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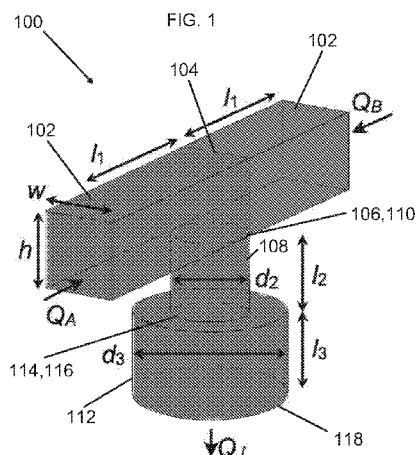
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(54) Title: PRINthead AND METHOD FOR 3D PRINTING OF MULTIPLE MATERIALS



(S7) Abstract: A printhead for 3D printing of multiple materials comprises a nozzle body including (1) at least two ink delivery channels joined together at a downstream end of each channel and comprising a single outlet, (2) a transition channel having an inlet connected to the single outlet of the ink delivery channels, where the transition channel comprises a width d_2 , and (3) an expansion channel having an inlet connected to an outlet of the transition channel, where the expansion channel has a width d_3 greater than the width d_2 . The expansion channel also includes an outlet for extrusion therethrough of a continuous filament comprising more than one material.

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PRINTHEAD AND METHOD FOR 3D PRINTING OF MULTIPLE MATERIALS

RELATED APPLICATIONS

[0001] The present patent document claims the benefit of priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Serial No. 62/133,039, filed on March 13, 2015, and hereby incorporated by reference in its entirety.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under contract number DE-AC02-06CH11357 awarded by the Department of Energy (DOE) and contract number 2012-120625000003 awarded by the Central Intelligence Agency (CIA). The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present disclosure is related generally to three-dimensional printing (3D) printing and more particularly to 3D printing of multiple materials, which may be referred to as multi-material 3D printing.

BACKGROUND

[0004] The ability to integrate both form and function within printed objects may be the next frontier in 3D printing. To move beyond prototyping, new materials and flexible printing platforms may be required. One promising method, sometimes referred to as direct ink writing, utilizes viscoelastic inks in an extrusion-based process to fabricate structures ranging from electronic devices and battery electrodes to structural composites and vascularized 3D tissues. This printing approach has been utilized for high-throughput fabrication and for architectures incorporating multiple materials; however, constructing such architectures often involves sequentially printing individual materials using multiple nozzles. The

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drawbacks of printing one material at a time include the need to carefully align each nozzle as well as to start and stop ink flow on demand without introducing defects.

BRIEF SUMMARY

[0005] A printhead for 3D printing of multiple materials comprises a nozzle body including (1) at least two ink delivery channels joined together at a downstream end of each channel and comprising a single outlet, (2) a transition channel having an inlet connected to the single outlet of the ink delivery channels, where the transition channel comprises a width d_2 , and (3) an expansion channel having an inlet connected to an outlet of the transition channel, where the expansion channel has a width d_3 greater than the width d_2 . The expansion channel also includes an outlet for extrusion therethrough of a continuous filament comprising more than one material.

[0006] According to one embodiment, a method of printing multiple materials out of a single printhead comprises providing a nozzle body including at least a first ink delivery channel and a second ink delivery channel in fluid communication with a nozzle outlet. A first ink formulation is forced to flow through the first ink delivery channel while the second ink formulation is prevented from flowing through the second delivery channel. Thus, a continuous filament comprising only the first ink formulation over a first predetermined length thereof is extruded through the nozzle. The second ink formulation is then forced to flow through the second ink delivery channel while the first ink formulation is prevented from flowing through the first delivery channel. The continuous filament being extruded from the nozzle outlet thus comprises only the second ink formulation over a second predetermined length thereof, and a single continuous filament comprising multiple materials is 3D printed.

[0007] According to another embodiment, a method of printing multiple materials out of a single printhead comprises providing a nozzle body comprising at least a first ink delivery channel and a second ink delivery

channel in fluid communication with a nozzle outlet. A first ink formulation is forced to flow through the first ink delivery channel while a second ink formulation is forced to flow through the second delivery channel. Thus, a continuous filament comprising the first ink formulation and the second ink formulation over a predetermined length thereof is extruded through the nozzle outlet.

[0008] The terms “comprising,” “including,” and “having” are used interchangeably throughout this disclosure as open-ended terms to refer to the recited elements (or steps) without excluding unrecited elements (or steps).

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 shows a schematic of an exemplary multi-material microfluidic printhead.

[0010] FIG. 2 shows (top) an image of the exemplary multi-material printhead connected to two independently-actuated syringe pumps to control the flow of inks through the nozzle, and (bottom) a close-up image of the printhead while two different ink formulations are fed into the nozzle body from the syringe pumps.

[0011] FIG. 3A shows a side-view schematic of the exemplary multi-material printhead and an exemplary flow path of ink formulations A and B through the nozzle body.

[0012] FIG. 3B shows plots of predetermined volumetric flow rates in the syringe pumps and corresponding pressures in the ink delivery channels.

[0013] FIG. 3C shows images of the exemplary printhead during operation as the flow of ink formulation A and ink formulation B are switched, where the white lines have been added to the images to highlight the edges of the channels. The scalebar indicates 400 μm .

[0014] FIG. 3D is a schematic illustration of a fluid flow model.

[0015] FIG. 4 shows rheological flow curves of polydimethylsiloxane (PDMS) ink formulations employed in this work, where the filled symbols

correspond to data taken on a rotational rheometer and the hollow symbols indicate data taken using a capillary rheometer.

[0016] FIGs. 5A-5D show the impact of printing pulse strength on print quality for $Q_s = 20 \mu\text{L}/\text{min}$. Specifically, FIG. 5A shows an exemplary printed filament laden with quantum dots at $Q_p = 1600 \mu\text{L}/\text{min}$, where the scale of the image is consistent with the abscissa below; FIG. 5B shows representative intensity profiles along the filament length for a number of pulses values, as well as corresponding profiles predicted by a model; FIG. 5C shows transition length; and FIG. 5D shows standard deviation in filament width over the range of pulses tested. In all cases $Q_w = Q_p - Q_s$.

[0017] FIG. 6A shows an image of a 1D extruded filament containing alternating bands of differently-colored PDMS with a width of $420 \mu\text{m}$, an image of a 2D “H” pattern of total width 14 mm printed by switching materials, and an image of a 3D four-layer log pile structure with a 1 mm center-to-center spacing of the filaments, where the cross-section is displayed underneath.

[0018] FIG. 6B shows ribbons of alternating bands of different PDMS materials with different elastic moduli. The ribbons are initially 5 mm in width. Two degrees of interdigitation of the materials result in two different necking behaviors.

DETAILED DESCRIPTION

[0019] Multi-material 3D printing using a microfluidic printhead specifically designed for seamlessly switching between two flowable (e.g., viscoelastic) materials “on-the-fly” during printing is described herein. Also described is an analytical model developed to determine the relationships between the ink rheology, printing parameters (e.g., applied pressure and printing speed), and printed filament composition. The ability to print multiple materials from the same nozzle in a programmable manner opens new opportunities for creating functional matter with encoded compositional and property gradients defined solely by print path.

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[0020] Referring to FIG. 1, an exemplary printhead for multi-material 3D printing includes a nozzle body 100 comprising two ink delivery channels 102 joined together at a downstream end 104 of each channel 102 and comprising a single outlet 106. A syringe pump or other ink supply mechanism 120 may be in fluid communication with each of the ink delivery channels 102 for controlling the flow of ink into the nozzle body 100, as shown in the top image of FIG. 2. Components described as being “in fluid communication” are positioned relative to each other such that fluid flowing from one component can reach the other component. As will be discussed further below, a different ink formulation may be controllably flowed into each ink delivery channel 102. Generally speaking, the nozzle body 100 may include at least two, at least three, at least four, or at least five and up to 10 or up to 20 of the ink delivery channels 102.

[0021] The nozzle body 100 may also include a transition channel 108 downstream of the ink delivery channels 102, and an expansion channel 112 downstream of the transition channel 108. More specifically, the transition channel 108 may have an inlet 110 connected to the single outlet 106 of the ink delivery channels 102 and an outlet 116 connected to an inlet 114 of the expansion channel 112. The transition channel 108 may have a width d_2 , and the expansion channel 112 may have a width d_3 greater than the width d_2 to help achieve a sharp transition between different ink formulations. The expansion channel also has an outlet 118 through which a continuous filament comprising more than one material may be extruded.

