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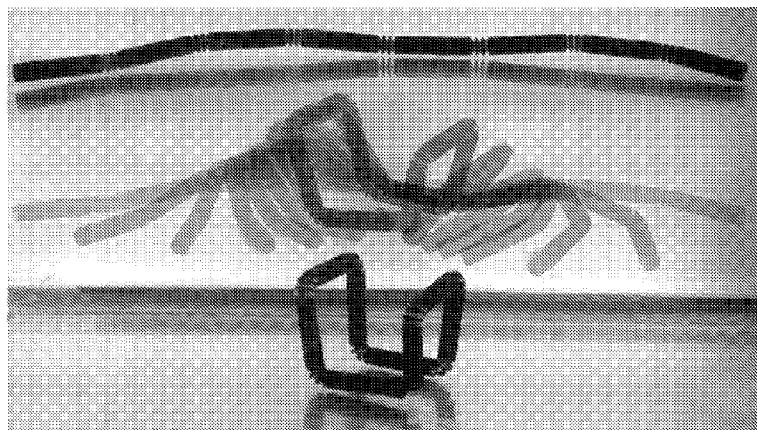


FIG. 5

(57) Abstract: The combination of 3D printing technology plus the additional dimension of transformation over time of the printed object is referred to herein as 4D printing technology. Particular arrangements of the additive manufacturing material(s) used in the 3D printing process can create a printed 3D object that transforms over time from a first, printed shape to a second, predetermined shape.



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**OBJECT OF ADDITIVE MANUFACTURE WITH ENCODED PREDICTED
SHAPE CHANGE****RELATED APPLICATION(S)**

[0001] This application claims the benefit of U.S. Provisional Application No. 61/930,521, filed on January 23, 2014. This application also claims the benefit of U.S. Provisional Application No. 61/912,056, filed on December 5, 2013. The entire teachings of the above applications are incorporated herein by reference.

**COMMON OWNERSHIP UNDER JOINT RESEARCH AGREEMENT 35 U.S.C.
102(c)**

[0002] The subject matter disclosed in this application was developed, and the claimed invention was made by, or on behalf of, one or more parties to a joint Research Agreement that was in effect on or before the effective filing date of the claimed invention. The parties to the Joint Research Agreement are the Massachusetts Institute of Technology, located in Cambridge, Massachusetts, USA; and Stratasys Ltd., an Israeli company located at 2 Holzman Street, Rehovot, Israel 76124, and Stratasys, Inc., a Delaware corporation located at 7665 Commerce Way, Eden Prairie, Minnesota 55344 (collectively, "Stratasys").

BACKGROUND OF THE INVENTION

[0003] Traditional manufacturing typically involves molded production of parts and other components having a fixed shape, and those individual components are frequently assembled into more complex structures. The process is often expensive and can involve a significant amount of manual labor, and molds used in the production are expensive to manufacture and have singular design structure.

[0004] Three-dimensional (3D) printing has been used to create static objects and other stable structures, such as prototypes, products, and molds. Three dimensional printers can convert a 3D image, which is typically created with computer-aided design (CAD) software, into a 3D object through the layerwise addition of material. For this reason, 3D printing has become relatively synonymous

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with the term “additive manufacturing.” In contrast, “subtractive manufacturing” refers to creating an object by cutting or machining away material to create a desired shape.

SUMMARY OF THE INVENTION

[0005] Existing 3D printing technologies hold a promise of an ability to mass-produce customized components by substantially reducing the time and materials necessary, which can consequently increase efficiency. However, in some cases existing technology may still require additional processes, for example labor-intensive sorting and assembly of the 3D printed components in order to arrive at a desired final product.

[0006] Embodiments described herein provide another dimension to 3D printing technology. Particular arrangements of the additive manufacturing materials used in the 3D printing process can create a printed 3D object that transforms over time from a first, printed shape to a second, predetermined shape. Therefore, the combination of 3D printing technology plus the additional dimension of transformation over time of the printed object is referred to herein as 4D printing technology. This 4D printing technology in some cases provides a number of benefits over 3D printing technology. In particular, some physical objects made through a 3D printing process that might otherwise have necessitated assembly or other post-processing of printed parts can be rapidly manufactured and assembled without requiring post-printing assembly, thereby reducing the time and costs associated with assembly. Objects can be printed in a first shape and transformed to a second, predetermined shape at a later time. For example, the objects can be printed and transported in a first shape that is flat, and then expanded to a second shape at a later time, such as upon arrival at a customer’s location. This can permit more efficient shipping because the first (*i.e.*, shipping) shape is more flat and requires a smaller shipping volume. Printing flat objects also requires significantly less printing time, thereby also reducing the overall fabrication costs.

[0007] Objects can be designed by reference to a second shape, and computer software loadable from a non-transient computer-readable medium can be used to

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calculate the first shape in which an object is printed for subsequent transformation to at least one second shape.

[0008] Disclosed herein is an object. The object can be made from an additive manufacturing material. The additive manufacturing material can have a response to an external stimulus and be configured to cause a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the external stimulus. The external stimulus can be non-biasing with respect to the predicted transformation from the first manufactured shape to the second manufactured shape.

[0009] The external stimulus can be a temperature change. The additive manufacturing material can have a glass transition temperature of approximately 0°C to approximately 150°C, or approximately 75°C to approximately 90°C.

[0010] The additive manufacturing material can be a first additive manufacturing material, and the object can have a second additive manufacturing material arranged relative to the first additive manufacturing material to enable the predicted transformation of the object from the first manufactured shape to the second manufactured shape in response to the external stimulus. The second additive manufacturing material can have a second response to either the first external stimulus or to a second external stimulus to enable a corresponding second predicted transformation of the object to a third manufactured shape. The first and second additive manufacturing materials can compose the entire object.

[0011] The object can further include a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, and can have a third response to the first external stimulus, the second external stimulus, or a third external stimulus to enable a corresponding third predicted transformation of the object to a fourth manufactured shape. The first, second, and third additive manufacturing materials can compose the entire object. The third additive manufacturing material can have a third response that modifies the properties of one or more of the first or second additive manufacturing materials. The property modified can be the stiffness of one or more of the first and second additive manufacturing materials.

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[0012] The external stimulus can be selected from the group consisting of a solvent, temperature change, electromagnetic energy, and pressure change.

[0013] The first and second additive manufacturing materials can be arranged to form a joint of the object. The joint can effect linear or rotational displacement of a first member of the object relative to a second member of the object. The joint can have at least one cylindrical disc or at least one rectangular member. Each of the first and second additive manufacturing materials composing the joint can have a three-dimensional structure. The joint can curl, fold, elongate linearly, decrease the size of a hole, form a curved crease, or expand linearly.

[0014] The first external stimulus can be a solvent. The first additive manufacturing material can be more hydrophilic than the second additive manufacturing material. The first additive manufacturing material can be formed of a polymerized formulation that includes one or more of hydrophilic acrylic monomers and oligomers. The first additive manufacturing material can be formed of a polymerized formulation that includes hydroxyethyl acrylate or poly(ethylene) glycol. The second additive manufacturing material can be formed of a polymerized formulation that includes one or more of hydrophobic acrylic monomers and oligomers. The second additive manufacturing material can be formed of a polymerized formulation that includes monomers of one or more of phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate. One or more of the first and second additive manufacturing materials can be formed of a polymerized formulation that further includes one or more of a photoinitiator, surface active agent, stabilizer, and inhibitor.

[0015] Also disclosed herein is a method for additive manufacturing of an object. The method can include dispensing an additive manufacturing material having a response to an external stimulus. The additive manufacturing material can be configured to cause a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the external stimulus. The external stimulus can be non-biasing with respect to the predicted transformation from the first manufactured shape to the second manufactured shape.

[0016] The first additive manufacturing material can have a glass transition temperature of approximately 0°C to approximately 150°C, or approximately 75°C

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to approximately 90°C. The method can further include exposing the object to an external stimulus, wherein the external stimulus is a temperature change.

[0017] The additive manufacturing material can be a first additive manufacturing material, and the method can further include dispensing a second additive manufacturing material arranged relative to the first additive manufacturing material to enable the predicted transformation of the object from the first manufactured shape to the second manufactured shape in response to the external stimulus. The external stimulus can be a first external stimulus, and the second additive manufacturing material can have a second response to either the first external stimulus or to a second external stimulus to enable a corresponding second predicted transformation of the object to a third manufactured shape. The first and second additive manufacturing materials can compose the entire object.

[0018] The method can further include dispensing a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, and having a third response to the first external stimulus, the second external stimulus, or a third external stimulus to enable a corresponding third predicted transformation of the object to a fourth manufactured shape. The first, second, and third additive manufacturing materials can compose the entire object. The third response of the third additive manufacturing material can modify the properties of one or more of the first or second additive manufacturing materials. The property modified can be the stiffness of one or more of the first and second additive manufacturing materials.

[0019] The first and second additive manufacturing materials can be arranged to form a joint of the object. The joint can effect linear or rotational displacement of a first member of the object relative to a second member of the object. The joint can have at least one cylindrical disc or at least one rectangular member. Each of the first and second additive manufacturing materials composing the joint can have a three-dimensional structure. The joint can curl, fold, elongate linearly, decrease the size of a hole, form a curved crease, or expand linearly.

[0020] The first additive manufacturing material can be more hydrophilic than the second material. The first additive manufacturing material can be formed of a polymerized formulation that includes one or more of hydrophilic acrylic monomers

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and oligomers. The first additive manufacturing material can be formed of a polymerized formulation that includes hydroxyethyl acrylate or poly(ethylene) glycol. The second additive manufacturing material can be formed of a polymerized formulation that includes one or more of hydrophobic acrylic monomers and oligomers. The second additive manufacturing material can be formed of a polymerized formulation that includes monomers of one or more of phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate. One or more of the first and second additive manufacturing materials can be formed of a polymerized formulation that further includes one or more of a photoinitiator, surface active agent, stabilizer, and inhibitor. The method can further include exposing the object to an external stimulus selected from the group consisting of a solvent, temperature change, electromagnetic energy, and pressure change. The external stimulus can be a polar solvent. The polar solvent can be selected from the group consisting of water, an alcohol, and combinations thereof.

[0021] Exposing the object to an external stimulus can cause one or more of curling, folding, stretching, shrinking, and curved creasing.

[0022] Also disclosed herein is an object of additive manufacture prepared according to the method described above. The method of forming the object can include dispensing an additive manufacturing material having a response to an external stimulus. The additive manufacturing material can be configured to cause a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the external stimulus. The external stimulus can be non-biasing with respect to the predicted transformation from the first manufactured shape to the second manufactured shape.

[0023] The first additive manufacturing material can have a glass transition temperature of approximately 0°C to approximately 150°C, or approximately 75°C to approximately 90°C. The method of forming the object can further include exposing the object to an external stimulus, wherein the external stimulus is a temperature change.

[0024] The additive manufacturing material can be a first additive manufacturing material, and the method can further include dispensing a second additive manufacturing material arranged relative to the first additive manufacturing

material to enable the predicted transformation of the object from the first manufactured shape to the second manufactured shape in response to the external stimulus. The external stimulus can be a first external stimulus, and the second additive manufacturing material can have a second response to either the first external stimulus or to a second external stimulus to enable a corresponding second predicted transformation of the object to a third manufactured shape. The first and second additive manufacturing materials can compose the entire object.

[0025] The method of forming the object can further include dispensing a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, and having a third response to the first external stimulus, the second external stimulus, or a third external stimulus to enable a corresponding third predicted transformation of the object to a fourth manufactured shape. The first, second, and third additive manufacturing materials can compose the entire object. The third response of the third additive manufacturing material can modify the properties of one or more of the first or second additive manufacturing materials. The property modified can be the stiffness of one or more of the first and second additive manufacturing materials.

[0026] The first and second additive manufacturing materials can be arranged to form a joint of the object. The joint can effect linear or rotational displacement of a first member of the object relative to a second member of the object. The joint can have at least one cylindrical disc or at least one rectangular member. The joint can curl, fold, elongate linearly, close a hole, form a curved crease, or expand linearly.

[0027] The first additive manufacturing material can be more hydrophilic than the second material. The first additive manufacturing material can be formed of a polymerized formulation that includes one or more of acrylic monomers and oligomers. The first additive manufacturing material can be formed of a polymerized formulation that includes hydroxyethyl acrylate. The second additive manufacturing material can be formed of a polymerized formulation that includes one or more of hydrophobic acrylic monomers and oligomers. The second additive manufacturing material can be formed of a polymerized formulation that includes monomers of one or more of phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate. One or more of the first and second additive manufacturing

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materials can be formed of a polymerized formulation that further includes one or more of a photoinitiator, surface active agent, stabilizer, and inhibitor. The method of forming the object can further include exposing the object to an external stimulus selected from the group consisting of a solvent, temperature change, electromagnetic energy, and pressure change. The external stimulus can be a polar solvent. The polar solvent can be selected from the group consisting of water, an alcohol, and combinations thereof.

[0028] Exposing the object to an external stimulus can cause one or more of curling, folding, stretching, shrinking, and curved creasing.

[0029] Further disclosed herein is a non-transient computer readable medium having stored thereon a sequence of instructions. When executed by a processor, the sequence of instructions can cause an apparatus to access a database that includes first parameters of additive manufacturing materials, access the database that includes second parameters for arranging one or more additive manufacturing materials relative to each other to form at least a portion of an object having a first manufactured shape in an absence of an external stimulus and having a second, predicted manufactured shape in a presence of, or following exposure to, an external stimulus, and calculate, as a function of the first and second parameters, a sequence of machine-controllable instructions that, when provided to a machine, programs the machine to produce the object in the first manufactured shape.

[0030] The database can further include parameters of an environment in which the object will be employed. The sequence of instructions can further cause the apparatus to calculate machine-controllable instructions as a function of the environment or adjust the previously calculated machine-controllable instructions as a function of the environment.

[0031] The external stimulus can be one or more of a solvent, temperature change, electromagnetic energy, and pressure change. The machine-controllable instructions can cause the apparatus to dispense a first additive manufacturing material. The machine-controllable instructions can cause the apparatus to dispense a second additive manufacturing material in an arrangement relative to first additive manufacturing material to enable a predicted transformation of the object from a

first manufactured shape to a second manufactured shape in response to the first external stimulus.

[0032] The external stimulus can be a first external stimulus, and the predicted transformation can be a first predicted transformation and can further include a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, wherein the third additive manufacturing material has a third response to the first external stimulus or a second external stimulus to enable a corresponding second predicted transformation of the shape of the object in response to the first or second external stimulus.

[0033] The database can include a library of joints. The joints can include one or more of a curling joint, a folding joint, a linear elongation joint, a joint that decreases the size of a hole, a curved-crease joint, and a linear expansion joint.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

[0035] The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating embodiments of the present invention.

[0036] FIG. 1 is a schematic representation of an arrangement of a low swelling material and a high swelling material.

[0037] FIG. 2 is a schematic representation of an arrangement of a low swelling material and a high swelling material that can form a folding joint.

[0038] FIG. 3A is a computer generated model of an object formed by an additive manufacturing process that can fold upon, or following, exposure to an external stimulus.

[0039] FIG. 3B is a computer generated model of an object formed by an additive manufacturing process that has folded after exposure to an external stimulus.

[0040] FIG. 4A is a top view of a schematic representation of an arrangement that can produce a folding transformation upon, or following, exposure to an external stimulus.

[0041] FIG. 4B is a perspective view of a schematic representation of an arrangement that can produce a folding transformation upon, or following, exposure to an external stimulus.

[0042] FIG. 4C is a top view of a schematic representation of an arrangement that has undergone a folding transformation after exposure to an external stimulus.

[0043] FIG. 4D is a perspective view of a schematic representation of an arrangement that has folded after exposure to an external stimulus.

[0044] FIG. 4E is a top view of a schematic representation of an arrangement having a plurality of joints that can fold to form a Hilbert curve in the shape of a cube upon, or following, exposure to an external stimulus.

[0045] FIG. 4F is a perspective view of a schematic representation of an arrangement having a plurality of joints that has folded to form a Hilbert curve in the shape of a cube after exposure to an external stimulus.

[0046] FIG. 5 is a series of time-lapsed photographs showing a transformation from a cylindrical object to a Hilbert curve in the shape of a cube.

[0047] FIG. 6 is a table having four columns that: a) describe a type of joint; b) provide a computer aided design (CAD) of the joint; c) show an experimental representation of the joint after exposure to an external stimulus; and d) illustrate a simulation showing the predicted shape of the joint after exposure to an external stimulus.

[0048] FIG. 7A is a top view of a schematic representation of an arrangement of a generally cylindrical object having a series of joints that can transform into an object that spells the letters "MIT."

[0049] FIG. 7B is a side view of a schematic representation of an arrangement of a generally cylindrical object having a series of joints that can transform into an object that spells the letters "MIT."

[0050] FIG. 7C is a schematic representation of an arrangement of a generally cylindrical object having a series of joints that has transformed into an object that spells the letters "MIT" after exposure to an external stimulus.

