Tampereen yliopisto

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STATE-OF-THE-ART, CHALLENGES, APPLICATIONS AND FUTURE PROSPECTS IN 4D PRINTING TECHNOLOGY

Bachelor of Science Thesis
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ABSTRACT

Valtteri Nikkanen: State-of-the-art, Challenges, Applications and Future prospects in 4D printing technology
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4D printing is a new emerging technology that enables new possibilities for many fields of science and technology. 4D printing can move some of the intelligence away from complicated sensor and computer connectivity directly to the material itself. The goal of this thesis is to give an up-to-date overview what 4D printing is, how does it work and what does it entail. It will also examine what state the technology is in presently and what applications it enables in the future.

The thesis is split into parts where the types of stimuli, smart materials, challenges and applications are examined. A few examples of the already achieved 4D structures and their self-actuations are shown in figures in the thesis. The thesis is a literature review, so no new research has been conducted. Used sources are published and peer-reviewed texts that are available online because of the ongoing pandemic and because the technology is new and there is not a lot of printed material about it. Sources are also mainly from the past decade to try and give a current view of the technology.

As a result of the examination, it can be said that 4D printing has immense potential for a wide variety of technological and scientific fields. However, 4D printing is still in its early stages and has challenges that it needs to overcome before it is at its maximum potential and can be used commercially or in many of the applications that it can enable in the future. For example, biomedical applications that could save lives. Tissue printing new organs instead of relying on donor organs can make the organs available faster and making it possible to personalize them for each patient.

Keywords: 4D printing, smart materials, Additive manufacturing

PREFACE

The subject of this thesis was chosen in large part because of my own interest to 3D printing and the possibilities that it alone enables. 4D printing brings a new dimension to the traditional 3D printing which makes it even more interesting with all the possibilities that non-static structures enable. Great interest were especially the applications that 4D printed structures can make happen in the future.

I would like to thank my instructor Luis Gonzalez Moctezuma for being patient with me, flexible with the scheduling and guiding me through this new thing for both of us. A warm thank you goes to my friends and family also who have had to listen to me complain about the writing process for almost a year.

Tampere, 5.5.2022

Valtteri Nikkanen

CONTENTS

LIST OF FIGURES

SYMBOLS AND ABBREVIATIONS

AM	Additive Manufacturing or 3D/4D printing, manufacturing by adding material instead of subtracting material
CAD	Computer Aided Design, software that is used to design something with a computer
FDM	Fused Deposition Modelling, 3D printing principle where material is melted and extruded through a small hole
SLA	Stereolithography, 3D printing principle using vat photopolymerization of resin for example
SLM	Selective Laser Melting, 3D printing principle where usually metal powder is melted with a laser
SCE	Shape Change Effect, the effect of smart material changing its shape
SMP	Shape Memory Polymer, polymeric material that can hold a shape until a correct stimulus is provided
SCM	Shape Changing Material, material capable of changing its shape in response to a stimulus
SMM	Shape Memory Material, material capable of holding a temporary shape until a correct stimulus is provided
DIW	Direct-Ink-Writing, 3D printing principle based on writing with ink material
SMA	Shape Memory Alloy, alloy based smart material that can hold a shape until a correct stimulus is provided
NiTi	Nitinol, nickel titanium alloy that has shape memory properties and can be classified as a shape memory alloy
Tg	Glass transition temperature, temperature where the material becomes pliable but is not melted
PCG	Photochromic Chromophore Group, molecules included into other material that are reactive to light
UV	Ultraviolet (light), used in curing or as a trigger mechanism for some materials
PLA	Polylactic acid, common plastic used in 3D printing
ABS	Acrylonitrile butadiene styrene, common plastic used in 3D printing
ITOP	Integrated Tissue Organ Printer, printer used to print biocompatible tissue structures

1. INTRODUCTION

Additive Manufacturing (AM) also known as 3D printing has slowly become a standard manufacturing method since it was invented in 1984 by Charles W. Hull [15*]. 3D printing technology is especially used for fast, cheap, and easy prototyping instead of large-scale manufacturing. AM methods work on the principle of adding more material layer by layer until the finished structure is made. AM has grown with great speed in the past two decades and is presently a multibillion-dollar industry [35]. Consumer level 3D printers of many different working principles are cheap to buy and easy to use. The materials required for 3D printing are also readily available from multiple different companies. Computer assisted design (CAD) software is intuitive to use and even free for a consumer to use. In 2013 Tibbits [43] working as a researcher at MIT proposed a manufacturing technique to create 3D printed structures that can change on their own over time. This variation to AM is now also referred to as 4D printing which is 3D printing with time being the 4th dimension. 4D structures are made with smart materials capable of reacting to a specific stimulus. As a reaction to the stimulus these 4D structures can change their shape, functionality, or other properties.

Creating 4D printed structures require 5 different parts: Smart materials, 3D printing facility, mathematical modelling, stimulus, and an interaction mechanism. This thesis will focus on the smart materials and stimuli and briefly examine what goes into the mathematical modelling. 3D printers are already existing and relatively widely used which is why they won't be looked at too closely, but examples will be mentioned. Interaction mechanisms may require some amount of ingenuity with combining the desired stimulus with the structure, but this is not anything especially revolutionary or straightly related to the act of 4D printing so this part of the 4D structures will not be detailed too accurately. Smart materials are materials that enable and perform the change in the structure. There are various materials used in 4D printing capable of this. Different kinds of smart materials and examples of shape changing structures made with them will be examined later. 3D printing facility or 3D printer is needed to generate the structure. This printer needs to be able to work with the chosen smart material, so a correct printer working with the right manufacturing principle needs to be chosen. 4D structures can be made with traditional 3D printers with a variety of different manufacturing principles, extrusion-based 3D printing like fused deposition modelling (FDM), vat photopolymerization-based 3D printing like stereolithography (SLA) and powder-based 3D printing such as selective laser melting (SLM) [4]. There are many other forms of AM that could also be used in 4D printing. Mathematical modelling is required to plan the 4D structure in advance and calculate the correct manufacturing layout and structure for the printer to print. The process of modelling is still difficult as the more powerful software, which can consider the different material properties, is needing development and will be looked closer in the challenges section. Normal slicing 3D printing software is not enough when the structure must change from a static structure into a dynamic one. Mathematical modelling is also done to reduce the amount of testing needed to achieve the desired shape change effect in the 4D structure. Stimulus is the driving force for the smart material to perform the desired reaction. Stimulus can be a physical, chemical, or a biological in its nature depending on the smart material that is used. Different stimuli and how they work with smart materials are examined later. Lastly an interaction mechanism for the stimuli and the 4D structure is needed. Interaction mechanism bluntly means how the stimulus is able to reach and affect the structure. Possibilities for these are endless and could be very case specific.

This thesis covers the current state of 4D printing material and stimulus research. The goal is to create a somewhat comprehensive overview of 4D printing technologies current state and future outlook. The sources used are publications made in the last decade to create a current and up-to-date view of where the technology is at today as the whole concept of 4D printing is new and the technology is in its early steps but rapidly advancing. There are some older sources especially about the smart materials as there has been research about them for a longer period. The thesis also looks at the challenges that 4D printing faces including what needs to be done to overcome them. Possible applications and future of the technology are also examined.

In the second chapter this thesis looks at different available stimulus types used in triggering the smart materials and the 4D printed structures made from them. An example use case is described for each of the stimulus types. Third chapter examines closer all the different known smart material types. The mechanism of how they work, and their advantages and disadvantages are looked at. Fourth chapter focuses on the current challenges facing the 4D printing technology and what needs to be done to advance toward commercialization. The challenges are split into three distinct categories that are then examined. Fifth chapter takes a closer look the possible applications and the future of the technology. Four fields of great interest and potential are picked out for a more in depth look for how 4D printing could benefit them.

