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Polymer Inkjet Printing: Construction of Three-Dimensional Structures at Micro-Scale by Repeated Lamination

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Abstract: Solution-based, direct-write patterning by an automated, computer-controlled, inkjet technique is of particular interest in a wide variety of industrial fields. We report the construction of three-dimensional (3D), micro-patterned structures by polymer inkjet printing. A piezoelectric, drop-on-demand (DOD) inkjet printing system and a common polymer, PVA (poly(vinyl alcohol)), were explored for 3D construction. After a systematic preliminary study with different solvent systems, a mixture of water and DMSO was chosen as an appropriate solvent for PVA inks. The use of water as a single solvent resulted in frequent PVA clogging when the nozzles were undisturbed. Among the tested polymer ink compositions, the PVA inks in a water/DMSO mixture (4/1 v/v) with concentrations of 3 to 5 g/dL proved to be appropriate for piezoelectric DOD inkjet printing because they were well within the proper viscosity and surface tension range. When a dot was printed, the so-called 'coffee-ring effect' was significant, but its appearance was not prominent in line printing. The optimal polymer inkjet printing process was repeated slice after slice up to 200 times, which produced a well-defined, 3D micro-patterned surface. The overall results implied that piezoelectric DOD polymer inkjet printing could be a powerful, solid-freeform, fabrication technology to create a controlled 3D architecture.

Keywords: inkjet printing, direct writing, 3D construction, micro-patterning, viscosity, surface tension.

Introduction

An inkjet printer is a familiar piece of equipment used in both the home and office. Most versions of inkjet printers work with only two dimensional (2D) materials, such as organic color inks. However, there is a growing interest in its use in non-graphical applications in a broad area of micro-engineering industries.[1-4] In essence, an inkjet printer is a simple dosing robot. Materials are only deposited in a desired location. The technology of inkjet printing has been rapidly developing. The size of the printed droplets has been steadily decreasing; currently inkjet printers can eject droplets of only a few pico-liters. The corresponding increase in resolution allows inkjet printing to fabricate complex shapes with features in micrometer ranges with the aid of computational topology design (CTD). Inkjet printing has been widely employed for electronic devices such as light emitting diodes (LEDs),[5,6] and thin film transistors (TFTs)[7-9] because of its simplicity, low cost, and flexibility. Recently, inkjet printing has been adapted to biomedical applications because most advanced biomedical devices require micro-scale patterning of biological molecules including proteins, peptides, and DNA.[3,10-15] Rapid prototyping technologies such as inkjet printing may play a key role in biosensors, immunoassays, cell-culture devices, tissue engineering, drug delivery devices, and high throughput drug screening.

The use of polymer inks in inkjet printing makes it possible to produce three dimensional (3D) printing. Three dimensional inkjet printing using polymer inks can be termed 'solid freeform fabrication' (SFF) or layered manufacturing. Both terms identify a mold-less manufacturing method and sequential deposition of slices to build up an object. Indeed, the fusion of polymeric materials and inkjet technologies offers exciting possibilities to develop 3D printers which can make anything, anywhere.[16] It is quite surprising, therefore, how little information has been published on how quality inkjet printing with polymers depends on polymer concentration, type of solvent, polymer ink composition, and other processing variables.

In this study, we explored the integration of polymeric materials into piezoelectric DOD inkjet systems to construct 3D micro-structure. The 3D printability of polymer ink was

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systemically investigated under different conditions by varying firing voltage, solvent composition, polymer concentration, viscosity, and surface tension. Finally, we fabricated a precisely micro-patterned 3D architecture through repeated lamination up to 200 times, and characterized its surface topography.

Experimental

Materials. Poly(vinyl alcohol) (PVA) was purchased from Sigma-Aldrich. A mixture of distilled water and dimethyl sulfoxide (DMSO) was used as a solvent. Polyimide (PI) films were supplied by KORON, Seoul, Korea.

Inkjet Printer. Printing was conducted on a piezoelectric DOD inkjet printer (Dimatrix Materials Printer, DMP-2800) manufactured by Dimatix Inc (Santa Clara, CA, USA). The printing area is approximately 200 mm×300 mm with an adjustable Z height. The substrate stage is a hotplate controlled by a regulator so that the substrate can be heated up to 70 °C. A CCD camera equipped with an LED light was installed to monitor drop ejection.