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[0051] FIG. 7D is a schematic illustrating an example joint that can be used to spell letters upon, or following, exposure to an external stimulus.

[0052] FIG. 7E is a schematic illustrating the example joint of FIG. 7D after exposure to an external stimulus.

[0053] FIGS. 8A-8D are a series of time-lapsed photographs showing a transformation from a generally cylindrical object to an object that spells the letters "MIT."

[0054] FIG. 9A is a top view of a schematic representation of an object that can transform into a cube having solid sides upon, or following, exposure to an external stimulus.

[0055] FIG. 9B is perspective view of a schematic representation of two panels having a joint that can fold upon, or following, exposure to an external stimulus.

[0056] FIG. 9C is a side view of a schematic representation of two panels having a joint that has folded upon exposure to an external stimulus.

[0057] FIG. 9D is a perspective view of a schematic representation of two panels having a joint that can fold upon, or following, exposure to an external stimulus.

[0058] FIG. 9E is a side view of a schematic representation of two panels having a joint that has folded after exposure to an external stimulus.

[0059] FIG. 9F is a schematic representation of an object that has transformed into a cube having solid sides after exposure to an external stimulus.

[0060] FIG. 10A is a computer generated model of an object formed by an additive manufacturing process that can transform into a cube upon, or following, exposure to an external stimulus.

[0061] FIG. 10B is a computer generated model of an object formed by an additive manufacturing process that has transformed into a cube after exposure to an external stimulus.

[0062] FIGS. 11A-D are a series of time-lapsed photographs showing a transformation of an object formed by an additive manufacturing process into a cube upon, or following, exposure to an external stimulus.

[0063] FIG. 12A is a schematic representation of an arrangement of joints that can effect linear elongation.

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[0064] FIG. 12B is a photograph of an object of additive manufacture having an arrangement of joints that can effect linear elongation.

[0065] FIG. 13A is a schematic representation of an object formed by an additive manufacturing process that can undergo a curling transformation upon, or following, exposure to an external stimulus.

[0066] FIG. 13B is a simulation showing the predicted shape of the object of FIG. 13A after exposure to an external stimulus.

[0067] FIG. 13C is a simulation showing the predicted shape of the object of FIG. 13A after exposure to an external stimulus.

[0068] FIG. 13D is a series of photographs of an object formed by an additive manufacturing process at various times before and after exposure to an external stimulus. The photographs show an object that can undergo an curling transformation upon, or following, exposure to an external stimulus.

[0069] FIG. 14 is a block diagram of a 3D printing apparatus.

[0070] FIGS. 15A-B are schematic representations of an arrangement of two low swelling materials and a high swelling material.

[0071] FIGS. 16A-C are schematic representations of an arrangement of materials that can be used in a temperature-based system.

[0072] FIG. 17 is a schematic representation of an arrangement of materials that can undergo a hole closing transformation.

[0073] FIG. 18A is four photographs of an object of additive manufacture that can undergo a curved crease transformation.

[0074] FIG. 18B is three photographs of an object of additive manufacture that can undergo a curved crease transformation.

[0075] FIG. 19 is three photographs of an object of additive manufacture that can transform into an octahedron.

[0076] FIG. 20 is a series of photographs showing folding joints having differentially-spaced cylindrical discs.

[0077] FIG. 21 is a series of photographs showing folding joints having differentially-spaced cylindrical discs.

[0078] FIG. 22A is a computer generated model of a linear expander formed by an additive manufacturing process that can expand upon, or following, exposure to an external stimulus.

[0079] FIG. 22B is a computer generated model of a linear expander formed by an additive manufacturing process that has expanded upon exposure to an external stimulus.

[0080] FIG. 22C is a series of photographs showing the transformation of a linear expander upon exposure to an external stimulus.

[0081] FIGS. 23A-C are photographs showing curling.

DETAILED DESCRIPTION OF THE INVENTION

[0082] A description of example embodiments of the invention follows.

[0083] As used herein, the term “object” and “objects” refers to physical objects produced by an additive manufacturing process.

[0084] As used herein, the term “a,” as used in describing “a first additive manufacturing material,” “a second additive manufacturing material,” and “a third additive manufacturing material,” means “at least one.” It should be understood that first, second, and third additive manufacturing materials are often described herein for ease of convenience; however, any number of additive manufacturing materials can be used to create a range of transformations over time in various combinations at joints or other locations of objects or objects in their entireties.

[0085] As used herein, the term “manufactured shape” refers to a predetermined geometrical shape. For example, a manufactured shape is different from a shape that would occur if an additive manufacturing material were simply melted post-manufacturing in an uncontrolled manner. Thus, a manufactured shape can be the shape of an object as it is produced by an additive manufacturing apparatus, such as a 3D printer. A manufactured shape can also be a shape having a distinct structure and/or function. In other words, a shape that is not a predetermined shape is not a manufactured shape. An object according to embodiments disclosed herein can have a first manufactured shape and at least one second manufactured shape, wherein a predicted transformation occurs to change a state of a manufactured object from the first manufactured shape to the at least one second manufactured shape. It

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should be understood that the term “predetermined” does not mean that every parameter, such as volume, angle, stiffness, etc., is known in advance, but rather that a shape is considered to be a manufactured shape generally predicted at the time of manufacturing the object. Depending upon the type of transformation, the actual shape may differ from the predetermined shape by $\pm 5\%$, $\pm 10\%$, $\pm 30\%$, or $\pm 50\%$.

[0086] As used herein, the term “non-biasing,” as used with respect to an external stimulus, means that the external stimulus does not apply a mechanical or other force on the object in order to transform the object from one manufactured shape to another manufactured shape that is different from the transformation(s) encoded in the object, as described herein. For example, exposing an object to an external stimulus, such as exposure to a solvent, temperature change, electromagnetic energy (*e.g.*, light), or pressure change is a non-biasing external stimulus because it does not apply a mechanical force more in any particular spatial direction.

4D Printing

[0087] Four dimensional (4D) printing is a novel process that entails the multi-material printing of objects having the capability to transform over time. As described herein, three of the dimensions are spatial, and the fourth dimension refers to the transformation of an object over time. For example, printed structures can transform from a first shape into at least one second shape due to exposure to at least one external stimulus.

[0088] Multi-material three-dimensional (3D) printing technologies can allow for fabrication of 3D objects having a heterogeneous composition. For example, 3D printed objects can be composed of two or more materials that differ in one or more of their physical and chemical properties. The Objet[®] line of 3D printers (Stratasys Ltd., Israel) can be used for the 3D printing of multi-material objects. Such printers are described in U.S. Patent Nos. 6,569,373; 7,225,045; 7,300,619; and 7,500,846; and U.S. Patent Application Publication Nos. 2013/0073068 and 2013/0040091, each of the teachings of which being incorporated herein by reference in their entireties. The Stratasys[®] Connex[™] multi-material printers provide multi-material Polyjet[™] printing of materials having a variety of properties, including rigid and

soft plastics and transparent materials, and provide high-resolution control over material deposition.

[0089] Printing materials having differing physical or chemical properties provides a user with the capability of programming object structure and composition in order to achieve specific functionality. For example, different combinations of a first, or a first and second (or more), additive manufacturing materials can form complex objects that cannot be generated otherwise in a single process. Among other uses, single or multi-material 3D printing can be used to generate heterogeneous objects having areas of different stiffness. When the shape of these areas have a preferred orientation, an object having anisotropic properties can be formed. One example is an object having different properties (*e.g.*, elastic modulus) in different directions (*e.g.*, X/Y/Z). Property gradients can also be formed by gradually modifying the ratio of components having different properties. For example, the ratio of low and high swell components can be modified over a specific line or plane in the 3D object. Layered structures can be made, where a rigid component is wrapped or placed over a soft component. Alternatively, a soft component can be wrapped or layered over a rigid component, or the structure can include more than two layers. This is used, for example, for functional living hinge construction. An object can be printed in a first shape that, upon exposure to an external stimulus, transforms into a second, predetermined shape. For example, a gradient of the first and second additive manufacturing materials can be varied to cause more or less curvature during the transformation.

[0090] Current 3D printers can also utilize support materials. For example, a support material can support a 3D printed object during the printing process, which may be desirable or necessary if the object has a shape that cannot support itself (*e.g.*, the shape has overhangs that, without support material or support material constructions, would not be printable). The support material can be positioned prior to beginning the 3D printing process, or it can be printed by the 3D printer substantially simultaneously with the printing of the additive manufacturing material. In some cases, the support material can be removable after the printing process is complete (*e.g.*, by mechanical force, such as by use of a water-jet

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apparatus). Typically, the support material is removed before transforming the object from a first shape into a second shape.

[0091] One of skill in the art will understand that in all of the specific examples described herein, it may be necessary to cure (*e.g.*, polymerize) the object of additive manufacture (*i.e.*, the formulation or formulations that make up the cumulative layers of the object). For example, it may be necessary to cure the object prior to removal of support material, if any, and transformation of the shape of the object.

[0092] It should be understood that while many of the embodiments described herein include at least two additive manufacturing materials, other embodiments can employ a single, given manufacturing material. The additive manufacturing operations can, for example, include applying more layers of the given additive manufacturing material in certain locations and fewer, or none, in others to encode a response to an external stimulus to cause a predicted transformation to the shape of the object.

[0093] Using the ability to print several materials with different properties simultaneously and control the placement of each material in 3D, the listed abilities and examples are made possible.

Joints

[0094] The object can have a first shape having joints. The joints can be formed of different material types, such as a high swelling material and a low swelling material. Upon exposure to an external stimulus, the high swelling material can swell, causing a transformation in the shape of the joint. For example, the joint can curl, fold, stretch, shrink, and form a curved crease.

[0095] In one embodiment, a joint can curl. For example, a curling joint can be formed by creating an object having a layer of a low swelling material adjacent to a layer of a high swelling material. Upon, or after, exposure to an external stimulus, the object will curl away from the high swelling material (*i.e.*, the low-swelling material will be on the inside of the curl).

[0096] In one embodiment, a joint can fold. In one particular embodiment, the joint can fold approximately 90° in either the clockwise or counterclockwise direction. In another embodiment, a high swelling material expands so that two or

more portions of low swelling material contact each other. The portions of low swelling material are shaped so that their forced interaction restricts the degree of curvature.

[0097] In another embodiment, concentric rings of a high swelling material can be alternated with concentric rings of a low swelling material along a longitudinal axis. Upon, or after, exposure to an external stimulus, the high swelling material expands, resulting in linear elongation.

[0098] In another embodiment, a hole or lumen decreases in size upon exposure to an external stimulus. A cylindrical object can have an exterior portion formed of a low swelling material and an interior portion formed of a high swelling material, wherein the interior portion has a lumen. Upon, or after, exposure to an external stimulus, the high swelling material in the interior of the joint expands and decreases the diameter of the lumen.

[0099] In another embodiment, the joint can form a curved crease upon exposure to an external stimulus. A curved crease can form when low swelling portions of a structure constrain the deformation of a joint in a way that creates deformation along other directions. A first example can be formed from concentric, alternating rings of high and low swelling material. A second example can be formed by depositing a gradient of two additive manufacturing materials. The center of the object can be a low swelling material while the periphery is a high swelling material.

[00100] In another embodiment, the joint can undergo linear expansion. A linear expander can have a first end portion and a second end portion that are formed, at least partially, of a low swell material. The first and second end portions are connected via two low swell portions that have curves that are mirror images of each other. For example, the low swell portion on the left travels upwards from the first end portion, curves counterclockwise for approximately 90°, then curves clockwise for approximately 180°, then curves counterclockwise for approximately 90°. The low swell portion on the left has three distinct adjacent high swell portions. A first high swell portion is affixed on the lower, exterior portion of the low swell material curve. A second high swell portion is affixed on the middle, interior portion of the low swell material. A third high swell portion is affixed on the upper, exterior portion of the low swell material. The low swell portion on the right travels along a

trajectory that is a mirror image of low swell portion on the left, and the high swell portions on the right are similarly mirror images. Upon exposure to an external stimulus, the three high swell portions expand, causing the linear expander to expand. In other words, the linear expansion joint has portions connected by an arrangement of low and high swelling materials that form curling joints, the synergistic effect of which is to provide linear expansion.

[00101] In general, the joints disclosed herein have a three dimensional structure, which differs from joints that have only a two dimensional structure. For example, some of the joints have portions that mechanically interfere with each other to attune the amount of folding.

Solvent-Based Transformation

[00102] In one embodiment, an additive manufacturing system can deposit at least two different additive manufacturing materials. After solidification (e.g., polymerization), the two additive manufacturing materials can have differing degrees of swelling upon exposure to an external stimulus. As illustrated in FIG. 1, a high swelling material 10 can be printed adjacent to a low swelling material 20. The high swelling material 10 has a first response to an external stimulus, and the low swelling material 20 has a second response to an external stimulus. In this example, the first response is a greater degree of swelling upon exposure to the external stimulus, and the second response is a lesser degree of swelling upon exposure to the external stimulus. In many cases, the low swelling material 20 has a minimal or undetectable response to the external stimulus. In the arrangement of FIG. 1, exposure to an external stimulus causes the high swelling material 10 to swell more than the low swelling material 20. As a result, the object transforms from a first shape into a second shape by curling. The extent of distortion depends primarily on three factors. First, a greater relative degree of swelling between the two materials leads to a greater degree of deformation. Second, the relative stiffness of the high and low swelling materials affects the extent of distortion. A stiffer high swelling material and a softer low swelling material will permit greater deformation. However, a very soft low swelling material can be inefficient in creating deformation and, alternatively, the overall structure may expand but not change

shape. In other words, if the low swelling material is very soft, it will not exert enough force to resist the high swelling material, so overall shape will not change. Third, a thicker high swelling layer or a thinner low swelling material (or both) will cause greater deformation.

[00103] A variety of combinations of high and low swelling materials can be used. Typically, the high and low swelling materials will be selected based on their response to a particular external stimulus. One example of an external stimulus involves exposing the object to a solvent. As one example, the solvent can be water, and the high swelling material 10 is more hydrophilic than the low swelling material 20. Stated differently, the low swelling material 20 is more hydrophobic than the low swelling material 10. Alternatively, the external stimulus can be exposure to a humid environment.

[00104] The high swelling material 10 can be a 3D printable material that swells in an aqueous solvent. Particular types of materials include UV-curable materials and other thermosetting materials. After deposition of formulations and during the printing process, the deposited material can be exposed to UV light or heat to cure (*e.g.*, polymerize) the material, resulting in a cured additive manufacturing material having hydrophilic properties. One particular example is a hydrophilic material that can be produced by polymerizing a formulation formed of one or more hydrophilic monomers and oligomers. Suitable examples are hydroxyethyl acrylate and poly(ethylene) glycol. Other examples include formulations composed of vinyl ethers, acrylamides, and/or epoxides.

[00105] A suitable UV-curable formulation resulting in a hydrophilic material after polymerization can include approximately 50 to 90 percent of hydrophilic acrylic monomers and approximately 60 to 80 percent of oligomers. More preferably, a suitable formulation for a hydrophilic material can include approximately 60 to 80 percent of a hydrophilic acrylic monomer and approximately 10 to 20 percent of oligomers.

[00106] A generalized formulation for a hydrophilic material is disclosed in Table 1, which shows the approximate ranges of components.

Amount by weight (percent)	Component
50 - 90%	Hydrophilic acrylic monomer
10 - 50%	Hydrophobic oligomer
1 - 3%	Photoinitiator
0.1 - 0.2%	Surface active agent
0.1 - 0.2%	Stabilizer or inhibitor

Table 1

[00107] One particular example of a formulation for producing a hydrophilic material is disclosed in Table 2. In the particular formulation disclosed in Table 2, the hydrophilic monomer is hydroxyethyl acrylate; the hydrophobic oligomer is composed of a difunctional bisphenol A based epoxy acrylate; the photoinitiator is an alphahydroxyketone; the surface active agent is a silicone containing surface additive; and the inhibitor is a hydroquinone.

Amount by weight (grams)	Component
70	Hydroxyethyl acrylate
15	Difunctional bisphenol A based epoxy acrylate
2	Alphahydroxyketone
0.1	Silicone containing surface additive
0.2	Hydroquinone

Table 2

[00108] For the hydrophilic material described in Table 2, a suitable external stimulus can be a polar solvent, such as water or an alcohol.

[00109] The low swelling material 20 can be a 3D printable material that does not swell, or that swells minimally, when exposed to an aqueous solution. A formulation that includes one or more of hydrophobic acrylic monomers and

oligomers is an example of a formulation that, after curing (*e.g.*, polymerization), results in a hydrophobic material. Suitable examples are disclosed in U.S. Patent No. 7,851,122, the entire teachings of which are incorporated herein by reference. Particularly suitable examples include phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate.

[00110] Each of the hydrophilic and hydrophobic formulations can include one or more of a photoinitiator, stabilizer, surfactant, or colorant.

[00111] In one embodiment, it is possible to obtain a material having controlled hydrophilicity by simultaneous deposition of low and high hydrophilic formulations in predetermined ratios. For example, this procedure can be used to produce a gradient of hydrophilicity within the material.