2. TYPES OF STIMULI

Stimulus is a core part of 4D structures working. They are a necessity in triggering the shape change effect (SCE) in the smart material. There are many different stimuli that can be used for 4D structures. The type of stimuli used is dependent on the chosen smart material, use case and design of the structure. The stimuli can be categorized into three different classes of stimuli: physical, chemical, and biological. Physical stimuli include temperature, light, water, electric field, and magnetic field. Chemical stimuli include pH level and different chemicals. Lastly biological stimuli include different enzymes and glucose. [36] The stimuli can be used in combination with each other when interacting with multimaterial structures to achieve the desired outcome for the structure behavior. Stimuli can be direct or indirect in how they work. Temperature, water, pH, chemicals, and the biological stimuli are all direct stimuli. Light, electric field, and magnetic field are indirect stimuli. Different types of stimuli have different advantages and disadvantages associated with them. These are based on the interaction mechanism or what the operating principle is. The different materials and their more specific interactions with different types of stimuli is examined later in this paper.

2.1 Temperature

Temperature is one of the most used stimuli in 4D printed structures, especially in shape memory polymers (SMPs). [2] Heat reactive smart materials most usual way of reacting is bending, folding, or twisting. Temperature is a direct physical stimulus when categorized into one the three stimulus classes. Temperature as a stimulus is based in the inequalities in the structure’s internal stresses. Advantage of temperature stimulus is that it is controllable and adjustable. Many temperature-responsive smart materials have a slow response to the stimulus and using temperature can be complicated from the design of the part to the interaction mechanism between the stimulus and the 4D structure [8]. Temperature as a stimulus has a few disadvantages. Heat transferal is slow and inefficient as it must be done by radiating or conducting. Heating the material can be a slow process and if the heating must be even across the material the process becomes even more complicated and slow. In addition to the problems in heating up the structures cooling the heated-up material back down can take a relatively long time which makes the response time slow.

Ge et al. [10] created a multimaterial gripper that was able to pick up objects when exposed an external heat stimulus. The gripper design is shown in Figure 1. Depending on the programming the gripper was either able to grip an object or release the grip when exposed to the heat stimulus. The grippers were constructed with multiple materials. The joints were made of the SMP material, and the grippers tips were different material with a different stiffness to ensure a firm contact with the target object.

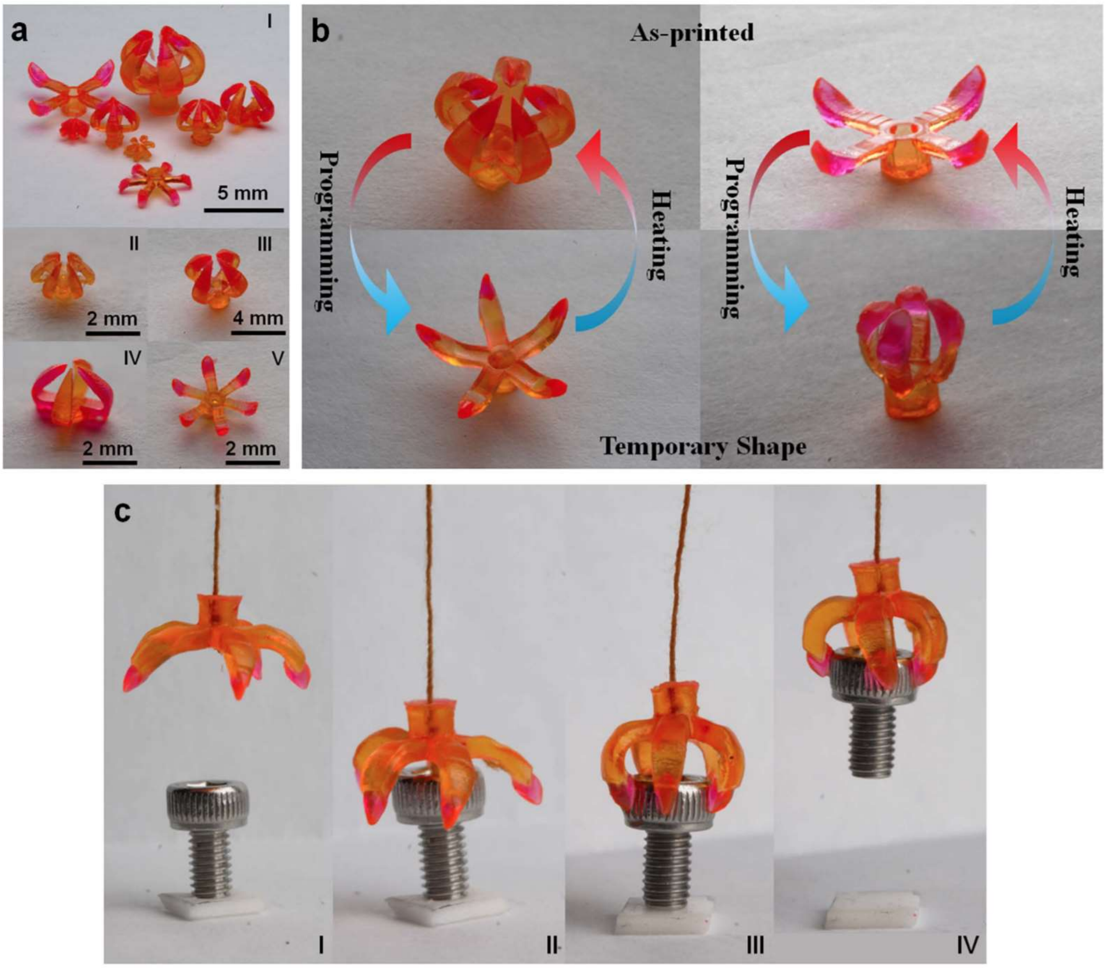

Figure 1: Multimaterial grippers. A) different sizes and designs of the gripper. B) Shows the different programming done to the gripper. Left one is gripping as a reaction to the heat stimulus and right one is loosening its grip. C) Shows a timelapse of the gripper picking up an object.[10]

2.2 Water/moisture

Water reactive smart materials mostly swell and expand as a reaction to the stimulus as they absorb the water into the structure. The 4D structure is made of the expandable hydrophilic material and a rigid material. The shape changing mechanism is driven by the different swelling ratios of the materials used to construct the structure. Shape change comes from the energy of the active shape changing material. When the structure is designed correctly with the active and rigid materials a complex swelling based shape-change can be achieved. The size and direction of the swelling can be controlled by the rigid material in the structure. This mechanism is also naturally reversible as the material dries so the original shape can be achieved. [29] Moisture, like temperature, is a direct physical stimulus when categorized into a stimulus class.

Mulakkal et. Al [31] created a 4D printed flower that laid flat and as a reaction to drying gained the 3D flower shape and again when hydrated reverted back to the flat structure form. The flower was made from a mix of a composite made of CMC polymer and fiber pulp (composite), clay, cellulose-hydrogel made of

CMC-Na and hydroxyethyl cellulose (gel), and citric acid as a crosslinking agent. The flower structure and its creation process are shown and explained in more detail in figure 2.