PVA Ink Preparation and Characterization. PVA was dissolved in a mixture of distilled water and dimethyl sulfoxide (DMSO) at different polymer concentrations. The polymer solution was stirred for 3 h at room temperature and then was passed through a syringe filter (pore size 0.2 μm) to eliminate insoluble particles. The viscosity was measured with a digital viscometer (LVDV II+ Pro, Brookfield Engineering Laboratories, MA, USA). The surface tension was measured with a dynamic contact angle analyzer (DCA-312, CAHN instruments Inc., Cerritos, CA, USA).

Inkjet Printing. The inkjet printability of PVA inks was investigated under different processing conditions. The plate temperature was set to 38 °C. The head temperature of a cartridge varied between a range of 30~50 °C and the firing voltage varied over a range of 16~40 V. The jetting rate was about 23 drop/s. Common photographic papers or flexible PI films (KORON) were used as a substrate.

Surface Topography. The pattern morphology and spatial distribution of the resulting polymer deposits after solvent drying were investigated by a high accuracy non-contact surface profiler (Nano surface profiler NV-P2020, Nano System, Korea).

Results and Discussion

Inkjet Printing Systems. Two commonly used inkjet systems are thermal and piezoelectric.[2,17] In both systems, an acoustic pulse ejects ink droplets through a nozzle. The pulse can be generated either thermally or piezoelectrically. In a thermal drop-on-demand (DOD) inkjet printer, a vapor bubble that ejects an ink droplet is formed by local heating. Thermal DOD inkjet systems use water as a solvent. Therefore, they are not preferred for 3D polymer inkjet printing due to solvent restriction because only water-soluble polymers can be used in a thermal DOD inkjet printing system. In contrast, piezoelectric DOD inkjet printing employs piezoelectric materials. The deformation of piezoelectric materials causes a sudden volume change and hence generates an acoustic pulse. The piezoelectric inkjet system is the method of choice for 3D polymer inkjet printing because it does not impose a solvent restriction. That is, any soluble polymers in organic solvents can be used in piezoelectric DOD inkjet printing.

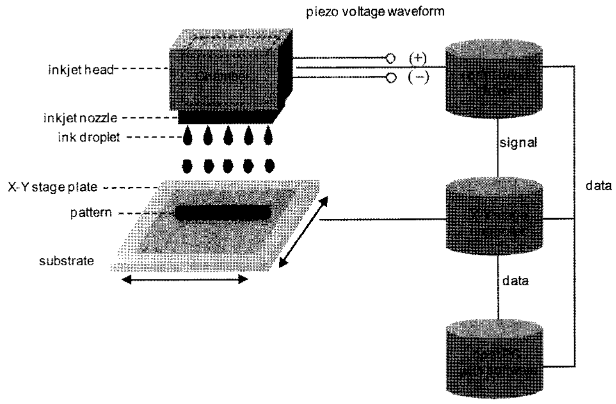

Figure 1. A diagram of the piezoelectric drop-on-demand (DOD) polymer inkjet printing system in the present study.

Figure 1 schematically represents the piezoelectric DOD inkjet printing system used in the present study. The piezoelectric inkjet printer consists of an inkjet head with multi-nozzles, a print head driver, an X-Y stage plate, an X-Y stage controller, and a host computer with software. The inkjet head is composed of a piezoelectric transducer, nozzles, ink pumping chambers, fluid inlet passages, and manifolds. When a voltage is applied to the piezoelectric transducer, the transducer deforms and creates a mechanical vibration. These vibrations create acoustic waves, which in turn force polymer ink out of the chamber through nozzles.[18] Each cartridge has 16 nozzles linearly spaced at 254 μm. A nozzle internal diameter is 21.5 μm. The typical drop volume is about 10 pL. The nozzle is activated by a voltage pulse, of which the voltage amplitude, the pulse width, and the frequency are adjustable through computer software. A positioning system controls the movements of the nozzle in an XYZ station.

