(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 September 2016 (15.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/145309 A1

(51) International Patent Classification:
H05K 1/03 (2006.01) *H05K 3/16* (2006.01)
H05K 1/02 (2006.01) *C09D 11/033* (2014.01)

(21) International Application Number:
PCT/US2016/022005

(22) International Filing Date:
11 March 2016 (11.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/131,778 11 March 2015 (11.03.2015) US

(71) Applicant: **PRESIDENT AND FELLOWS OF HARVARD COLLEGE** [US/US]; 17 Quincy Street, Cambridge, MA 02138 (US).

(72) Inventors: **LEWIS, Jennifer, A.**; 3 Grant Street, #3, Cambridge, MA 02138 (US). **BUSBEE, Travis, A.**; 17 Willow Avenue, Apt. 2, Somerville, MA 02144 (US). **VALENTINE, Alexander, D.**; 19 Pleasant Street. Apt. 4, Cambridge, MA 02139 (US). **LIND, Johan, U.**; 2 Lime Street, Apt. 41, Boston, MA 02108 (US).

(74) Agent: **RITTNER, Mindy, N.**; Brinks Gilson & Lione, P.o. Box 10087, Chicago, IL 60610 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2016/145309 A1

(54) Title: 3D PRINTED FLEXIBLE ELECTRONIC DEVICE

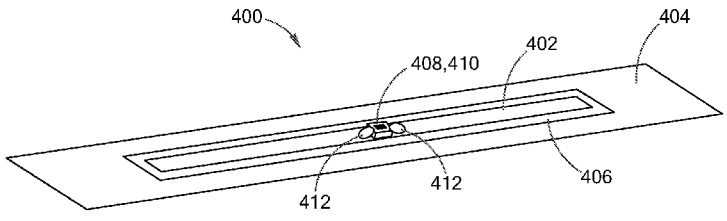


FIG. 4A

(57) Abstract: A method of 3D printing a flexible electronic device comprises depositing one or more conductive filaments in a pre-determined pattern on a substrate, where the one or more conductive filaments comprise a conductive ink formulation comprising a polar solvent, a thermoplastic elastomer, and a plurality of electrically conductive particles. The polar solvent is evaporated to dry the one or more conductive filaments, thereby forming a 3D printed conductive structure on the substrate.

3D PRINTED FLEXIBLE ELECTRONIC DEVICE

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. 62/131,778, filed on March 11, 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 S-875-040-017 awarded by the Air Force Research Laboratory/RXAS and contract number B606991 awarded by the Lawrence Livermore National Laboratory. 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.

BACKGROUND

[0004] The development of stretchable electronics is paving the way for advancements in soft robotics, wearable sensors and flexible displays, among other technologies. In some cases, building functional soft electronic devices can require integrating soft materials with rigid, wafer-based electronic components. Also or alternatively, stretchable electronics may be combined with flexible substrates or fabrics that can undergo a wide range of motion. To move beyond prototyping, new materials and fabrication methods may be needed to integrate diverse components together and realize a fully functional soft electronic device.

BRIEF SUMMARY

[0005] A 3D printed conductive structure for a flexible electronic device comprises a plurality of electrically conductive particles at least partially embedded in a thermoplastic elastomer and arranged to define a percolating conductive pathway therethrough. The 3D printed conductive structure comprises a predetermined geometry and may be supported by a flexible substrate comprising a sheet, textile, adhesive or laminate.

[0006] An ink formulation for 3D printing a flexible electronic device comprises a thermoplastic elastomer dissolved in a polar solvent.

[0007] A method of 3D printing a flexible electronic device comprises depositing one or more conductive filaments in a predetermined pattern on a substrate, where the one or more conductive filaments comprise a conductive ink formulation comprising a polar solvent, a thermoplastic elastomer, and a plurality of electrically conductive particles. The polar solvent is evaporated to dry the one or more conductive filaments, thereby forming a 3D printed conductive structure on the substrate.

[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 continuous filament being extruded through a deposition nozzle and deposited on a substrate, where in this example the continuous filament is extruded from a conductive ink formulation that includes a polar solvent, thermoplastic polyurethane (TPU) and silver (Ag) flakes.

[0010] FIG. 2 shows the stretchability of the conductive structure formed upon drying the continuous filament of FIG. 1.

[0011] FIG. 3A shows an exemplary strain gauge and FIG. 3B shows an exemplary multi-electrode array formed by 3D printing. Both conductive structures are printed from an Ag-TPU conductive ink formulation.

[0012] FIGs. 4A and 4B are schematics of an exemplary 3D printed flexible electronic device, where FIG. 4B shows a close-up view of the mid-portion of FIG. 4A. FIG. 4C provides mechanical data, specifically Young's modulus, for exemplary soft and stiff insulating materials (TPU) and exemplary soft and stiff conductive materials (Ag-TPU).

[0013] FIGs. 5A-5C show deposition nozzles carrying out pick and place maneuvers with exemplary electronic components.

[0014] FIGs. 6A-6D show images of an exemplary LED array formed by a combination of 3D printing steps to deposit conductive and insulating filaments on the flexible substrate as well as pick and place maneuvers to place the LEDs and other functional components.

[0015] FIGs. 7A-7C are plots showing the impact of drying temperature and time on the electrical conductivity of conductive structures printed from ink formulations comprising Ag flakes, TPU and dimethylformamide (DMF).

[0016] FIGs. 8A-8C show the electrical and mechanical properties of conductive structures, which are 3D printed from ink formulations comprising Ag flakes, TPU and DMF, as a function of silver volume fraction; FIGs. 8D-8F show $\Delta R/R_0$ and resistance of conductive structures including 36 vol.% Ag as a function of % strain and strain cycle.

[0017] FIGs. 9A and 9B show the impact of total solids loading on the viscosity and storage modulus of conductive ink formulations including a silver volume fraction of 36 vol.%.

[0018] FIGs. 10A and 10B show the impact of silver volume fraction on the viscosity and storage modulus of conductive ink formulations including a solids loading of 40%.

[0019] FIGs. 11A-11D show tape cast conductive structures formed from Ag-TPU and encapsulated in polydimethylsiloxane (PDMS) and the resistance of these structures while being strained.

[0020] FIGs. 12A and 12B show images of 3D printed electrode arrays for biological stimulation.

[0021] FIG. 13 shows a 3D printed lab-on-a-chip (heart-on-a-chip) device for sensing cellular mechanical forces.

[0022] FIGs. 14A-14F show an exemplary process in which 3D printing of insulating and conductive filaments is combined with pick and place maneuvers to build a multi-material flexible electronic device that includes a number of functional components.

[0023] FIGs. 15A-15B provide data showing how resistance varies as a function of strain and time for a 3D printed conductive structure with and without a strain limiting layer.

[0024] FIG. 16 shows how resistance in a 3D printed conductive filament can be decreased without sacrificing significant lateral resolution.

[0025] FIG. 17 shows how increasing the volume fraction of silver particles in a 3D printed conductive filament increases the Young's Modulus of the conductive structure formed after drying.

DETAILED DESCRIPTION

[0026] A 3D printed conductive structure for a flexible electronic device comprises a plurality of electrically conductive particles at least partially embedded in a thermoplastic elastomer. The electrically conductive particles form a percolating conductive pathway through the thermoplastic elastomer in both strained and unstrained states. The 3D printed conductive structure may function as, for example, an interconnect, electrode, antenna or a sensor in a flexible electronic device. In some cases, the 3D printed conductive structure may be combined with a stretchable insulating structure formed by 3D printing or another method to provide electrical isolation and, in some cases, local strain relief. Such flexible electronic devices may exhibit significant free-form stretching and straining while maintaining full electrical function, an extremely useful characteristic when compared to existing products based on rigid printed circuit boards and

inflexible wires. In addition, the devices may have a mechanical integrity sufficient to withstand linear strains of from greater than 0% to 100% without mechanical breakage. Depending on the application, the flexible electronic devices may be designed to be biocompatible. Such devices may find application in electronics, biometric sensing, energy harvesting, implantable stimulation and monitoring, lab-on-a-chip (*e.g.*, heart-on-a-chip) technology, electrocardiograms (ECG/EKGs), wearable healthcare technology, or others.

[0027] The 3D printed conductive structure has a predetermined geometry that may be determined by the 3D printing process. Referring to FIG. 1, 3D printing or direct write fabrication is an extrusion-based process that entails flowing an ink formulation having suitable rheological properties through a deposition nozzle, which is moving relative to an underlying substrate. As the deposition nozzle (and/or substrate) is moved in an x-, y-, and/or z-direction, a continuous filament comprising the ink formulation may be extruded through the nozzle and deposited on the substrate in a desired configuration or pattern. 3D structures may be built up layer-by-layer using this approach. The rheology of the ink formulation influences the printability, height, and morphology of structures that can be fabricated. At rest, the ink formulation may have a sufficiently high elastic storage modulus, G', and shear yield strength to partially or fully maintain the printed shape. Under a shear stress, the ink formulation ideally exhibits significant shear thinning to allow flow through the deposition nozzle without requiring prohibitively high driving pressures.

[0028] In the example of FIG. 1, a conductive ink formulation comprising conductive silver flakes, a thermoplastic polyurethane and a polar solvent is extruded to deposit a conductive filament on the substrate. Upon drying, the conductive filament is transformed into a highly stretchable conductive structure, as shown in FIG. 2.

[0029] Typically, 3D printing is carried out at or near room temperature and drying occurs at an elevated temperature after printing to remove the

solvent from the ink formulation. It is contemplated that 3D printing may alternatively take place at an elevated temperature at which the ink formulation is in a molten or semi-solid state (*e.g.*, fused filament fabrication (FFF)). In such a case, no solvent is used, and thus the drying step may be replaced with a cooling step to solidify the molten or semi-solid material.

[0030] At simplest, the predetermined geometry of the 3D printed conductive structure may be a straight and/or curved line defined by the path of the deposition nozzle as the continuous filament is deposited on the substrate. More complex geometries may be formed by depositing one or more of the continuous filaments in any desired two- or three-dimensional pattern that may include one or more layers. For example, FIG. 3A shows an exemplary strain gauge and FIG. 3B shows an exemplary multi-electrode array formed by 3D printing a conductive ink formulation comprising silver flakes dispersed in a polar solvent including thermoplastic polyurethane. The predetermined geometry of the 3D printed conductive structure may be selected to minimize or in some cases maximize strain-dependent resistance changes. For example, if the 3D printed conductive structure is intended to function as a strain sensor, then it may be beneficial to have a geometry (such as the elongated serpentine pattern of the strain gauge of FIG. 3A) that maximizes strain-dependent resistance changes in a particular direction. On the other hand, for a 3D printed conductive structure having another function, it may be beneficial to select a geometry that minimizes strain-dependent resistance changes. In the latter case, it may be possible to limit the amount of strain experienced by the 3D printed conductive structure by printing a strain-limiting region or layer having a predetermined stiffness adjacent to the conductive structure. The stiffness of the 3D printed conductive structure and the stiffness of the strain limiting region or layer may be determined by the selection of the thermoplastic elastomer.

[0031] The term “thermoplastic elastomer” may be understood to refer to a polymer, copolymer or a physical mix of polymers that has both thermoplastic and elastomeric (rubber-like) characteristics. Thermoplastic

elastomers may exhibit high stretchability at room temperature and may also be processable as a melt at elevated temperatures, in contrast to thermosetting polymers. The thermoplastic elastomer may comprise a thermoplastic polyurethane (TPU), a styrenic block copolymer (TPE-s), a thermoplastic olefin (TPE-o), an elastomeric alloy (e.g., TPE-v or TPV), a thermoplastic copolyester, and/or a thermoplastic polyamide. The thermoplastic elastomer may be selected to have suitable mechanical properties (*e.g.*, a desired Shore hardness) to impart the desired stiffness or pliability to the printed structure. For example, the thermoplastic elastomer may be a stiff thermoplastic elastomer comprising, in some embodiments, a Shore hardness of greater than 70A, or at least about 80A. Alternatively, the thermoplastic elastomer may be a soft thermoplastic elastomer comprising, in some embodiments, a Shore hardness of 70A or less, 50A or less, or 35A or less. The Shore hardness may be determined according to ASTM Standard D 2240.

[0032] Thermoplastic polyurethane, or TPU, is used in a number of examples described in this disclosure and has been found to be suitable for forming conductive and insulating structures having a range of stiffnesses. Thermoplastic polyurethanes having different values of Shore hardness are available commercially. For example, stiff thermoplastic polyurethanes having Shore hardnesses greater than 70A, such as Elastollan® TPU 1180A, which has a Shore hardness of 80A, may be obtained from BASF Corp. In another example, soft thermoplastic polyurethanes having Shore hardnesses of 70A or less, such as Elastollan ® Soft 35A, which has a Shore hardness of 35A, are also commercially available from BASF Corp.

[0033] The 3D printed conductive structure may be disposed on a substrate which is formed by 3D printing or prefabricated using another method. The substrate may be a flexible substrate comprising a sheet, textile, adhesive or laminate. In one example, the substrate may be formed from a polymer, such as polydimethylsiloxane, or a thermoplastic elastomer. In another example, the substrate may be formed of woven or unwoven

filaments or fibers (*e.g.*, synthetic or natural fibers). In yet another example, the substrate may be a pressure-sensitive adhesive layer suitable for adhering to human skin. In some cases, the substrate may be a sacrificial substrate that is removed after forming the conductive structure. The substrate may comprise an insulating material and, in some cases, may take the form of the insulating structure described below.

[0034] The electrically conductive particles of the 3D printed conductive structure may comprise a conductive material such as silver, carbon, nickel, platinum, palladium, aluminum, or another conductive metal or alloy. The electrically conductive particles may be anisotropic so as to align better when a strain is applied to the conductive structure and to mitigate any unwanted resistance change. For example, the conductive particles may take the form of microscale or nanoscale rods, tubes, fibers, wires or flakes (*e.g.*, microtubes or nanotubes, microfibers or nanofibers, nanowires, etc.). The electrically conductive particles may have a particle size in the range of about 1 nm to about 100 microns, and more typically from about 100 nm to about 10 microns.

[0035] The electrically conductive particles may be present in the conductive structure at a concentration of from about 15 wt.% to about 95 wt.%, where the thermoplastic elastomer accounts for the balance (*e.g.*, from about 5 wt.% to 85 wt.%). For example, in the case of conductive particles comprising a metal such as silver, the concentration may be from about 50 wt.% to about 95 wt.%. For conductive particles comprising carbon, a concentration of from about 15 wt.% to about 30 wt.% may be used. A series of experiments carried out to determine an optimal amount of silver flakes relative to the thermoplastic elastomer are described in the examples below.

[0036] In terms of volume percentage, the electrically conductive particles may be present at a concentration (with respect to the total volume of thermoplastic elastomer and conductive particles) in the range of from about 20 vol.% to about 60 vol.%. The concentration may also be from about 25

vol.% to about 45 vol.%, or preferably from about 32 vol.% to about 40 vol.%, in order to maximize the electromechanical properties of the 3D printed conductive structure. For example, the concentration of the electrically conductive particles may be at least about 25 vol.%, at least about 30 vol.%, or at least about 35 vol.%. Typically, the concentration is no higher than 50 vol.%, no higher than 45 vol.%, or no higher than 40 vol. %.