[0022] The nozzle body 100 may be a monolithic body having a single-piece construction. Alternatively, the nozzle body may be a modular body comprising a multi-piece construction with a number of pieces assembled and secured together. The nozzle body may be fabricated by molding, 3D printing, machining or other methods known in the art. In some instances, the nozzle body may be assembled from commercially available and/or custom-fabricated parts.

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[0023] A close-up view of an exemplary custom-designed and fabricated microfluidic printhead for printing multiple inks through a single nozzle is shown in the lower image in FIG. 2. During printing, the nozzle is typically stationary and the substrate is translated using a 3-axis, motion-controlled gantry. Generally speaking, however, either (or both) of the nozzle and an underlying substrate may be configured for motion. Two independently-actuated syringe pumps may alternately or simultaneously push the inks through the two ink delivery channels and into the transition channel at the outlet of the nozzle. In the exemplary printhead of FIGs. 1 and 2, the ink delivery channels have a square transverse cross-section ($h = w = 200 \mu\text{m}$) with hydraulic diameter $d_1 = 200 \mu\text{m}$ and an approximate length $l_1 = 1000 \mu\text{m}$ (1 mm). The transition and expansion channels have diameters $d_2 = 200 \mu\text{m}$ and $d_3 = 400 \mu\text{m}$, respectively, and their lengths are $l_2 = l_3 = 200 \mu\text{m}$.

[0024] During serial printing of multiple inks, the small size of the transition channel can reduce the transition volume of the nozzle, taken as $V_T \approx \frac{\pi}{4} d_2^2 (h + l_2) = 12.6 nL$, thereby expediting the switching process between inks. The expansion channel is included to sharpen the transition between different materials in the printed filaments, as illustrated in FIG. 3A, for which the minimum estimated transition length is $L_T = \frac{4}{\pi} V_T / d_3^2 = 100 \mu\text{m}$. The magnitude of the transition length is typically close to the magnitude of the diameter d_3 . The small dimensions of the junction region may also mitigate the growth of interfacial instabilities between the materials, which can otherwise adversely affect the transition sharpness.

[0025] Each of the ink delivery channels may be oriented at an angle of from about 30° to about 90° with respect to a longitudinal axis of the transition channel. In the example shown in FIG. 1, the angle is 90° . Each channel may have a length l_1 , a width w and a height h , as discussed above, with a square, rectangular, triangular or semi-circular cross-section. The length l_1 is typically from about 0.5 mm to about 2 mm. A ratio of the width w to the height h may be from about 1 to about 1.5, and each of the width w

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and the height h may have a value in the range from about 10 microns to about 400 microns. The cross-sectional area of each ink delivery channel may be constant or may increase along the length of the channel in a direction away from the single outlet. Preferably, the width w of each of the ink delivery channels at the downstream end does not exceed the width d_2 of the transition channel at the inlet.

[0026] The longitudinal axis of the transition channel may be aligned with a longitudinal axis of the expansion channel, as shown in the exemplary printhead of FIG. 1. Typically, a length l_2 of the transition channel is from about 10 microns to about 400 microns. Each of the transition channel and the expansion channel may have a circular cross-section, where the width d_2 is a diameter d_2 and the width d_3 is a diameter d_3 . A ratio of d_3/d_2 may be at least about 1.5, or at least about 2. The width d_2 is typically from about 10 microns to about 400 microns, and the width d_3 is typically from about 20 microns to about 800 microns. The cross-section may be constant as a function of length, as shown. Alternatively, the cross-sectional area of one or both of the transition and expansion channels may vary along the length thereof.

[0027] In some embodiments, as shown in FIG. 1, there is no transition region between the transition channel and the expansion channel; that is, the width d_2 may exhibit an abrupt increase to the width d_3 . This may help to promote a sharper transition during serial printing of different inks. Alternatively, the printhead may be designed to include a transition region between the transition channel and the expansion channel where the width d_2 gradually increases to the width d_3 .

[0028] An extrusion-based method of printing multiple materials out of a single printhead, such as that described above in reference to FIG. 1, is set forth here. The method entails providing a nozzle body comprising at least a first ink delivery channel (for delivery of a first ink formulation into the nozzle body) and a second ink delivery channel (for delivery of a second ink formulation into the nozzle body) in fluid communication with a nozzle outlet.

The first and second ink formulations may flow through the nozzle outlet serially (e.g., alternately) during all or part of the extrusion-based printing method, as described in a first example below. Alternatively, the first and second ink formulations may flow through the nozzle outlet simultaneously during all or part of the extrusion-based printing method, also as described below.

[0029] Independently controlled pumps may be used to control the flow through the first and second ink delivery channels. More specifically, the first ink delivery channel may be operatively connected to a first pump and a second ink delivery channel may be operatively connected to second pump. Structures and/or devices that are “operatively connected” may be understood to be directly or indirectly connected such that the action of one device (e.g., the first pump) may have an effect on the other device (e.g., the first ink delivery channel). The flow may be volume-controlled or pressure-controlled.

[0030] For example, each of the first and second ink formulations may be forced to flow through the respective first and second delivery channels at a steady volumetric flow rate, which may lie in the range of from about 10 $\mu\text{L}/\text{min}$ to about 100 $\mu\text{L}/\text{min}$. Volume-controlled flow may be advantageous for precisely dispensing the desired volume of ink through the printhead. The first ink formulation may flow at a first steady volumetric flow rate Q_1 and the second ink formulation may flow at a second steady volumetric flow rate Q_2 , where Q_1 is controlled independently from Q_2 . The steady volumetric flow rate of the first ink formulation may thus be the same as or different from that of the second ink formulation.

[0031] Alternatively, each of the first and second ink formulations may be forced to flow through the respective first and second delivery channels at a steady pressure, which may lie in the range of 1 to 200 psi, or from about 5 kPa to about 1400 kPa, for example. The pressure applied to the first ink formulation may be the same as or different than the pressure applied to the second ink formulation.

[0032] In one example of the extrusion-based printing method, a first ink formulation may be forced to flow through the first ink delivery channel while a second ink formulation is prevented from flowing through the second delivery channel. Thus, a continuous filament comprising only the first ink formulation over a first predetermined length thereof may be extruded through the nozzle outlet. The second ink formulation may then be forced to flow through the second ink delivery channel while the first ink formulation is prevented from flowing through the first delivery channel. Accordingly, the continuous filament being extruded from the nozzle outlet may comprise, over a second predetermined length thereof, only the second ink formulation. The alternate flowing of the first and second ink formulations as described above may be repeated multiple times during the extrusion, if desired. Using this approach, a single continuous filament comprising multiple materials or ink compositions may be fabricated. The materials may alternate along all or part of the length of the single continuous filament.

[0033] In a second example of the method, a first ink formulation may be forced to flow through the first ink delivery channel while a second ink formulation is forced to flow through the second delivery channel. Thus, a continuous filament comprising both the first ink formulation and the second ink formulation over a predetermined length thereof may be extruded through the nozzle outlet. A single continuous filament comprising multiple materials may be fabricated according to this approach. Due to the simultaneous flowing of the first and second ink formulations, the multiple materials may be present together (*e.g.*, adjacent to each other laterally across the filament) along all or part of the length of the single continuous filament.

[0034] It is also contemplated that flow of the first and second ink formulations through the nozzle outlet may occur serially or alternately during one or more parts and simultaneously during other part(s) of the extrusion-based printing method. For example, alternating between flow of the first and second ink formulations as described above may comprise a

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transitioning step where simultaneous flow of the first and second inks can occur. For example, after forcing the first ink formulation through the first delivery channel but before forcing the second ink formulation through the second delivery channel, there may be a transition where the first ink formulation is being withdrawn from the first ink delivery channel and the second ink formulation is being introduced into the second delivery channel. The continuous filament being extruded from the nozzle outlet may thus comprise both the first ink formulation and the second ink formulation over a transition length thereof. The transition length may be sandwiched between the first predetermined length, which comprises only the first ink formulation, and the second predetermined length, which comprises only the second ink formulation. Over the transition length, a volume ratio of the first ink formulation to the second ink formulation may range from greater than 0 to less than 1. Typically, the transition length is about 600 microns or less.