Temperature-Based Transformation

[00112] In another embodiment, an additive manufacturing process can be used to print an object having a first shape. This temperature-based transformation can occur where the first and second additive manufacturing materials have significantly different coefficients of thermal expansion.

[00113] In one example, the object can soften when heated a first time, and external force can be applied to transform the object into a second shape. When cooled down, the object retains the second shape. When heated a second time, the object reverts to the first shape. Thus, the energy externally applied in the first deformation is released upon exposure to an external stimulus, the second heating.

[00114] In another example, a shape can be printed from two additive manufacturing materials, a high swelling material and a low swelling material. The shape can be immersed in hot water and deformed. The low-swelling material softens due to the heat and allows the swelling material to deform to the shape as it swells. The shape is then cooled and dried at ambient temperature to yield a cool, dry, deformed shape because as it cools, the low swelling material becomes rigid again and prevents the shape from reverting as the high swelling material dries and contracts. The shape is then exposed to heat, which causes the shape to revert to the originally printed shape.

[00115] Several different types of 3D printable materials are suitable. Typically, the material is rigid below its glass transition temperature (T_g) but soft and flexible above its T_g . One particular material is the Objet VeroWhitePlus RGD835 (Stratasys Ltd., Israel), which is rigid and stiff at room temperature but very soft and flexible at 90°C. As another example, the Objet DurusWhite RGD30 material (Stratasys Ltd., Israel) is rigid and stiff at room temperature but very soft and flexible at 75°C. In one embodiment, the T_g can range from approximately 75° to approximately 90°C. One of skill in the art will recognize, however, that the T_g is not restricted to the range of approximately 75°C to approximately 90°C. Rather, a wide variety of thermosetting plastics are suitable, and the T_g can be any temperature that is suitable for the particular application, *e.g.*, approximately 0°C to approximately 150°C.

[00116] More complex predicted transformations are also contemplated. For example, an object can be printed from multiple materials, each of which has a different T_g , thereby allowing several shape transformations that occur at different temperatures.

[00117] In addition, temperature-based materials can be combined with swelling-based systems to create an object that transforms in response to both exposure to solvent and temperature changes. For example, a rigid hydrophobic material with a T_g of approximately 60°C can be combined with a hydrophilic material. When placed in hot water, the first material softens and the hydrophilic material swells, causing transformation. When removed to room temperature, the first material becomes rigid again and retains its shape, even when the swollen material dries. To reverse the first transformation, the deformed structure can be heated, which causes the rigid material to soften and the object to revert to its original shape.

Pressure-Based Transformation

[00118] In another embodiment, an external stimulus can be a change in pressure. For example, a cylindrical object having a multimaterial composition can be printed by a 3D printer. The exterior of the cylinder can be made of a first material that is relatively rigid. The interior of the cylinder can be a second material that is a soft, elastomer or other elastomer-like material (*e.g.*, polymerized Objet Tango Plus

FLX930 material). The cylinder can have a lumen through the middle. In response to a change in pressure, the second material will change, thereby causing deformation and changing the shape of the object.

Electromagnetic Energy-Based Transformation

[00119] In another embodiment, an external stimulus can be exposure to electromagnetic energy. For example, an object can be formed of two different materials having differential absorption characteristics of electromagnetic energy. Upon, or following, exposure to electromagnetic energy, a first material will heat up more than a second material. The electromagnetic energy can be within the infrared, visible, ultraviolet, or other portion of the electromagnetic spectrum.

Apparatus and Non-Transient Computer Readable Medium for 4D Printing

[00120] Figure 14 is a block diagram of an apparatus for multimaterial 3D printing. Stored on the non-transient computer readable medium 510 is a sequence of instructions. When executed by a processor 520, the sequence of instructions causes a processor to access a database 530 that includes first parameters of additive manufacturing materials and second parameters for arranging the additive manufacturing materials relative to each other to form at least a portion of a shape of an object having a first shape in an absence of an external stimulus and having a second, predicted shape in a presence of, or following exposure to, the external stimulus. The processor 520 can access the non-transient computer readable medium 510 and the database 530 either via a local connection or via a computer network. The processor can calculate, as a function of the first and second parameters, a sequence of machine-controllable instructions that, when provided to a 3D printing apparatus 540, programs the 3D printing apparatus 540 to produce the object in the first shape.

[00121] The database can further include parameters of an environment in which the object will be employed. The sequence of instructions can further cause the processor 520 to calculate machine-controllable instructions as a function of the environment or adjust the previously calculated machine-controllable instructions as a function of the environment. The external stimulus can be exposure to a solvent,

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temperature change, electromagnetic energy, or pressure changes. The machine-controllable instructions can cause the 3D printing apparatus 540 to dispense a first additive manufacturing material and a second additive manufacturing material in an arrangement relative to each other to enable a predicted transformation of the shape in response to the external stimulus. The external stimulus can be a first external stimulus, and the predicted transformation can be a first predicted transformation.

[00122] The machine-controllable instructions can further cause the 3D printing apparatus 540 to dispense a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both. The third additive manufacturing material can have a third response to the first external stimulus or a second external stimulus to enable a corresponding second predicted transformation of the shape of the object in response to the first or second external stimulus.

EXEMPLIFICATION

Example 1: Formation of a Cube

[00123] In this example, a generally cylindrical object transforms into a first generation of a fractal Hilbert curve in the shape of a cube.

[00124] FIG. 2 is a schematic representation of an arrangement of a low swelling material and a high swelling material that can form a folding joint. The object has a generally cylindrical shape. Two cylindrical discs 30 are spaced apart by a horizontal member 40. The high swelling material 10 is placed on one side of the horizontal member 40. The cylindrical discs 30 and horizontal members 40 are made of a low swelling material. For example, the high swelling material can be more hydrophilic than the low swelling material. Stated differently, the low swelling material can be more hydrophobic than the high swelling material. The cylindrical discs 30 function as angle limiters. Upon exposure to an external stimulus, the cylindrical discs 30 force the joint to fold to an approximately 90° angle. In order to change the curvature of the joint, the spacing or diameter of the cylindrical discs can be changed. Increasing the spacing between the cylindrical discs creates a more acute angle. If the cylindrical discs are spaced more closely together, very little folding will occur because the discs will contact each other and prevent further folding. The number of discs can also be modified as well.

[00125] FIGS. 3A and 3B are computer generated models of an object formed by an additive manufacture process that can fold upon, or following, exposure to an external stimulus. FIG. 3A is a photograph of the object prior to exposure to an external stimulus, and FIG. 3B is a photograph of the object after exposure to an external stimulus. In this particular embodiment, the high swelling material 10 is more hydrophilic than the low swelling material 20, and the external stimulus is exposure to water. As shown in FIG. 3B, the high swelling material has expanded in size relative to the low swelling material, causing a predicted bend in the joint.

[00126] FIGS. 4A-F are schematic representations of an arrangement of folding joints that can form a cube. The cube is formed from a series of joints similar to those shown in FIGS. 2, 3A, and 3B. The edges of the cube are formed from low swelling cylindrical material 51-58. The joints 61-67 are orientated so that the generally cylindrical shape transforms into a cube. For example, joint 62 is rotated 90° relative to joint 61 in order to align the cylindrical materials 51-58 to form the edges of a cube.

[00127] FIG. 5 is a series of time-lapsed photographs showing a transformation from a cylindrical object to a cube. The top image shows the generally cylindrical first shape of the object. As printed in a first shape, the object is approximately 18 inches long. The middle image shows several superimposed photographs that illustrate the predicted change of the object over time. The bottom image is a photograph of the object after the transformation has been completed.

Geometrically, the cube is the first generation of a fractal Hilbert curve, where a single line is drawn through all eight points of the cube without overlapping or intersecting. In this particular example, the low swelling material was Objet VeroBlackPlus RGD875, and the high swelling material was a formulation of the hydrophilic type described in Tables 1 or 2. The object was immersed in hot water for approximately 15 to 30 minutes.

[00128] One of skill in the art will understand that the timeframe of the transformation from a first shape to a second shape can depend on a variety of factors. Increasing the solvent temperature can decrease the amount of time required for the transformation. For example, a similar transformation as in FIG. 5 using cold water can require one hour or longer. In some cases, the transformation upon

exposure to water can be reversible or partially reversible. Removing the object from the water after it has transformed to the second shape can cause it to revert back to the first shape. However, the object may not be completely straight, and for this reason it may only partially reverse to the first shape.

Example 2: Transformation from a Cylinder to Letters

[00129] In this example, a generally cylindrical object transforms into a series of letters that spell “MIT.”

[00130] FIG. 6 is a table having four columns that: A) describe a type of joint; B) provide a computer aided design (CAD) of the joint; C) show an experimental representation of the joint after exposure to an external stimulus; and D) illustrate a simulation showing the predicted shape of the joint after exposure to an external stimulus. Each of the joints in FIG. 6 can be used to curve an object of additive manufacture upon exposure to an external stimulus. Each of the joints has a different arrangement of high swelling material 10 and low swelling material 20, and thus each joint curves differently, as are illustrated in the experimental and simulated curvature (columns C and D). The joint designated Elbow-“bi” is particularly effective for creating larger curvatures, though each of the joints listed, as well as modifications and hybrids thereof, can provide suitable curvature. In the VoxCAD simulation, the low swelling material was assigned a modulus of 2 GPa and a thermal expansion of zero. The high swelling material was assigned a modulus of 100 MPa and a thermal expansion of $0.03^{\circ}\text{C}^{-1}$. Water expansion was simulated by increasing the temperature to 50°C . In general, all of the joints illustrated in FIG. 6 are folding joints, though each folds slightly differently.

[00131] FIGS. 7A and 7B are schematic representations of an arrangement of a generally cylindrical object having a series of joints that can transform into an object that spells the letters “MIT.” FIG. 7A is a top view, and FIG. 7B is a side view. The letters are formed from low swelling material 221-239 with intervening high swelling material 210. Upon exposure to an external stimulus, the high swelling material 210 expands, and the curved corners of the low swelling materials 221-239 are forced together to form joints, thereby resulting in the schematic representation shown in FIG. 7C, which spells the letters “MIT.”

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[00132] FIG. 7D is a schematic illustrating an example joint having low swelling materials 240 and 241 with intervening high swelling material 210. Upon exposure to an external stimulus, the high swelling material expands, and the two low swelling materials 240 and 241 are forced toward each other, resulting in the joint illustrated in FIG. 7E. The relative curvature near the point of contact between the two low swelling materials 240 and 241 causes a predicted folding at the joint. By appropriately orientating the low swelling materials 221-239, an object can be created that predictably curves in 90° angles in both the clockwise and counterclockwise directions.

[00133] FIGS. 8A-D is a series of time-lapsed photographs showing a transformation from a generally cylindrical object to an object that spells the letters "MIT." The object corresponds to that illustrated in FIGS. 7A-E. FIG. 8A shows the generally cylindrical first shape of the object. As printed in a first shape, the object is approximately one foot long. FIG. 8B shows several superimposed photographs that illustrate the predicted change of the object over time. FIG. 8C is a photograph of the object after the transformation has been completed. FIG. 8D is a series of non-superimposed photographs showing the predicted change of the object over time. In this particular example, the low swelling material was Objet VeroBlackPlus RGD875, and the high swelling material was a formulation of the hydrophilic type described in Tables 1 or 2. The object was immersed in hot water for approximately 15 to 30 minutes.

Example 3: Formation of a Cube with Solid Sides

[00134] This example demonstrates surface transformations. A two-dimensional flat plane was printed. The flat plane corresponds to the six unfolded surfaces of a cube. At each of the joints, a strip of high and low swelling material is arranged so that the object transforms from a first shape to a second shape upon exposure to an external stimulus. The arrangement of high and low swelling material at each joint enables a 90° curvature so that the faces of the cube curve toward each other and stop curving upon reaching the second, predetermined shape. When submerged in water, the first shape transforms into a closed surface cube with filleted edges.

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[00135] FIGS. 9A-F are schematic representations of an object of additive manufacture that can transform into a cube having solid sides after exposure to an external stimulus. FIG. 9A is a top view of the object, which is formed from six panels 320, one for each face of the cube, with joints that fold upon exposure to an external stimulus. In the embodiment shown in FIGS 9A-F, each joint has four rectangular members 330. While the embodiment shown has four rectangular members, the joint can have greater or fewer rectangular members. The panels 320 and rectangular members 330 are formed from a low swelling material. Each of the joints is characterized by high swelling material 310 that connects the adjacent rectangular members 330. FIGS. 9B and 9D are schematic illustrations of two panels 320 having a joint that can fold upon exposure to an external stimulus. FIGS. 9C and 9E are schematic illustrations of two panels 320 having a joint that has folded after exposure to an external stimulus. FIG. 9F is a schematic illustration of the object of additive manufacture illustrated in FIG. 9A after exposure to an external stimulus.

[00136] FIG. 10A is a computer-generated model of an object formed by an additive manufacturing process that can transform into a cube upon exposure to an external stimulus. FIG. 10B is a computer-generated model of the object of FIG. 10A that has transformed into a cube after exposure to an external stimulus. FIG. 11A is a photograph of the object of additive manufacture of FIG. 10A. FIG. 11B shows several superimposed photographs that illustrate the predicted change of the object over time. FIG. 11C is a photograph of the object after the transformation has been completed. FIG. 11D is a series of non-superimposed photographs showing the predicted change of the object over time. In this particular example, the low swelling material was Objet VeroBlackPlus RGD875, and the high swelling material was a formulation of the hydrophilic type described in Tables 1 or 2.

Example 4: Linear Elongation

[00137] In this example, the linear elongation of a hollow cylinder is demonstrated.

[00138] FIG. 12A is a schematic representation of an arrangement of joints that can effect linear elongation. In the embodiment shown, the object is shaped to form

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a hollow cylinder. The object has alternating rings of high swelling material 410 and low swelling material 420. Upon exposure to an external stimulus, the high swelling material 410 expands, and the net effect is that the hollow cylinder expands along its longitudinal axis. In this particular example, the low swelling material was Objet VeroBlackPlus RGD875, and the high swelling material was a formulation of the hydrophilic type described in Tables 1 or 2.

[00139] FIG. 12B is a photograph of an object of additive manufacture that is similar to the schematic representation of FIG. 12A. The photographs depict the linear elongation of the object of additive manufacture upon exposure to an external stimulus.

Example 5: Curved Crease #1

[00140] In this example, a thin disc undergoes a curling transformation.

[00141] FIGS. 13A-D depict an object of additive manufacture that undergoes a curling transformation upon, or following, exposure to an external stimulus. FIG. 13A is a schematic representation of an object formed by an additive manufacturing process that can undergo a curling transformation upon, or following, exposure to an external stimulus. The center of the object is a low swelling material (depicted in red) while the periphery is a high swelling material (depicted in purple). The object is formed with a gradient in the distribution of material from the center to the periphery. Manufacturing an object with a gradient in the material distribution is particularly difficult to achieve through conventional, subtractive manufacturing processes.

[00142] FIGS. 13B and 13C are simulations showing the predicted shape of the curling of FIG. 13A after exposure to an external stimulus. The difference between FIGS 13B and 13C is that FIG. 13B is a simulation at a shorter duration of time after exposure to an external stimulus than FIG. 13C.

[00143] FIG. 13D is a photograph of an object formed by an additive manufacturing process that can undergo a curling transformation upon, or following, exposure to an external stimulus. The image on the left is the initial shape of the object as printed. The image in the middle is the object after exposure to water for 30 minutes. The image on the right is the object after exposure to water for 4 hours.

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In the later stages of deformation, the initial symmetry was broken, and a wavy circumference shape was attained. This transformation is generally referred to as a curved crease. In this particular example, the low swelling material was Objet VeroBlackPlus RGD875, and the high swelling material was a formulation of the hydrophilic type described in Tables 1 or 2.

[00144] Thus, FIGS. 13A-D illustrate that complex distributions of low and high swelling material can generate complex distortion behavior.

Example 6: Hole Closure

[00145] This example describes a self-healing structure, wherein a hole or lumen decreases in size upon exposure to an external stimulus. As illustrated in FIG. 17, a cylindrical object can be printed having a high swelling material 710 deposited in the interior and a low swelling material 720 on the exterior. Upon exposure to an external stimulus, the high swelling material 710 in the interior of the cylinder expands to decrease the diameter of the hole 730.

[00146] In a first iteration of this example, the low swelling material 720 can be relatively rigid, and the high swelling material 710 can be a soft elastomer or elastomer-like material (*e.g.*, polymerized Objet Tango Plus FLX930 material). The external stimulus can be a change in pressure, which causes the high swelling material 710 to expand and decrease the volume of the lumen.

[00147] In a second iteration of this example, the low swelling material 720 can be Objet VeroBlackPlus RGD875, and the high swelling material can be a formulation of the hydrophilic type described in Tables 1 or 2. The external stimulus can be exposure to water, which causes the high swelling material 710 to expand and decrease the volume of the lumen.