[0037] Referring now to FIGs. 4A and 4B, a 3D printed flexible electronic device 400 may comprise the 3D printed conductive structure 402 described above and an insulating structure 404 disposed adjacent to the 3D printed conductive structure 402. In some cases, the insulating structure 404 may overlie, underlie, and/or encapsulate the 3D printed conductive structure 402, and the insulating structure 404 may or may not be in direct contact with the 3D printed conductive structure 402. The insulating structure 404 may comprise a thermoplastic elastomer which is the same as or different from the thermoplastic elastomer of the 3D printed conductive structure 402. The insulating structure may be electrically insulating and thus may not include electrically conductive particles. In some cases, the insulating structure 404 may not comprise a thermoplastic elastomer, but rather may comprise another polymer, such as polydimethylsiloxane (PDMS).

[0038] The insulating structure 404 may be formed by 3D printing or another fabrication method. The insulating structure 404 may have any desired geometry, particularly if formed by 3D printing, where a continuous filament comprising a thermoplastic elastomer or another polymer may be deposited on the substrate. At simplest, the insulating structure 404 may comprise a straight and/or curved line which may be defined by the path of the deposition nozzle. More complex geometries may be formed by depositing one or more of the continuous filaments in any desired two- or three-dimensional pattern that may include one or more layers.

[0039] The 3D printed conductive structure 402 may have a higher stiffness than the insulating structure 404. This may be due at least in part to the stiffening effect of the electrically conductive particles that impart

electrical conductivity to the conductive structure 402, as shown in FIG. 17 for silver particles in a thermoplastic polyurethane. Thus, even if the conductive and insulating structures 402,404 comprise the same thermoplastic elastomer having the same Shore hardness, the 3D printed conductive structure may exhibit a higher stiffness. Due to the sometimes significant difference in stiffnesses between the conductive and insulating structures 402,404, as revealed by the exemplary data of FIG. 4C, it may be beneficial to include a strain limiting region 406 between the 3D printed conductive structure 402 and the insulating structure 404. The strain limiting region 406 may have a lower stiffness than the 3D printed conductive structure 402 and a higher stiffness than the insulating structure 404, in one embodiment. Referring to FIG. 4C, the strain limiting region 406 may have, for example, a stiffness (*e.g.*, Young's Modulus) corresponding to the "stiff TPU," while the 3D printed conductive structure 402 has the stiffness of the "soft AgTPU" and the insulating structure 404 has the stiffness of the "soft TPU." The strain limiting region 406 may help to prevent unintended strains from being transmitted to the 3D printed conductive structure 402 during flexing or deformation of the flexible electronic device 400.

[0040] Accordingly, the strain limiting region 406 may comprise a thermoplastic elastomer having a Shore hardness higher than that of the thermoplastic elastomer of the insulating structure 404. For example, the thermoplastic elastomer of the strain limiting region 406 may be a stiff thermoplastic polyurethane having a Shore hardness greater than 70A, while the thermoplastic elastomer of the insulating structure may be a soft thermoplastic polyurethane having a Shore hardness of 70A or less. In some cases, the Shore hardness of the stiff thermoplastic polyurethane may be at least about 80A and the Shore hardness of the soft thermoplastic polyurethane may be about 50A or less. The strain limiting region 406 may also be electrically insulating, and thus may be referred to as an insulating strain limiting region 406.

[0041] It is also possible that – despite the stiffening effect of the electrically conductive particles – the 3D printed conductive structure 402 may have a lower stiffness than the insulating structure 404. For example, the 3D printed conductive structure 402 may be fabricated from a thermoplastic elastomer having a much lower Shore hardness than the insulating structure 404, thereby offsetting the stiffening effect of the conductive particles. In such a case, the strain limiting region 406 positioned between the insulating structure 404 and the 3D printed conductive structure 402 may have a higher stiffness than the 3D printed conductive structure but a lower stiffness than the insulating structure 404, and thus the strain limiting region 406 may serve to limit the strain transmitted to the insulating structure 404. The strain limiting region 406 may thus comprise a thermoplastic elastomer having a Shore hardness lower than that of the thermoplastic elastomer of the insulating structure 404.

[0042] It is further contemplated that, in any of the examples described herein, the strain limiting region 406 may have a stiffness that is the same as that of either the 3D printed conductive structure 402 or the insulating structure 404. It is also contemplated that the strain limiting region 406 may have a graded stiffness, where the stiffness increases or decreases (*e.g.*, linearly, stepwise, exponentially or in another fashion) across the strain limiting region 406 from the 3D printed conductive structure 402 to the insulating structure 404. Such a graded structure of the strain limiting region 406 may be obtained by 3D printing adjacent filaments formed from thermoplastic elastomers having different Shore hardnesses.

[0043] As indicated above, the strain limiting region 406 may be formed by 3D printing and may have any desired 3D-printable geometry. The predetermined geometry of the strain limiting region may be as described above for the insulating structure and/or the 3D printed conductive structure. Typically, the geometry of the strain limiting region 406 is determined by the geometry of the 3D printed conductive structure 402 since the strain limiting

region 406 may be positioned directly adjacent thereto. The benefit of printing a stiffer ink formulation along the print path of a softer conductive ink formulation in terms of the impact on the electrical resistance of the conductive structure may be understood in reference to FIGs. 15A and 15B, which are described in the Examples below.

[0044] The 3D printed flexible electronic device may further comprise a plurality (two or more) of the 3D printed conductive structures, where each conductive structure may be formed by 3D printing to have a desired geometry and position. For example, referring again to FIG. 3B, the 3D printed flexible electronic device may comprise an array of electrodes, where each electrode has a position optimized for electrical stimulation of a specific region of an individual. Each of the 3D printed conductive structures comprises a plurality of electrically conductive particles at least partially embedded in an electrically insulating material comprising a thermoplastic elastomer, as described above. An insulating structure may be adjacent to each 3D printed conductive structure, and in some or all cases a strain limiting region may be disposed between the insulating structure and the 3D printed conductive structure, also as described above.

[0045] The 3D printed flexible electronic device 400 may further include a functional component 410, such as the LED 408 shown in FIGs. 4A and 4B, electrically connected to the 3D printed conductive structure 402. The functional component 410 may be an active electronic component, a passive electronic component, an optoelectronic component, an electromechanical component, a piezoelectric component, a biometric component and/or a sensor. The functional component 410 may be prefabricated and incorporated into the flexible electronic device 400 using a pick and place maneuver, as described below. It is also contemplated that the functional component 410 may be formed by 3D printing during fabrication of the flexible electronic device 400.

[0046] Since the functional component 410 may be a rigid component with a significantly higher stiffness than that of the 3D printed conductive

structure 402, it may be beneficial to include a strain limiting region 412 between the functional component 410 and the 3D printed conductive structure 402. The strain limiting region 412 may have a higher stiffness than the 3D printed conductive structure 402 and a lower stiffness than the functional component 410. In some embodiments, the strain limiting region 412 may have a stiffness that is the same as that of the 3D printed conductive structure 402. Due to its placement between the functional component 410 and the 3D printed conductive structure 402, the strain limiting region 412 may be electrically conductive so as to provide an electrical path between the two, and thus may be referred to as a conductive strain limiting region 412.

[0047] Referring again to FIG. 4C, the conductive strain limiting region 412 may have, in one example, a stiffness corresponding to the "stiff AgTPU," while the 3D printed conductive structure 402 has the stiffness of the "soft AgTPU." The conductive strain limiting region 412 may comprise a thermoplastic elastomer having a higher Shore hardness than the thermoplastic elastomer of the 3D printed conductive structure 402. For example, the thermoplastic elastomer of the conductive strain limiting region 412 may be a stiff thermoplastic polyurethane having a Shore hardness of greater than 70A, or at least about 80A, and the thermoplastic elastomer of the 3D printed conductive structure 402 may be a thermoplastic polyurethane having a Shore hardness of 70A or less, or about 50A or less. The conductive strain limiting region 412 may include electrically conductive particles at least partially embedded in the thermoplastic elastomer and arranged to define a percolating conductive pathway through some or all of the conductive strain limiting region 412, thereby imparting the desired electrical conductivity.

[0048] As with the insulating strain limiting region 406, the conductive strain limiting region 412 may be formed by 3D printing and may have any desired 3D-printable geometry. The predetermined geometry of the conductive strain limiting region 412 may be as described above for the

insulating structure and/or the 3D printed conductive structure. It is also contemplated that the conductive strain limiting region 412 may have a graded stiffness, where the stiffness increases or decreases (*e.g.*, linearly, stepwise, exponentially or in another fashion) across the strain limiting region 412 from the 3D printed conductive structure 402 to the functional component 410. Such a graded structure of the strain limiting region 412 may be obtained by 3D printing adjacent filaments formed from thermoplastic elastomers having different Shore hardnesses and/or different amounts of conductive particles.

[0049] Also described herein are conductive and insulating ink formulations having a rheology suitable for 3D printing of flexible electronic devices. Arriving at a suitable ink formulation is a challenge due to the various processing and property requirements of 3D printed conductive and insulating structures. For example, a solvent that can effectively dissolve a thermoplastic elastomer while still remaining volatile for post-deposition evaporation may be required for printing. In addition, an ideal ink formulation is engineered to dry quickly without sacrificing the aesthetics (*e.g.*, transparency) and integrity (*e.g.*, edge continuity) of the printed structure. The conductive ink formulations may have additional requirements, such as exhibiting both a high conductivity and high stretchability, as well as enduring high strains without electrical breakdown or mechanical failure. Also important is minimizing the change in resistance of the 3D printed conductive structure as a function of strain cycle, which may be referred to as cyclic $\Delta R/R_0$.

[0050] The ink formulation may comprise a thermoplastic elastomer dissolved in a polar solvent. The ink formulation may be a conductive ink formulation that further includes a plurality of electrically conductive particles and, in some cases, a surfactant or dispersing agent to improve the dispersion of the conductive particles. A suitable surfactant or dispersing agent may comprise, for example, a long chain fatty acid with a carboxylic acid head. The ink formulation may alternatively be an insulating ink

formulation that does not include the electrically conductive particles. By combining suitable insulating and conductive ink formulations in a multi-material 3D printing approach, entire functional, stretchable, and flexible electrical devices may be fabricated using additive manufacturing (*e.g.*, 3D printing) alone.

[0051] The electrically conductive particles may comprise a conductive material selected from among gold, silver, carbon, nickel, platinum, palladium, aluminum, and other conductive metals and/or alloys, as described above. The electrically conductive particles may be anisotropic so as to align better under an applied strain and mitigate any unwanted resistance change. In addition, anisotropic particles may undergo alignment during 3D printing, as described for example in International Patent Application No. PCT/US2015/015148, entitled "Three-Dimensional (3D) Printed Composite Structure and 3D Printable Composite Ink Formulation," and filed on February 10, 2015, which is hereby incorporated by reference in its entirety. This alignment during printing may promote formation of a percolating conductive pathway in the printed conductive structure. The conductive particles may take the form of microscale or nanoscale rods, tubes, fibers, wires or flakes (*e.g.*, microtubes or nanotubes, microfibers or nanofibers, nanowires, etc.). The electrically conductive particles may have a particle size in the range of about 1 nm to about 100 microns, and more typically from about 100 nm to about 10 microns.

[0052] The thermoplastic elastomer may have any of the characteristics described above and may comprise a thermoplastic polyurethane (TPU), a styrenic block copolymer (TPE-s), a thermoplastic olefin (TPE-o), an elastomeric alloy (e.g., TPE-v or TPV), a thermoplastic copolyester, and/or a thermoplastic polyamide. The thermoplastic elastomer may be a stiff thermoplastic elastomer comprising, in some embodiments, a Shore hardness of greater than 70A, or at least about 80A. Alternatively, the thermoplastic elastomer may be a soft thermoplastic elastomer comprising,

in some embodiments, a Shore hardness of about 70A or less, or about 50A or less.

[0053] The polar solvent may comprise one or more of the following: dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dimethylformamide (DMF), dibasic ester (DBE), N-methyl-2-pyrrolidone (NMP), alkyl ester, dichloromethane, glycol ether, glycol ether acetate and water (H_2O). For example, the polar solvent may include two of the above polar solvents, such as DMF and THF. The volume ratio of the two polar solvents (*e.g.*, DMF to THF) may be in the range of from 15:85 to about 25:75, for example, 20:80.

[0054] The ink formulation may further include one or more rheological modifiers, such as one or more of the following: fumed silica, surface functionalized treated fumed silica, associative thickeners, and non-associative thickeners. An exemplary associative thickener that may be suitable for the ink formulation comprises a hydrophobically modified ethoxylated urethane resin (HEUR). Typically, a total solids loading in the ink formulation is from about 15% to about 50% by volume.

[0055] A method of 3D printing a flexible electronic device comprises depositing one or more conductive filaments in a predetermined pattern on a substrate to form a 3D printed conductive structure. Each conductive filament may be extruded as a continuous filament from a deposition nozzle moving relative to the substrate, as shown in FIG. 1. The one or more conductive filaments comprise a conductive ink formulation including a polar solvent, a thermoplastic elastomer, a plurality of electrically conductive particles, and optionally a surfactant or dispersant. For example, the thermoplastic elastomer may be a soft thermoplastic elastomer (*e.g.*, TPU) as described above having a Shore hardness of about 70A or less, and thus the conductive ink formulation may be referred to as a soft conductive ink formulation, and the one or more conductive filaments may be referred to as one or more soft conductive filaments. The polar solvent may be evaporated to dry the conductive filament(s) and form a 3D printed conductive structure.

[0056] The 3D printed conductive structure can be both mechanically and electrically tuned by varying the concentration and type(s) of electrically conductive particles in the conductive ink formulation. For example, the conductive ink formulation may be engineered for high sensitivity to low strains for sensor applications, for high robustness and low sensitivity to strain for wiring applications, and for high biocompatibility for biometric sensing applications. The concentration and characteristics of the thermoplastic elastomer may also influence the mechanical properties of the conductive structure.

[0057] The method may further comprise depositing one or more insulating filaments in a predetermined pattern on the substrate to form an insulating structure adjacent to and/or in contact with the conductive structure. Each insulating filament may be extruded as a continuous filament from a deposition nozzle moving relative to the substrate. The deposition nozzle may be the same as or different from the deposition nozzle used for depositing the conductive filament(s), and the deposition of the insulating and conductive filaments may be carried out in serial or in parallel. The one or more insulating filaments may comprise an insulating ink formulation including a thermoplastic elastomer and a polar solvent. For example, the thermoplastic elastomer may be a soft thermoplastic elastomer (*e.g.*, TPU) as described above having a Shore hardness of about 70A or less, and thus the insulating ink formulation may be referred to as a soft insulating ink formulation, and the one or more insulating filaments may be referred to as one or more soft insulating filaments. The polar solvent may be evaporated to dry the insulating filament(s) and form an insulating structure. The properties of the insulating structure, which may function as an effective packaging, encapsulating, supporting and/or strain limiting material, may be controlled by varying the concentration and/or characteristics (*e.g.*, type, hardness) of thermoplastic elastomer employed in the insulating ink formulation.