[0035] Switching between the first and second ink formulations may entail applying decompressive and compressive pressure pulses to the first and second ink delivery channels, respectively. More specifically, withdrawing the first ink formulation from the first ink delivery channel may comprise applying a withdrawal pulse to the first ink delivery channel, thereby decompressing the first ink formulation, and introducing the second ink formulation into the second delivery channel may comprise applying an infusion pulse to the second ink delivery channel, thereby compressing the second ink formulation.

[0036] Similarly, alternating from flow of the second ink formulation to flow of the first ink formulation may comprise a transitioning step where, after forcing the second ink formulation through the second delivery channel, the second ink formulation is withdrawn from the second ink delivery channel while the first ink formulation is introduced into the first delivery channel. The withdrawal of the second ink formulation may comprise applying a withdrawal pulse to the second ink delivery channel, thereby decompressing the second ink formulation, and introducing the first

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ink formulation may comprise applying an infusion pulse to the first ink delivery channel, thereby compressing the first ink formulation. The continuous filament being extruded from the nozzle outlet may thus comprise both the second ink formulation and the first ink formulation over a transition length thereof, as described above. The transitioning may be carried out during the extrusion as desired to alternate the flow through the ink delivery channels. Consequently, the first and second predetermined lengths, which respectively comprise only the first and only the second ink formulations, may be separated along the length of the continuous filament by transition lengths.

[0037] The process is described for the case where the nozzle body comprises two ink delivery channels. However, the nozzle body used in the method may have any of the features described in this disclosure and is not limited to two ink delivery channels. For example, the nozzle body may include a plurality of ink delivery channels, where each ink delivery channel may be employed to deliver a different ink formulation. Accordingly, the continuous filament may comprise a plurality of ink formulations (e.g. different ink formulations A, B, C, and D) that alternate in a predetermined manner along the length of the continuous filament and/or which are printed simultaneously along a given length or lengths of the continuous filament, as described above. For example, a continuous filament may include along a first predetermined length only ink formulation A, along a second predetermined length only ink formulation B, along a third predetermined length only ink formulation C, and along a fourth predetermined length only ink formulations B and D. The continuous filament may further comprise transition lengths between the predetermined lengths that comprise, in this example, both ink formulations A and B, both ink formulations B and C, and the three ink formulations C, B and D, respectively. The switching of the inks may be carried out by withdrawing and introducing the ink formulations into the respective ink delivery channels as described above.

[0038] Each of the infusion and withdrawal pulses may be applied for a time duration of from about 0.5 sec to about 2 sec. Applying the infusion pulse may comprise increasing the pressure or the volumetric flow rate, depending on whether the printing process is pressure-controlled or flow rate-controlled. Similarly, applying the withdrawal pulse may comprise decreasing the pressure or the volumetric flow rate. Typically, each pulse is applied at a pulse strength of from about 20 to about 100 times the steady volumetric flow rate. For example, the infusion pulse may be applied at a pulse strength of from about 200 $\mu\text{L}/\text{min}$ to about 2000 $\mu\text{L}/\text{min}$, or from about 600 $\mu\text{L}/\text{min}$ to about 1600 $\mu\text{L}/\text{min}$, and the withdrawal pulse may be applied at a pulse strength from about -200 $\mu\text{L}/\text{min}$ to about -2000 $\mu\text{L}/\text{min}$.

[0039] A typical pumping protocol of set flow rates and corresponding pressures is provided in FIG. 3B. During steady printing of one ink (A) over time t_s , the pumping flow rate on syringe A is $Q_{p,A} = Q_s$, while $Q_{p,B} = 0$ for the other ink (B). The corresponding pressures in the syringes are $P_A = P_s$ and $P_B = P_m$. To generate the desired switching transition between the two inks, the pressures in syringes A and B may fall and rise, respectively, by $\Delta P_p = P_s - P_m$ within a fixed period of time t_p . To expedite this pressure change, an infusion pulse $Q_{p,B} = Q_p$ on syringe B and a withdrawal pulse $Q_{p,A} = -Q_w$ on syringe A may be simultaneously applied to rapidly compress and decompress the inks in each syringe. After this pulsing period, steady printing rates are resumed with $Q_{p,A} = 0$ and $Q_{p,B} = Q_s$. The process is reversed to switch back from ink B to A.

[0040] System compressibility can cause significant transient periods in microfluidic printheads as pressures adjust to sudden changes in imposed flow rates, and this can attenuate the sharpness of the transition between different inks, as illustrated in FIG. 3C. To develop a framework to qualitatively understand the effects, the printhead may be modeled as a combination of connected syringes (capacitors) and microchannels (resistors) with flow rates (current) that instantaneously adjust to the

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pressure drops (voltage) according to the Herschel-Bulkley (HB) model. For the model to be applicable, it is assumed that the pumps reliably and accurately achieve the set flow rates and they start and stop instantaneously, and the effects of compressibility can be described by a constant isothermal compressibility coefficient $\beta \equiv -\frac{1}{V}(\frac{\partial V}{\partial P})_T$ of the system, where $V = V_A = V_B$ is the net ink volume in each syringe. To achieve a steady flow rate through the nozzle outlet, it is preferred to maintain a constant pressure within the junction $P_j = P^* = P_0 + \Delta P_2(Q_s)$, where $\Delta P_2(Q_s)$ is the pressure drop from the junction to the outlet at Q_s . Hence, $P_s = P^* + \Delta P_1(Q_s)$, where $\Delta P_1(Q_s)$ is the pressure drop over the upstream channel between the syringe and the junction region. The minimum syringe pressure over the printing cycle may be described as $P_m = P^* + \Delta P_Y$, where $\Delta P_Y = 4 \frac{l_1}{d_1} \tau_Y$ is the minimum pressure drop below which the yield stress of the material is sufficient to prevent any appreciable flow from the syringe into the junction region. Accordingly, it can be shown that the desired pulse and withdrawal values to achieve full transition between materials during the pulsing step can be determined from:

$$Q_{p,FT} \approx Q_{w,FT} + Q_s \approx \frac{V}{t_p} \beta \Delta P_p \quad (1)$$

[0041] Hence, to attain low variations in the filament diameter, the ideal withdrawal flow rate can be determined from $Q_{w,FT} = Q_{p,FT} - Q_s$.

Consequently, for all printed structures, the value of the withdrawal pulse may be selected so that $Q_w = Q_p - Q_s$.

[0042] The method described herein may be applicable to any ink formulation. Broadly speaking, the ink formulations employed for printing may comprise a flowable material, such as a viscoelastic material. More specifically, the ink formulation may comprise a shear-thinning material. In one example, the ink formulations comprise a polymer, such as polydimethylsiloxane (PDMS).

[0043] To demonstrate the multi-material printing capabilities of the printhead described above, model viscoelastic inks based on PDMS elastomers of varying composition are printed in one-, two-, and three-dimensional architectures. Referring to Table 1, five exemplary PDMS inks are formulated using a combination of 2-part SE 1700 (Dow Corning), anhydrous hexanes (95% purity, Sigma Aldrich), and silicone oil (Thermo Fisher Scientific). Red Silc Pig silicone pigment (Smooth-On) and CdSeS/ZnS 6 nm quantum dots (QD) with emission peaks at either 490 nm or 630 nm (Sigma Aldrich) are added as color modifiers. The ratio of base and catalyst is varied for certain inks to affect the compliance of the printed structure after curing.

Table 1. Exemplary Elastomer Ink Formulations (in wt.%)

<i>Ink</i>	<i>PDMS Base</i>	<i>PDMS Catalyst</i>	<i>Silicone Oil</i>	<i>Red Pigment</i>	<i>Red QD</i>	<i>Green QD</i>	<i>Hexane</i>
A	83.0	0	16.6	0	0.4	0	0
B	83.0	0	16.6	0	0	0.4	0
C	78.6	7.8	0	3.6	0	0	10
D	81.8	8.2	0	0	0	0	10
E	87.1	2.9	0	0	0	0	10

[0044] The rheological behavior of the PDMS inks under steady shear is shown in FIG. 4. The filled symbols correspond to data taken on a rotational rheometer and the hollow symbols indicate data taken using a capillary rheometer. Both the Bagely correction and the Weissenberg-Rabinowitsch correction were applied to the capillary data. The black solid line is the fit of the HB model to formulations A and B. The ink exhibits a shear thinning response with an apparent viscosity of $\eta = 91 \text{ Pa}\cdot\text{s}$ at a shear rate of $\dot{\gamma} = 10 \text{ s}^{-1}$ and a shear yield stress of $\tau_Y = 550 \text{ Pa}$. The ink is well described by the HB model:

$$\tau = \eta(\dot{\gamma})\dot{\gamma} = \tau_Y + K\dot{\gamma}^n \quad (2)$$

[0045] where $K = 80 \text{ Pa}\cdot\text{s}^{0.65}$ is the consistency index, and $n = 0.66$ is the power-law exponent.