[00148] In a third iteration of this example, the low swelling material 720 can be relatively rigid that does not change shape appreciably upon exposure to electromagnetic energy (*e.g.*, light), and the temperature of the high swelling material 710 can increase upon exposure to electromagnetic energy (*e.g.*, light). The high swelling material 710 can then expand similarly to the temperature-response embodiment described below in reference to Example 8. For example the low swelling material 720 can be a clear plastic that allows light to penetrate.

Example 7: Three Material Systems

[00149] In another embodiment, first and second additive manufacturing materials are low swelling materials having different rigidity that are arranged relative to a third, high swelling additive manufacturing material. The amount of deformation can be adjusted by altering the relative amounts of the first and second low swelling materials. As illustrated in FIGS. 15A and 15B, a high swelling material 610 can be printed adjacent to a first low swelling material 620, which, in turn, is printed adjacent to a second low swelling material 630. The relative thickness of the first and second low swelling materials 620 and 630 can be adjusted to control the amount of deformation. In one particular embodiment, the first low swelling material 620 can have a lower rigidity than the second low swelling material 630. Using a thicker layer of the second low swelling material 630 that has a higher rigidity or a thinner layer of the first low swelling material that has a lower rigidity, or both as illustrated, can decrease the amount of deformation. Increasing the thickness of the high swelling material 610 can also have the same effect. The technique is not limited to only three materials, but rather any particular number of low and/or high swelling materials can be printed, such as three, four, five, or more. In another particular embodiment, the first low swelling material 620 can have a higher rigidity than the second low swelling material 630. In other embodiments, the relative positions of the high swelling material 610, the first low swelling material 620, and the second low swelling material 630 can be adjusted. For example, the first low swelling material 620 can be on top, the high swelling material 610 can be in the middle, and the second low swelling material 620 can be on the bottom.

Example 8: Temperature-Based Transformation

[00150] FIGS. 16A-C illustrate an object of additive manufacture for use in a temperature-based transformation. An object having a shape can be printed from two additive manufacturing materials, a high swelling material 660 and a low swelling material 670, as illustrated in FIG. 16A. The shape can be immersed in hot water and deformed to yield the object of FIG. 16B, which is then cooled and dried

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at ambient temperature to yield a cool, dry, deformed shape. The shape is then exposed to heat, which causes the shape to revert to the originally printed shape, as illustrated in FIG. 16C.

[00151] Several different types of 3D printable materials are suitable. Typically, the material is rigid below its glass transition temperature (T_g) but soft and flexible above its T_g . One particular material is the Objet VeroWhitePlus RGD835 (Stratasys Ltd., Israel), which is rigid and stiff at room temperature but very soft and flexible at 90°C. As another example, the Objet DurusWhite RGD30 material (Stratasys Ltd., Israel) is rigid and stiff at room temperature but very soft and flexible at 75°C. In one embodiment, the T_g can range from approximately 75° to approximately 90°C. One of skill in the art will recognize, however, that the T_g is not restricted to the range of approximately 75°C to approximately 90°C. Rather, a wide variety of thermosetting plastics are suitable, and the T_g can be any temperature that is suitable for the particular application, *e.g.*, approximately 0°C to approximately 150°C.

Example 9: Curved Crease #2

[00152] This example describes a curved crease formation.

[00153] An object of additive manufacture can be printed in a first shape. The first shape is generally annular. The first shape is printed with concentric, alternating rings of high swelling and low swelling material.

[00154] The top two photographs of FIG. 18A illustrate the generally annular shape and concentric, alternating rings of high and low swelling material. The bottom two photographs of FIG. 18A illustrate the object after exposure to an external stimulus. As can be seen, the object develops a wavy curve that is generally referred to as a curved crease. FIG. 18B is additional photographs of the same object of FIG. 18A.

Example 10: Octahedron

[00155] This example describes the formation of an octahedron.

[00156] FIG. 19 is a series of photographs of an object of additive manufacture that can fold to form an octahedron. The photograph on the left illustrates the object

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as printed. The photograph in the middle is a series of superimposed time-lapsed photographs showing the transformation from the printed shape into an octahedron upon exposure to an external stimulus. The photograph on the right is the object after exposure to an external stimulus and shows the complete transformation to an octahedron.

Example 11: Joint spacing

[00157] FIG. 20 is a series of photographs of joints having differentially-spaced discs. The joints on the left side of the photograph have cylindrical discs that are more closely spaced together, while the joints on the right side of the photograph have joints that are spaced farther apart. The joints having more closely spaced cylindrical discs do not fold as much as the joints having greater spacing between the cylindrical discs.

[00158] Fig. 21 is another series of photographs of joints having differentially-spaced discs. The joints on the left side of the photograph have cylindrical discs that are more closely spaced together, while the joints on the right side of the photograph have joints that are spaced farther apart. The joints having more closely spaced cylindrical discs do not fold as much as the joints having greater spacing between the cylindrical discs.

[00159] While the spacing is illustrated with respect to joints having a cylindrical disc, one of skill in the art will understand that the principle is similarly applicable to joints having rectangular members, such as those described in FIGS. 9A-F, 10A-B, and 11A-D.

Example 12: Linear Expander

[00160] This example describes the formation of a linear expander.

[00161] FIG. 22A is a schematic representation of a linear expander as formed by an additive manufacturing process. The linear expander has a first end portion 730 and a second end portion 740 that are formed, at least partially, of a low swell material. The first and second end portions 730 and 740 are connected via two low swell portions 720 that have curves that are mirror images of each other. The low swell portion 720 on the left travels upwards from the first end portion 730, curves

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counterclockwise for approximately 90°, then curves clockwise for approximately 180°, then curves counterclockwise for approximately 90°. The low swell portion 720 on the left has three distinct adjacent high swell portions 711, 712, and 713. The high swell portion 711 is affixed on the lower, exterior portion of the low swell material curve. The high swell portion 712 is affixed on the middle, interior portion of the low swell material 720. The high swell portion 713 is affixed on the upper, exterior portion of the low swell material 720. The low swell portion 720 on the right travels along a trajectory that is a mirror image of low swell portion 720 on the left, and the high swell portions on the right are similarly mirror images. Upon exposure to an external stimulus, the high swell portions 711, 712, and 713 expand, causing the linear expander of FIG. 22A to transform into the linear expander of FIG. 22B. In other words, the linear expansion joint has portions connected by an arrangement of low and high swelling materials that form curling joints, the synergistic effect of which is to provide linear expansion.

[00162] FIG. 22C is a series of time-lapsed photographs showing the transformation of a linear expander from a first shape to a second, predetermined shape upon exposure to an external stimulus.

Example 13: Curling

[00163] This example describes the formation of a curling joint.

[00164] FIGS. 23A-C are photographs of an object of additive manufacture that can curl upon, or following, exposure to an external stimulus. In these particular examples, an object of additive manufacture is formed having a low swelling layer adjacent to a high swelling layer. Upon, or after, exposure to an external stimulus, the object will curl away from the high swelling material (*i.e.*, the low-swelling material will be on the inside of the curl).

[00165] The teachings of all patents, published applications and references cited herein are incorporated by reference in their entirety.

[00166] While this invention has been particularly shown and described with references to example embodiments thereof, it will be understood by those skilled in

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the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. An object, comprising:
an additive manufacturing material, the additive manufacturing material having a response to an external stimulus and being configured to cause a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the external stimulus, the external stimulus being non-biasing with respect to the predicted transformation from the first manufactured shape to the second manufactured shape.
2. The object of claim 1, wherein the external stimulus is a temperature change.
3. The object of claim 2, wherein the additive manufacturing material has a glass transition temperature of approximately 0°C to approximately 150°C.
4. The object of claim 3, wherein the additive manufacturing material has a glass transition temperature of approximately 75°C to approximately 90°C.
5. The object of claim 1, wherein the additive manufacturing material is a first additive manufacturing material and wherein the object has a second additive manufacturing material arranged relative to the first additive manufacturing material to enable the predicted transformation of the object from the first manufactured shape to the second manufactured shape in response to the external stimulus.
6. The object of claim 5, wherein the second additive manufacturing material has a second response to either the first external stimulus or to a second external stimulus to enable a corresponding second predicted transformation of the object to a third manufactured shape.
7. The object of claim 5, wherein the first and second additive manufacturing materials compose the entire object.

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8. The object of claim 5, further comprising a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, and having a third response to the first external stimulus, the second external stimulus, or a third external stimulus to enable a corresponding third predicted transformation of the object to a fourth manufactured shape.
9. The object of claim 8, wherein the first, second, and third additive manufacturing materials compose the entire object.
10. The object of claim 8, wherein the third additive manufacturing material has a third response that modifies the properties of one or more of the first or second additive manufacturing materials.
11. The object of claim 10, wherein the property modified is the stiffness of one or more of the first and second additive manufacturing materials.
12. The object of claim 5, wherein the external stimulus is selected from the group consisting of a solvent, temperature change, electromagnetic energy, and pressure change.
13. The object of claim 5, wherein the first and second additive manufacturing materials are arranged to form a joint of the object.
14. The object of claim 13, wherein the joint is a means for effecting linear or rotational displacement of a first member of the object relative to a second member of the object.
15. The object of claim 14, wherein the joint has at least one cylindrical disc.
16. The object of claim 14, wherein the joint has at least one rectangular member.
17. The object of claim 14, wherein each of the first and second additive manufacturing materials composing the joint has a three-dimensional structure.

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18. The object of claim 14, wherein the joint is a means for curling.
19. The object of claim 14, wherein the joint is a means for folding.
20. The object of claim 14, wherein the joint is a means for linear elongation.
21. The object of claim 14, wherein the joint is a means for decreasing the size of a hole.
22. The object of claim 14, wherein the joint is a means for forming a curved crease.
23. The object of claim 14, wherein the joint is a means for linear expansion.
24. The object of claim 5, wherein the external stimulus is a solvent.
25. The object of claim 24, wherein the first additive manufacturing material is more hydrophilic than the second additive manufacturing material.
26. The object of claim 25, wherein the first additive manufacturing material comprises a polymerized formulation comprising one or more of hydrophilic acrylic monomers and oligomers.
27. The object of claim 26, wherein the first additive manufacturing material is comprises a polymerized formulation comprising hydroxyethyl acrylate or poly(ethylene) glycol.
28. The object of claim 24, wherein the second additive manufacturing material comprises a polymerized formulation comprising one or more of hydrophobic acrylic monomers and oligomers.
29. The object of claim 28, wherein the second additive manufacturing material comprises a polymerized formulation comprising monomers of one or more of phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate.

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30. The object of claim 24, wherein one or more of the first and second additive manufacturing materials comprises a polymerization formulation that comprises one or more of a photoinitiator, surface active agent, stabilizer, and inhibitor.
31. A method for additive manufacturing of an object, the method comprising:

dispensing an additive manufacturing material having a response to an external stimulus, the additive manufacturing material being configured to cause a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the external stimulus, the external stimulus being non-biasing with respect to the predicted transformation from the first manufactured shape to the second manufactured shape.
32. The method of claim 31, wherein the additive manufacturing material has a glass transition temperature of approximately 0°C to approximately 150°C
33. The method of claim 32, wherein the first additive manufacturing material has a glass transition temperature of approximately 75°C to approximately 90°C.
34. The method of claim 32, further comprising exposing the object to an external stimulus, wherein the external stimulus is a temperature change.
35. The method of claim 31, wherein the additive manufacturing material is a first additive manufacturing material and further comprising dispensing a second additive manufacturing material arranged relative to the first additive manufacturing material to enable the predicted transformation of the object from the first manufactured shape to the second manufactured shape in response to the external stimulus.
36. The method of claim 35, wherein the external stimulus is a first external stimulus and wherein the second additive manufacturing material has a second response to either the first external stimulus or to a second external

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stimulus to enable a corresponding second predicted transformation of the object to a third manufactured shape.

37. The method of claim 36, wherein the first and second additive manufacturing materials compose the entire object.
38. The method of claim 36, further comprising dispensing a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, and having a third response to the first external stimulus, the second external stimulus, or a third external stimulus to enable a corresponding third predicted transformation of the object to a fourth manufactured shape.
39. The method of claim 38, wherein the first, second, and third additive manufacturing materials compose the entire object.
40. The method of claim 38, wherein the third response of the third additive manufacturing material modifies the properties of one or more of the first or second additive manufacturing materials.
41. The method of claim 40, wherein the property modified is the stiffness of one or more of the first and second additive manufacturing materials.
42. The method of claim 35, wherein the first and second additive manufacturing materials are arranged to form a joint of the object.
43. The method of claim 42, wherein the joint is a means for effecting linear or rotational displacement of a first member of the object relative to a second member of the object.
44. The method of claim 42 wherein the joint has at least one cylindrical disc.
45. The method of claim 42, wherein the joint has at least one rectangular member.

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46. The method of claim 42, wherein each of the first and second additive manufacturing materials composing the joint has a three-dimensional structure.
47. The method of claim 42, wherein the joint is a means for curling.
48. The method of claim 42, wherein the joint is a means for folding.
49. The method of claim 42, wherein the joint is a means for linear elongation.
50. The method of claim 42, wherein the joint is a means for decreasing the size of a hole.
51. The method of claim 42, wherein the joint is a means for forming a curved crease.
52. The method of claim 42, wherein the joint is a means for linear expansion.
53. The method of claim 35, wherein the first additive manufacturing material is more hydrophilic than the second material.
54. The method of claim 53, wherein the first additive manufacturing material comprises a polymerized formulation comprising one or more of hydrophilic acrylic monomers and oligomers.
55. The method of claim 54, wherein the first additive manufacturing material comprises a polymerized formulation comprising hydroxyethyl acrylate or poly(ethylene) glycol.
56. The method of claim 35, wherein the second additive manufacturing material comprises a polymerized formulation comprising one or more of hydrophobic acrylic monomers and oligomers.
57. The method of claim 56, wherein the second additive manufacturing material comprises a polymerized formulation comprising monomers of one or more of phenoxy ethyl acrylate, trimethylol propane triacrylate, and isobornyl acrylate.

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58. The method of claim 35, wherein one or more of the first and second additive manufacturing materials a polymerized formulation further comprising one or more of a photoinitiator, surface active agent, stabilizer, and inhibitor.
59. The method of claim 31, further comprising exposing the object to an external stimulus selected from the group consisting of a solvent, temperature change, electromagnetic energy, and pressure change.
60. The method of claim 59, wherein the external stimulus is a polar solvent.
61. The method of claim 60, wherein the polar solvent is selected from the group consisting of water, an alcohol, and combinations thereof.
62. The method of claim 59, wherein exposing the object to an external stimulus causes one or more of curling, folding, stretching, shrinking, and curved creasing.
63. A non-transient computer readable medium having stored thereon a sequence of instructions that, when executed by a processor, causes an apparatus to:
 - access a database that includes first parameters of additive manufacturing materials;
 - access the database that includes second parameters for arranging one or more additive manufacturing materials relative to each other to form at least a portion of an object having a first manufactured shape in an absence of an external stimulus and having a second, predicted manufactured shape in a presence of, or following exposure to, an external stimulus; and
 - calculate, as a function of the first and second parameters, a sequence of machine-controllable instructions that, when provided to a machine, programs the machine to produce the object in the first manufactured shape.
64. The non-transient computer readable medium of claim 63, wherein the database further includes parameters of an environment in which the object will be employed, and wherein the sequence of instructions further causes the apparatus to calculate machine-controllable instructions as a function of

the environment or adjust the previously calculated machine-controllable instructions as a function of the environment.

65. The non-transient computer readable medium of claim 63, wherein the external stimulus comprises one or more of a solvent, temperature change, electromagnetic energy, and pressure change.
66. The non-transient computer readable medium of claim 63, wherein the machine-controllable instructions cause the apparatus to dispense a first additive manufacturing material.
67. The non-transient computer readable medium of claim 66, wherein the machine-controllable instructions cause the apparatus to dispense a second additive manufacturing material in an arrangement relative to first additive manufacturing material to enable a predicted transformation of the object from a first manufactured shape to a second manufactured shape in response to the first external stimulus.
68. The non-transient computer readable medium of claim 63, wherein the external stimulus is a first external stimulus and the predicted transformation is a first predicted transformation and further comprising a third additive manufacturing material arranged relative to the first or second additive manufacturing materials, or both, wherein the third additive manufacturing material has a third response to the first external stimulus or a second external stimulus to enable a corresponding second predicted transformation of the shape of the object in response to the first or second external stimulus.
69. The non-transient computer readable medium of claim 63, wherein the database includes a library of joints.
70. The non-transient computer readable medium of claim 69, wherein the library of joints includes one or more of a curling joint, a folding joint, a linear elongation joint, a joint that decreases the size of a hole, a curved-crease joint, and a linear expansion joint.