[0058] To evaporate the polar solvent, the conductive and/or insulating filaments may be heated to a temperature in the range of about 50°C to about 135°C. Typically, the heating is carried out for a time period ranging from about 30 minutes to about 3 hours.

[0059] The substrate may be a flexible substrate comprising a sheet, textile, adhesive or laminate. In one example, the substrate may be formed from a polymer, such as polydimethylsiloxane, or a thermoplastic elastomer. In another example, the substrate may be formed of woven or unwoven filaments or fibers (*e.g.*, synthetic or natural fibers). In yet another example, the substrate may be a pressure-sensitive adhesive layer suitable for adhering to human skin. In some cases, the substrate may be a sacrificial substrate that is removed after forming the conductive structure. The substrate may comprise an insulating material and may serve as one of the insulating structures.

[0060] The method may further comprise electrically connecting a functional electronic component to the 3D printed conductive structure by a manual or automated pick and place maneuver. The pick and place maneuver may be carried out using the same deposition nozzle employed for 3D printing by generating a vacuum instead of a positive pressure in the nozzle. The vacuum is selected to be strong enough to counteract gravitational forces on small electronic components, such as resistors and LEDs, allowing them to be readily picked up, transported to the desired location, and placed on the substrate. FIGs. 5A-5C show deposition nozzles carrying out pick and place maneuvers with exemplary electronic components.

[0061] The pick and place maneuver may be carried out before, during and/or after the one or more conductive filaments is deposited, and multiple pick and place maneuvers may be carried out to place a number of electronic components on the substrate. FIGs. 6A-6D show images of an exemplary LED array formed by a combination of 3D printing steps to deposit conductive and insulating filaments on the flexible substrate as well

as pick and place maneuvers to place the LEDs and other functional components. The one or more insulating filaments may be deposited before, during or after the functional component is manually or automatically picked and placed.

[0062] As indicated above, the one or more conductive filaments may comprise one or more soft conductive filaments extruded from a conductive ink formulation comprising a soft thermoplastic elastomer. Also or alternatively, the one or more insulating filaments may comprise one or more soft insulating filaments extruded from an insulating ink formulation comprising a soft thermoplastic elastomer (which may be the same as or different from that of the soft conductive filament(s)).

[0063] The method may further entail depositing one or more stiff insulating filaments in a predetermined pattern on the substrate in contact with the one or more soft conductive filaments, so as to form, after drying, a strain limiting structure (or, more specifically, an insulating strain limiting structure) on the substrate. The stiffness of the strain limiting structure may have a stiffness that lies between that of the conductive structure and the insulating structure. The one or more stiff insulating filaments may comprise a stiff insulating ink formulation including a stiff thermoplastic elastomer and a polar solvent, where the stiff thermoplastic elastomer of the stiff insulating ink formulation comprises a higher Shore hardness than the soft thermoplastic elastomer of one or both of the conductive and insulating ink formulations used to form the conductive and insulating structures, respectively. The one or more stiff insulating filaments may alternatively have a higher Shore hardness than the soft thermoplastic elastomer of the soft conductive ink formulation used to form the conductive structure. In either case, evaporating the polar solvent may comprise drying the one or more stiff insulating filaments, thereby forming the insulating strain limiting structure on the substrate between the 3D printed conductive structure and the insulating structure. The evaporation of the polar solvent may be carried out as described above.

[0064] The method may further comprise depositing one or more stiff conductive filaments in a predetermined pattern on the substrate in contact with the functional component, so as to form, after drying, a strain limiting structure (or, more specifically, a conductive strain limiting structure) on the substrate. The one or more stiff conductive filaments may comprise a stiff conductive ink formulation comprising a polar solvent, a stiff thermoplastic elastomer, and a plurality of electrically conductive particles, where the stiff thermoplastic elastomer of the stiff conductive ink formulation comprises a higher Shore hardness than the soft thermoplastic elastomer of the soft conductive ink formulation, which is used to form the 3D printed conductive structure. In this case, evaporating the polar solvent may comprise drying the one or more stiff conductive filaments, thereby forming the conductive strain limiting structure on the substrate between the functional component and the 3D printed conductive structure. The evaporation of the polar solvent may be carried out as described above.

[0065] Each of the above-described continuous filaments (*e.g.*, the soft conductive filaments, the soft insulating filaments, the stiff conductive filaments and the stiff insulating filaments) may be extruded from a conductive or insulating ink formulation that comprises a thermoplastic elastomer (*e.g.*, thermoplastic polyurethane) having the desired hardness or softness in order to produce a conductive or insulating component, or strain limiting region, having the desired stiffness. The soft or stiff insulating filaments may be deposited before, during and/or after the soft or stiff conductive filaments are deposited. Also, any of the above-described filaments may be deposited directly on the substrate or on a previously-deposited filament or portion of a filament.

[0066] Although a single deposition nozzle is shown in FIG. 1, a plurality of deposition nozzles may be employed for 3D printing. For example, two or more, three or more, four or more, five or more and up to N nozzles may be used for extruding the filaments, where $1 \leq N \leq 1024$; more typically, N is no more than 512, no more than 256, no more than 128, or no more than 64.

The conductive and insulating filaments, including soft and stiff conductive filaments, and soft and stiff insulating filaments (and referred to collectively as “the filaments”), may be extruded from the N nozzles sequentially in a serial deposition process or simultaneously in a parallel deposition process, and each nozzle may contain the same or a different ink. It is also contemplated that the deposition may include both parallel and serial deposition steps. To facilitate sequential or serial printing, the nozzles can be independently controlled in the z-direction.

[0067] Each nozzle may have an inner diameter of from about 10 microns to about 1 mm in size, and more typically from about 50 microns to about 500 microns. The size of the nozzle may be selected depending on the desired continuous filament diameter. Depending on the injection pressure and the nozzle translation speed, the filament may have a diameter ranging from about 10 microns to about 10 mm, and more typically from about 100 microns (0.1 mm) to about 1 mm. The nozzles may be moved and the filaments may be deposited at print speeds as high as about 3 m/s (*e.g.*, from about 1 cm/s to about 3 m/s), and are more typically in the range of from about 1 mm/s to about 500 mm/s, from about 0.1 mm/s to about 100 mm/s, or from about 0.5 mm/s to about 10 mm/s.

[0068] The inks fed to the one or more nozzles may be housed in separate syringe barrels that may be individually connected to a nozzle for printing by way of a Luer-Lok™ or other connector. The extrusion of each of the continuous filaments may take place under an applied or injection pressure of from about 1 psi to about 1000 psi, from about 10 psi to about 500 psi, or from about 20 psi to about 100 psi. The pressure during extrusion may be constant or it may be varied. By using alternative pressure sources, pressures of higher than 100 psi and/or less than 1 psi, for example, may be applied during printing. A variable pressure may yield a continuous filament having a diameter that varies along the length of the filament. The extrusion is typically carried out at ambient or room temperature conditions (*e.g.*, from about 18°C to about 25°C).

[0069] During the extrusion and deposition of each continuous filament, the nozzle may be moved with respect to the substrate along a predetermined 2D or 3D pathway (*e.g.*, from (x_1, y_1, z_1) to (x_2, y_2, z_2)) with a positional accuracy of within ±200 microns, within ±100 microns, within ±50 microns, within ±10 microns, or within ±1 micron. Accordingly, the continuous filaments may be deposited on the substrate with a positional accuracy of within ±200 microns, within ±100 microns, within ±50 microns, within ±10 microns, or within ±1 micron.

[0070] It is also contemplated that the ink formulations described above but without the polar solvent may be employed in a 3D printing process carried out at an elevated temperature. In this case, the thermoplastic elastomer may be heated to a molten or semi-solid state for deposition of the one or more conductive filaments and the one or more insulating filaments in a process that may be referred to as fused filament fabrication (FFF). The drying step described above may in this case be replaced with a cooling step to solidify the molten or semi-solid material.

Examples

Solvent System for TPU Insulating Structures

[0071] Stiff and soft insulating ink formulations are fabricated using thermoplastic polyurethanes of different Shore hardness values dissolved in two polar solvents combined in various ratios. The two polar solvents are N-N-dimethylformamide (DMF), which has a boiling point of 153°C and a vapor pressure of 3.9 Torr, and tetrahydrofuran (THF), which has a boiling point of 66°C and a vapor pressure of 3.9 Torr. The stiff ink formulation includes Elastollan 1180A, and the soft ink formulation includes Elastollan Soft 35A. The ratios of DMF to THF range from 100:0 to 0:100 in terms of volume. 3D printing is carried out using a deposition nozzle having an inner diameter of 410 microns at a height above the substrate of 0.4 mm, a print speed of 17 mm/s, and a constant pressure of 18 psi. Insulating structures (*e.g.*, simple meanders and continuous films) formed by 3D printing the stiff and soft

insulating ink formulations are evaluated based on four criteria: extent of drying (*e.g.*, wetness or tackiness of structures); transparency; edge continuity; and presence of bubbles. All of the observations are made at 5 minutes post-printing. The results are summarized in Table 1 below, and show that an ideal ratio of DMF:THF may be 20:80 for insulating ink formulations comprising either soft or stiff TPU.

Table 1. Summary of Insulating Ink Formulation Characteristics as a Function of Solvent

	DMF:THF	Extent of Drying	Edge Continuity	Transparent?	Bubbles?
Soft TPU (35A)	100:0	Wet	Poor	No	No
	80:20	Wet	Poor	No	No
	40:60	Wet	Poor	No	No
	30:70	Wet	Good	Yes	No
	20:80	Tacky	Good	Yes	No
	0:100	N/A	N/A	N/A	N/A
Stiff TPU (1180A)	100:0	Wet	Poor	No	No
	80:20	Tacky	Poor	No	No
	40:60	Tacky	Poor	No	No
	30:70	Tacky	Poor	Yes	No
	20:80	Tacky	Good	Yes	No
	0:100	Tacky	Good	Yes	Yes

Drying of Conductive Ink Formulations

[0072] Experiments are carried out to evaluate the effect of drying temperature and time on the electrical conductivity of structures printed from conductive ink formulations comprising silver flakes, thermoplastic polyurethane (Elastollan Soft 35A) and DMF as the solvent. The results shown in FIGs. 7A-7C suggest that 50°C and 2 hours is an optimal temperature and time for evaporation of the solvent.

Characterization of Conductive Ink Formulations

[0073] Conductive ink formulations comprising thermoplastic polyurethane (Elastollan Soft 35A) dissolved in DMF and including various volume fractions of silver flakes are mixed using a planetary mixer. The silver flakes have a particle size of 2-4 μm (Inframat Corp.) and are incorporated into the conductive ink formulations in the following amounts: 15, 18, 21, 24, 27, 30, 33, 36, 39, 42 and 45 vol.%.

[0074] Continuous filaments having a linear geometry are 3D printed from the conductive ink formulations and then heated at 50°C for 2 hours to evaporate the solvent prior to electrical testing. The cross-sectional area of the resulting conductive structures is measured with a profilometer and the conductivity is determined by a four-point probe measurement.

[0075] Conductive structures having a dogbone geometry (gauge length of 1.5 cm) suitable for mechanical testing are formed by tape casting the conductive ink formulations, followed by heating at 50°C for 2 hours to evaporate the solvent. Mechanical tests are carried out on an Instron testing system. Strain to failure (or stretchability) and electrical failure are evaluated using a displacement rate of 0.1 mm/s (strain rate of 0.00667 s^{-1}).

[0076] FIGs. 8A-8C show the electrical and mechanical properties of the conductive structures as a function of silver volume fraction. It is desirable to maximize conductivity, stretchability and the strain to percolation breakdown (or strain to electrical failure), while minimizing cyclic $\Delta R/R_0$. By comparing the relationships shown in these figures, an optimal loading of about 36 vol. % silver is identified. In FIGs. 8D-8F, $\Delta R/R_0$ and resistance are examined as a function of % strain and strain cycle, respectively, for conductive structures including 36 vol.% Ag.

[0077] The impact of total solids loading and silver flake volume fraction on the viscosity and storage modulus of conductive ink formulations. In FIGs. 9A and 9B, the silver volume fraction (after fully drying the conductive ink formulation) is held constant at 36 vol.% while the solids loading is varied from 20 vol.% to 45 vol.%. In FIGs. 10A and 10B, the solids loading

(%) is held constant at 40 vol.% while the volume fraction of silver flakes is varied from 28 vol.% to 48 vol.%.

3D Printing and Characterization of Flexible Electronic Devices

[0078] Conductive ink formulations comprising silver flakes dispersed in thermoplastic polyurethane (Ag-TPU) and carbon particles (carbon black) dispersed in thermoplastic polyurethane (CB-TPU) are prepared and used to fabricate flexible electronic devices. Dimethylformamide (DMF) is employed as the solvent for both ink formulations.

[0079] The Ag-TPU formulation includes DMF and 33 wt.% TPU (Elastollan Soft 35A) dissolved in the solvent. Silver flakes having a particle size of about 2-5 microns are included in the formulation at a concentration of 85 wt.% (with respect to the TPU). All components are mixed together using a planetary mixer. Conductive structures having linear, serpentine and other geometries are prepared by a molding technique using stencils. A resistivity of 5.72×10^{-5} $\Omega \cdot$cm, which is equivalent to approximately 3% of the conductivity of bulk silver, and a conductivity of 1.75×10^{4} S/cm are measured for the conductive structures.

[0080] The CB-TPU formulation includes DMF and 33 wt.% TPU (Ellastolan Soft 35A) dissolved in the solvent. Carbon black obtained from Cabot Corp. (Boston, MA) is included in the formulation at a concentration of 25 wt.% (with respect to the TPU). All components are mixed together using a planetary mixer. Conductive structures having various geometries are 3D printed from the CB-TPU conductive ink formulation using a deposition nozzle having an inner diameter of 200 microns. The printing is carried out at room temperature under constant-pressure flow conditions.

[0081] Referring to FIGs. 11A-11D, stenciled conductive structures formed from Ag-TPU are encapsulated in PDMS and strained while the resistance is monitored. The conductive structure of FIG. 11B has a linear geometry and the conductive structure of FIG. 11D has a serpentine geometry. The resistance of the linear conductive structure changes by

approximately 10-fold during a 20% strain, but then returns to its baseline resistance without breaking. This demonstrates the robustness of the conductive structures to high strains, as well as their potential use as strain sensors. The conductive structure printed in the serpentine pattern exhibits a small change in resistance, from 1.84 ohms to 1.91 ohms, over the course of one hundred 20% strain cycles, which demonstrates the potential of the conductive structures for use as interconnects in a flexible electronic device.

[0082] The Ag-TPU conductive ink formulation is also employed to 3D print an electrode array for biological stimulation applications, as shown in FIGs. 12A and 12B. In this example, Ag-TPU is printed with TPU in patterned layers, which are then encapsulated in PDMS to make a robust three-dimensional electrode device with embedded wiring.