Polymer Inks and Printability. The most crucial part of a polymer inkjet printing system is the ink and its physical properties such as solubility, vapor pressure, viscosity, and surface tension.[1,2,19-21] The selection of solvent is the first step for polymer ink formulation. The homogeneity of polymer ink is a prerequisite because poor solvents lead to polymer precipitation and eventual clogging of the nozzle. The viscosity should be suitably low because the power generated by a piezoelectric DOD printer is limited.[2,5,21] However, too much dilution leads to an increase in the number of layers required for

Table I. Basic Properties of the Solvents

Solvent Property	Solvent	
	Water	Dimethyl sulfoxide
Boiling Point (°C)	100.0	189.0
Vapor Pressure (mmHg @20 °C)	17.5	0.1
Surface Tension (mN/m)	72.8	43.5
Viscosity (mP·s @20 °C)	1.0	2.0

construction of three dimensional polymer structures. Surface tension is responsible for spherical liquid drops emerging from nozzles.[2,19,20] It is also important to adjust operating parameters such as jetting voltage and firing frequency to successfully jet viscoelastic fluids.

In this study, a number of potential solvents were investigated for inkjet printability. After a systematic study with several solvent systems, a mixture of water and DMSO was chosen as a solvent for PVA inks. Table I details the basic properties of solvents used in the present study. The drying behavior of a small droplet is significantly different from that of a macroscopic droplet because of its high surface-to-volume ratio.[22,23] When water was used as a solvent of PVA, its evaporation time was incredibly short, within a few seconds. The use of water as a single solvent resulted in frequent PVA clogging, especially when the nozzle was undisturbed. The addition of the non-volatile solvent DMSO with a boiling point of 189 °C significantly relieved the clogging phenomenon. When absent or erratic drop firing was observed, the immediate action taken was to increase the nozzle voltage and to run a few cleaning cycles.

It has been reported that the optimum viscosity for inkjetable fluids in piezoelectric DOD inkjet printing is 3~20 mPa·s.[19] Figure 2 shows the viscosities of PVA solutions in water/DMSO mixture (4/1 v/v) at different temperatures ranging

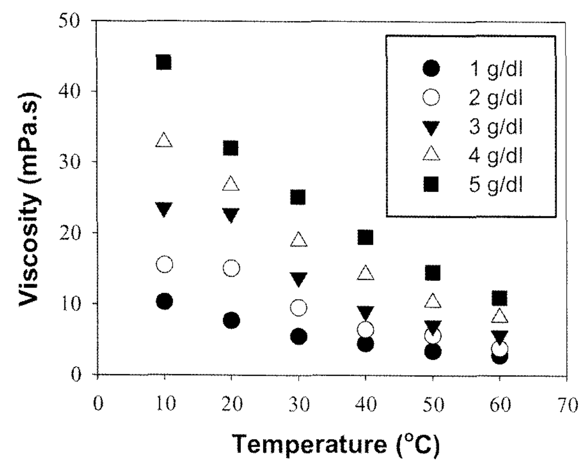

Figure 2. Viscosities of PVA inks at different temperatures and different PVA concentrations. A mixture of distilled water/DMSO (4/1 v/v) was used as a solvent.

Table II. Surface Tensions of PVA Solutions

Samples	Surface Tension (mN/m)
Water	71.96
DMSO (Dimethyl sulfoxide)	43.54
Water/DMSO (4/1 v/v)	58.86
PVA 1 g/dL in Water/DMSO (4/1 v/v)	44.52
PVA 2 g/dL in Water/DMSO (4/1 v/v)	36.70
PVA 3 g/dL in Water/DMSO (4/1 v/v)	41.53
PVA 4 g/dLin Water/DMSO (4/1 v/v)	37.96
PVA 5 g/dL in Water/DMSO (4/1 v/v)	41.90

from 10 to 70 °C. All solutions exhibited an exponential dependence of viscosity on PVA concentration with different sensitivities depending on temperature. Among the tested ink samples, '3 to 5 g/dL concentrations of PVA at 30~50 °C' were selected for further study because they are well within the proper viscosity range.

The surface tension should be high enough to prevent dripping of the ink from the nozzle and low enough to allow spreading over the substrate, typically in the range 30~70 mN/m.[19,20] Table II contains the surface tensions of PVA solutions in water/DMSO (4/1 v/v) at different PVA concentrations. The addition of DMSO (20%) decreased the surface tension of water. Furthermore, the presence of PVA in inks significantly decreased their surface tensions. However, all measured surface tensions were in a range suitable for inkjet