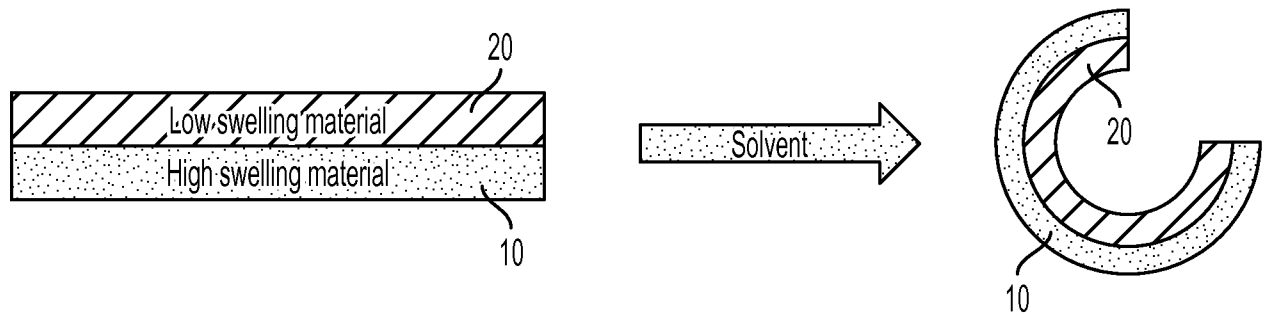


FIG. 1

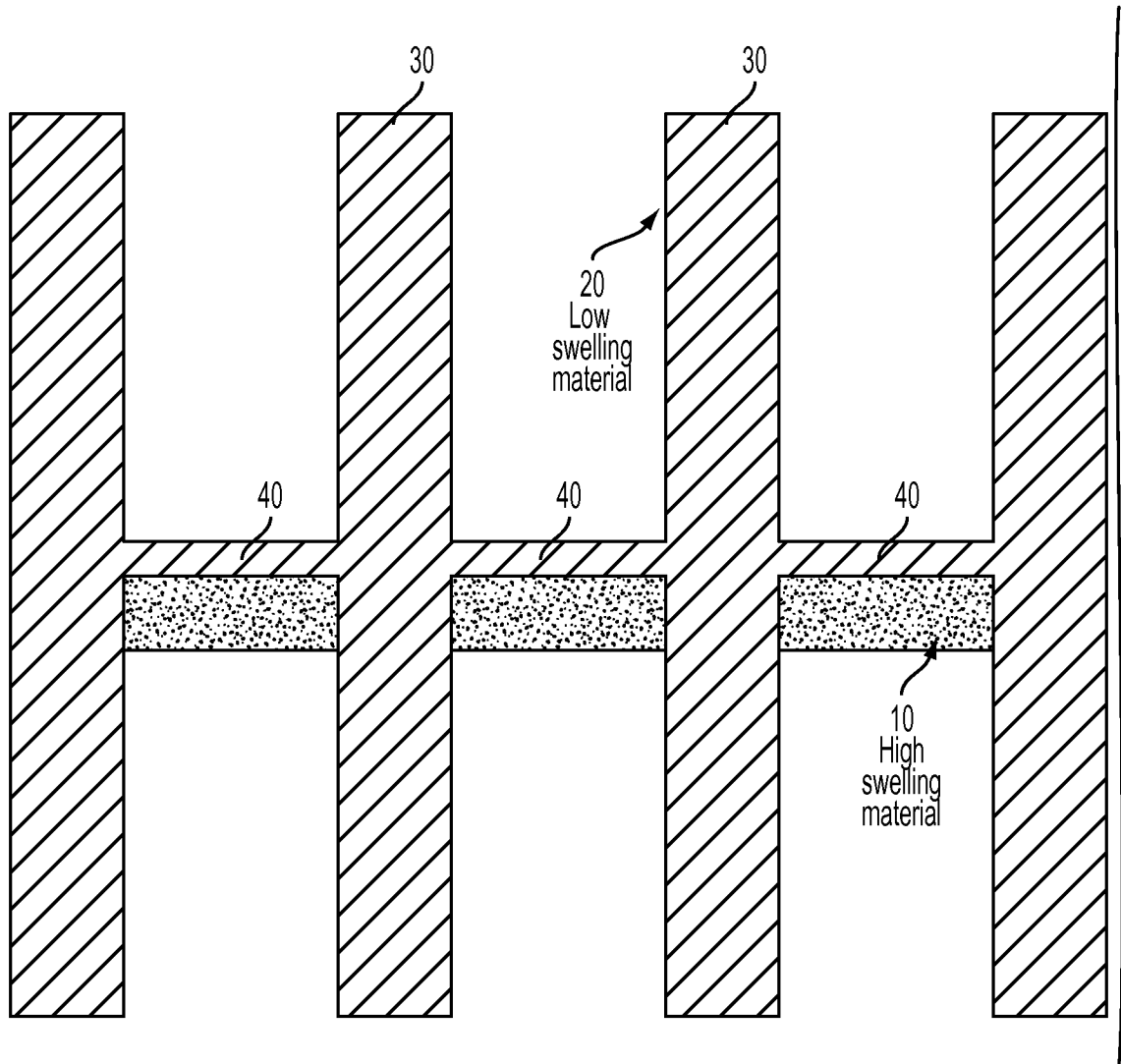


FIG. 2

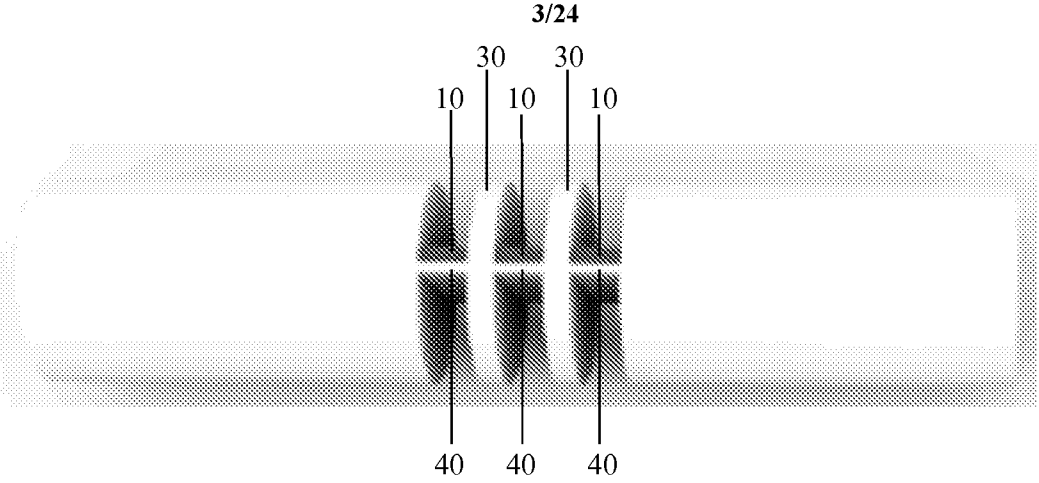


FIG. 3A

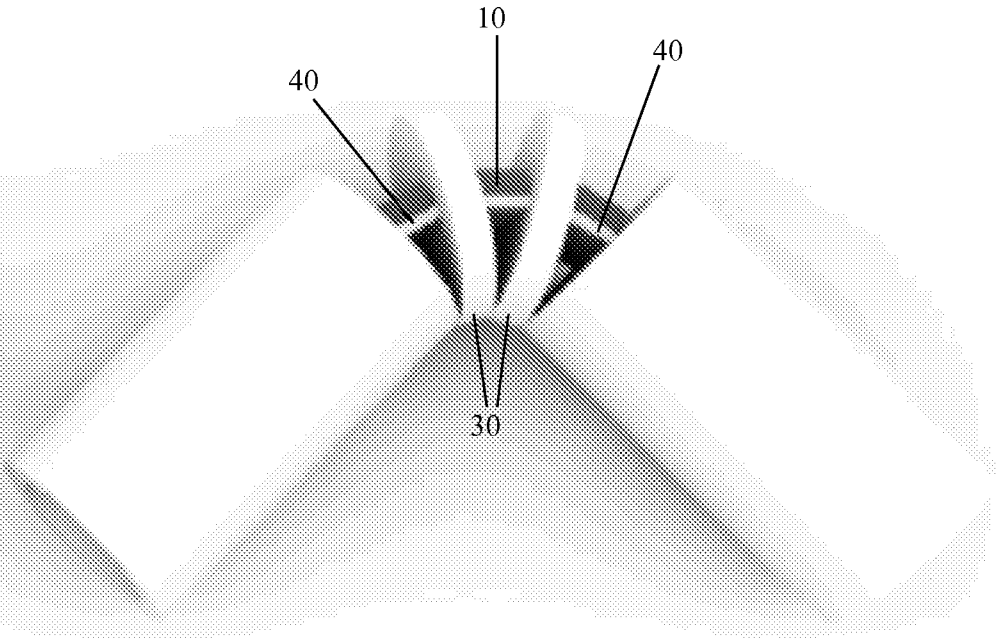


FIG. 3B

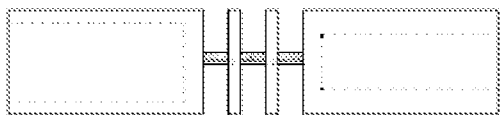


FIG. 4A

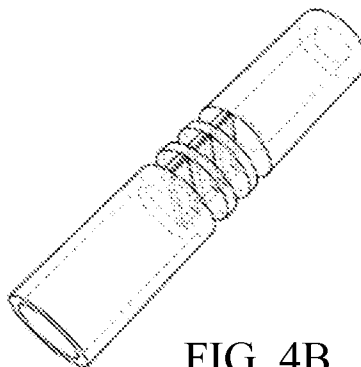


FIG. 4B

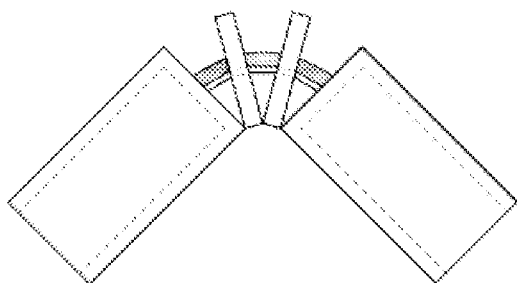


FIG. 4C

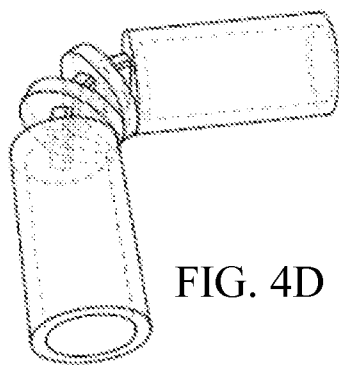


FIG. 4D

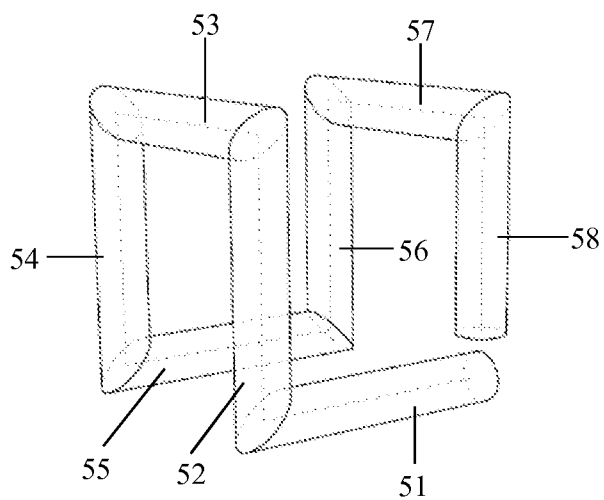


FIG. 4F

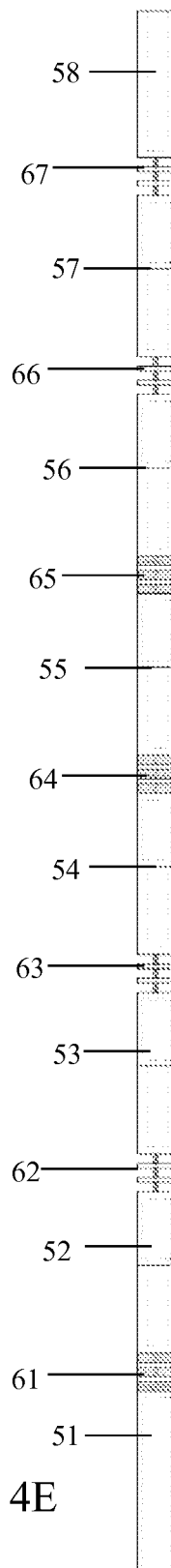


FIG. 4E

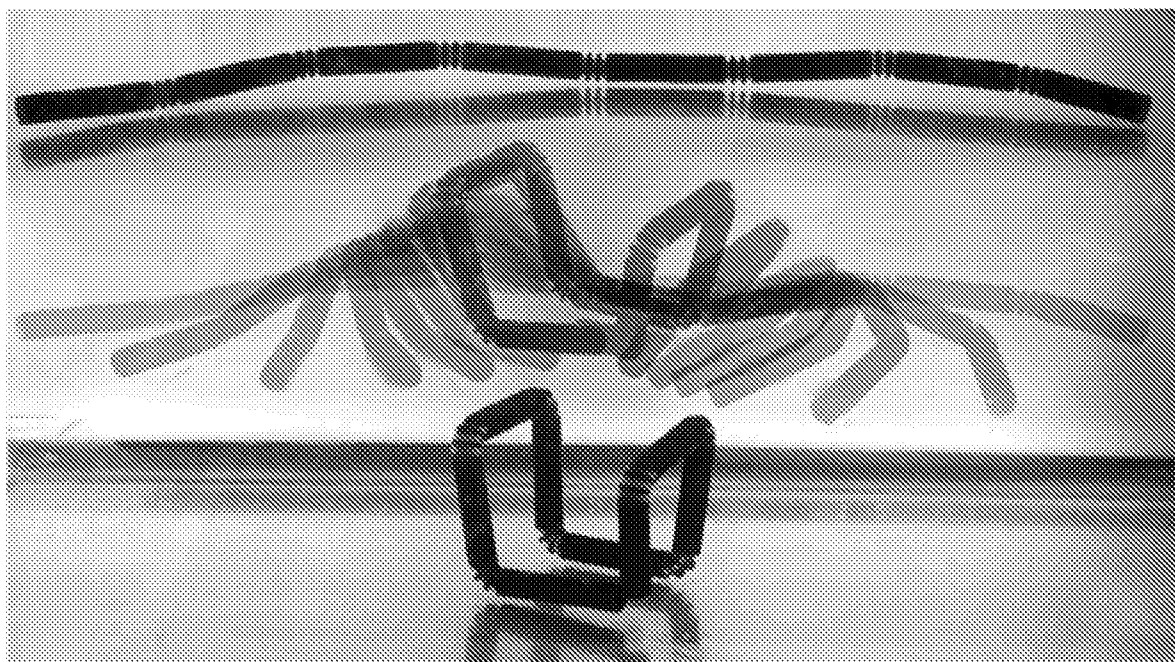


FIG. 5

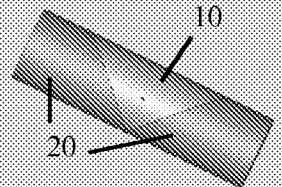
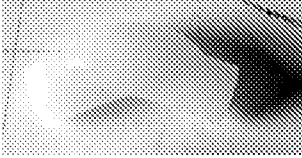
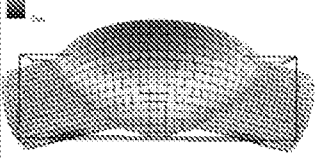
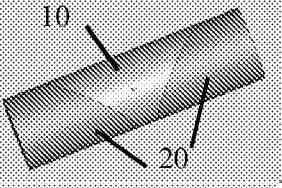
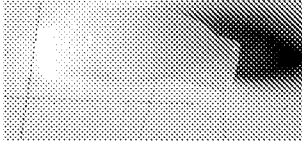
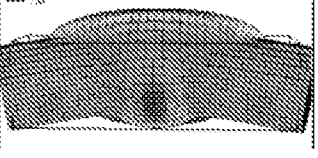
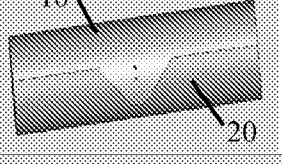
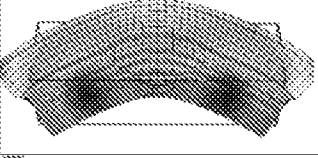
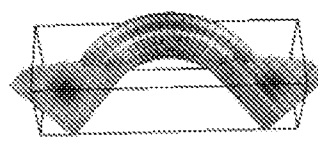
A) structure	B) CAD	C) experiment	D) simulation
Simple elbow			
Elbow+space			
Elbow+extra expander			
Elbow-“bi”			

