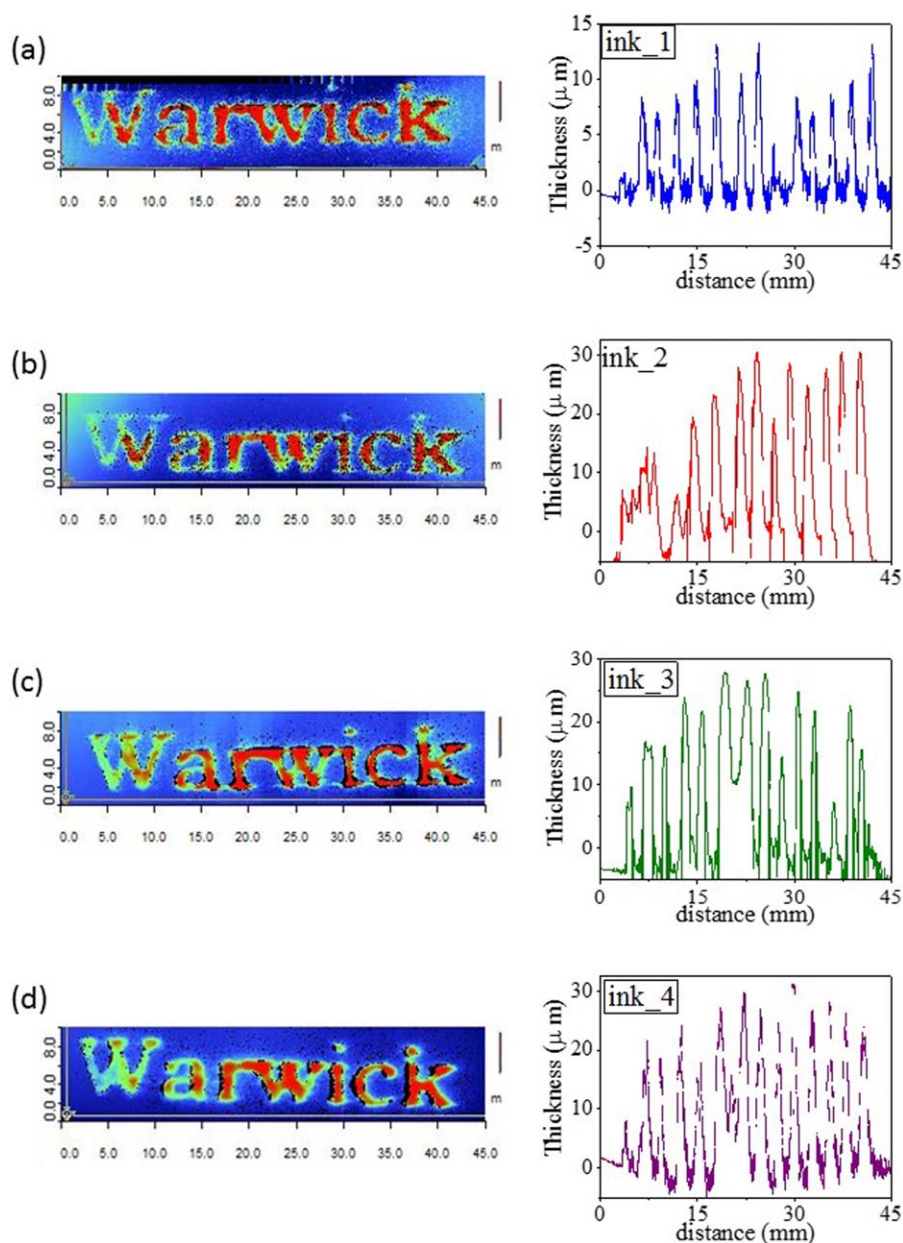
**Figure 10.** Optical micrographs of inkjet printing PVOH (a) 25 and (b) 100 layers.

First, it is observed that addition of pigment to the ink results in a lowering of the viscosity and a reduction of the standard deviation, respectively. Based on these observations it can be seen that the addition of the pigment has a positive impact on the stability of the inks. Second, it has been observed that inks based on PVOH\_B demonstrate a large standard deviation (more significant effect observed for Ink\_5) and hence instabilities are likely to be induced during the printing process.

Furthermore, the ink stability was evaluated by also monitoring the pH of the all formulated inks. The pH is a very important parameter in water-based solutions as it provides key information about both the properties (drying, foaming, and viscosity) and stability of the ink. For example, an ink with a low-pH (acidic) is corrosive and can reduce the lifetime of the cartridge.<sup>13</sup> On the contrary, a high-pH condition can result in a decreased viscosity, likely due to changes in the conformation of the polymer molecules,<sup>14</sup> and affects as well the ink's drying



**Figure 11.** (a) Visible microscope image of the cross-section of the 100 layers; (b) chemical image generated using the peak at  $1245\text{ cm}^{-1}$ ; (c) FTIR spectra collected on a particular point from the printed structure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 12.** Surface and thickness profiles of the printed “Warwick” logo using (a) Ink\_1, (b) Ink\_2, (c) Ink\_3, and (d) Ink\_4. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

time (changes in colligative properties of the water solvent). After all we can conclude that overall pH-neutral inks have a few important benefits: First, it guarantees a stable process; Second, it ensures a good lifetime of the printhead and third is more environmentally friendly. As shown in Figure 7 in the case of PVOH\_A solutions, after preparation and for the next few days, the inks were initially at pH6 and then sharply increased to pH7 where pH remained fairly constant. The results of pH tests define the formulated solutions as “pH neutral inks”. However, a not very well defined pH trend was displayed by PVOH\_B inks [Figure 7(b)].