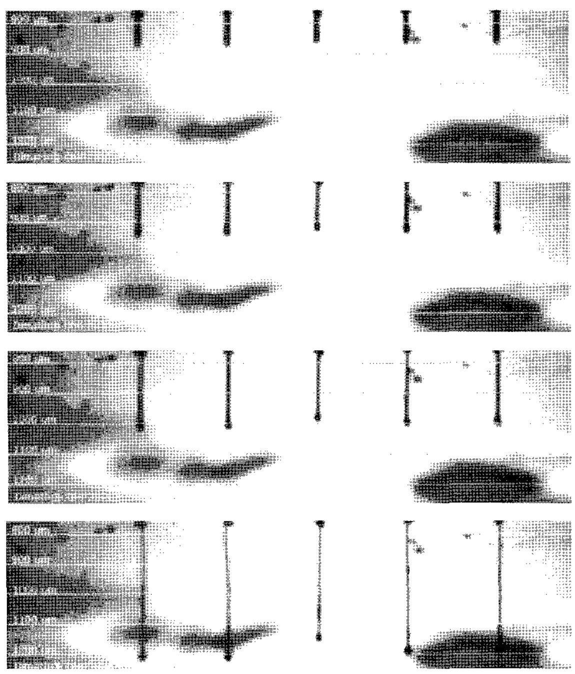

Figure 3. Series of pictures showing droplet ejection as a function of time. PVA concentration 4 g/dL in water/DMSO mixture (4/1 v/v), firing voltage 28 V, temperature 31 °C.

printing. The appropriate jetting voltage and firing frequency were determined to be 20~30 V and 3 kHz, respectively, through systematic studies under several conditions.

Figure 3 shows optical photographs of PVA ink drops generated at 4 g/dL PVA. The polymer concentration influenced inkjet printability through viscosity. At polymer concentrations above 5 g/dL, the polymer solution droplet remained attached to the nozzle under the same jetting voltage. Even though the firing voltage was increased up to 40 V, most nozzles did not eject polymer ink droplets. That is, at higher polymer concentrations, elastic stresses led to the bouncing back of a polymer droplet and finally withdrawal of the droplet. Secondly, the presence of polymer in the ink caused the formation of a long tail connecting drop and nozzle. The decrease in PVA concentration of the solution slightly reduced the tail formation. However, as previously described, lowering polymer concentration compromises the number of layers required for the construction of 3D polymer structures.

Inkjet Printed Dot and Line Morphologies. Figure 4(a-c) shows a typical dried pattern of a PVA ink droplet on PI substrate. A PVA solution (3 g/dL) in water/DMSO (4/1 v/v) was jetted at 22 V and 38 °C. Despite its high boiling point, the droplet dried within a few seconds, due to the high surface-to-volume ratio. Figure 4(c) shows the cross-sectional profile of the dot. When a droplet of around 20 μm diameter landed on the PI substrate, it spread on the substrate to become a circle with a diameter of 45~50 μm. The dot was shaped like a volcano due to the so-called 'coffee-ring effect'.[24-28] Since the evaporation rate of the outer region is greater than that of the inner region, convective flow is generated to replenish solvent at the outer region. As the drop evaporated, the polymers accumulated at the edge and were depleted at the center. The average height at the edge of the dot was around 0.13 μm. This coffee-ring effect could be controlled by manipulating the evaporation profile of drying droplets.[26]

The printed one-layer lines are shown in Figure 4(d-f). A PVA solution (3 g/dL) in water/DMSO (4/1 v/v) was jetted at 22 V and 38 °C. Figure 4(e) represent thickness profiles across lines, showing the thickness variation perpendicular to the printing direction. The width and the height of the line were 160~200 μm and 0.25~0.30 μm, respectively. This indicates that the line was three to four times wider and two times higher than the dot. It should be noted that the coffee-ring effect in dot printing was not dominant in line printing. Shallow craters rarely appeared on top of the line. The isolated drops from multiple nozzles overlapped and merged, which resulted in a smooth, straight line.