FIG. 6



FIG. 7A

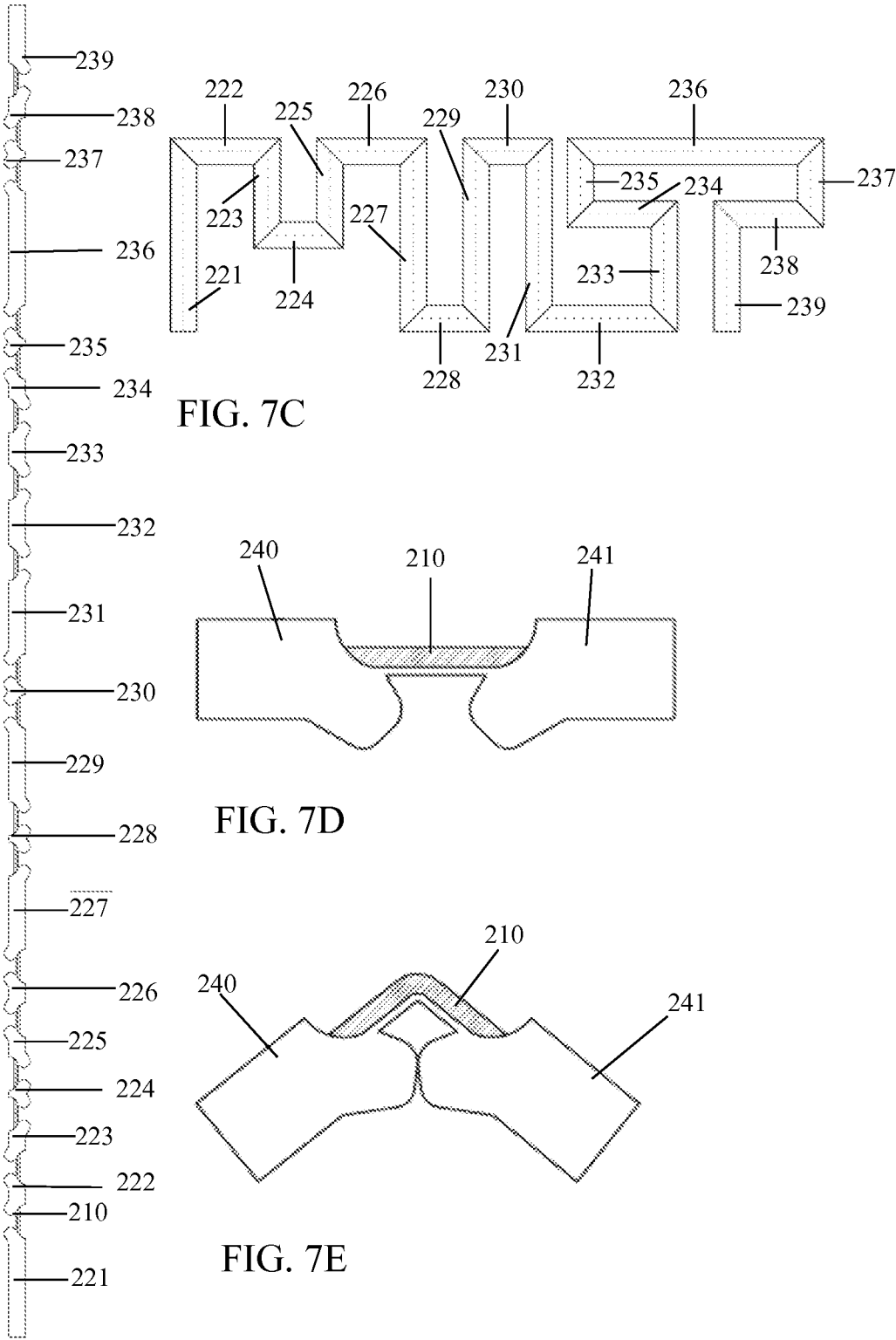


FIG. 7B

FIG. 7E

FIG. 8A

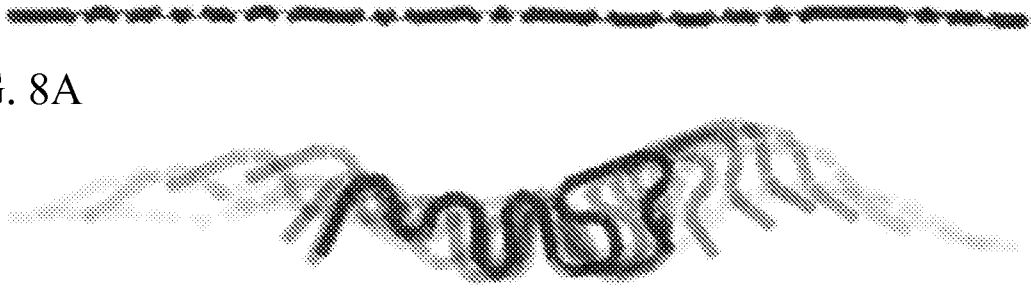


FIG. 8B

FIG. 8C

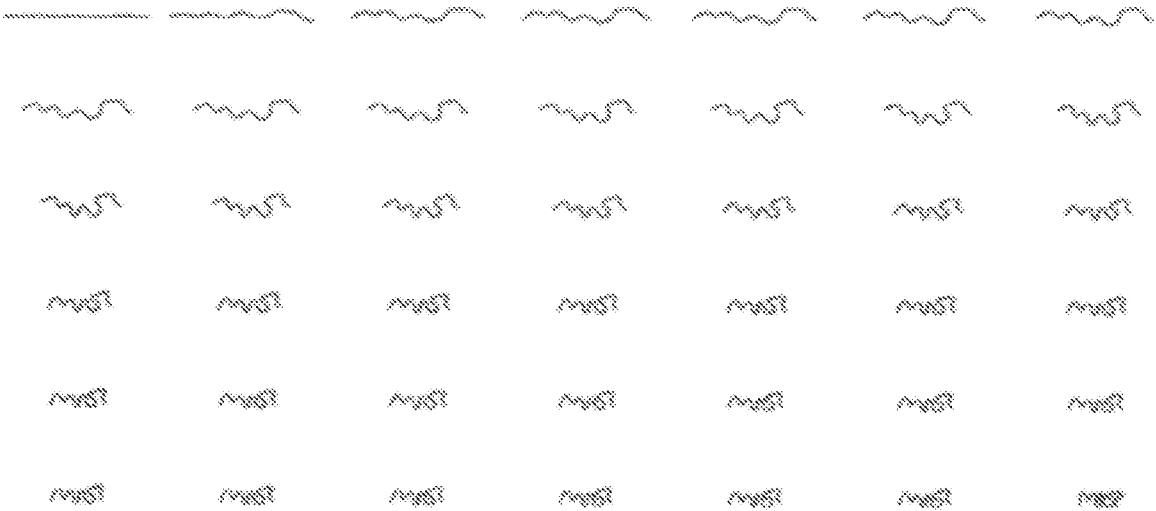
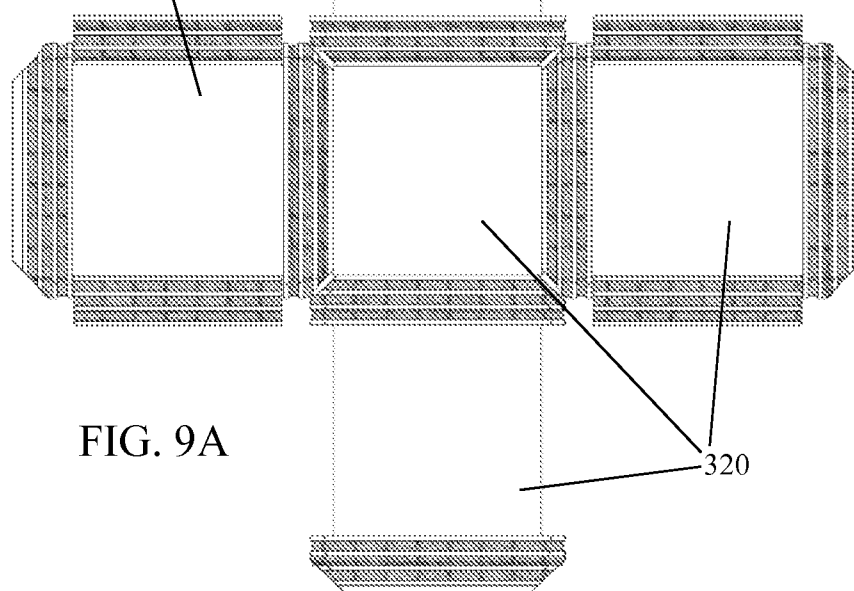
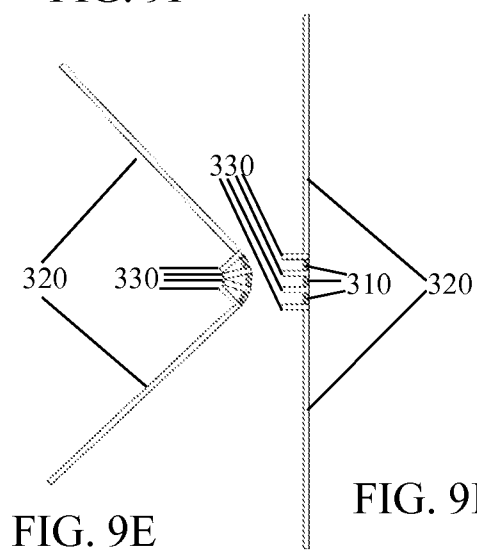
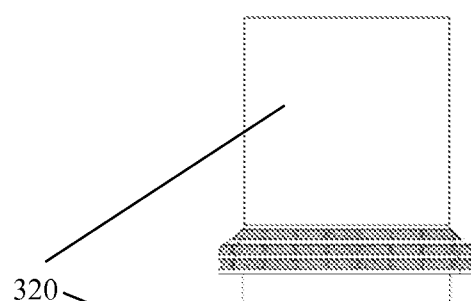
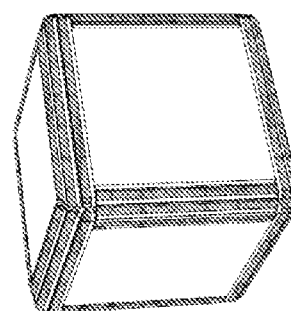
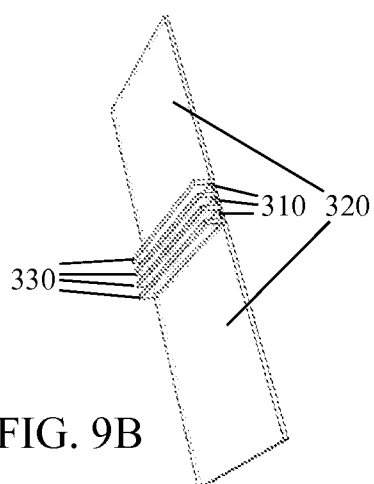
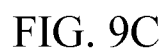


FIG. 8D



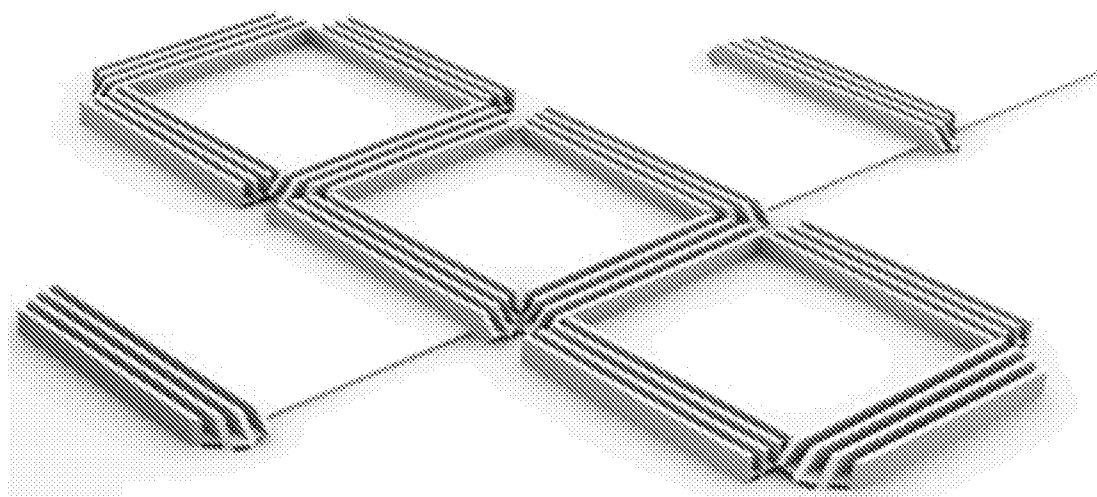


FIG. 10A

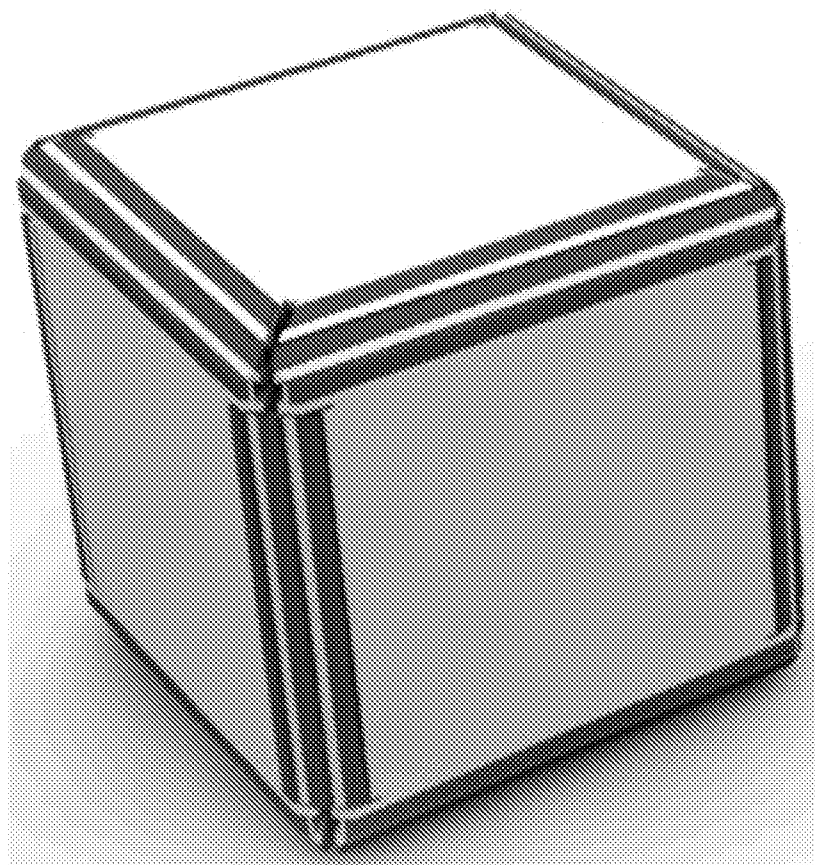


FIG. 10B

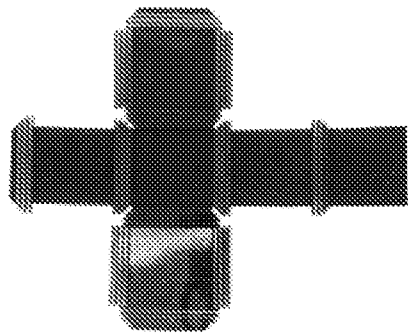


FIG. 11A

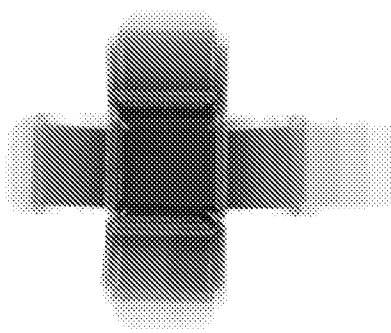


FIG. 11B

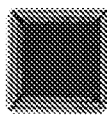


FIG. 11C

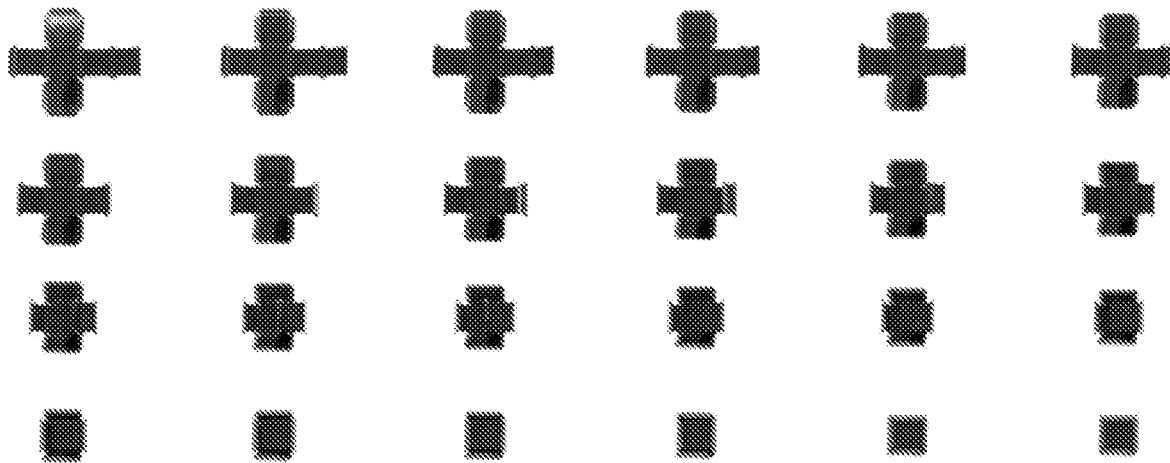


FIG. 11D

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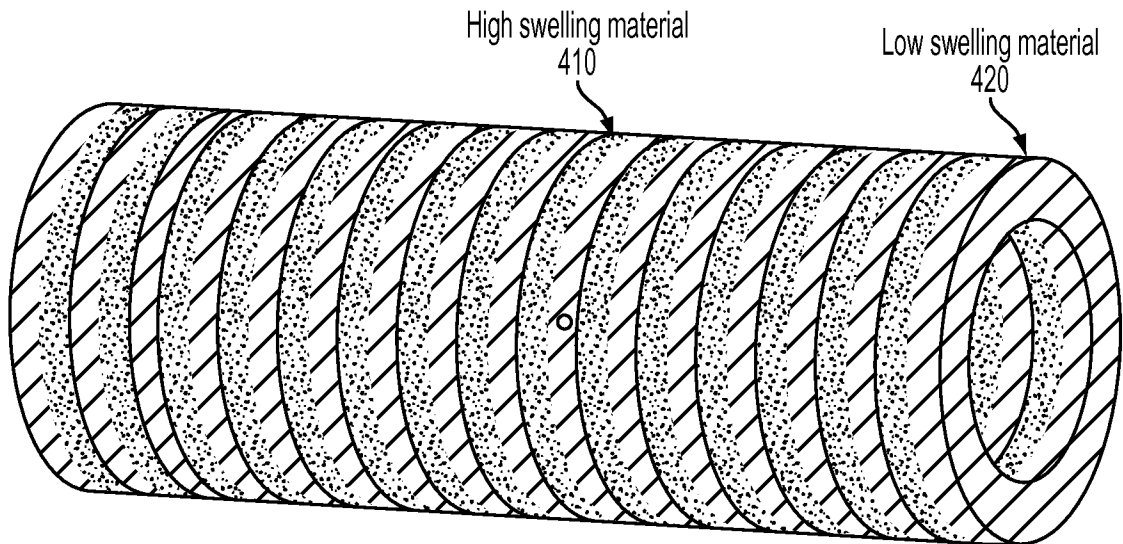