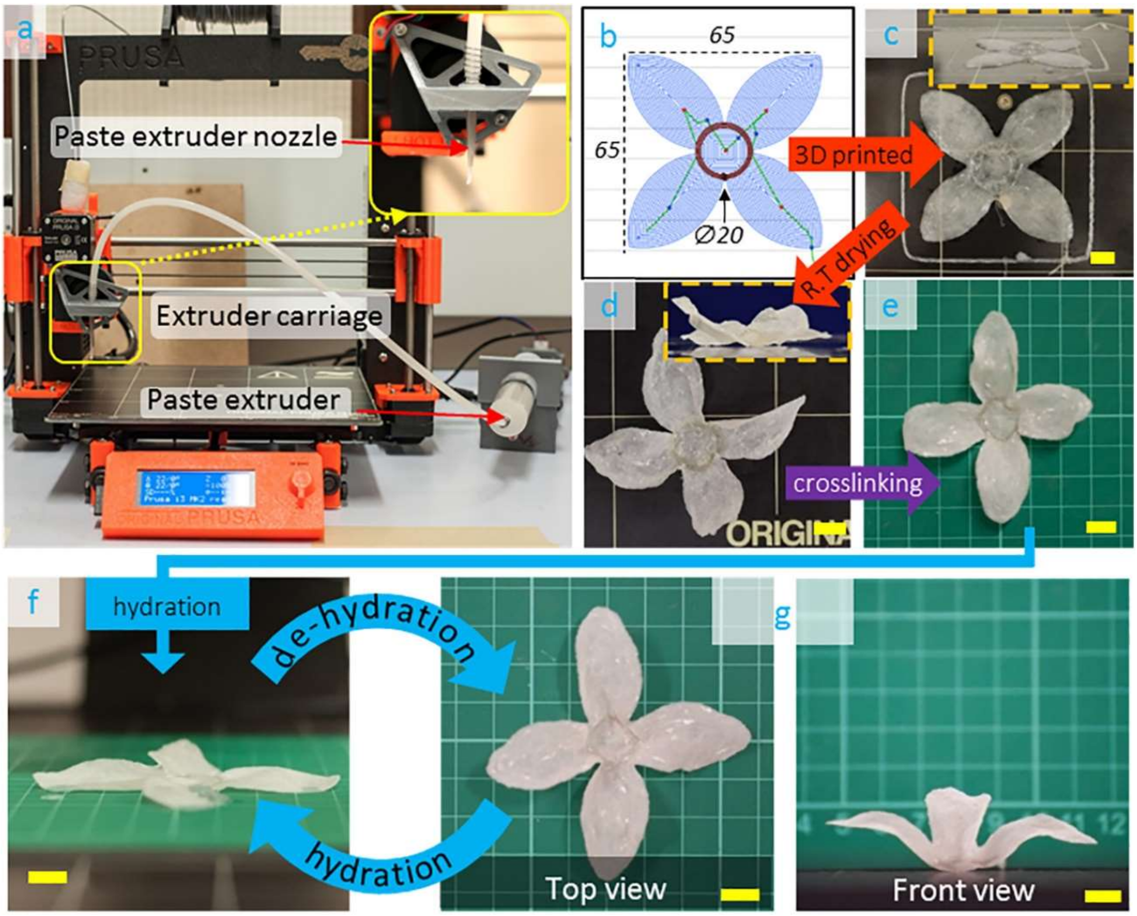

Figure 2: 4D printing of the hydration reacting flower structure. A) Shows the printing setup. B) Print path for the structure based on the CAD model, dimensions are in mm. Blue area in the picture is composite, clay and citric acid mixture while the red area is just gel and citric acid. C) Is the printed structure. D) Is the printed structure drying at room temperature starting the shape change. E) Is the structure after crosslinking to retain the correct 3D shape. F) Flat hydrated structure. G) Dehydrated 3D flower shape. [31]

2.3 Light

Photoreactive smart materials react to light as a stimulus. This type of smart material can as a response to the stimulus change color or its shape. Different wavelengths of light can be used to trigger different shape change effects in a structure. Light as a stimulus is based on a photo-thermal effect in the smart material or the light causes the materials temperature to rise causing the change in the geometry. Light as a stimulus can be remote controlled and has a high resolution in its control which are advantages for it use. Light is a complicated stimulus to use. Light is an indirect stimulus unlike temperature or moisture, and it does not cause damage to cells like increasing the temperature of the material [8]. Because of this it is extremely applicable in medical science. For example, structures that are inserted into a patient can be remotely activated with light waves. Different medical applications for 4D printed structures are more closely examined later in the thesis.

Jeong et al. [16] demonstrated the effect of different shape changes in a single structure under different color lights when they by using red light got the structure to bend into an n-shape under red light and then under blue light they got the structure to revert to its original shape. If the structure was first exposed to blue light it bent into a u-shape and then after red light reverted into the flat shape. Materials used in the experiment were photoreactive SMPs. The structure was made of blue (Verocyan) and yellow (Veroyellow) digital SMP materials that absorbed red and blue light differently. The light absorption caused the material to heat up above its Tg and bend while the other material stayed rigid causing the change in the structures shape.

2.4 Electric field

Electrical field as a stimulus works by causing a temperature change inside the structure also known as electro-thermal effect. The electric field causes current to run through conducting particles that have been introduced to the material that then heat up. This temperature change in the material causes a physical reaction that changes the structures geometry. Electric field is a fast stimulus but can be inconvenient because of the interaction mechanism as it requires a strong enough electric field to be generated around the target structure. Electrical field similarly to light can be used as a remote-control stimulus. [8] Smart material infused with conducting material particles could be able to react to an indirect electric field and cause a reaction in the structure. Electric field as a stimulus is a physical and an indirect one.

Miriyev et al. [27] created a soft artificial muscle that could expand as a reaction to the heat generated in a wire with electric current running through it. The material used was elastic silicone rubber with ethanol mixed in it. When heated the liquid ethanol pores in the material vaporize and expanded causing the whole structure to grow. The silicone ethanol mix is 3D printable, and the artificial muscle used in the experiment was 3D printed. Although the electricity used as a stimulus acted as a stimulus because of the heat generated because of the resistance in the wire.

2.5 Magnetic field

Magnetic field as a stimulus is based on magnetic material like iron nanoparticles such as Fe_2O_3 and Fe_3O_4 in the smart material. Similarly, to electric fields the interaction mechanism can be difficult to operate and manage as it requires a potent enough magnetic field to be generated around the target structure. [8] Magnetic field as a stimulus is a physical and an indirect one. Compared to temperature or water stimuli magnetic fields are fast acting [53]. In small applications like grippers and other small actuators electromagnets could be a straightforward way to generate the required magnetic field to trigger the SCE. Electromagnets are easy to control and can be small so the structure does not need to be stationary but can be moved with relative ease. For even smaller applications this would be even less of an issue as the target area where the structure is would be easy to cover in the desired magnetic field.

Breger et al. [7] thermo-magnetically responsive soft microgrippers. The microgrippers were hydrogel based with some stiffer polymer segments for added grip. The hydrogel was infused with iron nanoparticles Fe_2O_3 to create the magnetic response for the structure. The grippers were strong enough to excise come cells out of a tissue sample.

2.6 Chemical stimuli

There are different kinds of chemical stimuli. The change of pH value and different chemicals can be used as trigger mechanisms for some smart materials. SCEs in chemical stimuli responsive materials are swelling, dissolving, and softening [49]. This type of SCE is mostly conducted in water environments because of the ease of changing the pH value of the liquid or easy mixing of trigger chemicals into the liquid. The aqueous environment is suitable for hydrogel materials shape change, so they are widely used with chemical stimuli. Chemical stimuli are especially interesting for biomedicine use as there is clear pH deviation in different parts of the human body. There are also possible other chemical compounds in the human body that could be taken advantage of to be used as chemical stimulus. Microstructures that are responsive to these compounds could be used to diagnose or even for treatment.