[0046] To evaluate the ability to seamlessly transition between viscoelastic inks, two model inks comprising PDMS dyed with different fluorescent QDs (formulations A-B) are printed at a constant gap height of 400 μm and at a print speed of 2.65 mm/s ($Q_s = 20 \mu\text{L}/\text{min}$) over a controlled range of pulse strengths, $200 < Q_p < 2,000 \mu\text{L}/\text{min}$. The spatial distribution of each ink along the printed filament is determined using confocal microscopy coupled with image analysis. The transition length equals the distance along the filament over which the fraction of red ink F_A varies from 80% and 20%. A representative printed filament ($Q_p = 1,600 \mu\text{L}/\text{min}$) is shown adjacent to intensity profiles obtained from different pulse strengths in FIGs. 5A and 5B.

[0047] For pulse values below $Q_p < 600 \mu\text{L}/\text{min}$, the transition is too weak to determine a transition length according to the stated metric. For higher pulse values ($600 < Q_p < 1,200 \mu\text{L}/\text{min}$), the compression in the syringes is large enough to generate syringe pressures to drive transitions greater than 60%, with transition length monotonically decreasing with Q_p . These cases represent partial transition of the interface between the materials across the outlet of the nozzle. The minimum pulse value for full transition is $Q_{p,FT} = 1,200 \mu\text{L}/\text{min}$, corresponding to $\beta = 3.4 \times 10^{-8} \text{ Pa}^{-1}$ according to Eq. (1), which is within the range of compressibility for PDMS materials. This value of β is used to compare model predictions for the HB fluid against the experimentally measured transition length and standard deviation in filament width, as shown in FIGs. 5C and 5D. For pulse values between $1,200 < Q_p < 1,600 \mu\text{L}/\text{min}$ the transition length continues to decrease with increasing Q_p , but the variation in the filament width increases due to larger fluctuations in the junction pressure during the transition process. The transition length reaches a minimum of approximately 520 μm at $Q_p = 1,600 \mu\text{L}/\text{min}$. At higher values of $Q_p > 1,600 \mu\text{L}/\text{min}$, the transition length and the width variation increase with Q_p . This trend may be caused by sufficiently large suction pressures during ink withdrawal, causing partial

retraction of the filament into the syringe, as well as limitations in the pump accuracy and backlash between the syringe plunger and pump ram. To achieve sharp transitions, a pulse value $Q_p \geq 1,600 \mu\text{L}/\text{min}$ may be used as a starting point for printing (e.g., with PDMS inks (C-E)).

[0048] To demonstrate multi-material 3D printing of viscoelastic inks, one-, two- and three-dimensional (1D, 2D, and 3D) architectures composed of elastomeric inks of varying composition and mechanical properties are created, as shown in FIGs. 6A-6B. First, 1D continuous filaments with small alternating bands present along the length are printed to demonstrate repeated switching between two viscoelastic inks on a length scale corresponding to the filament diameter. Next, a 2D structure containing segments of varying lengths to form the letter H is printed. Then, 3D periodic structures are created in which material transitions occur in the gaps spanning across orthogonal filaments in the underlying layers. As a final demonstration, highly integrated 3D architectures composed of elastomeric materials with different mechanical stiffness are printed. Specifically, alternating bands of different inks are interdigitated in patterns to form printed matrices that exhibit different necking behavior. These initial demonstrations highlight the ability to programmably control the local compositional and mechanical properties within 3D printed objects.

[0049] Multi-material 3D printing using microfluidic printheads specifically optimized for patterning viscoelastic inks has been demonstrated. Also developed in the course of this work is an analytical model of viscoelastic ink flow, from which scaling relationships can be derived to enable printhead optimization. Using the printheads described herein, 3D architectures can be printed with sharp transitions between different materials from a single nozzle in a controlled and repeatable manner. In addition, 3D architectures may be patterned with programmable compositional and mechanical property gradients over length scales below the characteristic nozzle dimensions. The ability to rapidly switch between multiple inks within a

single nozzle printhead not only greatly simplifies tool path planning, but opens new opportunities for the programmable assembly of functional matter.

Experimental Section

[0050] *Elastomeric Inks:* Each ink is prepared by adding one component at a time, proceeding from left to right in Table 1. After each addition, the inks are mixed in a planetary centrifugal mixer (Thinky Mixer) at 2000 rpm for 180 seconds followed by 30 seconds of centrifugation. Inks A and B are mixed with 4 μL of QD suspended in toluene per gram of PDMS. Inks C and D are designed to print structures that could be cured, using a 1:10 ratio by mass of catalyst to base. Hexane serves as a rheological modifier to lower the viscosity and evaporates quickly upon printing. Ink C contains red pigment. Finally, Ink E contains a catalyst to base ratio of 1:30, yielding a more compliant elastomeric matrix than those with a 1:10 ratio.

[0051] *Ink Rheology:* The ink viscosity is measured at $\dot{\gamma} \lesssim 1 \text{ s}^{-1}$ using a 40-mm, 2° cone-and-plate on a stress-controlled rotational rheometer (AR2000ex, TA Instruments). At higher shear rates $1 \lesssim \dot{\gamma} \lesssim 1000 \text{ s}^{-1}$, the ink rheology is measured using a custom-built capillary rheometer. This system consists of a syringe pump (PHD Ultra, Harvard Apparatus), 1.0 mL glass Luer lock syringe (Hamilton Gastight), a diaphragm pressure transducer (PX44E0-1KGI, Omega Engineering) and disposable Luer lock needle tips (Norsdon EFD). Capillaries with inner radius $R = 514 \mu\text{m}$ lengths from $L = 12.9 \text{ mm}$, 25.4 mm, and 38.3 mm are used. The total pressure drop ΔP_{tot} across the transducer housing and capillary is measured over a range of imposed flow rates. These measurements are repeated using capillaries of the same diameter, but increasing lengths, and the Bagely correction is applied to determine the actual pressure drop across the capillary, ΔP_{cap} . These values are then related to the wall shear stress by $\tau_w = \frac{1}{2} R \Delta P_{cap}$. The Weissenberg-Rabinowitsch correction is applied to account for shear-thinning and to determine the true wall shear rate using:

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$$\dot{\gamma}_t = \frac{\dot{\gamma}_a}{3} \left[2 + \frac{d \ln \dot{\gamma}_a}{d \ln \tau_w} \right] \quad (3)$$

[0052] where $\dot{\gamma}_a = \frac{4Q}{\pi R^3}$ is the wall shear rate of a Newtonian fluid corresponding to the volumetric flow rate Q . Finally, a third order polynomial is fit to five consecutive data points to numerically determine the local differential correction term for each data point.

[0053] *Microfluidic Printheads:* The printheads are machined from acrylic (McMaster Carr) in four pieces using a CNC-mill (Wabeco). Two pieces formed the microchannels and the other two formed the tapped inlets for the inks. Polished (Buelar EcoMet250) surfaces are solvent welded together by soaking the surfaces in acetone for one minute then pressing them together. Fine features are preserved during solvent welding by infilling them with wax prior to solvent welding. The outlet is machined into the printhead after all four pieces are solvent-welded together. The nozzle body is then machined down and polished to remove excess materials and Leur lock adapters are screwed into the inlets. Finally, the wax is removed from the microchannels.

[0054] *Modeling Fluid Flow:* To model fluid flow through the microfluidic printhead, the Reynolds number given by: $Re = \rho U d_2 / \eta(\dot{\gamma})$ is first calculated, where ρ is the density of the fluid, $U = Q / \frac{\pi}{4} d_2^2$ is the mean velocity in the narrow section of the printhead, and $\eta(\dot{\gamma})$ is the rate dependent viscosity described by the HB model at the characteristic shear rate $\dot{\gamma} = U / d_2$ in the flow through the nozzle. Even at the highest flow rates $Re < 10^{-5}$, so the ink flow is laminar.