[0083] In another example shown in FIG. 13, a lab-on-a-chip device for sensing cellular mechanical forces is fabricated by 3D printing. Conductive structures comprising CB-TPU are printed and encapsulated in TPU to form thin cantilever beams onto which cells can adhere, reorganize, and apply mechanical forces. The cellular mechanical forces strain the cantilever beams, which induces a change in resistance measureable through 3D printed electrodes fabricated from a conductive silver ink. The end result is a functional, 8-layer, multi-material device.

Hybrid 3D Printing Process

[0084] In a multi-step process shown in FIGs. 14A-14F, printing of insulating and conductive inks is combined with pick and place maneuvers to build a multi-material flexible electronic device that includes a number of functional components. FIG. 14A shows 3D printing of an insulating structure or matrix comprising a thermoplastic polyurethane; FIG. 14B shows 3D printing of a soft conductive ink formulation comprising Ag-TPU on the insulating matrix and also the creation of voids for LEDs; FIG. 14C shows a pick and place maneuver to deposit an LED within one of the voids; FIG. 14D shows 3D printing of a stiffer conductive ink formulation along the path of the soft conductive ink formulation to form a stiff conductive structure

adjacent to a soft conductive structure; FIG. 14E shows the placement of a magnet in predetermined regions of the circuit using a pick and place maneuver; and FIG. 14F shows the final functioning flexible electronic device.

[0085] The benefit of printing a stiffer conductive ink formulation along the path of a previously printed soft conductive ink formulation can be understood in terms of the strain limiting effect of the stiffer conductive structure. FIGs. 15A and 15B show how the resistance of a conductive structure comprising Ag-TPU changes as a function of strain and time, respectively, with and without a strain-limiting layer comprising stiff TPU adjacent to the conductive structure. With the strain-limiting layer, the resistance of the conductive structure exhibits a much higher stability as a function of strain for a single strain cycle and as a function of time for successive applications of higher strains. The data show that the strain experienced by the conductive structure is reduced with the strain-limiting layer.

[0086] FIG. 16 shows a plot of resistance as a function of the number of layers deposited to form a 3D printed conductive structure, which in this example is a conductive trace. The inset images show cross-sectional views of the conductive trace having a varying number of layers. The data in FIG. 16 reveal that electrical resistance decreases as the number of layers increases. FIG. 17 shows how the volume fraction of conductive particles (silver flakes in this example) influence the Young's Modulus of the 3D printed conductive structure.

[0087] 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.

CLAIMS

1. A 3D printed conductive structure for a flexible electronic device, the 3D printed conductive structure comprising:

a plurality of electrically conductive particles at least partially embedded in a thermoplastic elastomer and arranged to define a percolating conductive pathway therethrough,

wherein the 3D printed conductive structure comprises a predetermined geometry.

2. The 3D printed conductive structure of claim 1 disposed on a flexible substrate comprising a sheet, textile, adhesive or laminate.

3. The 3D printed conductive structure of claim 1 or 2, wherein the predetermined geometry comprises one or more straight lines and/or one or more curved lines.

4. The 3D printed conductive structure of any one of claims 1-3, wherein the predetermined geometry is selected to minimize strain-dependent resistance changes.

5. The 3D printed conductive structure any one of claims 1-4, wherein the predetermined geometry is selected to maximize strain-dependent resistance changes.

6. The 3D printed conductive structure of any one of claims 1-5, wherein the electrically conductive particles comprise a conductive material selected from the group consisting of: gold, silver, carbon, nickel, platinum, palladium, aluminum, and other conductive metals and/or alloys.

7. The 3D printed conductive structure of any one of claims 1-6, wherein the thermoplastic elastomer is selected from the group consisting of: thermoplastic polyurethane, styrenic block copolymer, thermoplastic

olefin, elastomeric alloy, thermoplastic copolyester, and thermoplastic polyamide.

8. The 3D printed conductive structure of any one of claims 1-7, wherein the thermoplastic elastomer comprises a Shore hardness of 70A or less.

9. The 3D printed conductive structure of claim 8, wherein the Shore hardness is about 50A or less.

10. The 3D printed conductive structure of any one of claims 1-7, wherein the thermoplastic elastomer comprises a Shore hardness of greater than 70A.

11. The 3D printed conductive structure of claim 10, wherein the Shore hardness is at least about 80A.

12. The 3D printed conductive structure of any one of claims 1-11, wherein the electrically conductive particles are present at a concentration of from about 15 wt.% to about 95 wt.% relative to the thermoplastic elastomer.

13. The 3D printed conductive structure of claim 12, wherein the electrically conductive particles comprise a metal and the concentration is from about 50 wt.% to about 95 wt.%.

14. The 3D printed conductive structure of claim 12, wherein the electrically conductive particles comprise carbon and the concentration is from about 15 wt.% to about 30 wt.%.

15. The 3D printed conductive structure of any one of claims 1-14, wherein the electrically conductive particles are present at a volume percentage of from about 20 vol.% to about 60 vol.%.

16. The 3D printed conductive structure of any one of claims 1-15, wherein the electrically conductive particles are anisotropic and comprise rods, tubes, fibers, wires and/or flakes.

17. The 3D printed conductive structure of any one of claims 1-16, wherein the electrically conductive particles have an average particle size in the range of from about 100 nm to about 10 microns.

18. The 3D printed conductive structure of any one of claims 1-17 being selected from the group consisting of: sensor, antenna, interconnect, and electrode.

19. A 3D printed flexible electronic device comprising:

the 3D printed conductive structure of any one of claims 1-18; and

an insulating structure adjacent to the 3D printed conductive structure.

20. The 3D printed flexible electronic device of claim 19, wherein the insulating structure underlies, overlies and/or encapsulates the 3D printed conductive structure.

21. The 3D printed flexible electronic device of claim 19 or 20, wherein the insulating structure comprises a thermoplastic elastomer, and wherein the thermoplastic elastomer of the insulating structure is the same as or different from the thermoplastic elastomer of the 3D printed conductive structure.

22. The 3D printed flexible electronic device of any one of claims 19-21, wherein the thermoplastic elastomer of the insulating structure is selected from the group consisting of: thermoplastic polyurethane, styrenic block copolymer, thermoplastic olefin, elastomeric alloy, thermoplastic copolyester, and thermoplastic polyamide.

23. The 3D printed flexible electronic device of any one of claims 19-22, wherein the 3D printed conductive structure has a higher stiffness than the insulating structure.

24. The 3D printed flexible electronic device of any one of claims 19-23, wherein the insulating structure is formed by 3D printing.

25. The 3D printed flexible electronic device of any one of claims 19-24, further comprising a strain limiting region between the 3D printed conductive structure and the insulating structure, the strain limiting region comprising a lower stiffness than the 3D printed conductive structure and a higher stiffness than the insulating structure.

26. The 3D printed flexible electronic device of claim 25, wherein the strain limiting region comprises a thermoplastic elastomer having a higher Shore hardness than the thermoplastic elastomer of the insulating structure.

27. The 3D printed flexible electronic device of claim 26, wherein the thermoplastic elastomer of the strain limiting region is a stiff thermoplastic polyurethane having a Shore hardness greater than 70A, and wherein thermoplastic elastomer of the insulating structure is a soft thermoplastic polyurethane having a Shore hardness of 70A or less.

28. The 3D printed flexible electronic device of claim 27, wherein the Shore hardness of the stiff thermoplastic polyurethane is at least about 80A, and wherein the Shore hardness of the soft thermoplastic polyurethane is about 50A or less.

29. The 3D printed flexible electronic device of any one of claims 25-28, wherein the strain limiting region is formed by 3D printing.

30. The 3D printed flexible electronic device of any one of claims 25-29, wherein the stiffness of the strain limiting region is a graded stiffness

comprising a decrease across the strain limiting region from the 3D printed conductive structure to the insulating structure.

31. The 3D printed flexible electronic device of any one of claims 19-22, wherein the 3D printed conductive structure has a lower stiffness than the insulating structure.

32. The 3D printed flexible electronic device of claim 31, further comprising a strain limiting region between the 3D printed conductive structure and the insulating structure, the strain limiting region comprising a higher stiffness than the 3D printed conductive structure and a lower stiffness than the insulating structure.

33. The 3D printed flexible electronic device of claim 32, wherein the strain limiting region comprises a thermoplastic elastomer having a lower Shore hardness than the thermoplastic elastomer of the insulating structure.

34. The 3D printed flexible electronic device of claim 32 or 33, wherein the strain limiting region is formed by 3D printing.

35. The 3D printed flexible electronic device of any one of claims 32-34, wherein the stiffness of the strain limiting region is a graded stiffness comprising an increase across the strain limiting region from the 3D printed conductive structure to the insulating structure.

36. The 3D printed flexible electronic device of any one of claims 19-35, further comprising a functional component electrically connected to the 3D printed conductive structure.

37. The 3D printed flexible electronic device of claim 36, wherein the functional component is selected from the group consisting of: active electronic component, passive electronic component, optoelectronic

component, electromechanical component, piezoelectric component, biometric component and sensor.

38. The 3D printed flexible electronic device of claim 36 or 37, further comprising a strain limiting region disposed between the functional component and the 3D printed conductive structure, the strain limiting region being a conductive strain limiting region.

39. The 3D printed flexible electronic device of claim 38, wherein the conductive strain limiting region comprises a lower stiffness than the functional component, and a higher stiffness than the 3D printed conductive structure.

40. The 3D printed flexible electronic device of claim 39, wherein the conductive strain limiting region comprises:

a thermoplastic elastomer having a higher Shore hardness than the thermoplastic elastomer of the 3D printed conductive structure; and

electrically conductive particles at least partially embedded in the thermoplastic elastomer and arranged to define a percolating conductive pathway through some or all of the conductive strain limiting region.

41. The 3D printed flexible electronic device of claim 40, wherein the electrically conductive particles of the conductive strain limiting region comprise a conductive material selected from the group consisting of: gold, silver, carbon, nickel, platinum, palladium, aluminum, and other conductive metals and/or alloys.

42. The 3D printed flexible electronic device of claim 40 or 41, wherein the electrically conductive particles of the conductive strain limiting region comprise the same conductive material as the electrically conductive particles of the 3D printed conductive structure.

43. The 3D printed flexible electronic device of any one of claims 38-42, wherein the thermoplastic elastomer of the conductive strain limiting region is a stiff thermoplastic polyurethane having a Shore hardness greater than 70A, and wherein thermoplastic elastomer of the 3D printed conductive structure is a soft thermoplastic polyurethane having a Shore hardness of 70A or less.

44. The 3D printed flexible electronic device of claim 43, wherein the Shore hardness of the stiff thermoplastic polyurethane is at least about 80A, and wherein the Shore hardness of the soft thermoplastic polyurethane is about 50A or less.

45. The 3D printed flexible electronic device of any one of claims 38-44, wherein the conductive strain limiting region is formed by 3D printing.

46. The 3D printed flexible electronic device of any one of claims 19-45 being biocompatible.

47. The 3D printed flexible electronic device of any one of claims 19-46 having a mechanical integrity sufficient to withstand linear strains of from greater than 0% to 100% without mechanical breakage.

48. The 3D printed flexible electronic device of any one of claims 19-47 being selected from the group consisting of: biometric sensor, energy harvesting device, implantable stimulation and monitoring device, lab on a chip device, electrocardiogram device and wearable healthcare device.

49. An ink formulation for 3D printing a flexible electronic device, the ink formulation comprising:

a thermoplastic elastomer dissolved in a polar solvent.

50. The ink formulation of claim 49, further comprising a plurality of electrically conductive particles in the polar solvent.

51. The ink formulation of claim 49 or 50, further comprising a surfactant or dispersing agent for dispersing the electrically conductive particles in the polar solvent.

52. The ink formulation of any one of claims 49-51, wherein the thermoplastic elastomer is selected from the group consisting of: thermoplastic polyurethane, styrenic block copolymer, thermoplastic olefin, elastomeric alloy, thermoplastic copolyester, and thermoplastic polyamide.

53. The ink formulation of any one of claims 49-52, wherein the thermoplastic elastomer comprises a Shore hardness of greater than 70A, the thermoplastic elastomer being a stiff thermoplastic elastomer.

54. The ink formulation of claim 53, wherein the Shore hardness of the stiff thermoplastic elastomer is at least about 80A.

55. The ink formulation of any one of claims 49-54, wherein the thermoplastic elastomer comprises a Shore hardness of 70A or less, the thermoplastic elastomer being a soft thermoplastic elastomer.

56. The ink formulation of claim 55, wherein the Shore hardness of the soft thermoplastic elastomer is about 50A or less.

57. The ink formulation of any one of claims 49-56, wherein the polar solvent comprises one or more of: dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dimethylformamide (DMF), dibasic ester (DBE), N-methyl-2-pyrrolidone (NMP), alkyl ester, dichloromethane, glycol ether, glycol ether acetate and water (H_2O).

58. The ink formulation of claim 57, wherein the polar solvent includes DMF and THF.

59. The ink formulation of claim 58, wherein a volume ratio of the DMF to the THF is in the range of from 15:85 to about 25:75.

60. The ink formulation of claim 59, wherein the ratio is 20:80.

61. The ink formulation of any one of claims 50-60, wherein the electrically conductive particles comprise a conductive material selected from the group consisting of: gold, silver, carbon, nickel, platinum, palladium, aluminum, and other conductive metals and/or alloys.

62. The ink formulation of any one of claims 50-61, wherein the electrically conductive particles are anisotropic.

63. The ink formulation of any one of claims 50-62, wherein a volume loading of the electrically conductive particles is from about 25 vol.% to about 50 vol.%.

64. The ink formulation of any one of claims 49-63, further comprising one or more rheological modifiers selected from the group consisting of: fumed silica, surface functionalized treated fumed silica, associative thickeners, and non-associative thickeners.

65. The ink formulation of claim 64, wherein the associative thickener comprises a hydrophobically modified ethoxylated urethane resin (HEUR).

66. The ink formulation of any one of claims 49-65, wherein a total solids loading is from about 15% to about 50% by volume.

67. A method of 3D printing a flexible electronic device, the method comprising:

depositing one or more conductive filaments in a predetermined pattern on a substrate, the one or more conductive filaments comprising a conductive ink formulation comprising a polar solvent, a thermoplastic elastomer, and a plurality of electrically conductive particles; and

evaporating the polar solvent to dry the one or more conductive

filaments, thereby forming a 3D printed conductive structure on the substrate.

68. The method of claim 67, wherein the one or more conductive filaments are extruded from a deposition nozzle at room temperature prior to being deposited on the substrate.

69. The method of claim 67 or 68, further comprising depositing one or more insulating filaments in a predetermined pattern on the substrate adjacent to the one or more conductive filaments, the one or more insulating filaments comprising an insulating ink formulation including a thermoplastic elastomer and a polar solvent, and wherein evaporating the polar solvent further comprises drying the one or more insulating filaments, thereby forming an insulating structure on the substrate.

70. The method of claim 69, wherein the one or more insulating filaments are extruded from a deposition nozzle at room temperature prior to being deposited on the substrate.

71. The method of claim 69 or 70, wherein the insulating structure underlies, overlies and/or encapsulates the 3D printed conductive structure.