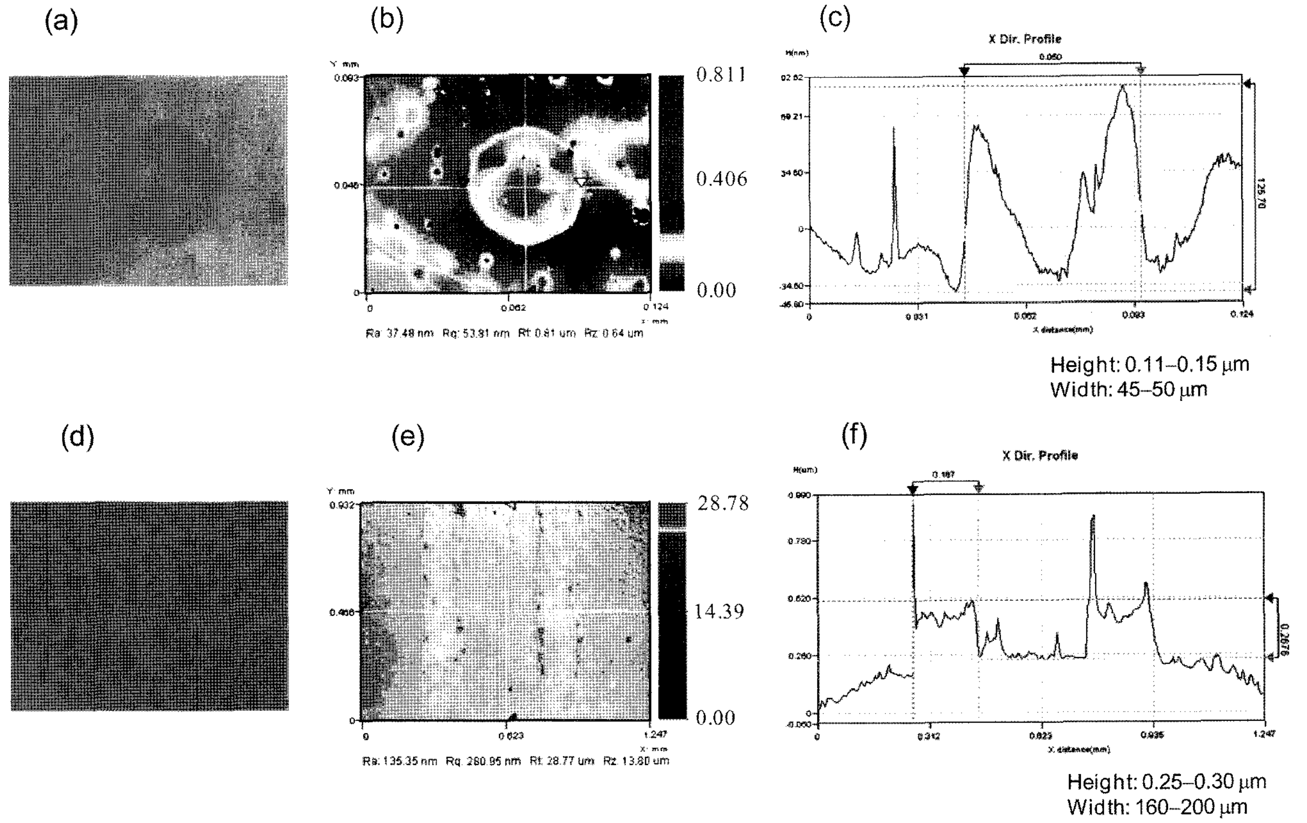

Figure 4. Optical photographs and cross-sectional profiles of an inkjet-printed droplet (a-c) and inkjet-printed lines (d-f). Inkjet conditions: PVA concentration 3 g/dL in water/DMSO mixture (4/1 v/v), firing voltage 22 V, temperature 32 °C.