Nadgorny et al. [32] created a printable hydrogel that was pH responsive. The hydrogel swelled in pH-levels above 4 and shrunk in pH level under 4. Chemical stimulus could be useful for example in biomedical applications. The printed structures could react when the pH-level changes to release medicine trapped inside the structure to medicate only the area that needs the medication.

3. SMART MATERIALS

Smart materials are a requirement in 4D printing. The materials can be split into two different types of materials. Shape changing materials (SCM) and shape memory materials (SMM). SCM changes its shape when provided with the correct type of stimulus but notably cannot hold the shape. When the stimulus is removed reverting to their original shape. SMMs however can hold their newly acquired shape when the stimulus is removed. SMM requires a programming step where the desired temporary shape is forced on the structure. Temporary shape is held by the material until an appropriate stimulus is applied when the structure reverts to its original permanent shape. [51] This shape memory effect is shown in Figure 3.

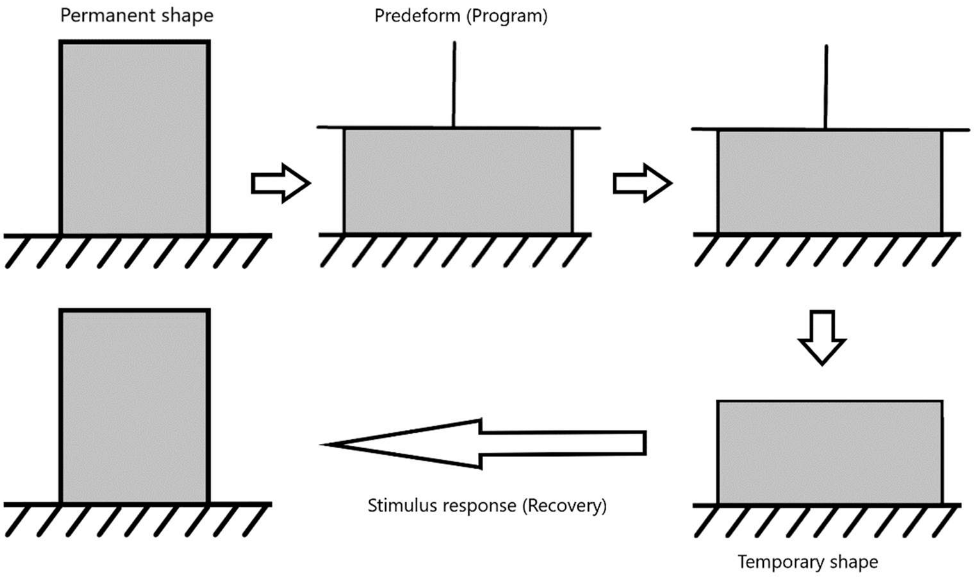

Figure 3: Explanation of the shape memory effect in SMMs

4D structures can have interesting functionalities based on the material properties. Self-assembly, self-actuation and self-repair are some of the most interesting of these functionalities. Structures that can self-repair have many possible applications in many different fields: pipes, tissue, or aerospace components are examples of applications where self-repair could be very useful. Difficult to reach parts that could repair themselves when damaged would be useful. Self-actuation could reduce the need for servos in robotics making them more autonomous and less bulky when complicated processes could be managed with only material properties. Gripping tasks not requiring multiple servos to control the gripping actuator but for example working with a remotely activatable electromagnets magnetic field could reduce the bulk and complexity of the required machinery. SCE in smart materials is usually folding, swelling, or twisting but can also include change in other material properties. The change in these properties is used to achieve the desired functionality in the 4D structures.

Type 1 stimulus responsive material is when the shape changes when a stimulus is applied and the shape reverses when the stimulus is removed. Type 2 stimulus responsive material is referring to dual shape memory. There are also one-way or two-way types of type 2 materials. One-way shape change requires a new programming step when two-way does not. Type 3 stimulus responsive materials are materials that are capable of triple shape memory or multiple shape memory meaning more than three memorized shapes. Type 3 shape memory material has one permanent shape and two or more temporary shapes. [2] Type 1 materials can also be described as SCMs which were described earlier described earlier. Type 2 and type 3 materials are SMMs which were also examined earlier.

Important for smart materials aside from their SCE capabilities is that the material can be used in additive manufacturing practice. If the smart material cannot be processed into a printable form, it is not suitable for 4D printing for obvious reasons. Hydrogels for example are not suitable for FDM printers but can be excellent for Direct-Ink-Writing (DIW) printing. Combining different smart materials with each other can negate the disadvantages of the materials and take the best properties from each material, creating a better more versatile result. SMPs and Hydrogels are the most used smart materials in 4D printing as alloys and metals are much more difficult and expensive to manufacture via printing.

3.1 Hydrogel

Hydrogel is gel like material but can be made more rigid by mixing the material with other materials. Hydrogels have good biological affinity and can be reversibly deformed in response to a correct type of stimulus. The swelling degree of hydrogels depends on the properties including crosslinking density and hydrophilicity, of the hydrogel material. Advantages for hydrogels is that they are biocompatible and are easy to print using direct ink for example DIW method of additive manufacturing principles. Hydrogel is also an easy-to-synthesize material that is adjustable and has a low cost. It is promising material for biomedical applications. Hydrogel can be responsive to different stimulus types. There are thermally responsive, light responsive and pH-responsive hydrogels in addition to the more basic moisture responsive hydrogels. [8]

Moisture responsive hydrogels work by absorbing moisture/water from their environment and swelling in response. The swelling of the hydrogel like other SCEs can be controlled by the construction of the 4D structure and material properties. When drying the hydrogel structure would revert its deformation.

Thermally responsive hydrogels are gels that change their volume when the environments temperature changes. Because the volume change response is caused by the swelling or collapse of the materials polymer chain itself the SCE is reversible [6]. One of the most studied thermally responsible hydrogel materials is Poly(N-isopropylacrylamide) (PNIPAm). PNIPAm has the capability to reversibly swell in response to a temperature change. Bakarich et al. [3] created a relatively fast, reversible, muscle-like linear actuation using printed hydrogel materials that were then incorporated into a smart valve to control water flow. The hydrogel they used was a mixture of PNIPAm and alginiate that swelled when exposed to temperatures of 60°C stopping/slowing the water flow through the valve and reopened when 20 °C water was ran over the printed hydrogel parts.

Light responsive hydrogels get the benefit of all light responsive materials, the benefit being that they do not require direct contact with the environmental stimulus. The light can be controlled remotely, its intensity can be configured, and it can be shined from desired directions to control the hydrogels swelling. One downside in light responsive hydrogels is that many of them are also reactive to UV light. Hydrogels can react to the light stimulus through molecular exchange or through changes in the physical or chemical properties like shape, swelling, viscosity or elasticity.[8] Schiphorst et al. [39] created a light responsive hydrogel water valve. The hydrogels deformation in the valve was reversible. The deformation process working in either way only took a couple of minutes making it also relatively fast when compared to other materials.

pH-responsive hydrogels volume change depends on the concentration of internal hydrogen ions in the structure in response to the change of pH in the environment. [21*,38] pH-value differences in the human body make pH-responsive hydrogels a good option together with hydrogels good biological affinity for biomedicine applications [8]. Hu et al. [14] 4D printed pH-responsive hydrogel structures resembling flowers. The printed structures were extremely small, and the study proposes microscale 4D printing of hydrogels would have great applications in biomedicine.