FIG. 12A

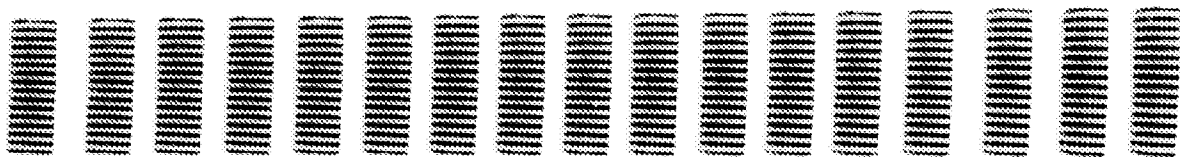


FIG. 12B

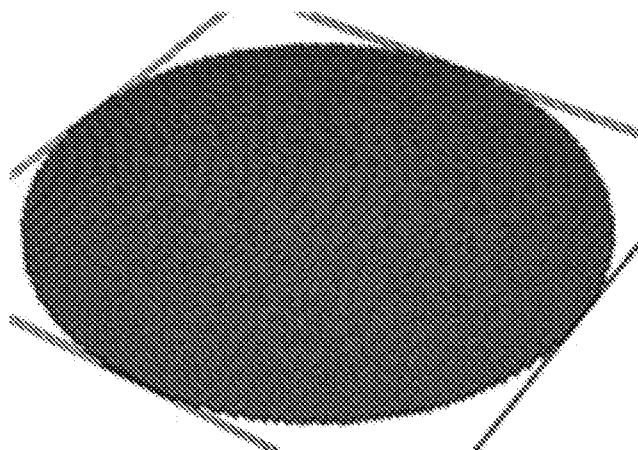


FIG. 13A

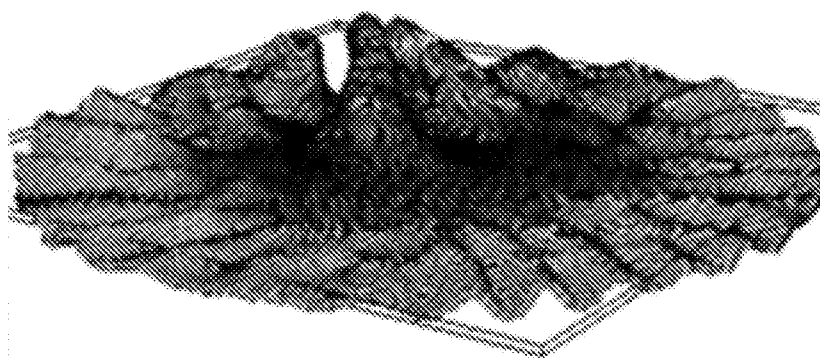


FIG. 13B

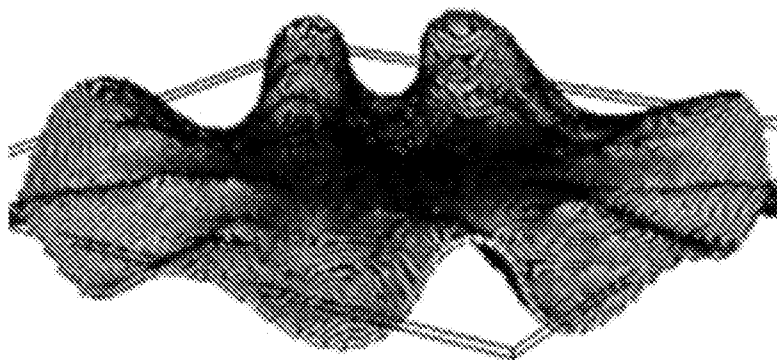


FIG. 13C

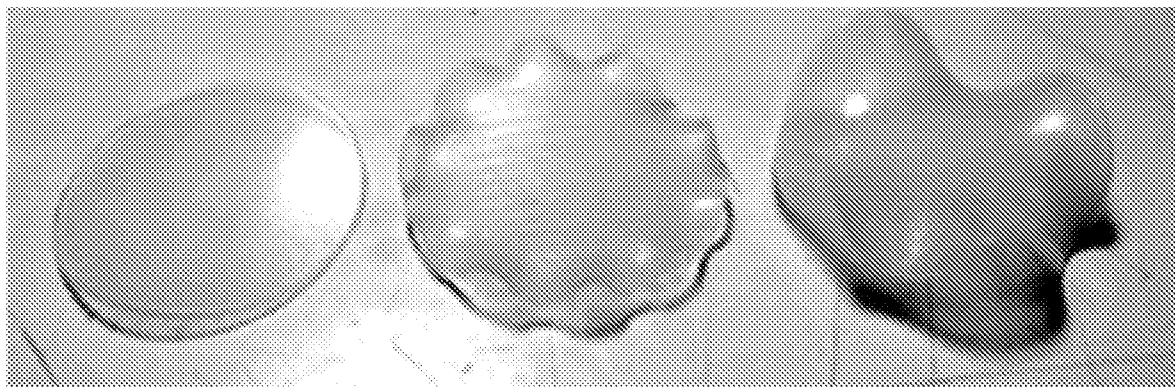


FIG. 13D

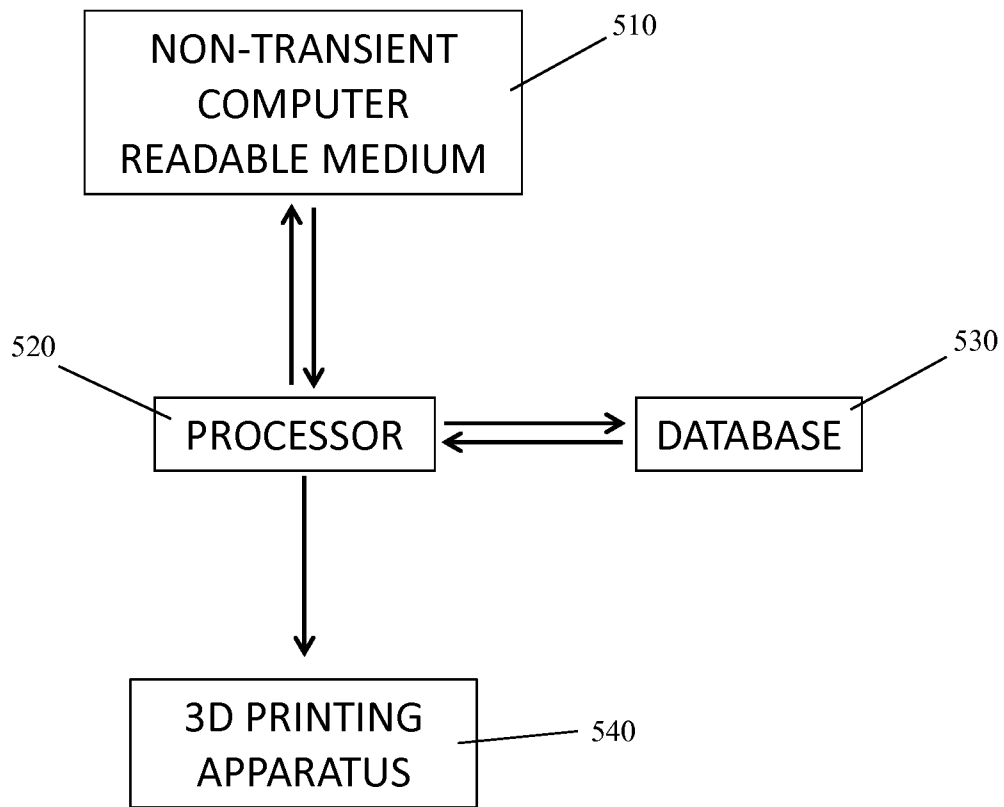


FIG. 14

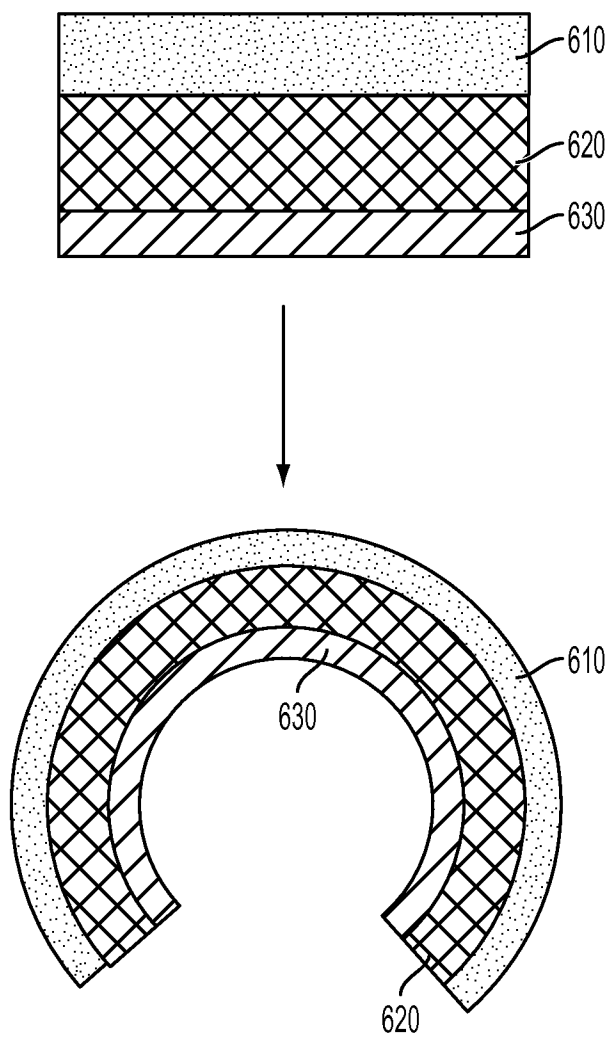


FIG. 15A

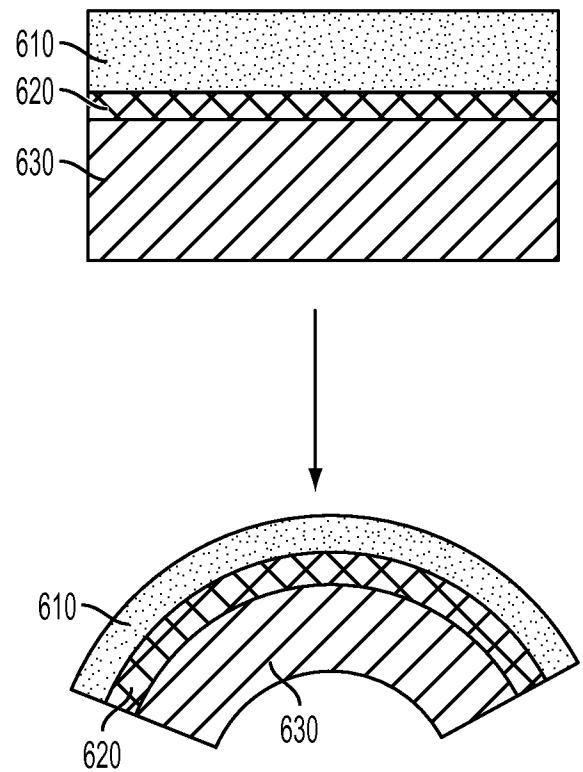


FIG. 15B

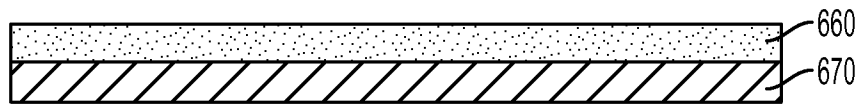


FIG. 16A

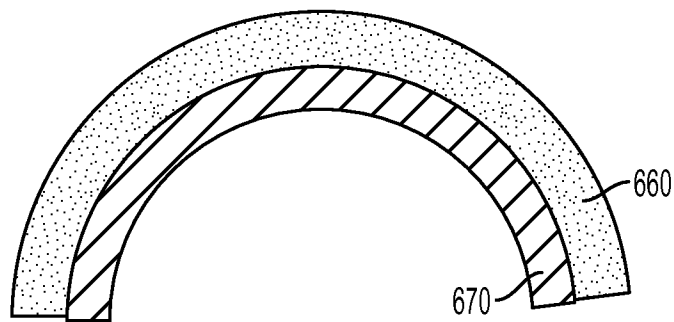


FIG. 16B

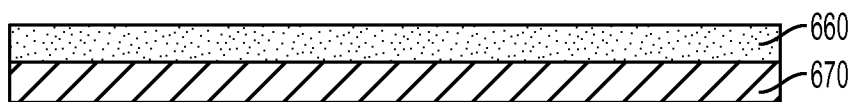


FIG. 16C

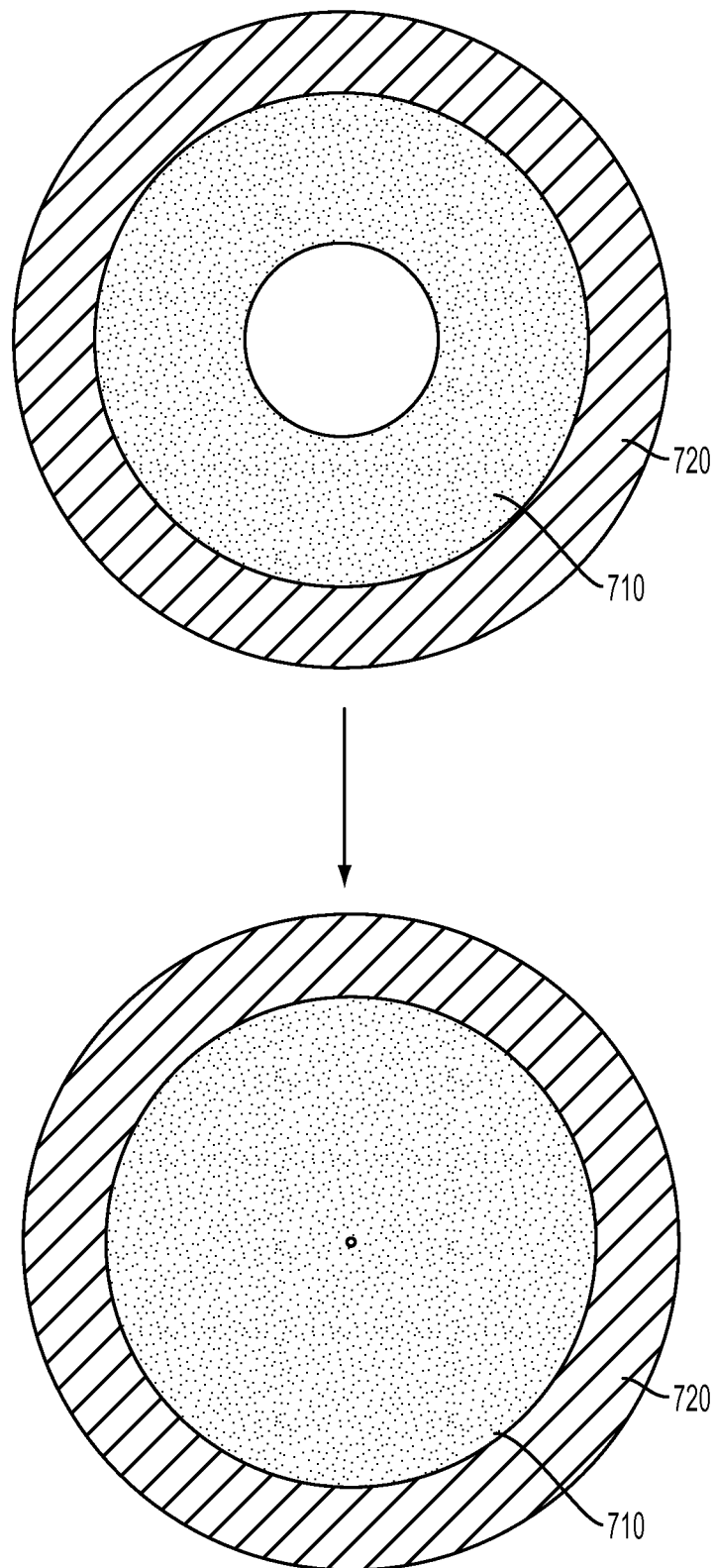


FIG. 17

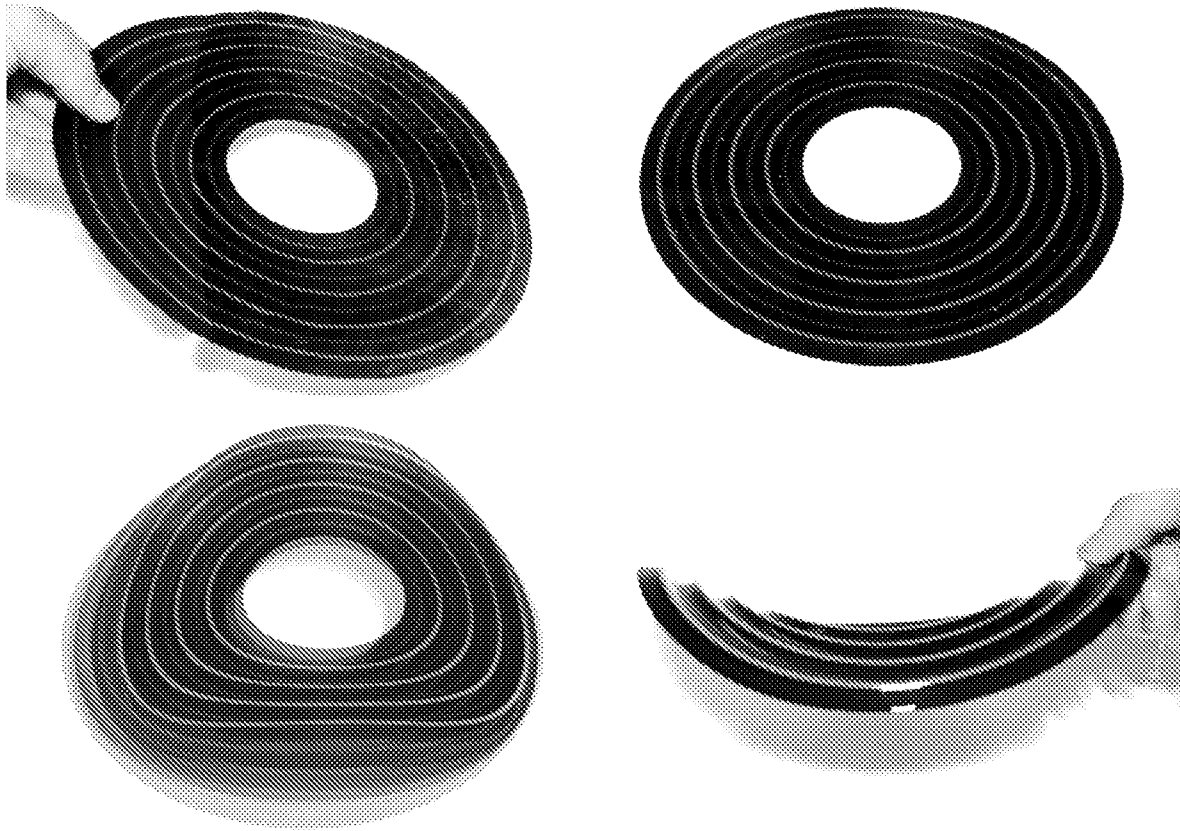


FIG. 18A

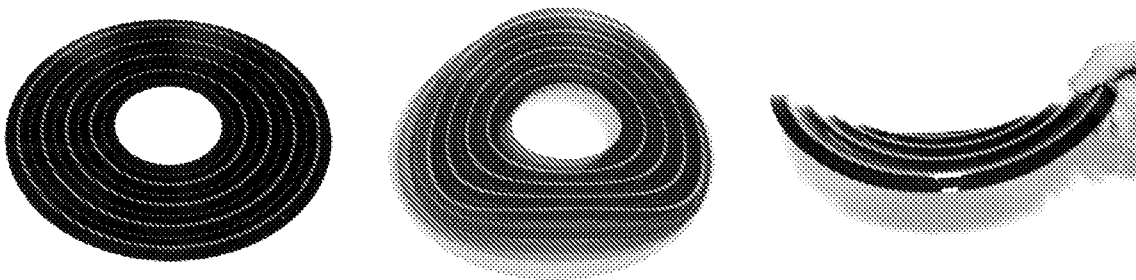


FIG. 18B

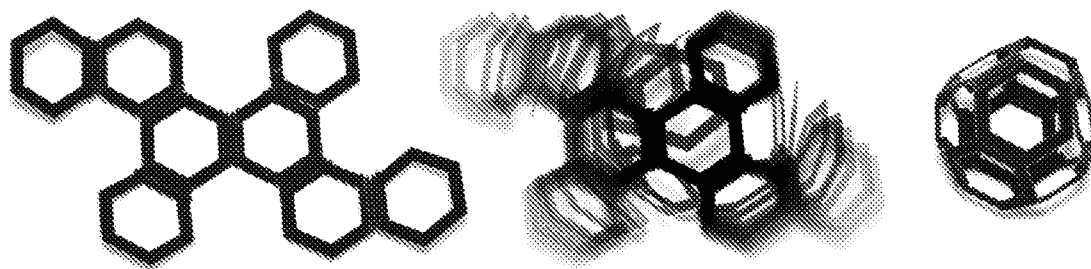


FIG. 19

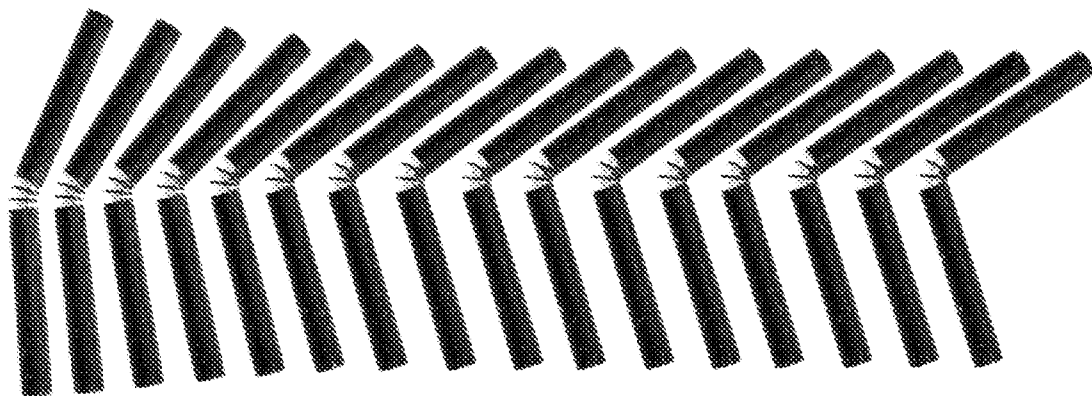


FIG. 20

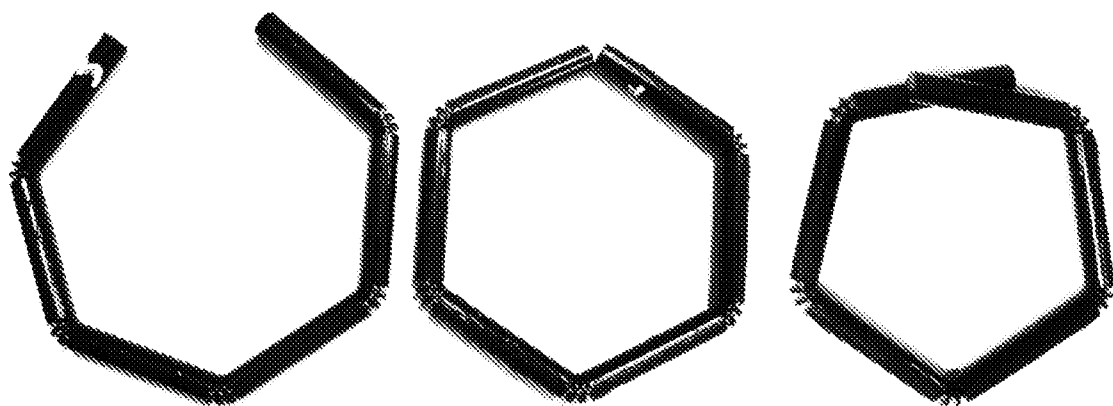


FIG. 21

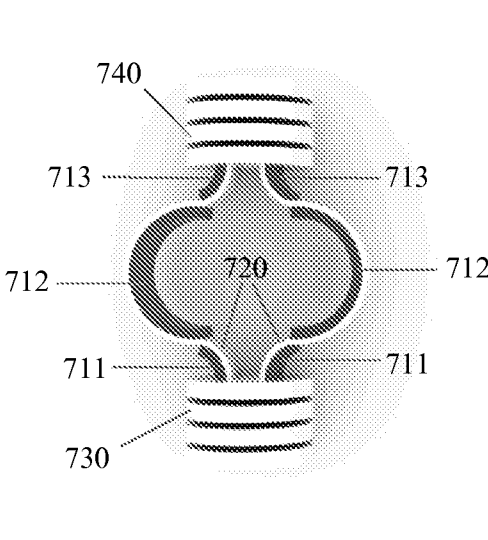


FIG. 22A

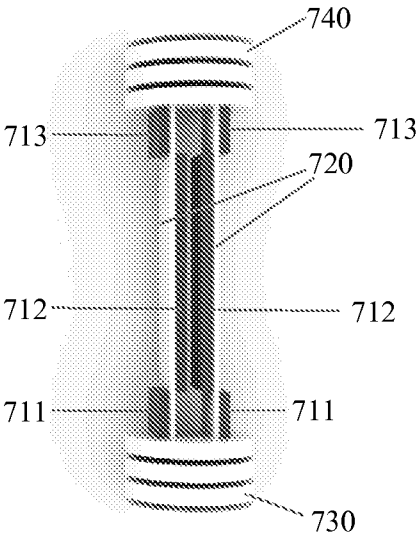


FIG. 22B

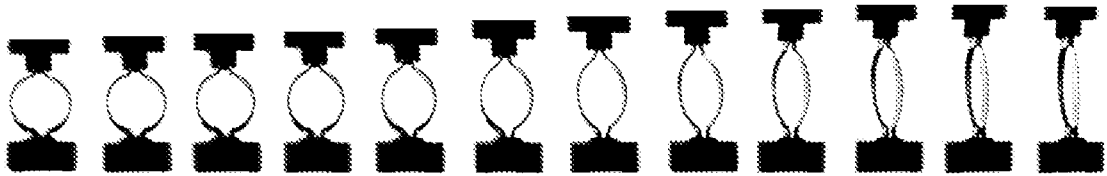


FIG. 22C

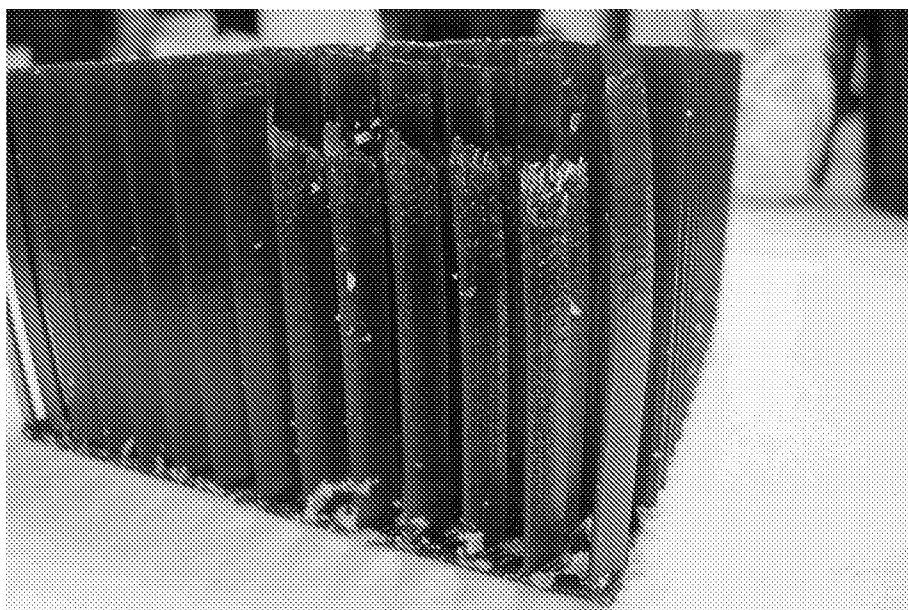


FIG. 23A

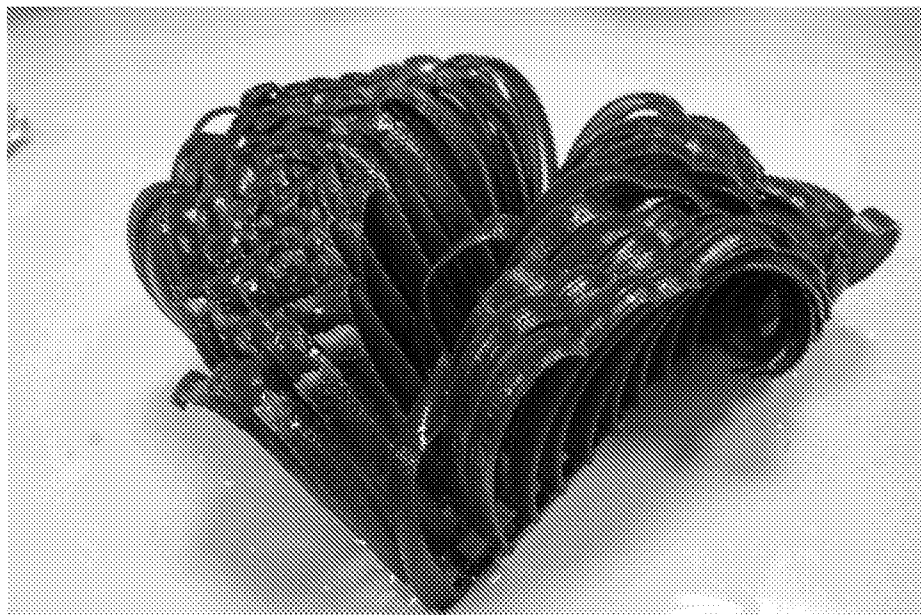


FIG. 23B



FIG. 23C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/018373**A. CLASSIFICATION OF SUBJECT MATTER****B29C 67/00(2006.01)i**

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)

B29C 67/00; B28B 1/14

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: additive manufacturing, 3D print, 3-dimensional print, 4D, 4-dimensional print, swell, hydrophile, stimulus, transformation, self-assembly