Furthermore, the long-term viscosity of the PVOH-based inks (Ink\_1–Ink\_6) were investigated. The viscosity of the

fluids was tested immediately and at 6 months after formulation. However, it should be underline that in meantime all fluids were stored in sealed beakers at room temperature. All inks based on PVOH\_A (Inks 1–4) demonstrated an excellent stability behavior as can be seen in Figure 8. Conversely, the experimental results showed that inks based on the low molecular PVOH grade (Inks 5 and 6) are not stable solutions by displaying a large variation of viscosity over time (Figure 8).

Overall, the both short and long terms stability tests demonstrated that the inks based on low molecular weight grade (PVOH\_B) do not meet the stability requirements for inkjet printing. Moreover, has been observed that the addition of

pigment has a positive effect on the stability of the formulated fluids.

Furthermore, the wetting behavior of the PVOH-based inks was investigated. All inks demonstrated a good level of wettability with the contact angle on the glass substrate in the range of 40–55°. Adding pigment to the solution leads to a higher wettability of the ink to the substrate, with a reduced contact angle of 25° observed. Also, the evolution of the contact angle with time was assessed (Figure 9 for Inks\_1 and 2), and it has been found that a rapid decrease in contact angle takes place in the first second of contact and gaining an equilibrium after that initial period [Figure 9 (e)]. The drop/surface interaction is quite a complex process and is governed by different forces such as inertial, capillary, and gravitational; a comprehensive study was published by Derby.<sup>15</sup> We propose that the fast decrease of the contact angle in our case can be associated with the rapid infiltration of ink into the porous glass substrate controlled by capillary forces. In Addition, adding pigment to the solution leads to a higher wettability of the ink to the substrate, with a reduced contact angle of 25° observed.

It is true that the size of the dispersed fluid (droplet volume) has a strong influence on the wettability due to the both gravity force and rate of evaporation. For study of the wetting behavior, 3  $\mu\text{L}$  ( $\sim 3$  mm diameter) droplets of fluid were placed on the substrate from a needle, whereas during inkjet deposition from the Konica Minolta piezoelectric print-head, 42 pL ( $\sim 100$   $\mu\text{m}$  diameter) droplets were deposited. However, Taylor *et al.*<sup>16</sup> demonstrated that water contact angles from picolitre volume droplets are comparable with those obtained from microlitre volume droplets. Overall, based on the work of Taylor *et al.*, we can conclude that in our case the wetting and the time-dependant results obtained from microliter volume droplets adequately describe the behavior of picolitre ink droplets.

Microscopic images of the inkjet printing of PVOH with 25 and respectively 100 layers are shown in Figure 10.

A coffee ring effect can be observed in the case of 25 printed layers [Figure 10(a)]. However, this is a very well-known defect in the inkjet printing sector<sup>17,18</sup> and it is generated by the back-flow of ink from the drop middle to the edge. Moreover, there is a visible difference, that is, the quality is much improved and no presence of the coffee ring defects detected when 100 layers were printed [Figure 10(b)].

In order to further evaluate the quality of the multilayer printed structures, Imaging Microscopy coupled with an FT-IR spectrometer was used. This technique is very useful in identifying defects (inclusions in polymer films), separation of the layers, and the chemical map of the deposited structure. Figure 11(a) shows the cross-section microscope image of 100 printed layers. FTIR mapping measurements were then performed and a chemical image [Figure 11(b)] was produced by showing the distribution of the strong FTIR band at 1245  $\text{cm}^{-1}$ , that is, present in the printed layers but not in the substrate. Closer evaluation of the optical image reveals a continuous structure with no sign of separation between layers. A few defects in the form of small inclusions were observed inside of the printed pattern. There-

fore, the multilayer thickness can be calculated using this technique and has been found that the thickness of 100 printed layers is 88  $\mu\text{m}$ .

The surface profile and the thickness uniformity of a 100 ink-jet printed layers were performed by using a Contour GT-K 3D optical microscope. The collected images (Figure 12) reveal the presence of some poorly covered areas especially at the first letter of the pattern that are reflected as well as on the thickness uniformity, that is, the thickness is not uniform over the entire scanned area with lower thickness on the first part of the pattern. We advance that this is caused by a well-known “first drop” effect in the printing process, in that the first propelled drop behaves differently in both quantity and quality from droplets that come after it, as has been demonstrated by Famili *et al.*<sup>19,20</sup>

## CONCLUSIONS

PVOH aqueous solutions with different additives (humectant, pigment) were formulated. Their rheological behavior was investigated and the experimental results demonstrated that all formulated inks display a combination of *pseudoplastic shear thinning and thixotropic* behaviors at low-shear rates and a *Newtonian* behavior at high-shear rates. All inks are neutral solution (pH7) that ensure a good lifetime of the print head. Therefore, the experimental results demonstrated that the formulated inks based on PVOH\_A grade show a good time stability. Conversely, the ink based on PVOH\_B, especially Ink\_5, shows a large standard deviation of viscosity, and an increase in viscosity over time, and this behaviour does not meet the requirements for the inkjet printing process. Moreover, it was successfully demonstrated that inkjet printing technology is capable of producing PVOH multilayers structures. The cross-section image of the 100 inkjet printed layers indicated that the structure was continuously built and there was no sign of barrier between individual layers. The surface profile data showed the presence of some imperfections and further work will be performed to improve the printing coverage.

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