3.2 SMA - shape memory alloy

Shape memory alloys (SMAs) are not a new concept as the first reported was in the late 1960s. Combining SMAs with additive manufacturing however is a new concept. SMAs fall into two categories, thermo- and magneto-responsive materials. Reversible martensitic transformation in the materials crystal lattice structure is the main mechanism behind shape recovery in SMAs. [49] SMAs have a few disadvantageous properties as they have complex manufacturing processes, high costs, they can be toxic and have limited recovery compared to other smart material types [36]. SMAs also have other limitations to consider when using them which include small usable strain, low actuation frequency, low controllability, and low accuracy [28]. Additive manufacturing of metals or alloys can also be complicated but there are AM principles that are applicable. Deterioration of the material is also a large concern in SMAs, multiple cycles of deformation can take a toll on the structure and cause issues in the shape formation.

Thermo-responsive materials are sensitive to temperature. Nitinol (NiTi) is a titanium and nickel alloy that has shape memory properties. NiTi is a thermos-responsive material that has the unique property of temperature-induced austenite-to-martensite phase transformation. Higher temperature phase for NiTi is the austenite phase and lower temperatures the martensitic phase. The phase change is achieved by heating or cooling the material. Transition temperatures for the austenite to martensitic phase can range from -100 to 150 depending on the material. Some SMAs require high temperatures, which can make them difficult to operate. [49] Problem with thermo-responsive materials is that they require heat transfer from the environment for the activation response and then they need to release that heat somewhere to achieve the reverse. The heat needs to be radiated or conducted somehow which can be slow and energy inefficient.

Magneto-responsive materials are responsive to magnetic fields. Actuation energy produced by magnetization is much higher than the energy produced by heat transfer. [49] The higher actuation energy also leads to the fact that compared to thermo-responsive SMAs the magneto responsive SMAs actuate at higher frequency because the energy is transferred via magnetic fields and not via inefficient heat transfer [28]. Magneto-responsive SMAs have limitations only working in low enough environmental temperatures. For example, measurements for the temperature limits for a magnetic shape memory material Ni-Mn-Ga martensite was measured to be around 173-315 K. [12]

3.3 SMP - shape memory polymer

Shape memory polymers or SMPs are a class of polymeric materials that have the shape memory capability of smart materials. SMPs can retain multiple shapes so they are type 2 and type 3 smart materials. There are SMPs that are reactive to multiple types of stimuli. [49] There are temperature, light, magnetic/electric field, chemically and water responsive SMPs [33]. That is by far the widest coverage of stimuli that any smart material types have. SMPs consist of two parts, one that is highly elastic and one that can reduce the stiffness of the polymer under the correct stimulus. After the correct stimulus, a transformation is triggered in the material and the stored strain energy is released, resulting in shape recovery. The shape recovery mechanism is completely different to SMAs. [8] SMPs have good qualities for a material, they have a lower cost and simpler manufacturing when comparing to other smart materials, they are lightweight especially when comparing to SMAs and SMPs extremely good recoverability and do not deteriorate as rapidly as SMAs. [49] SMPs also have limited high temperature application possibilities as polymers have a relatively low melting point. Some of the stimulus responses are achieved by implementing some stimulus sensitive molecules into the polymer material, the stimulus sensitive molecules then respond to the stimulus causing the SCE in the polymer material. Digital SMPs are polymer materials that are made by mixing two base materials at specific ratio to achieve the desired thermomechanical and shape memory behavior [26]. SMPs can be printed with more traditional AM methods than many other smart materials. Bodaghi et al. [5] printed a triple SMP with an FDM printer in their recent study on SMP 4D printing. FDM printers are relatively cheap and readily accessible to a wide hobbyist market which makes it that more interesting that 4D printing can in theory be achieved with existing and widespread equipment. Suriano et al. [41] demonstrate an SMP material with the self-healing ability of the material. The printed object has a cut area in it that it repairs with thermal treatment. Figure 4 shows the damage and result of the materials self-healing.

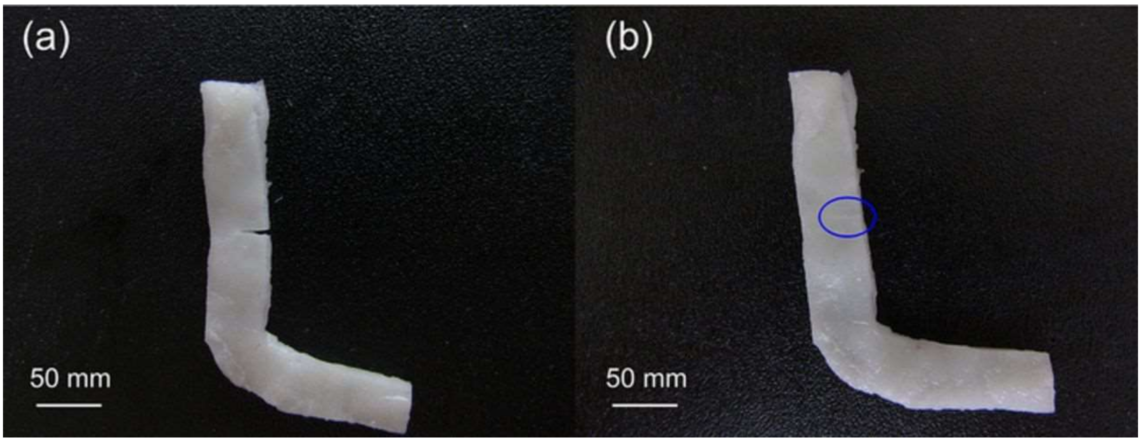

Figure 4: An L shaped piece of printed polymer material. a) the L shaped material has a partial cut in it b) after thermal treatment of 1 hour in 80°C keeping the cut area pressed together the cut is healed. [41]

Heat is the most used stimulus in 4D printing and thermo-responsive SMPs can be classified as thermoplastics and thermosets. Thermosetting SMP mixes the crosslinking agent with the polymer after heating the material to its melting point and then engaging the crosslinking reaction in the mold to achieve the structures initial shape [37]. SMPs that are capable of the so-called shape memory effect (SME) can transform from a temporary shape to a memorized shape when heated above their glass transition temperature (T_g). In this temperature the material loses its rigidity and becomes more flexible as it loses its internal stresses that keep it solid. [2] When the structure cools down below the T_g depending on the material and its properties the structure can either keep the new acquired shape or revert to its original one.

Light responsive polymers work by including an appropriate photochromic chromophore group (PCG) into the polymer material. When this material is then exposed to light, especially high energy light like ultra-violet (UV) light, PCG isomerization reaction is going to happen, and the molecule chain structure of the material is going to experience a significant change. The original shape can then be recovered on different wavelengths of UV light. [34] This type of SMP has all the advantages and disadvantages that other light responsive materials have which were examined earlier in this paper.

Chemically responsive polymers refer to polymers that change their shape when exposed to chemicals. pH-responsive polymers usual way to apply the stimulus is to soak the structure in acid solution which causes hydrogen ions to expand the molecular chain. When the structure is then exposed to a base solution the molecular chain will shrink and return the structure to its starting state. [11] The main mechanisms for this type of SMPs are softening, dissolving, and swelling [49]. The main advantage for chemical responsiveness is the biocompatibility and possibilities in biomedicine applications that they enable

Magnetic and electric field responsive polymers work similarly with each other. Polymers that are reactive to electrical fields there is some conductive material mixed in with the polymer material, materials used in this are graphene, metal nanoparticles and carbon nanoparticles. When the material is then exposed to electrical fields the heat generated by the current running through the material enabled by the reactive particles is used to trigger the SCE in the 4D structure. [49] Magnetic field responsive materials have magnetic responsive particles mixed in the polymer material, like ferromagnetic iron particles or something similar. Mechanisms work in SMPs the way that the stimuli have been explained to work earlier in this thesis.