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GE, Q. et al. "Active materials by four-dimension printing", Applied Physics Letters 103, 131901 2013, published online 23 September 2013	1-2,31,34,63,65-66
Y	See abstract; page 131901-4; fig. 5.	
A		5-7,12,24-25,35-37 ,53,59-62,67 3-4,8-11,13-23 ,26-30,32-33,38-52 ,54-58,64,68-70
Y	"4D Printing: Self-assembling parts in Action at TED2013" 29 April 2013	5-7,12,24-25,35-37 ,53,59-62,67
A	See page 1.	1-4,8-11,13-23 ,26-34,38-52,54-58 ,63-66,68-70
A	TIBBITS, S. "Design to Self-Assembly", Architectural Design, Volume 82, Issue 2, pages 68-73, Mar	1-70
A	WESTBROOK, K. K. et al. "A 3D finite deformation constitutive model for amorphous shape memory polymers: A multi-branch modeling approach for nonequilibrium relaxation process", 43, 2011, pages 853-869	1-70
	See abstract; pages 853-869.	



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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

03 September 2014 (03.09.2014)

Date of mailing of the international search report

03 September 2014 (03.09.2014)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/018373

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012-0133080 A1 (MOUSSA, K. et al.) 31 May 2012 See abstract; claims 1-20.	1-70
A	US 2012-0068378 A1 (SWANSON, W. J. et al.) 22 March 2012 See abstract; claims 1-20.	1-70

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/018373Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

US 2012-0133080 A1

31/05/2012

WO 2012-074950 A1

07/06/2012

US 2012-0068378 A1

22/03/2012

None