72. The method of any one of claims 69-71, the one or more insulating filaments being one or more soft insulating filaments and the insulating ink formulation being a soft insulating ink formulation comprising a soft thermoplastic elastomer, and

further comprising depositing one or more stiff insulating filaments in a predetermined pattern on the substrate in contact with the one or more conductive filaments,

wherein the one or more stiff insulating filaments comprises a stiff insulating ink formulation including a stiff thermoplastic elastomer and a polar solvent, the stiff thermoplastic elastomer of the stiff insulating ink formulation comprising a higher Shore hardness than the soft thermoplastic

elastomer of the soft insulating ink formulation, and

wherein evaporating the polar solvent further comprises drying the one or more stiff insulating filaments, thereby forming an insulating strain limiting structure on the substrate between the 3D printed conductive structure and the insulating structure.

73. The method of any one of claims 67-72, wherein evaporating the polar solvent comprises heating the polar solvent to a temperature in the range of about 50°C to about 135°C.

74. The method of claim 73, wherein the heating is carried out for a time period ranging from about 30 minutes to about 3 hours.

75. The method of any one of claims 67-74, wherein the conductive ink formulation further comprises a surfactant or dispersing agent.

76. The method of any one of claims 67-75, wherein the substrate is a flexible substrate comprising a sheet, textile, adhesive or laminate.

77. The method of any one of claims 67-76, further comprising electrically connecting a functional component to the 3D printed conductive structure by a pick and place maneuver.

78. The method of claim 77, the one or more conductive filaments being one or more soft conductive filaments and the conductive ink formulation being a soft conductive ink formulation comprising a soft thermoplastic elastomer, and

further comprising depositing one or more stiff conductive filaments in a predetermined pattern on the substrate in contact with the functional component,

wherein the one or more stiff conductive filaments comprises a stiff conductive ink formulation comprising a polar solvent, a stiff thermoplastic

elastomer, and a plurality of electrically conductive particles, the stiff thermoplastic elastomer of the stiff conductive ink formulation comprising a higher Shore hardness than the soft thermoplastic elastomer of the soft conductive ink formulation, and

wherein evaporating the polar solvent further comprises drying the one or more stiff conductive filaments, thereby forming a conductive strain limiting structure on the substrate between the functional component and the 3D printed conductive structure.

79. The method of any one of claims 77 or 78, wherein the depositing of the one or more insulating filaments is carried out before, during and/or after the functional component is manually or automatically picked and placed.

80. The method of any one of claims 69-79, wherein the depositing of the one or more insulating filaments is carried out before, during and/or after the depositing of the one or more conductive filaments.

81. The method of any one of claims 69-80, wherein the one or more conductive filaments and/or the one or more insulating filaments are deposited on a previously-deposited filament or portion of a filament on the substrate.

82. The method of any one of claims 67-81, wherein the substrate is a sacrificial substrate, and further comprising removing the substrate after forming the 3D printed flexible electronic device.