[0055] The governing equations for the evolution of the pressure in each syringe are determined from a mass balance on each syringe

$$V_A \beta \frac{dP_A}{dt} = Q_{p,A}(t) - Q_A(t) \quad (4)$$

$$V_B \beta \frac{dP_B}{dt} = Q_{p,B}(t) - Q_B(t) \quad (5)$$

[0056] where Q_A and Q_B are the net volumetric flow rates of material exiting each syringe. The syringe volumes are assumed to be equal ($V_A = V_B = V$) and are approximated as constant in time, since very small

volumes of ink are printed compared to the syringe volume. Density changes in the nozzle junction are neglected, and the flow rate through the nozzle is determined from a mass balance on the junction:

$$Q_J(t) = Q_A(t) + Q_B(t) \quad (6)$$

[0057] The relationship between pressure drop ΔP_i and net volumetric flow rate Q_i through any channel is determined by the equation for steady flow of a HB fluid through a cylindrical pipe with radius r_i and length l_i

$$Q_i = \pi r_i^3 \left(\frac{\sigma_Y}{K} \right)^m \frac{1}{m+1} \frac{\alpha^{m+1}}{(1-\alpha)^m} \left[1 - \frac{2\alpha}{m+2} + \frac{2\alpha^2}{(m+2)(m+3)} \right] \quad (7)$$

[0058] where $m \equiv 1/n$, $\alpha \equiv 1 - \tau_Y/\tau_W$, $\tau_W = \frac{1}{2} \frac{r_i}{l_i} \Delta P_i$. For Q_A and Q_B , $r_i = \frac{1}{2}d_1$, $l_i = l_1$ and $\Delta P_i = P_i - P_J$, while for Q_J , $r_i = \frac{1}{2}d_2$, $l_i = l_2$ and $\Delta P_i = P_J - P_0$ where $P_0 = 0$.

[0059] Eqs. (4)–(7) yield a system of coupled differential equations to determine the evolution of the pressures and flow rates in the nozzle. During the start-up process, $Q_A = Q_B = \frac{1}{2}Q_s$; hence, the initial conditions for pressures P_A , P_B and P_J are determined by implicitly solving Eq. (7) for these imposed flow rates. For Newtonian materials with the same viscosity μ , Eq. (7) becomes $Q_i = \frac{\pi r_i^4}{8\mu l_i} \Delta P_i$, for which Eqs. (4)–(5) are linear and can be solved exactly. However, for HB materials, Eqs. (4)–(5) are non-linear, but can be approximated using a first order Maclaurin series in time t to determine the evolution of the pressure profile

$$P_i(t + \Delta t) \approx P_i(t) + \frac{\Delta t}{V\beta} (Q_{p,i}(t) - Q_i(t)) \quad (9)$$

[0060] where Δt is the elapsed time of either the pulse $\Delta t = t_p = 0.5 \text{ sec}$ or the steady extrusion $\Delta t = t_s = 2 \text{ sec}$. This equation is sequentially evolved from the initial conditions until the long-term oscillatory state is attained.

[0061] *Multi-Material 3D Printing:* Inks (3 mL) are loaded into the syringes and then centrifuged in custom holders at 3,000 RPM (IEC Centra CL2, Thermo Scientific) for 1 hour. Hexane is then pulled into each syringe and

quickly expelled to assist with removal of air at the exit of the syringe. Inks are printed through the microfluidic printhead using two opposed syringe pumps (PHD Ultra, Harvard Apparatus).

[0062] A confocal microscope (LSM710, Zeiss) is used to image the printed filaments. A 7 x 7 array of z-stacks is generated using a commercial stitching algorithm (Imaris 7.6.4, Bitplane Scientific Software) from $\Delta z = 9$ μm increments. The intensity of each image is rescaled to compensate for the minimal level of speckling caused by QD aggregates in the PDMS. The slices are then summed and scaled to generate the final images, which are analyzed using Matlab (MathWorks) to determine the transition length and variation in filament width. This analysis is similar to the procedure for identifying edge sharpness according to the ISO-13660 protocols. Line edges are defined as the point from the top and bottom edge of the image for which the signal intensity is above the background noise for at least five consecutive pixels.

[0063] Since the printing speed is held constant, a large value of $Q_p \gg Q_s$ is important for purging the finite volume of the previous material in nozzle junction as quickly as possible to maintain abrupt transitions in the printed structure. There are, however, practical limitations on the upper bound of the pulse strength that can be imposed. Firstly, the derivation of Eq. (1) assumes that the transient pressure profile is purely due to material compression. Mechanical backlash in the syringe pump, syringe or nozzle, or the connections between these elements may also influence the pressure during the transition. Any air bubbles in the ink can strongly affect system compressibility. A further source of error may be related to a limited synchronization of the two pumps, defined by being Δt_{sync} out of synchronization. This error may arise at the beginning and ending of each transition when, for a short time, only one pump is running at the full pulse strength. The amount of ink pumped or not pumped during the beginning or end of the transition is given by $Q_p \Delta t_{sync}$. These complicating factors are

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dependent on the ink formulation, loading, and setup of the printing system. Thus, Eq. (1), though instructive, may be only qualitatively valid for this system, and calibration may be required for each material.

[0064] Although the present invention has been described in considerable detail with reference to certain embodiments thereof, other embodiments are possible without departing from the present invention. The spirit and scope of the appended claims should not be limited, therefore, to the description of the preferred embodiments contained herein. All embodiments that come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein. Furthermore, the advantages described above are not necessarily the only advantages of the invention, and it is not necessarily expected that all of the described advantages will be achieved with every embodiment of the invention.

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CLAIMS

1. A printhead for 3D printing of multiple materials, the printhead comprising:
 - a nozzle body comprising:
 - at least two ink delivery channels joined together at a downstream end of each channel and comprising a single outlet;
 - a transition channel having an inlet connected to the single outlet of the ink delivery channels, the transition channel comprising a width d_2 ; and
 - an expansion channel having an inlet connected to an outlet of the transition channel, the expansion channel comprising a width d_3 greater than the width d_2 ,
 - wherein the expansion channel comprises an outlet for extrusion therethrough of a continuous filament comprising more than one material.
2. The printhead of claim 1, wherein the nozzle body is a monolithic body comprising a single piece.
3. The printhead of claim 1, wherein the nozzle body is a modular body comprising multiple pieces.
4. The printhead of any one of claims 1-3, wherein each of the ink delivery channels is oriented at an angle of from about 30° to about 90° with respect to a longitudinal axis of the transition channel.
5. The printhead of claim 4, wherein the longitudinal axis of the transition channel is aligned with a longitudinal axis of the expansion channel.

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6. The printhead of any one of claims 1-5, wherein a cross-sectional area of each of the ink delivery channels is constant or increases along a length thereof in a direction away from the single outlet.

7. The printhead of any one of claims 1-6, wherein a cross-sectional area of each of the transition channel and the expansion channel is constant or variable along a length thereof.

8. The printhead of any one of claims 1-7, wherein a width w of each of the ink delivery channels at the downstream end does not exceed the width d_2 of the transition channel at the inlet thereof.

9. The printhead of any one of claims 1-8, wherein each of the ink delivery channels comprises a square, rectangular, triangular or semi-circular cross-section.

10. The printhead of any one of claims 1-9, wherein each of the ink delivery channels comprises a width w and a height h , and wherein a ratio of the width w to the height h is from about 1 to about 1.5.

11. The printhead of claim 10, wherein each of the width w and the height h is from about 10 microns to about 400 microns.

12. The printhead of any one of claims 1-11, wherein each of the transition channel and the expansion channel comprises a circular cross-section, the width d_2 being a diameter d_2 and the width d_3 being a diameter d_3 .

13. The printhead of any one of claims 1-12, wherein a ratio of d_3/d_2 is at least about 1.5.

14. The printhead of claim 13, wherein the ratio of d_3/d_2 is at least about 2.

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15. The printhead of any one of claims 1-14, wherein the width d_2 is from about 10 microns to about 400 microns.

16. The printhead of any one of claims 1-15, wherein the width d_3 is from about 20 microns to about 800 microns.

17. The printhead of any one of claims 1-16, wherein each of the ink delivery channels comprises a length l_1 of from about 0.5 mm to about 2 mm.

18. The printhead of any one of claims 1-17, wherein a length l_2 of the transition channel is from about 10 microns to about 400 microns.

19. The printhead of any one of claims 1-18, further comprising a transition region between the transition channel and the expansion channel where the width d_2 gradually increases to the width d_3 .

20. The printhead of any one of claims 1-18, wherein there is no transition region between the transition channel and the expansion channel, the width d_2 abruptly increasing to the width d_3 .