3.4 Composites and multi-materials

Fiber reinforced composite materials have been used in 3D printing for some time already. 4D printing smart composite materials is a natural step. This type of composite material is ideal for 4D printing because they have great properties for a smart material including great strength, durability, stiffness, and commercial availability [13]. 4D printing in combination with composite materials can be used to create strong and durable parts for heavy duty use in which SMPs for example would not be adequate due to high mechanical stresses.

Smart multi-materials are made by combining varied materials with each other. In this the design of the components plays a vital role as traditional materials don’t react to external stimuli. Combining varied materials with each other may be useful to achieve the desired result in the structures actuation or other desired properties. The problem here comes in linking and printing the smart material with the conventional material to create the finished structure. [20] Multi-materials can be used to achieve the desired stimulus response. One of the more widely known multi-material used in 4D printing are polyurethane based SMPs and composites made from them and carbon nanotubes which can also be printed via FDM which makes it so much more accessible for a wider audience [24]. Mao et al. [26] created a self-folding box that had smart materials in the hinges to achieve the folding. The hinges contained different smart materials so that the folding process could be controlled, and the desired amount of folding could be achieved at the correct hinges. Figure 5 shows the box and how the folding happens as a response to the stimulus.

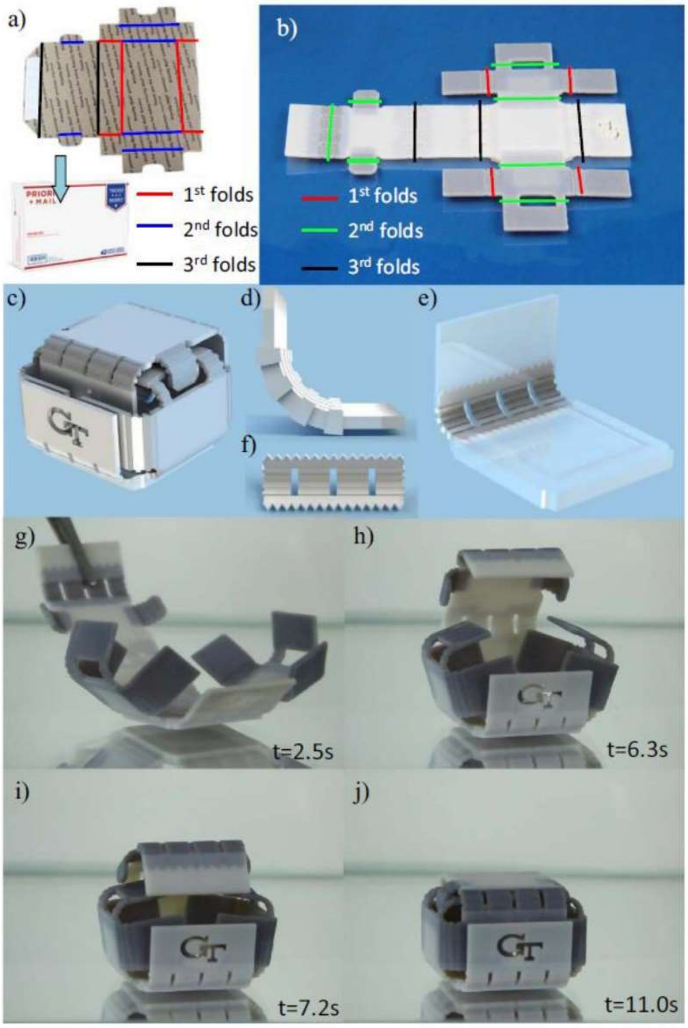

Figure 5: 3D folding of the multimaterial USPS shipping box. a) the USPS shipping box folds into a box in the showed sequence. b) a 3D printed sheet with varied materials in different hinges. c-f) More detailed pictures showing the design of the structure and hinges. g-j) When exposed to heat the box folds into the designed shape. [26]

These stronger and more specialized materials are ideal for aerospace applications for example where the strength of the material is of paramount importance [17]. The smart material functionalities like self-repair or self-assembly would be especially useful for aircraft or spacecraft parts where all the parts need to be in working order and their manual repair may be hard or even impossible in the case of spacecraft.

4. CHALLENGES OF 4D PRINTING

While 4D printing is a very promising technology and there has been a huge amount of research and real progress has already been made, the technology does still have a lot of challenges to overcome before it can be adopted in any serious capacity. 4D printing is still a new area of research as it was proposed as an idea only in the last decade. 3D printing as a technology while much more far along than 4D printing is itself still developing and wide acceptance and usage of 3D printing is still happening. Because additive manufacturing hasn’t really caught on just yet there are less resources spent on research in more sophisticated adaptations for it like 4D printing. Therefore, some of the challenges that 4D printing technology faces are the same challenges that AM in general is facing and having to overcome. When there is enough concrete evidence and AM has been further commercialized research in 4D printing will only accelerate. Challenges in 4D printing that are not inherently related to AM can be classified into three main categories: technological, material and design limitations [20].

4.1 Technological limitations

Stronger more sophisticated software that can be used to design how the 4D structure needs to work and can then create instructions through calculations for the 4D printer is needed. The software for 3D printers can make instructions for the 3D printers to achieve the desired 3D structure but this is not enough for the needs of 4D printing. The software needs to be able calculate how the printer needs to construct the part to achieve the desired stimulus response in the finished structure. Now designing 4D structures requires manual calculations and modelling from the researchers. That work needs to be delegated to software that knows and can adapt to different smart material properties. This is a required step to advance 4D printing so that it is not as difficult and costly to create simple actuations. The required software for 4D printing can be categorized into six distinct types of software: simulation, modelling, slicer, firmware, monitoring, and printing management [9].

Simulation would need to be able to accurately simulate the smart materials behavior to help design the printable structure. Autodesks “Project Cyborg” is a 4D printing software that optimizes the 4D printed structure through various simulations [9]. “Project Cyborg” at least was in development but no current information on it can be found so its fate is uncertain as of now. At Georgia Institute of Technology 4D printing was simulated using the ABAQUS software [26*, 25]. Modelling software is conventionally used to design 3D objects. Modelling software for 4D printing might differ from already existing CAD software in that it also would need to take into consideration the simulation and material properties to get the structure to behave as intended by the designer. Slicer software takes the 3D model of the structure and breaks it down to 2D layers for the printer to print. The printer’s firmware then reads the code from the slicer and transforms it into mechanical movement in the printer. Slicers for 4D printing would need to be a little more intelligent version of the slicers for 3D printers as it too would need to be able to take into consideration the desired actuation to plan the printer instructions to get the finished structure to work like it was designed to. Firmware refers to the software that turns the slicer instructions into instructions for the printer. Printer firmware needs to be up to par with new and improving printer technology of course but it should not need to be too intelligent or know about material properties as the software before it should be able to take care of the limitations and printer settings like 3D printer slicers and firmware work. Firmware is usually developed by the printer manufacturers but there are open-source alternatives at least for 3D printers. Monitoring software would be for the observation of the 4D structures transformation when exposed to correct stimulus. And printing management to control all the types of software needed and streamline the 4D printing process.