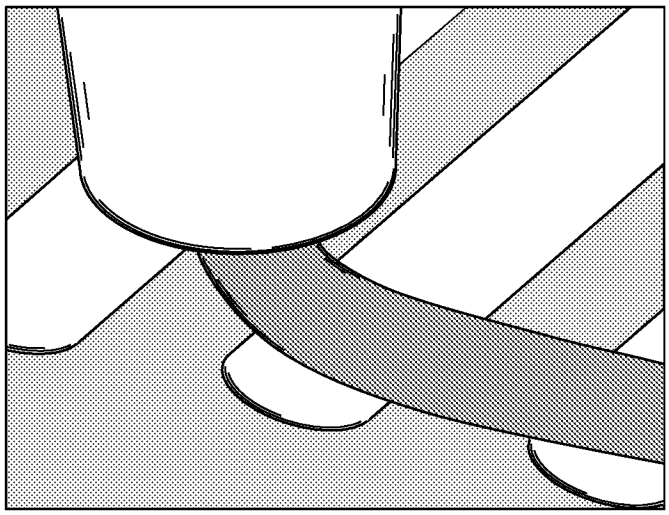


FIG. 1

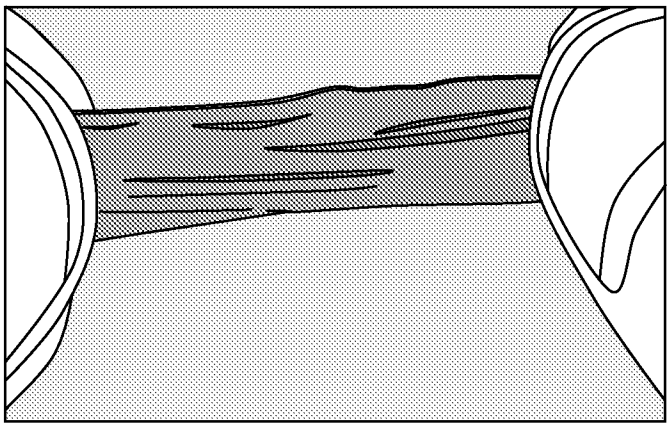


FIG. 2

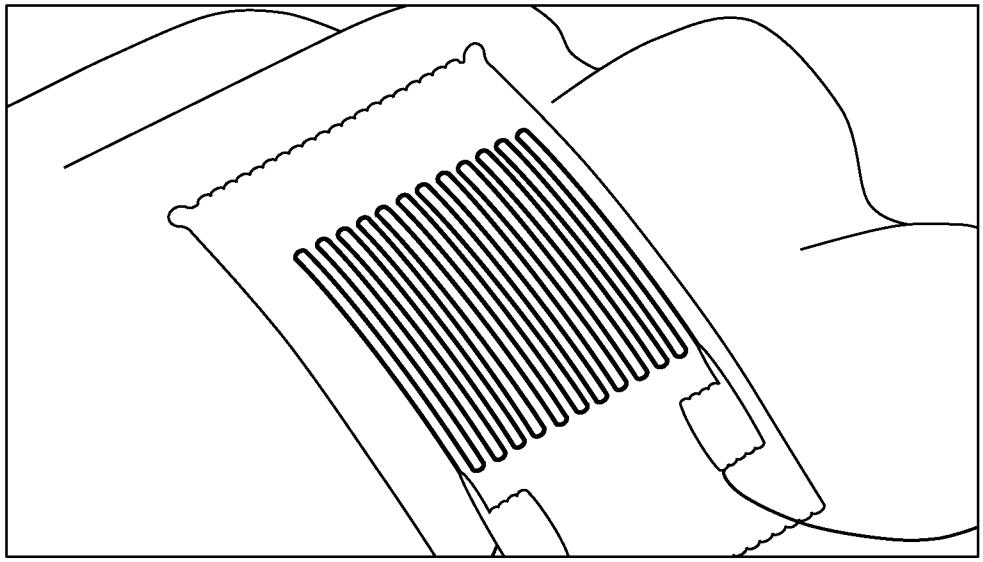


FIG. 3A

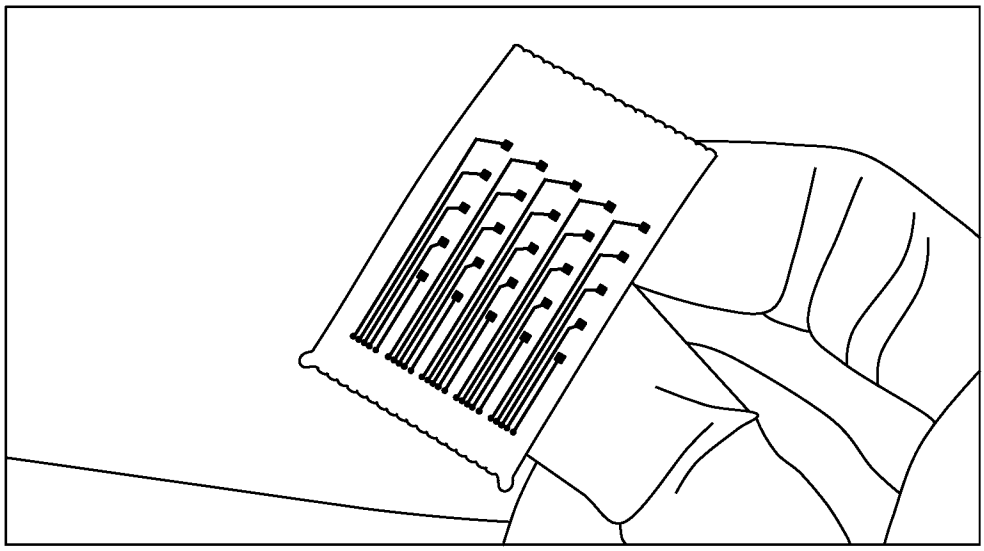


FIG. 3B

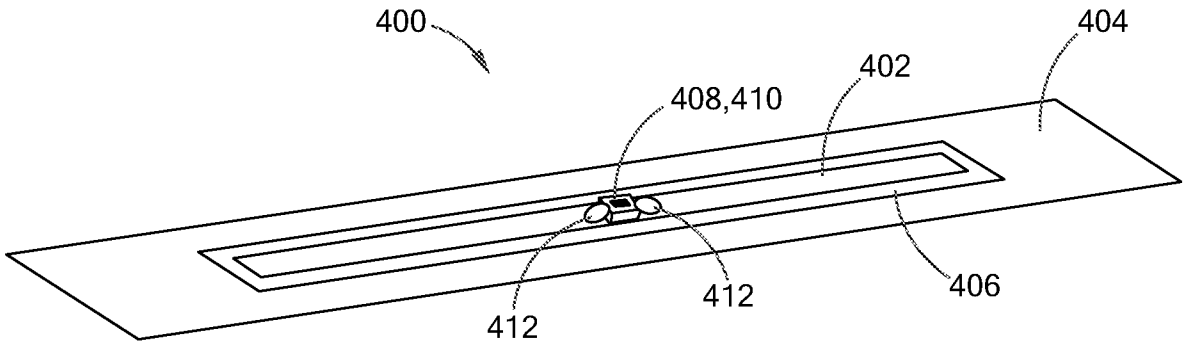

400
404
402
408,410
406
412
412

FIG. 4A

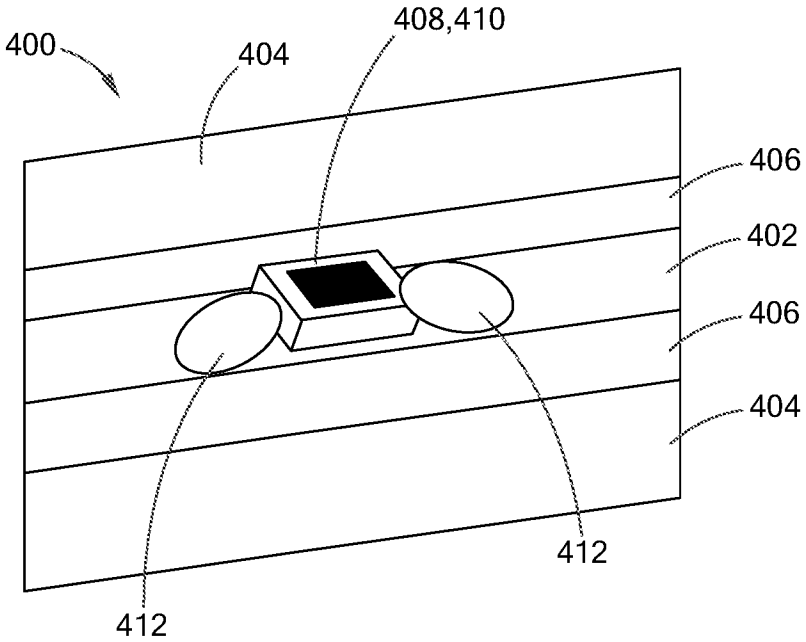

400
404
408,410
406
402
406
404
412
412

FIG. 4B

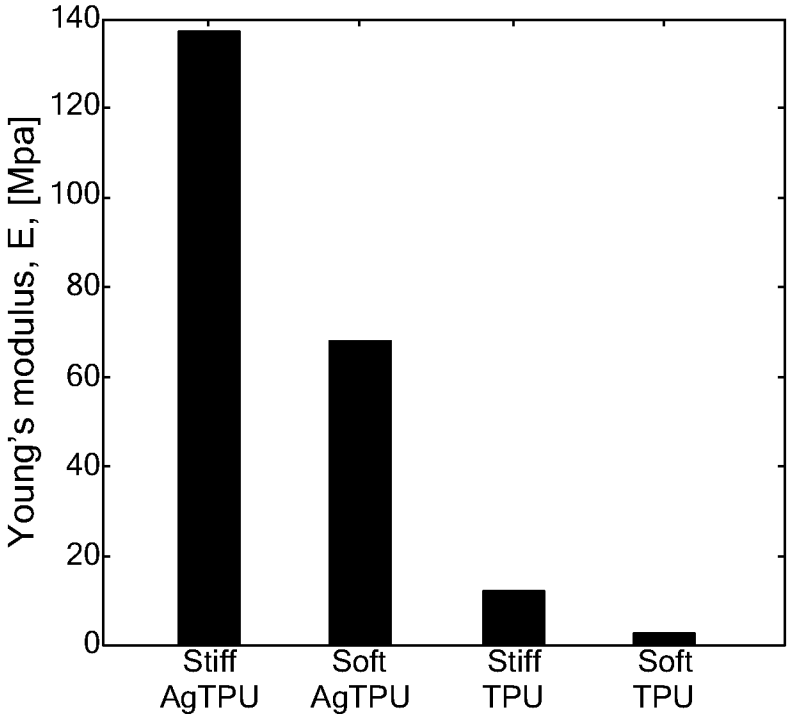


FIG. 4C

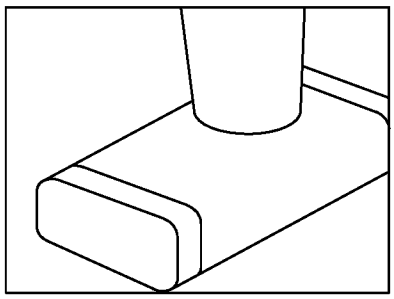


FIG. 5A

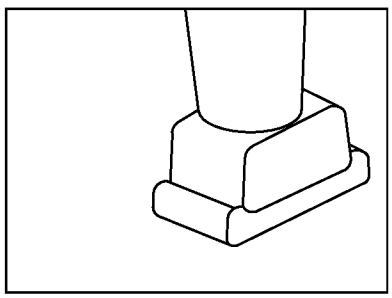


FIG. 5B

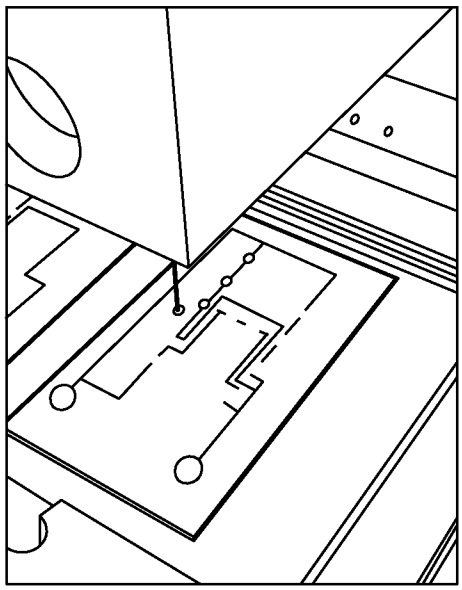


FIG. 5C

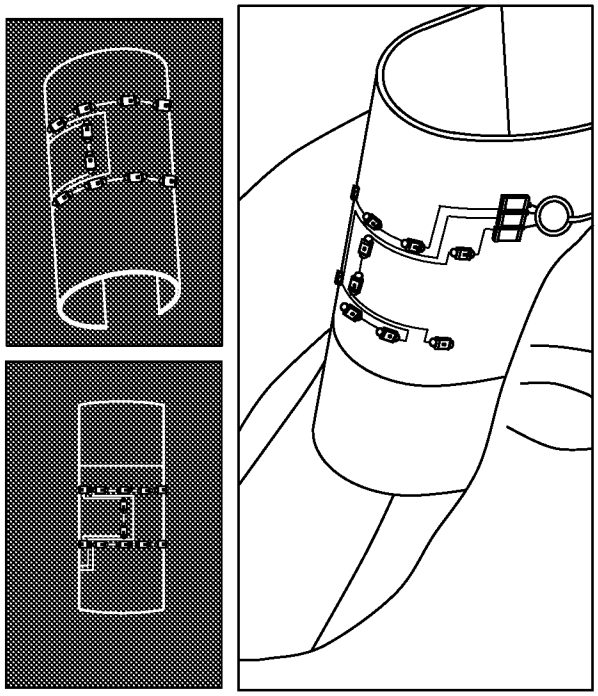


FIG. 6D

FIG. 6C

FIG. 6B

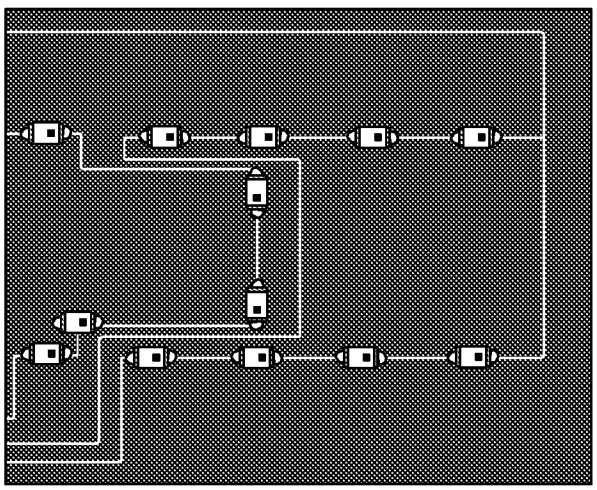


FIG. 6A

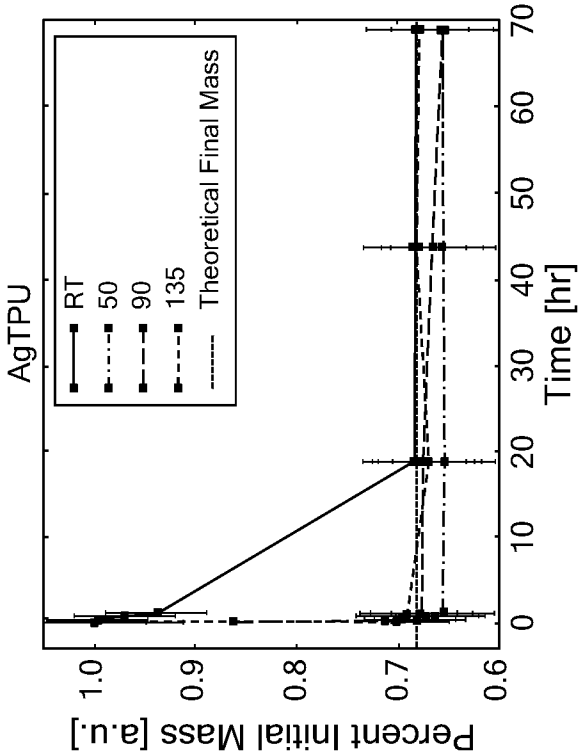


FIG. 7A

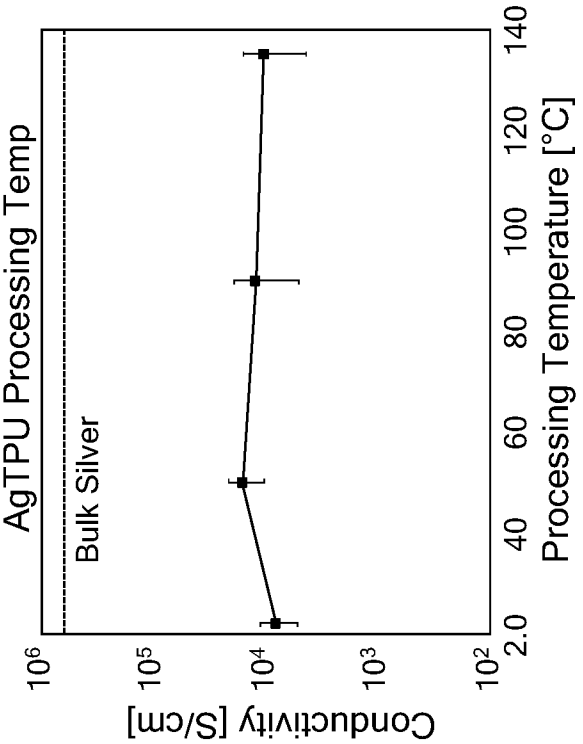


FIG. 7B

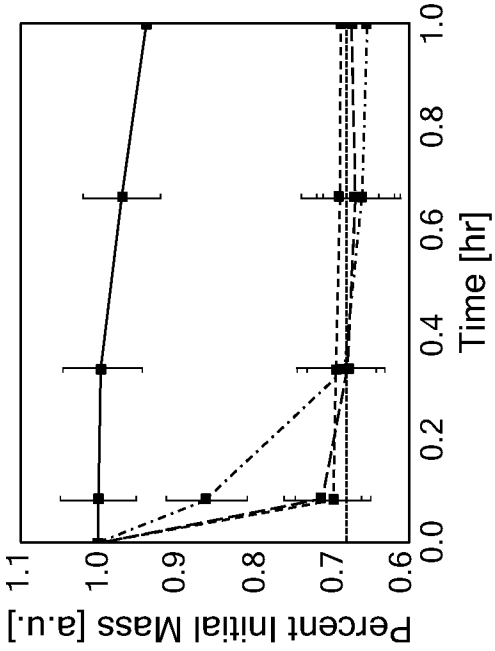


FIG. 7C

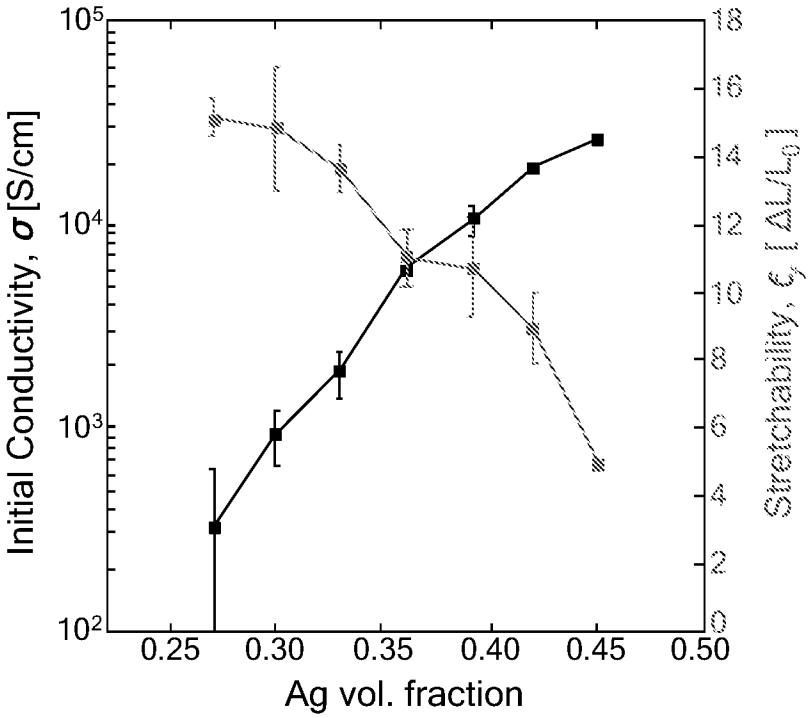

Initial Conductivity, σ [S/cm]
Stretchability, ε_f [ΔL/L_0]
Ag vol. fraction
10^5
10^4
10^3
10^2
0.25
0.30
0.35
0.40
0.45
0.50
0
2
4
6
8
10
12
14
16
18

FIG. 8A

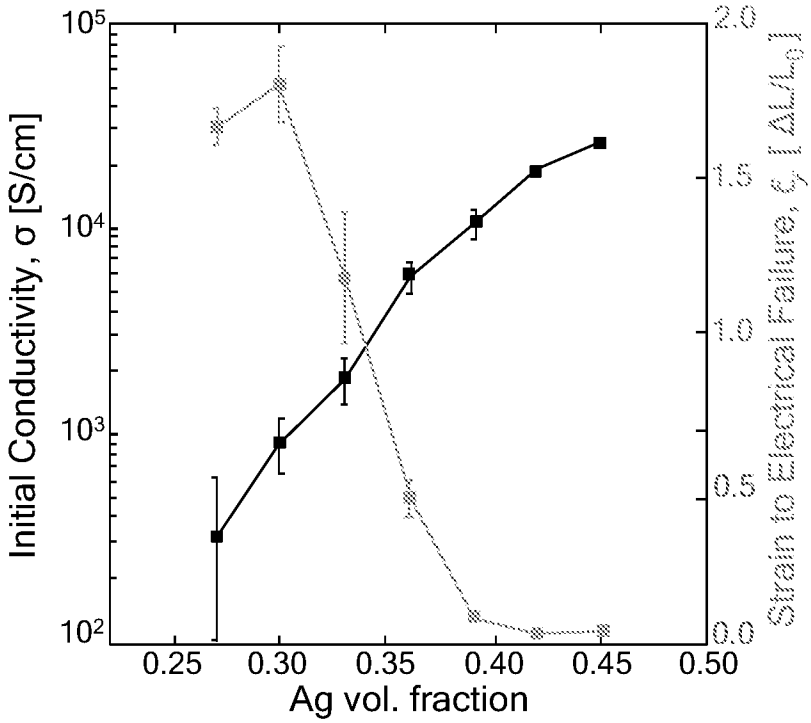

Initial Conductivity, σ [S/cm]
Strain to Electrical Failure, ε_f [ΔL/L_0]
Ag vol. fraction
10^5
10^4
10^3
10^2
0.25
0.30
0.35
0.40
0.45
0.50
0.0
0.5
1.0
1.5
2.0