21. A method of printing multiple materials out of a single printhead, the method comprising;

providing a nozzle body comprising at least a first ink delivery channel and a second ink delivery channel in fluid communication with a nozzle outlet;

forcing a first ink formulation to flow through the first ink delivery channel while preventing a second ink formulation from flowing through the second delivery channel, thereby extruding through the nozzle outlet a continuous filament comprising only the first ink formulation over a predetermined length thereof; and

forcing the second ink formulation to flow through the second ink delivery channel while preventing the first ink formulation from flowing

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through the first delivery channel, wherein the continuous filament being extruded from the nozzle outlet comprises only the second ink formulation over a predetermined length thereof,

thereby 3D printing a single continuous filament comprising multiple materials.

22. The method of claim 21, further comprising transitioning from the first ink formulation to the second ink formulation, the transitioning comprising, after forcing the first ink formulation to flow through the first delivery channel, withdrawing the first ink formulation from the first ink delivery channel while introducing the second ink formulation into the second delivery channel.

23. The method of claim 22, wherein withdrawing the first ink formulation from the first ink delivery channel comprises applying a withdrawal pulse to the first ink delivery channel, and wherein introducing the second ink formulation into the second delivery channel comprises applying an infusion pulse to the second ink delivery channel, thereby decompressing the first ink formulation while compressing the second ink formulation, wherein the continuous filament being extruded from the nozzle outlet comprises both the first ink formulation and the second ink formulation over a transition length thereof.

24. The method of claim 23, wherein the transition length is about 600 microns or less.

25. The method of any one of claims 23-24, wherein the infusion pulse and the withdrawal pulse are applied for a time duration of from about 0.5 sec to about 2 sec.

26. The method of any one of claims 21-25, wherein each of the first and second ink formulations is forced to flow through the respective first and second delivery channels at a steady volumetric flow rate.

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27. The method of claim 26, wherein the steady volumetric flow rate is from about 10 $\mu\text{L}/\text{min}$ to about 100 $\mu\text{L}/\text{min}$.

28. The method of claim 26 or 27, wherein the steady volumetric flow rate of the first ink formulation is the same as or different from that of the second ink formulation.

29. The method of any one of claims 23-28, wherein each of the infusion pulse and the withdrawal pulse is applied at a pulse strength of from about 20 to about 100 times the steady volumetric flow rate.

30. The method of any one of claims 23-29, wherein the infusion pulse is applied at a pulse strength of from about 200 $\mu\text{L}/\text{min}$ to about 2000 $\mu\text{L}/\text{min}$.

31. The method of claim 30, wherein the pulse strength is from about 600 $\mu\text{L}/\text{min}$ to about 1600 $\mu\text{L}/\text{min}$.

32. The method of any one of claims 23-31, wherein the withdrawal pulse is applied at a pulse strength from about -200 $\mu\text{L}/\text{min}$ to about -2000 $\mu\text{L}/\text{min}$.

33. The method of any one of claims 21-25, wherein each of the first and second ink formulations is forced to flow through the respective first and second delivery channels at a steady pressure.

34. The method of claim 33, wherein applying the infusion pulse comprises increasing the pressure and wherein applying the withdrawal pulse comprises decreasing the pressure.

35. The method of any one of claims 21-34, wherein the first ink delivery channel is operatively connected to a first pump and a second ink delivery channel is operatively connected to second pump.

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36. The method of any one of claims 21-35, wherein the ink formulation comprises a polymer.

37. The method of any one of claims 21-36, wherein the ink formulation comprises PDMS.

38. The method of any one of claims 21-37, further comprising repeating the forcing and applying as desired,
wherein, after forcing the second ink formulation to flow through the second delivery channel, a withdrawal pulse is applied to the second ink delivery channel while an infusion pulse is applied to the first ink delivery channel, thereby decompressing the second ink formulation while compressing the first ink formulation, wherein the continuous filament being extruded from the nozzle outlet comprises both the second ink formulation and the first ink formulation over a transition length thereof.

39. A method of printing multiple materials out of a single printhead, the method comprising;
providing a nozzle body comprising at least a first ink delivery channel and a second ink delivery channel in fluid communication with a nozzle outlet;

forcing a first ink formulation to flow through the first ink delivery channel while forcing a second ink formulation to flow through the second delivery channel, thereby extruding through the nozzle outlet a continuous filament comprising the first ink formulation and the second ink formulation over a predetermined length thereof.

40. The method of claim 39, wherein each of the first and second ink formulations is forced to flow through the respective first and second delivery channels at a steady volumetric flow rate.

41. The method of claim 39 or 40, wherein a volume ratio of the first ink formulation to the second ink formulation over the predetermined

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length of the continuous filament may range from greater than 0 to less than 1.

42. The method of any one of claims 39-41, wherein the first ink formulation flows at a first steady volumetric flow rate Q_1 and the second ink formulation flows at a second steady volumetric flow rate Q_2 , Q_1 being controlled independently from Q_2 .

43. The method of claim 39, wherein the first and second ink formulations are forced to flow through the respective first and second delivery channels at a steady pressure.