Another technological limitation is the 4D printer technology. Smart materials and 4D structures are different from conventional 3D printed structures and may require something more from the printer. Now most smart materials are manufactured with only one type of AM principle. For example, FDM printers have been used to print SMPs, but printing hydrogels require a more specialized, for example a DIW, printer. Printing technology that works for multiple types of smart materials would help 4D printing tremendously as it would lower the cost and amount of the required machinery required to create the designed structures in the best way possible. This type of printer technology does not exist as of now and requires more research into the materials and methods of 4D printing. Higher resolution 4D printers are also a necessity for applications that require precise parts like aerospace industry. AM is nowhere near as precise traditional subtractive manufacturing that works by removing material. Part of the reason for this is because traditional manufacturing has been around for longer and there has been more research that has gone into making machinery that meets the precision requirements of the different industries. A challenge AM now is to achieve comparable resolution if it to directly compete in industrial manufacturing instead of only working in prototyping capacity. Printers that can print multiple materials at the same time or work for varied materials would be a good step to make 4D printing more accessible, usable, and cost effective. There are FDM printers that have multiple extruders for 3D printing, but that AM method only works for a small selection of smart materials. In conclusion there needs to be more development in 4D printing technology to make 4D printing a viable manufacturing process. Developing commercially viable, user-friendly, and cost-effective printers is a necessity for the future of 4D printing [17]. Faster and cheaper printing is required to push 4D printing into the future.

4.2 Material limitations

As smart materials in general are a new concept and smart materials suitable for AM are an even newer concept. This makes them not available from many sources as there is no real market for them aside from the few researchers working on 4D printing. This is also a reason for the high cost of smart materials. For example, Verocyan used in an example of light responsive material earlier in reference costs over a 1000$ for 4kg of the material [45]. That is over 250 $/kg which is extremely expensive for anything but industrial use. The material is also designed to work in specific machinery further limiting the usage of this material type. The technology is new and there probably is no mass production of the typical smart materials like there is for 3D printer materials. Smart materials are, as it is in their name, smart, so it would be naïve to expect them to be comparable in price to conventional 3D printing materials like polylactic acid (PLA) or acrylonitrile butadiene styrene (ABS) plastics. The high price point and limited availability is however an obstacle in the diffusion and commercialization of the technology.

4D printing materials that are widely used are polymer or hydrogel based which both have limited high temperature application capabilities. 3D printable materials however contain some applicable ones for high temperatures. Smart composites and multi-materials that were examined get around this problem but are even newer than SMPs or hydrogels so require more research. It is imperative to develop smart materials that do not have limited compatibility and can function in multi-stimulus systems without issues [22].

Understanding and predicting how the smart materials react when exposed to more than one stimulus at a time remains unclear and difficult to predict [22]. Smart material deterioration after multiple response cycles may also prove to be a problem. This is especially problematic in biomedical applications where the function of the structures is extremely important to not have dysfunctional or broken parts inside a person for example. Deterioration could also show up by altering the structures stimulus response after a number of successful stimulus response cycles. New stronger and more durable materials or new fabrication methods are needed to solve the degradation issues.

Making sure that the whole actuation happens may be impossible to ensure excluding keeping the trigger stimulus active on the 4D structure for long enough time. Due to material properties or uneven application of the chosen stimulus all the smart material actuation might not happen, or it may take a long time. There is not much that can be done about this currently. The need for more reliable smart materials and interaction mechanisms is evident to advance 4D printing. Without advances in either of these the printed structures will not be dependable enough for real applications. There is also no effortless way to control the amount of actuation after the stimulus is provided which does not give much controllability on the actuators.

4.3 Design limitations

Mathematical modelling and the understanding and predicting the behavior of the smart materials is linked to the software aspect of the challenges in 4D printing. They are also big design challenges that software tries to solve. Understanding how the material needs to be and how it behaves when responding to stimulus is extremely important when designing 4D structures. Achieving this involves advanced simulation and topological transformation to achieve the requirements for manufacturing and material constraints. Designing 4D actuating structures with new and relatively unknown materials to achieve responses that can’t be truly seen until after the structure is tested is extremely difficult. This requires a high level of knowledge of the material and manufacturing process that is not reasonable to expect from 4D printing userbase. Which is why the design process has to be dedicated to software that can then predict how the material will react and then iterating from the simulations from the software to achieve the desired outcome for the structure.

When it comes to bioprinting and tissue printing a difficulty is with mimicking existing biological systems so that they would work similarly with the existing ones. Unfortunately, biological systems are difficult to simulate even with only computer systems not to mention imitating and replicating them with only smart material structures and their innate stimulus responses. However, designing 4D structures that can imitate existing systems accurately with biocompatible smart materials is a necessary step in applying the technology to biomedicine.

Printed structures need a mechanical straining to get them ready for the stimulus response which causes them to release the stored strain. If the 4D structures could be printed pre-strained it would make them more useful. Now there is not existing technology that would enable directly printing pre-strained structures. That makes them much more impractical when every structure has to be mechanically strained for it to function in the intended purpose.

Making 4D printing more accessible by simplifying the design process has to happen for the technology to get a wider acceptance and larger interest. Through steps like this it would lower the barrier of entry for companies and other research teams which in turn would accelerate the advancements.

5. APPLICATIONS AND FUTURE OF 4D PRINTING

4D printing is a rapidly growing industry and a promising area of research. According to estimations 4D printings global value will reach 537.8 million dollars by the year 2025 [1]. AM and 4D printing truly are a technology of the future and will shape day to day life in the future. The technology has gathered interest from a various field of science and technology as it has such a wide range of applications. Multi-disciplinary technology has potential applications in almost all anything with the only limitation being one's own imagination and of course the technology at least for now. In this thesis we will take a closer look at some of these applications. Many of these applications are still pure speculation and only to give ideas about what might be possible as the technology progresses. There are other potential applications in many different fields that are not mentioned here. Piping systems that are self-repairing when coming in contact with water. Using these structures in solar panels, making them follow the sunlight on their own. Manufacturing structures in small build volumes that can then self-deploy into larger structures. Printing food mixed with ingestion safe material that can change color when the food is unsafe to eat. The possibilities are endless and limited by nothing but imagination when the technology is matured.

Advancing AM technology in general can help in decentralizing and replacing traditional subtractive manufacturing. This would help in lowering the waste material created from manufacturing which is both economical and environmentally friendly. AM produces very little to no waste material unlike in conventional subtractive manufacturing. Decentralizing manufacturing can also reduce waste by changing the whole manufacturing outlook as mass producing may not be as necessary to lower manufacturing costs when the objects can be manufactured locally and directly from order from 4D printers. AM still has limitations that it needs to overcome. The continuous research, advancements and interest in new materials, manufacturing methods and new concepts like 4D printing are pushing it forward. 4D printing is a recent technology but has already gathered a lot of interest and progress has been made. Much of the interest is because of the possible applications that AM, and self-transforming stimulus responsive structures make possible. More research into every aspect of 4D printing is needed before the technology can be used for real manufacturing purposes. The advancement and potential of the technology is undeniable, and 4D printing will have a real effect on the world in the future.