FIG. 8B

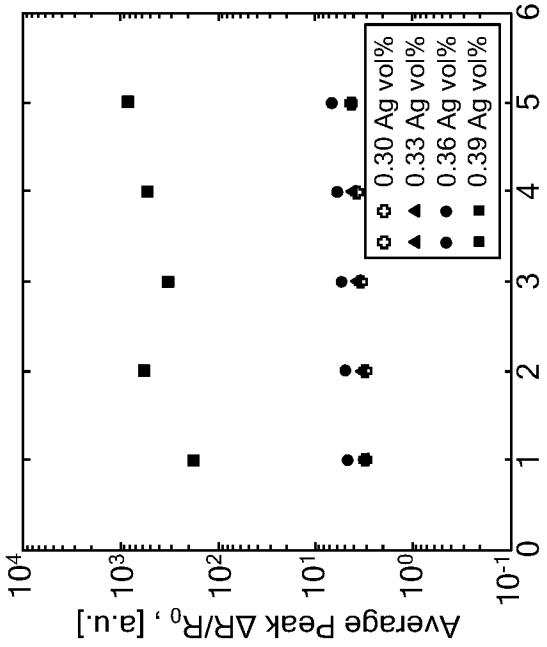


FIG. 8C

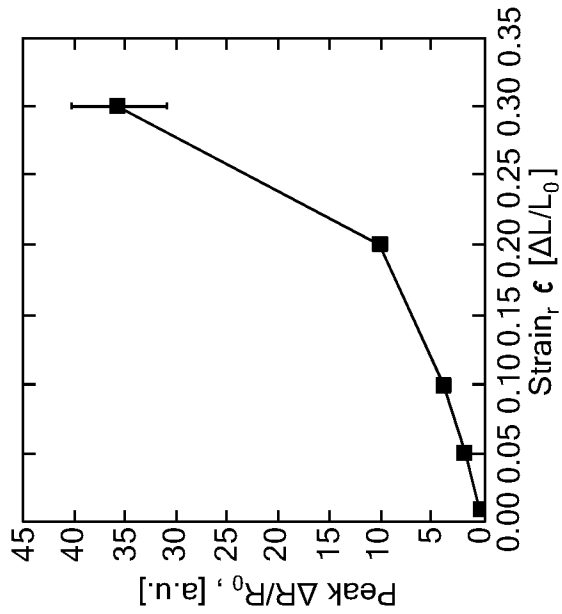


FIG. 8D

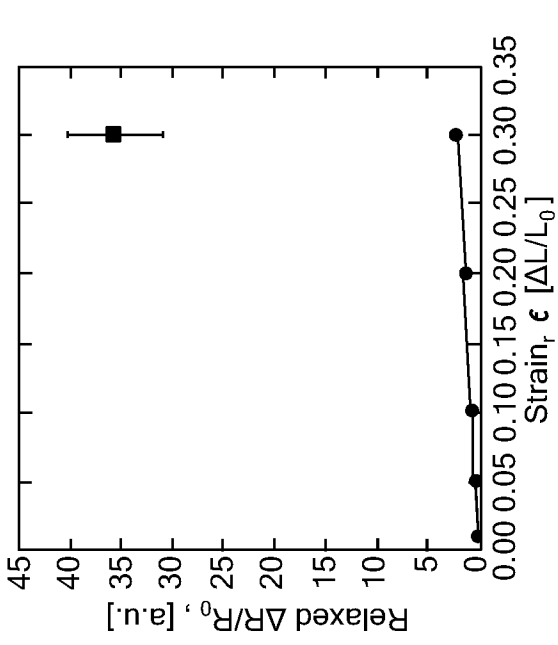


FIG. 8E

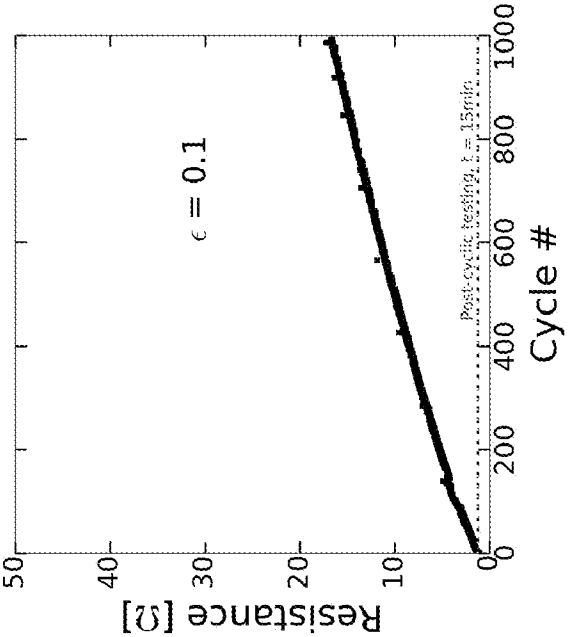


FIG. 8F

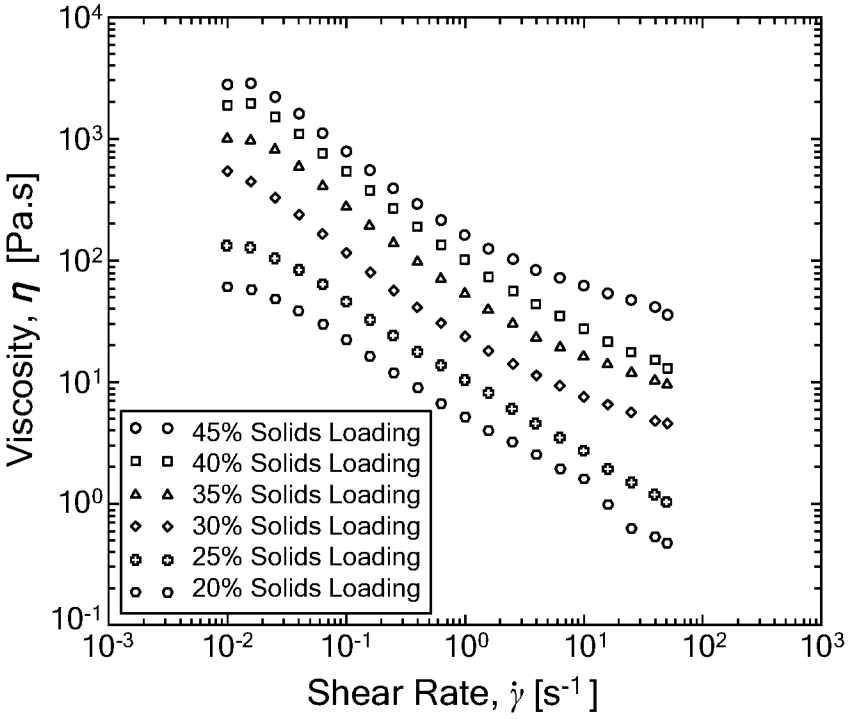

Viscosity, η [Pa.s]
Shear Rate, γ̇ [s-1]
45% Solids Loading
40% Solids Loading
35% Solids Loading
30% Solids Loading
25% Solids Loading
20% Solids Loading

FIG. 9A

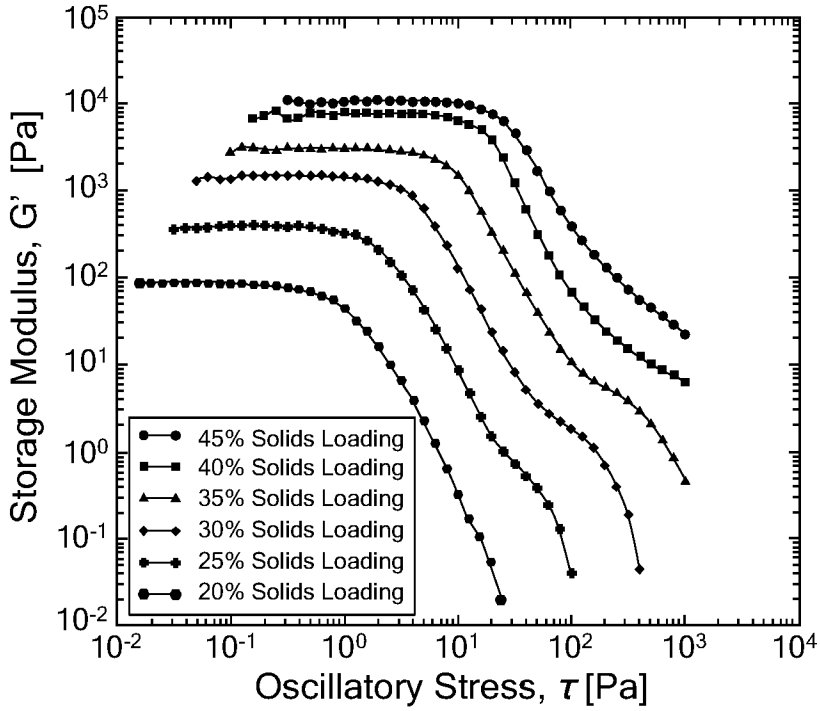

Storage Modulus, G' [Pa]
Oscillatory Stress, τ [Pa]
45% Solids Loading
40% Solids Loading
35% Solids Loading
30% Solids Loading
25% Solids Loading
20% Solids Loading