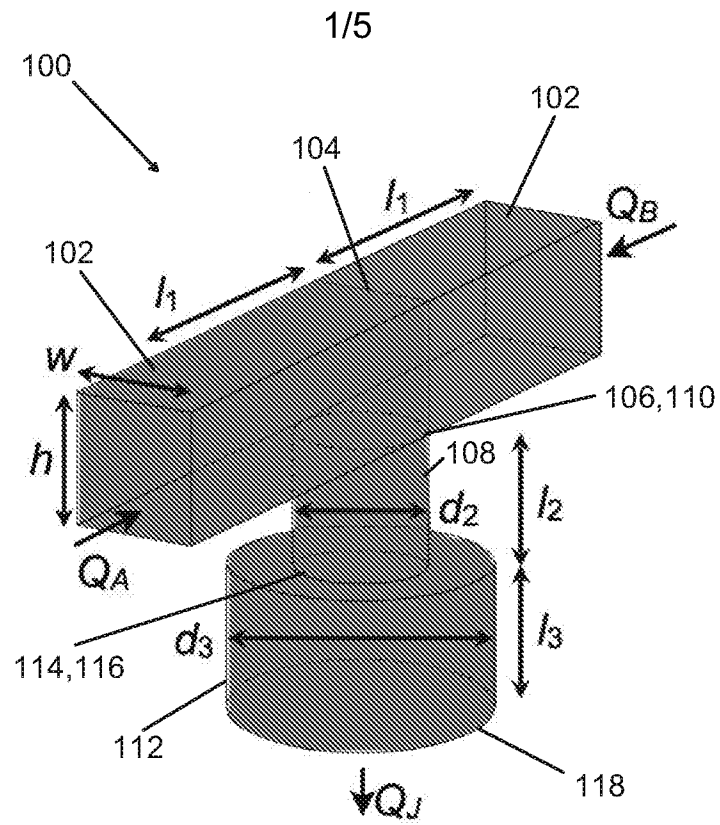


FIG. 1

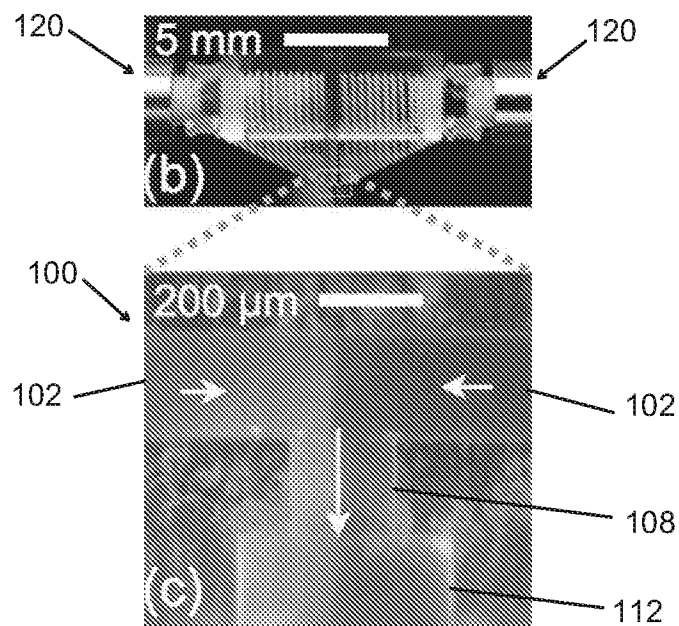


FIG. 2

FIG. 3A

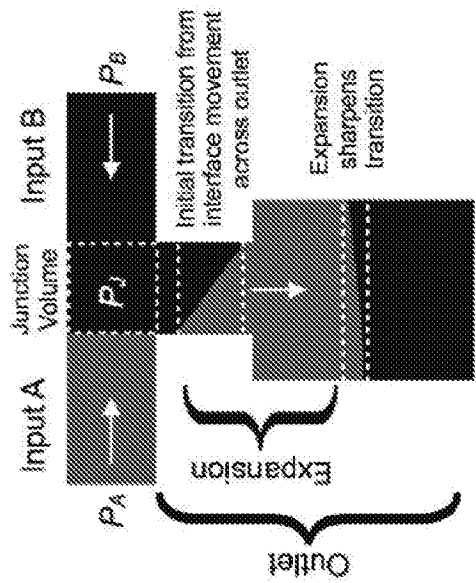


FIG. 3B

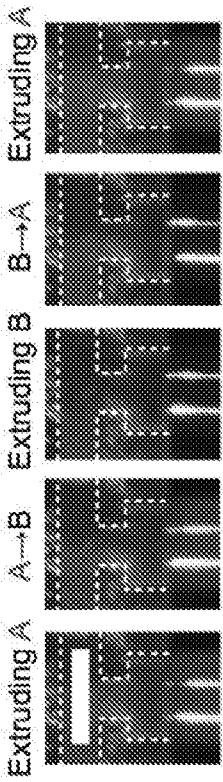
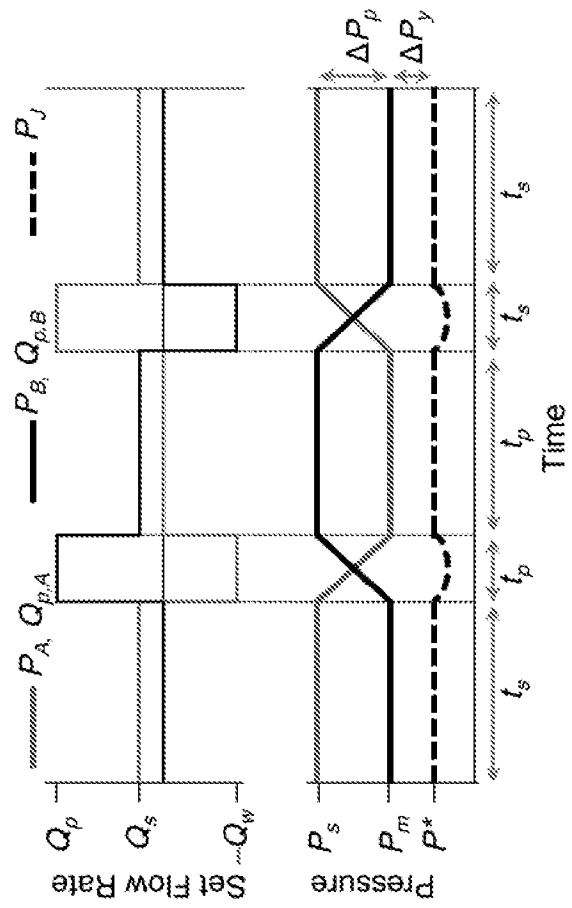


FIG. 3D

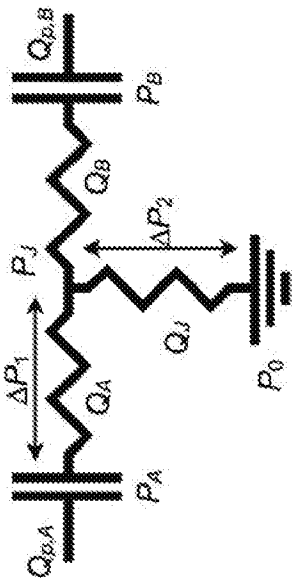


FIG. 3C

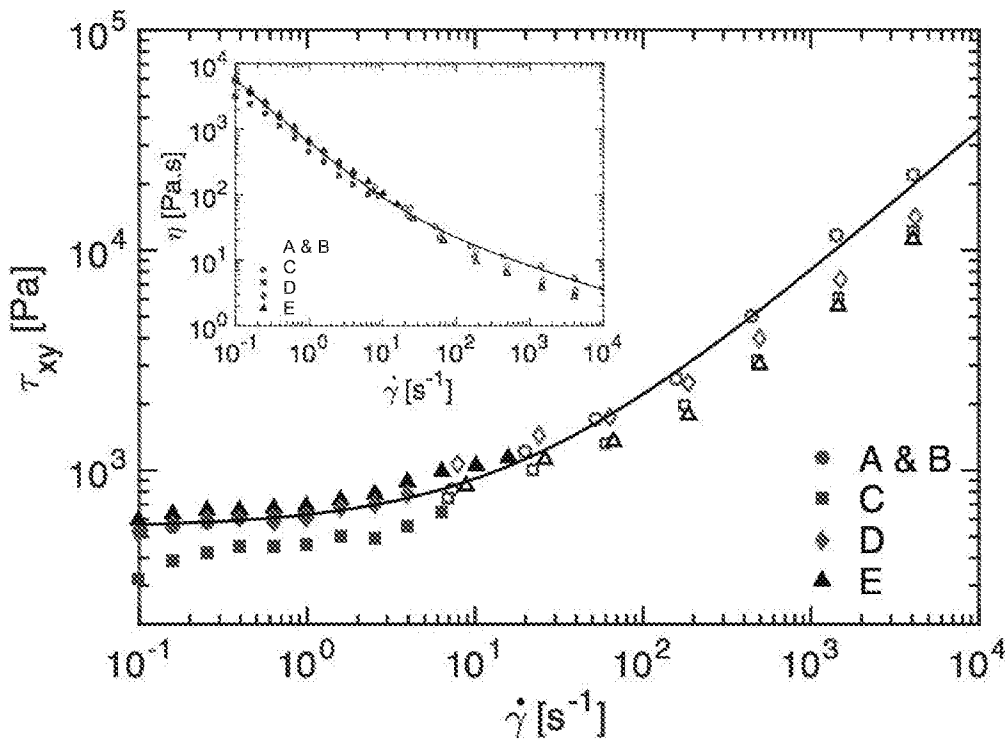


FIG. 4

FIG. 5A

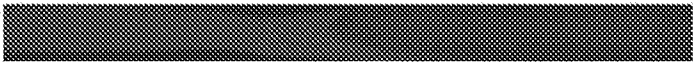
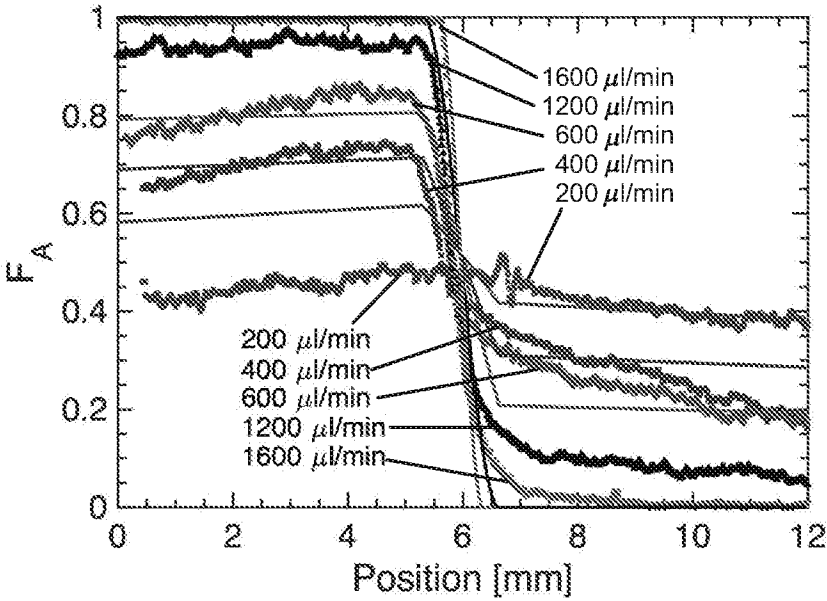