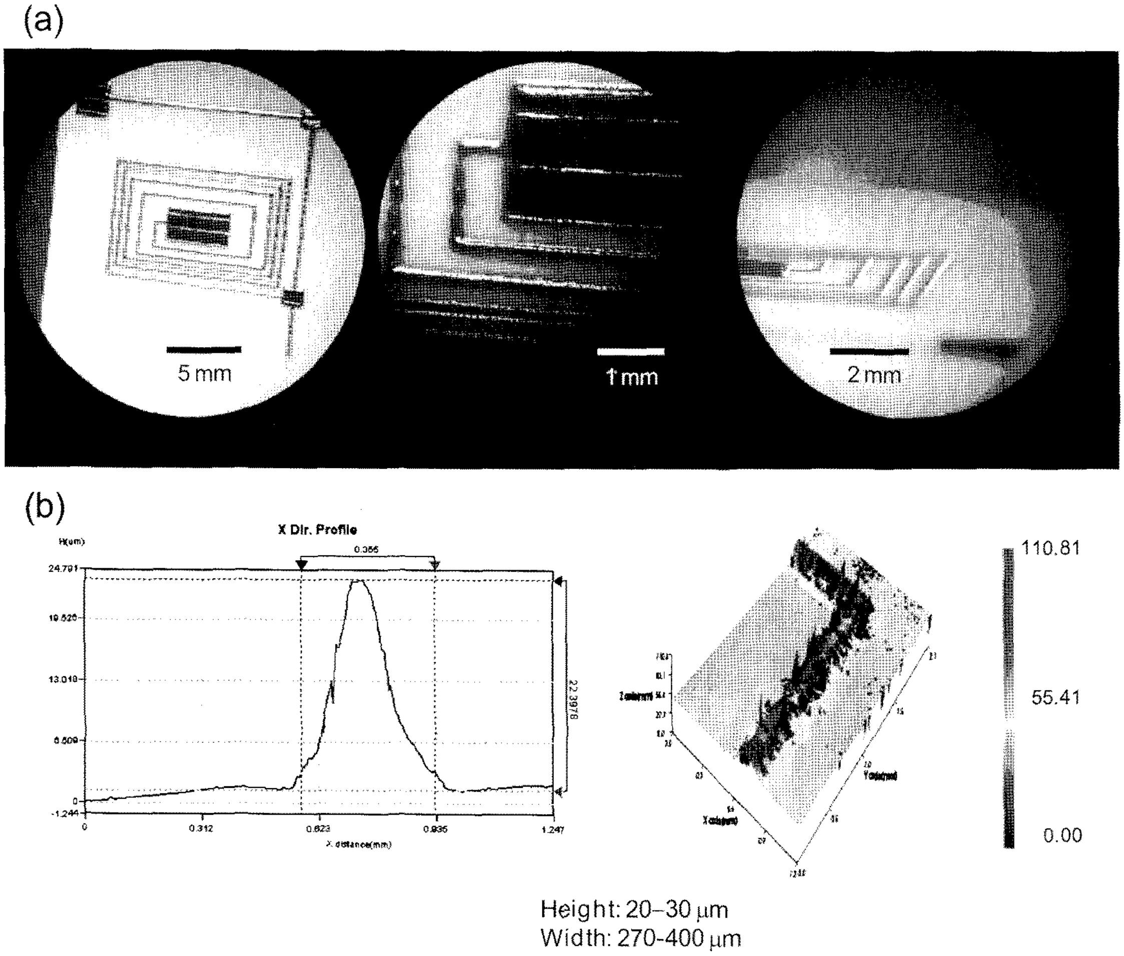

Figure 5. Optical photographs (a) and a cross-sectional profile (b) of a three-dimensional, micro-architecture fabricated by polymer ink-jet printing. A small amount of black ink was added to the polymer ink for visualization.

Fabrication of 3D Microstructures. Figure 5(a) shows a stereoscopic micrograph of a specific pattern prepared by polymer inkjet printing. The micro-pattern was drawn by CAD, and then the optimum inkjet processing determined by previous dot and line printings was repeated 200 times slice after slice on a photographic paper. Figure 5(b) shows cross-sections of a part of the pattern. The cross-sectional shape of the laminated line changed completely, displaying an isosceles triangle. The width at the bottom and the height at the center of the cross-section were 270~400 μm and 20~30 μm, respectively. The craters on top in dot and line printing did not appear on overprinting with layer-by-layer deposition. That is, the coffee-ring effect was not significant in 3D polymer construction. However, the triangular shape of the cross-section implies that the 'self-pinning effect' in repeated deposition might be another problem for creating precise 3D architecture with polymer inkjet printing. Overall results suggest that commercial inkjet printing technology could be applied to fabricate 3D micro-structures but more extensive, systematic studies on inkjet printability with polymers as a function of polymer structure, molecular weight, and solvent and substrate characteristics should be requisite to explore its possibilities and limitations.

Conclusions

We have explored the feasibility of a polymer inkjet printing technique for the construction of 3D micro-patterned structures. Through a systematic study with a variety of polymer inkjet variables such as firing voltage, temperature, solvent composition, viscosity, and surface tension, the polymer inkjet system was optimized. The repeated lamination of micro-patterned polymer layers under optimum inkjet condition produced a 3D polymer structure with good shape definition. This may represent a potential strategy for developing a 3D printer which can construct arbitrary complex 3D architecture. We consider polymer inkjet printing to be the method of choice in the near future for the fabrication of micro-patterned, multi-layered 3D structures, particularly in relation to micro-electronic devices.

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