FIG. 9B

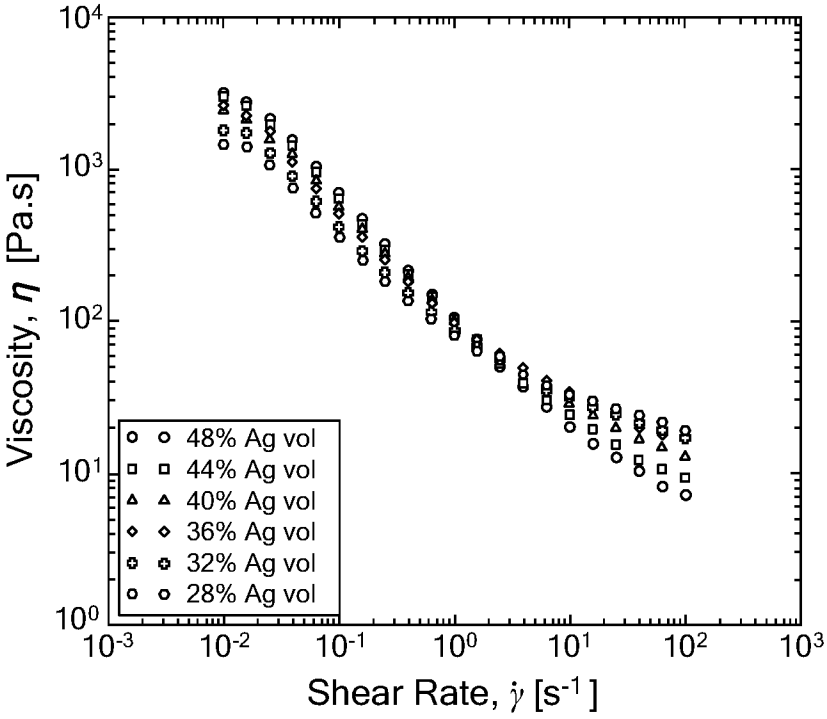


FIG. 10A

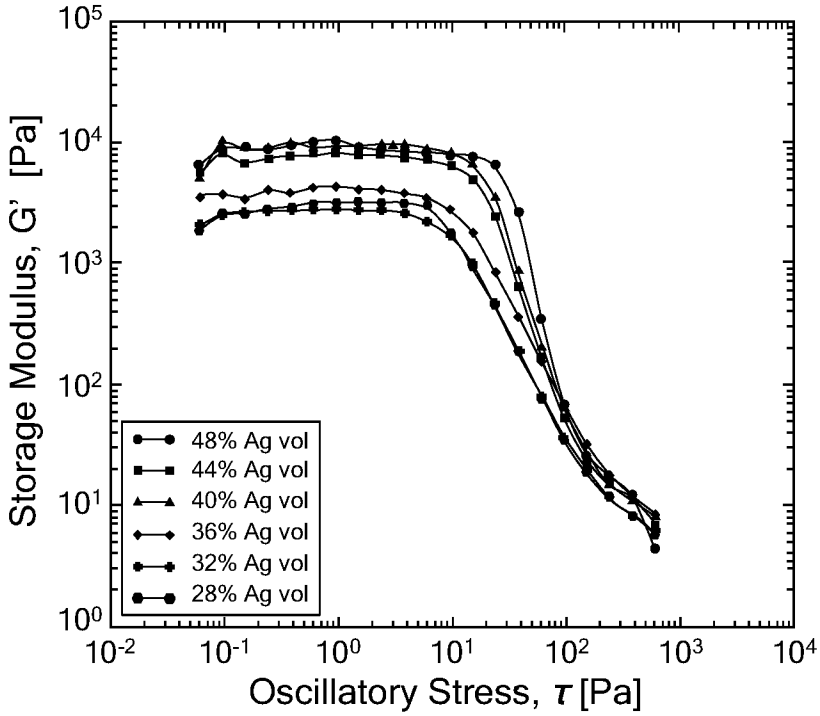


FIG. 10B

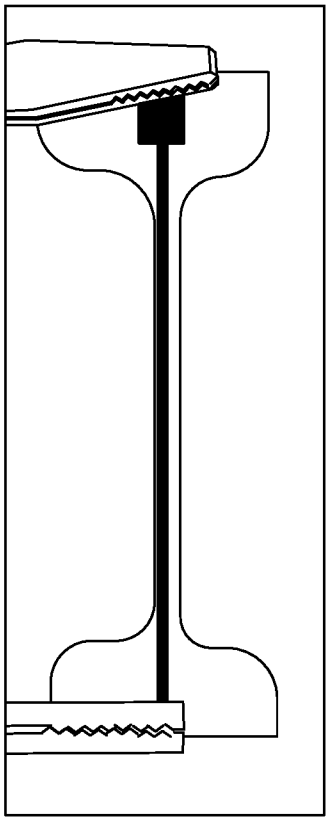


FIG. 11B

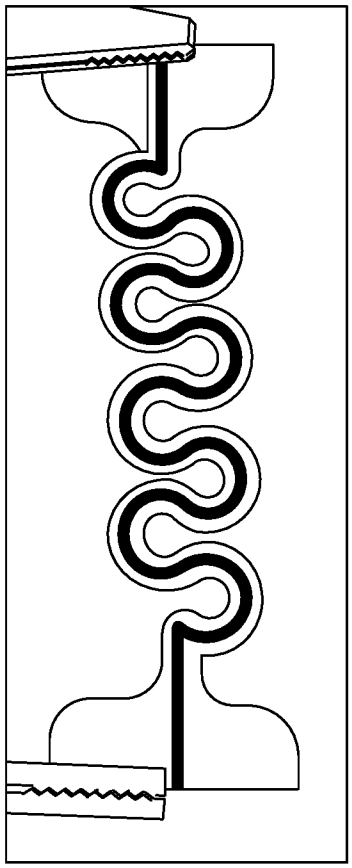


FIG. 11D

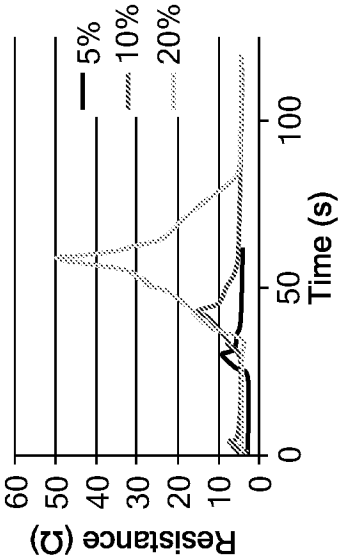


FIG. 11A

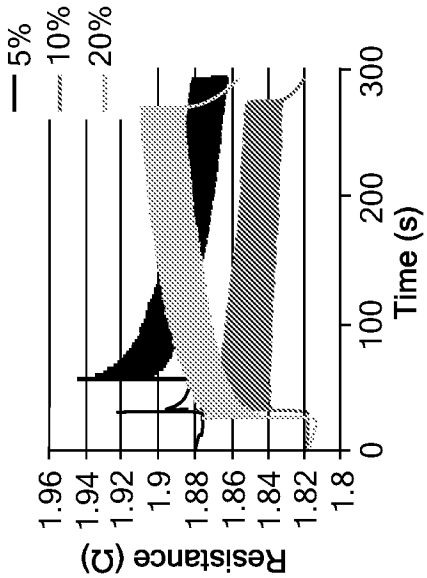


FIG. 11C

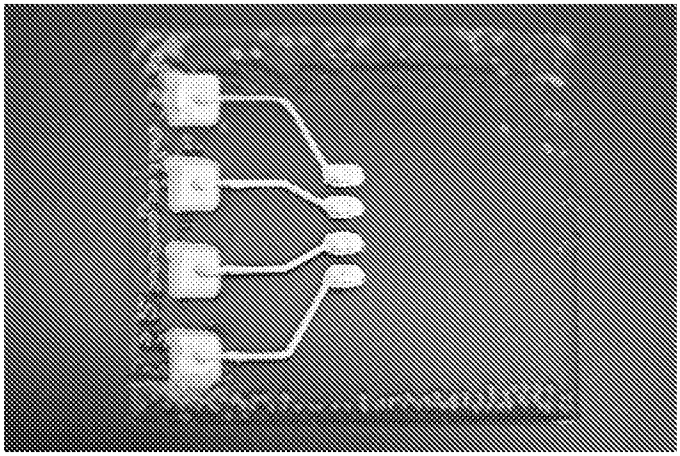


FIG. 12A

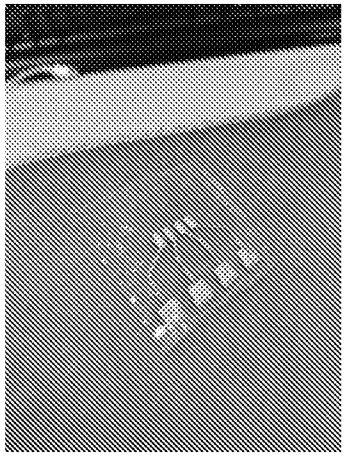


FIG. 12B

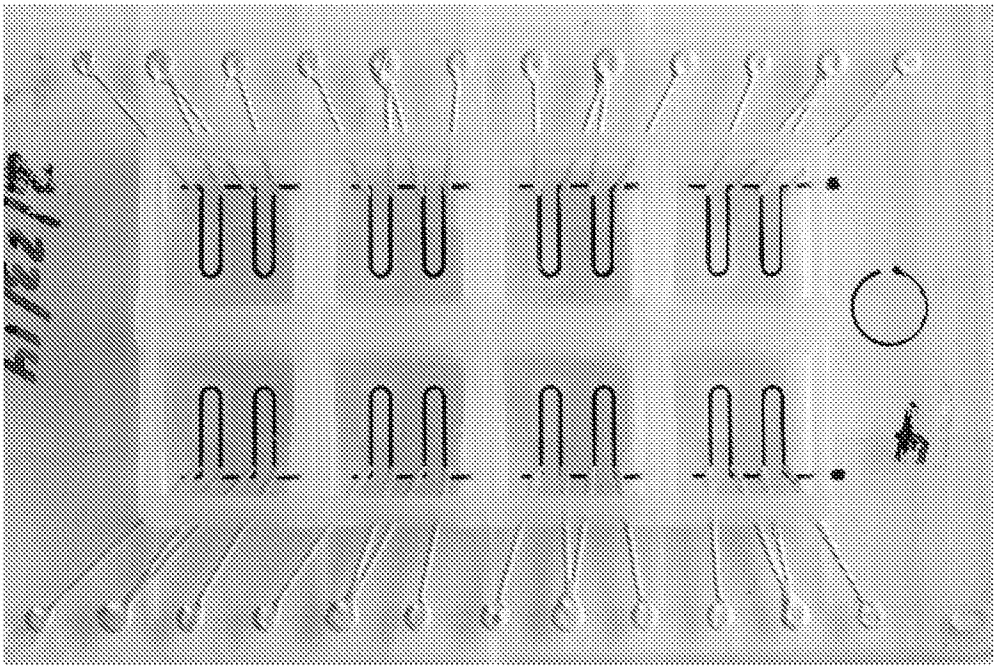


FIG. 13

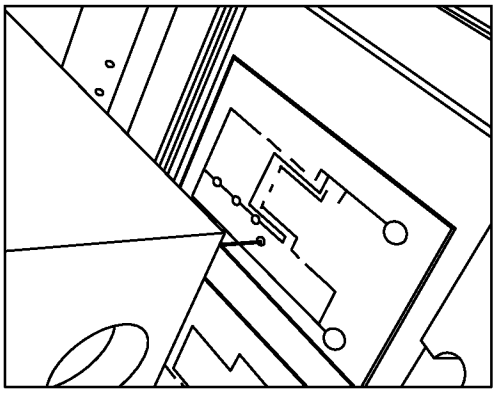


FIG. 14C

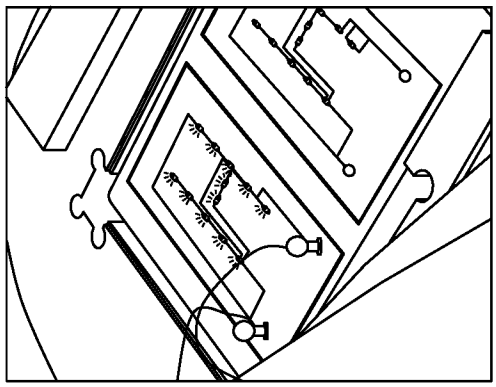


FIG. 14F

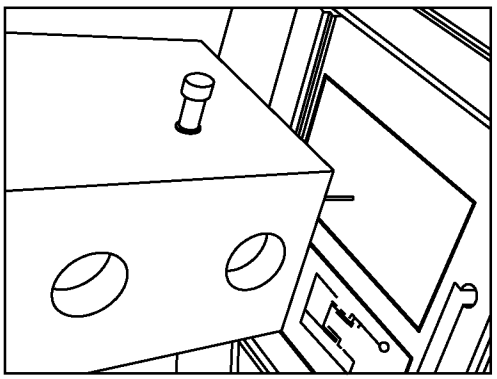


FIG. 14B

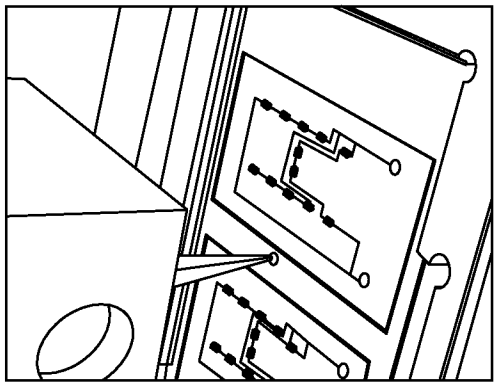


FIG. 14E

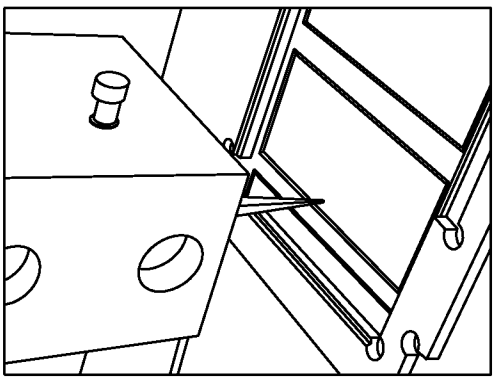


FIG. 14A

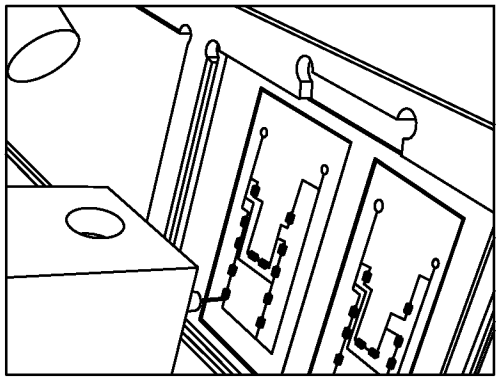


FIG. 14D

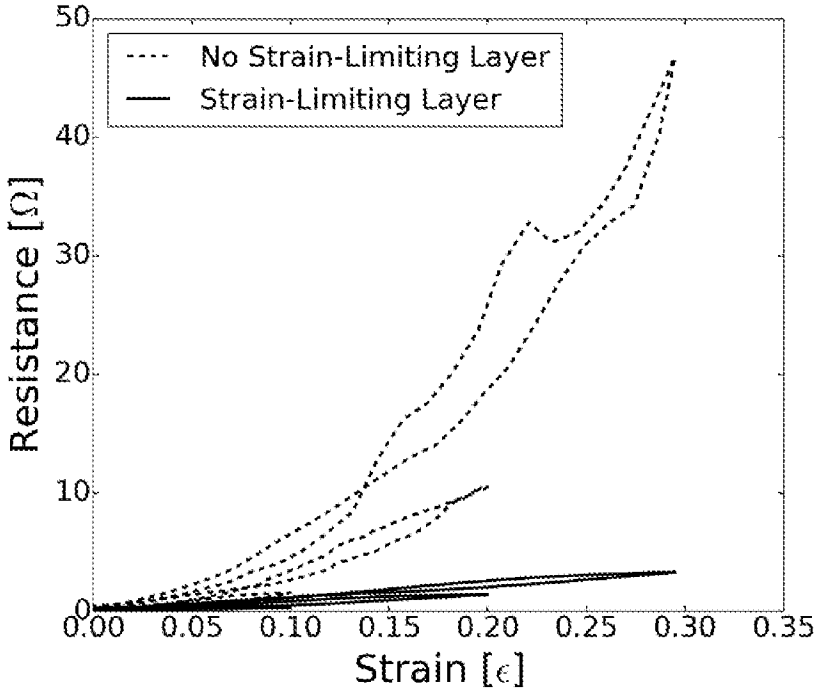


FIG. 15A

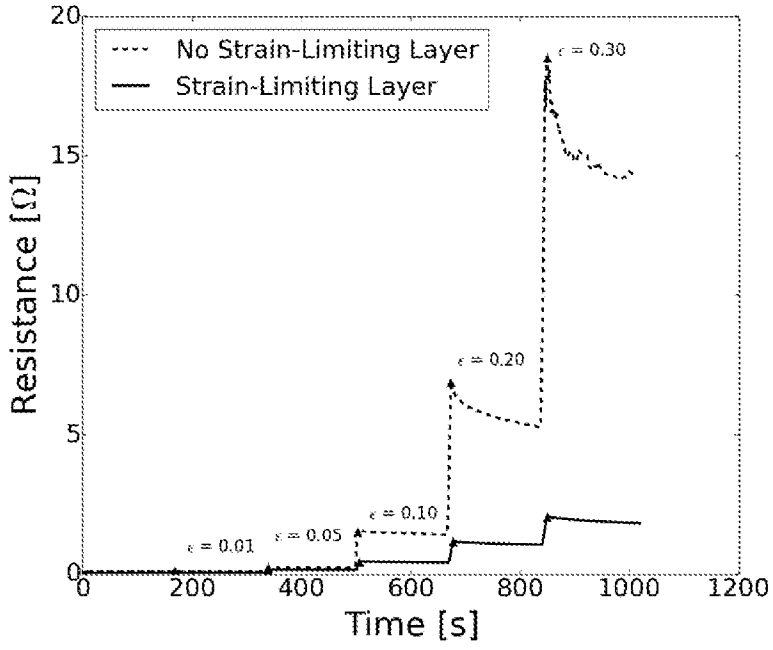


FIG. 15B

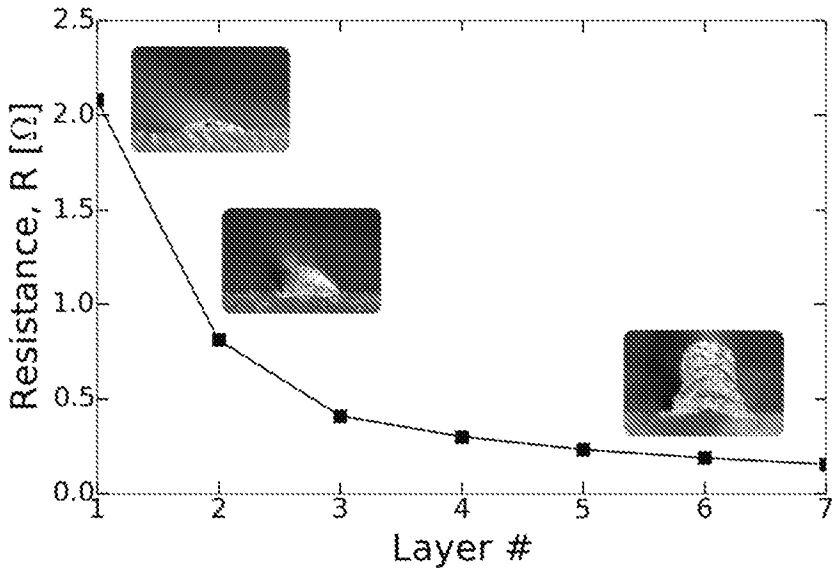

Resistance, R [Ω]
2.5
2.0
1.5
1.0
0.5
0.0
1
2
3
4
5
6
7
Layer #

FIG. 16

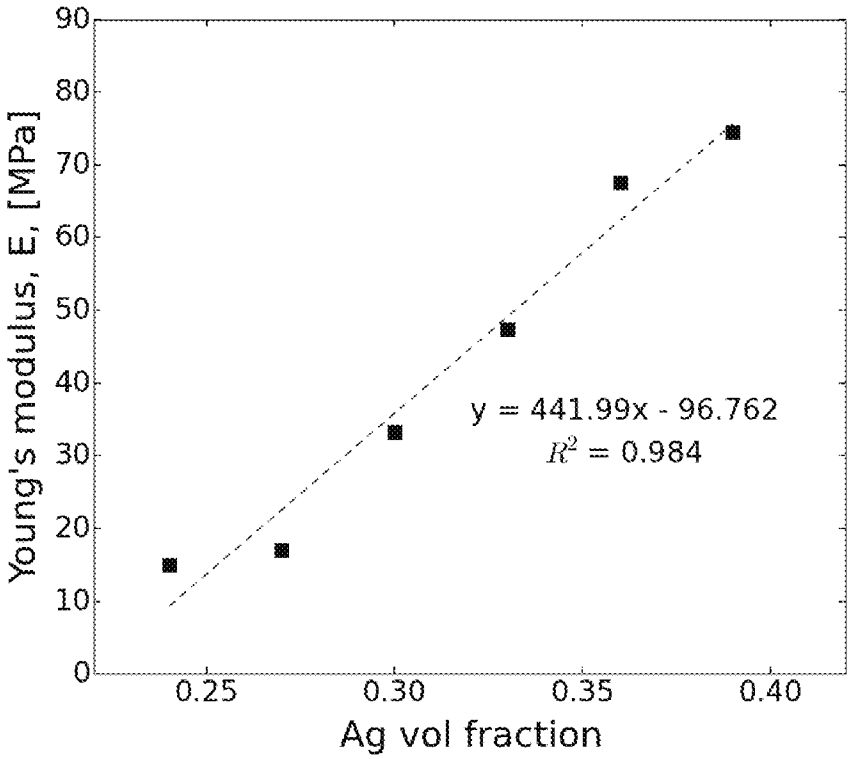

Young's modulus, E, [MPa]
90
80
70
60
50
40
30
20
10
0
0.25
0.30
0.35
0.40
Ag vol fraction
y = 441.99x - 96.762
R^2 = 0.984

FIG. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/022005

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H05K 1/03; H05K 1/02; H05K 3/46; C09D 11/033 (2016.01)
CPC - H05K 1/038; H05K 1/0283; H05K 1/02; H05K 3/4644; C09D 11/033 (2016.05)
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 - B41J 2/01; B41J 2/015; C09D 11/02; C09D 11/033; C09D 11/10; H05K 1/02; H05K 1/03; H05K 3/46
CPC - C09D 11/033; H05K 1/028; H05K 1/0283; H05K 1/038; H05K 3/46; H05K 3/4644; H05K 3/4691

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC 347/21; 438/455 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Patbase, Google Patents , Google
Search terms used: thermoplastic elastomer, 3D print, circuit

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2001/0036718 A1 (WILLIAMS) 01 November 2001 (01.11.2001) entire document	1-3
A	US 2013/0320467 A1 (BUCHANAN et al) 05 December 2013 (05.12.2013) entire document	1-3
A	WO 2014/113937 A1 (HENKEL IP & HOLDING GMBH et al) 31 July 2014 (31.07.2014) entire document	1-3
A	US 2010/0007692 A1 (VANMAELE et al) 14 January 2010 (14.01.2010) entire document	1-3

☐ 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	Date of mailing of the international search report
26 June 2016	28 JUL 2016
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/022005

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.: 4-48, 52-66, 71-82
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 supplemental page

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.:
1-3

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.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/022005

Continued from Box No. III Observations where unity of invention is lacking

This 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 fees must be paid.

Group I, claims 1-3, drawn to a 3D printed conductive structure for a flexible electronic device.
Group II, claims 49-51,67-70, drawn to 3D printing a flexible electronic device.

The inventions listed as Groups I-II 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 for the following reasons: the special technical feature of the Group I invention: define a percolating conductive pathway therethrough, wherein the 3D printed conductive structure comprises a predetermined geometry as claimed therein is not present in the invention of Group II. The special technical feature of the Group II invention: an ink formulation comprising a polar solvent as claimed therein is not present in the invention of Group I.

Groups I and II lack unity of invention because even though the inventions of these groups require the technical feature of 3D printed structure for a flexible electronic device; plurality of electrically conductive particles; a thermoplastic elastomer, this technical feature is not a special technical feature as it does not make a contribution over the prior art.

Specifically, US 2001/0036718 A1 (WILLIAMS) 01 November 2001 (01.11.2001) teaches 3D printed structure for a flexible electronic device (Paras. 32 and 76); plurality of electrically conductive particles (Para. 23); a thermoplastic elastomer (Para. 110).

Since none of the special technical features of the Group I or II inventions are found in more than one of the inventions, unity of invention is lacking.