FIG. 5B



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FIG. 5C

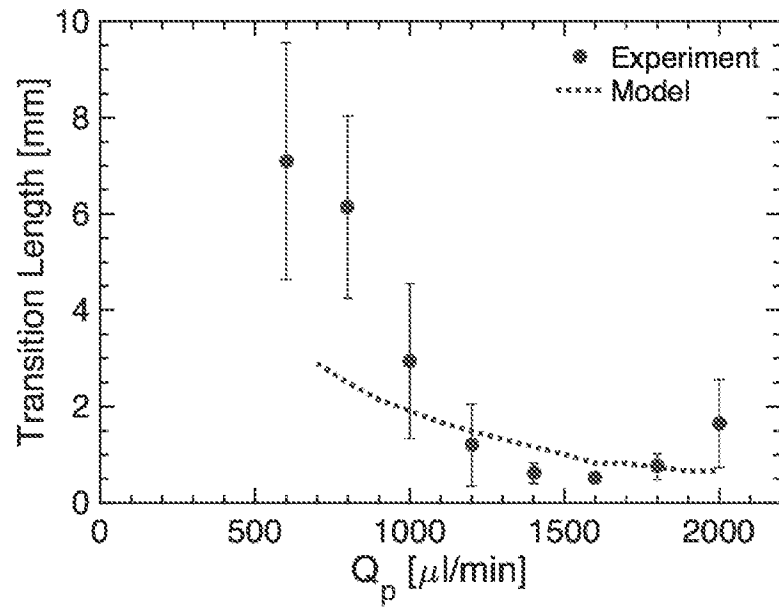


FIG. 5D

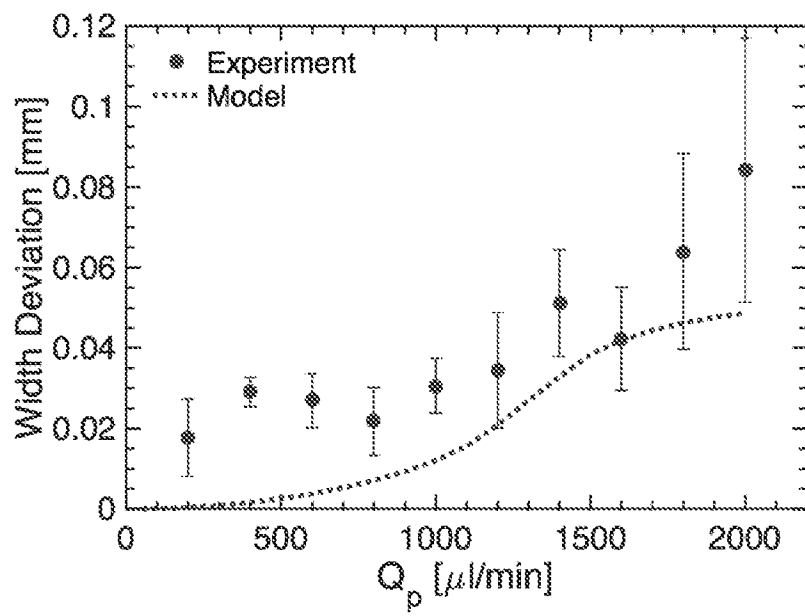


FIG. 6A

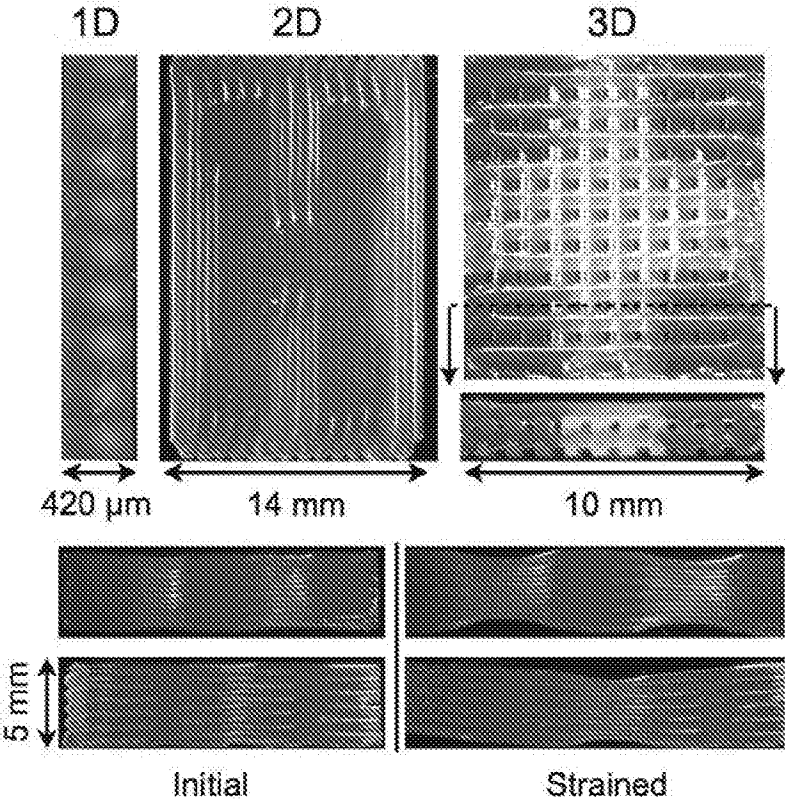


FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/21738

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 23/532; B41J 2/14; B29C 67/00 (2016.01)

CPC - H01L 23/532; B41J 2/14; B29C 67/0055

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): H01L 23/532; B41J 2/14, 2/16; B29C 67/00 (2016.01)

CPC: H01L 23/532; B41J 2/14, 2/16; B29C 67/0055, 67/0085

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google; Google Scholar; EBSCO; KEYWORDS: printhead 3D printing materials nozzle body ink delivery channels outlet inlet transition channel width expansion channel extrusion filament

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/209994 A2 (PRESIDENT AND FELLOWS OF HARVARD COLLEGE) December 31, 2014; figure 4; paragraphs [0078, 0080-0081]	1-5
Y	US 2014/0314954 A1 (LEWIS, J. et al.) October 23, 2014; figure 2; paragraphs [0050-0051]	1-5
A	US 8,827,684 B1 (SCHUMACHER, N. et al.) September 09, 2014; entire document	1-5

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 May 2016 (23.05.2016)

Date of mailing of the international search report

05 AUG 2016

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/21738

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-20, 26 38, 42
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-5

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

---Continued from Box III---

The application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fee must be paid.

Group I: Claims 1-5 are directed towards a printhead for 3D printing of multiple materials comprising: a transition channel having an inlet connected to the single outlet of the ink delivery channels, the transition channel comprising a width d_2 ; and an expansion channel having an inlet connected to an outlet of the transition channel.

Group II: Claims 21-25 are directed towards a method of printing multiple materials out of a single printhead, the method comprising: forcing a first ink formulation to flow through the first ink delivery channel while preventing a second ink formulation from flowing through the second delivery channel, thereby extruding through the nozzle outlet a continuous filament comprising only the first ink formulation over a predetermined length thereof; and forcing the second ink formulation to flow through the second ink delivery channel while preventing the first ink formulation from flowing through the first delivery channel, wherein the continuous filament being extruded from the nozzle outlet comprises only the second ink formulation over a predetermined length thereof.

Group III: Claims 30-41 are directed towards a method of printing multiple materials out of a single printhead, the method comprising: forcing a first ink formulation to flow through the first ink delivery channel while forcing a second ink formulation to flow through the second delivery channel, thereby extruding through the nozzle outlet a continuous filament comprising the first ink formulation and the second ink formulation over a predetermined length thereof.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. Group I has at least a transition channel; and an expansion channel that Groups II-III do not have. Group II has at least preventing a second ink formulation from flowing through the second delivery channel; and preventing the first ink formulation from flowing through the first delivery channel that Groups I & III do not have. Group III has at least extruding through the nozzle outlet a continuous filament comprising the first ink formulation and the second ink formulation over a predetermined length thereof that Groups I-II do not have.

The common technical features of Groups I-III are a printhead for 3D printing; a nozzle body; at least two ink delivery channels; and a continuous filament comprising more than one material.

These common features are disclosed by WO 2014209994 A2 to President and Fellows of Harvard College (hereinafter "Harvard") which discloses a printhead for 3D printing (3D printhead; paragraph [0008]); a nozzle body (printhead comprises at least one nozzle for extruding and depositing filaments; paragraph [0008]); at least two ink delivery channels (more than one nozzle may be used, where each nozzle has an internal cavity for allowing filaments to flow therethrough; paragraphs [0008, 0036]; claim 17 of Harvard); and a continuous filament comprising more than one material (unitary 3D functional part that is printed by 3D printer may comprise structural and conductive filaments (more than one material); paragraphs [0006, 0008]; claim 17 of Harvard).

Since the common technical features are previously disclosed by the Harvard reference, these common features are not special and so Groups I-III lack unity.