5.1 Soft robotics

In traditional robotics hard materials, like metals and hard plastics are used for developing robots. This reduces their capability of doing tasks that require flexibility. The usage of hard materials also means that the robots are unable to withstand large deformations without suffering from side effects. To overcome these problems of traditional robotics a field of soft robotics has been developed. These soft robots can be flexible, vary their stiffness when required and adjust to environmental conditions [10]. Soft robots also could change their shape and size flexibly as the situation needs. Soft robotics naturally require soft materials which 4D printing and smart materials should be able to support. 4D printed structures would suit the needs of soft robotics as the materials can be flexible, innately deform and withstand deformation and would be able to adjust to environmental conditions. 4D printing is moving the field of soft robotics towards material robotics by eliminating the need for expensive, error-prone and complex electromechanical devises such as motors, sensors and electronics, bulky components, power consumption from batteries or electricity and difficult assembly processes [42]. Self-assembly and self-repair properties in 4d structures is also advantageous in robotic applications. Self-repairing material helps the robot not get stranded or become dysfunctional when it is unreachable. Yuk et al. [48] fabricated grippers from hydrogel material that could catch and release a fish swimming in the water tank. Development of soft robotics will enable the replacement of the more traditional stiff robotics with highly responsive smart components. Soft robotic components would be able to perform in many different circumstances due to their flexibility. In the future incorporating artificial intelligence and machine learning with smart soft robotics would enable the formation of flexible and self-learning robotic units. Other examples and descriptions of soft robots fabricated via AM techniques can be found in the paper by Yap et al. [47].

Soft actuators are a key component of soft robotics. Conventional actuators are rigid which makes them unsuitable for use in soft robotics. Soft actuators would also be able to manipulate delicate objects that more rigid actuators would need a very extensive sensors and control-loops to manage. [54] Using 4D printing to manufacture these soft actuators could make the manufacturing process faster, cheaper, and simpler [52]. Then product from 4D printing could also be a smarter product thanks to the usage of smart materials eliminating the need for multiple components to achieve the desired actuation response. As of now actuation control for smart materials remains an issue for use in robotics.

4D printing could also enable the easy manufacturing of smart sensors. Soft robotics would require sensors for the closed control-loops in them, that are as flexible and stretchable as the robot itself [47]. Currently most of these soft sensors are made by embedding conventional rigid electronics into flexible substrates [23]. Making sensors from smart materials would reduce the need for rigid electronics by substituting them with material responses in reaction to stimuli from the environment. Truby et al. [44] report a method of creating soft somatosensitive actuators via embedded 3D printing which then enable haptic, proprioceptive and thermoceptive sensing.

5.2 Clothing, fashion, and apparel

Clothing and fashion industry has immense potential for 4D printing technology. Clothing that is both visually appealing and functional could be developed using 4D printing and smart materials. Clothes that can change their properties in response to a specific stimulus would be practical for a wide variety of uses. For outdoor clothing for example material that can change its own ventilation/insulation in response to outdoor temperature would be extremely practical. Clothing becoming water resistant when exposed to water and breathable when dry is a fitting example of applying smart materials into making clothing smarter and better. 4D printing could make this process relatively easy in the future. Impact and abrasion resistant clothing, especially for children, could help in keeping people safe from small bludgeons and keep the clothes in one piece during strenuous usage.

Clothing in health care sector and for clinical usage could also benefit from smart and adaptive clothing. When it comes to medical services small things like small deviations in the condition of the clothing the staff wears can have a real impact on human lives. Gloves that form fit to the hands of a surgeon instead of badly fitting or poorly made gloves can help surgeons performing vital operations can help them feel more in control by giving maximum amount of freedom for their hands [4]. Designing self-sterilizing materials could also help prevent possible infections without the need for time consuming and complicated sterilization processes. Another large industry that works with textiles is the multi-billion-dollar fashion industry.

Color, texture and shape changing clothing for fashion will enable a whole new avenue of design for fashion designers. Clothing could change the color of the material itself as a response to external light, jackets could change their shape or texture when exposed to water to achieve new and interesting clothes that are not possible today. Incorporating 4D structures and stimulus responsive materials into textiles will enable innovative designs in adaptive clothing.

Shoes are a good example for a piece of wearable apparel that has potential in just 3D printing. Making shoes is a straightforward process but making the end product more adaptable by using 4D printing and the smart materials it enables, could bring many potentially useful qualities. Qualities like “adaptive fit” where the shoe changes it shape and size as is automatically depending on the need and “one size fits all” which would change the size of the shoe based on the size of the users’ feet would enable form fitting custom shoes for everyone for a cheap price. Zarek et al. [50] created a smart heel for a shoe that as a response to heat transforms the flat heel of the shoe into a high heal. The transformation was triggered by an original hand dryer which makes the application easy and practical to use. The same ideas could be extended to the sportswear industry which is another clothing related multi-billion-dollar industry that could benefit from 4D printed structures. Athletic shoes that could adapt to different conditions like rain or sunshine, or different surface textures from hard streets to soft grass, or even adapt based on the use case the shoe is experiencing from running to the impact of playing football for example.

5.3 Defense and aerospace

War usually brings with itself new breakthrough technologies as they are needed. 4D printing won’t be any different if it is deemed applicable and useful as militaries all around the world are expected to operate in harsh and challenging conditions. The harsh environment may be caused by the region’s climate or the war zones chemical or biological effects. 4D printed structures could be useful with the many properties that they might have. The US military is funding research into implementing 4D printing and smart materials that come with it into fabrics and textiles for military use [4]. For example, textiles that could harden when coming into contact with sharp edges, change the color of the camouflage worn by soldiers in response to the amount sunlight or even bend light to help in hiding them. This type of technology would help protect the lives of the soldiers and help to conceal them on the battlefield. This type of technology could be used for other applications than clothing in the military. Deployable structures like self-deploying tents and smart parachutes are great examples that could be useful in the operations of the military forces. Smart material usage in arms, ammunition, ordnance, and combat vehicles is still unexplored aspect of 4D printing technology but may become a real area of research for military R&D teams and eventually have a real effect on the weapon industry. 4D printing technology could also help with maintenance with self-repairing parts in mission critical equipment. Adaptable equipment that changes properties by what the situation needs is a great future way to reduce the amount of load and equipment that the normal soldier needs to use and carry with them.

4D printing could also be applicable to aerospace applications especially because removing variables, weight and complexity from mission critical components makes them all the more reliable and efficient. 4D printing enables this by delegating those necessary functionalities directly to the material thus eliminating the need for assisting systems. Aircraft and spacecraft technology could benefit from these smart and light structures that have all the necessary requirements and can sustain the demanding conditions caused by high-altitudes, high speeds, and temperatures. Easy manufacturing process, self-repairing parts and self-assembling structures are all things that aerospace industry surely would find uses for. Wings for drones and larger aircraft that could change shape based on the situation or mission could be useful to make the crafts suitable for multiple purposes. 4D printed structures could be used for this kind of application because of their low weight and would be efficient and cheap to manufacture. Self-deployable reflectors in spacecraft would again reduce the amount of weight and complexity by implementing the functionality into the material [2]. Self-illuminating materials implemented into fabrics replacing lighting fixtures in air- and spacecrafts may help to reduce the weight and give more space to other supplies. This would also reduce the need for control systems for the lighting reducing the complexity in mundane tasks like lighting. 4D printing could enable the manufacturing of smart valves that automatically control air intake for engines [40]. Decentralized manufacturing enabled by AM could enable astronauts to print mission critical equipment from raw material on the job [1]. Printing parts or tools that have broken or are suddenly needed could be a real lifesaver when supply lines to established manufacturing do not exist or are too slow.

5.4 Biomedicine

Biocompatible 4D printing has huge potential in healthcare and medicine applications. 4D printed structures could be used for drug delivery, stents or even tissue and organ printing. Especially the organ printing could save lives by shortening the amount of time patients need to wait for suitable organs and donors. The printed organs and tissues could also be directly manufactured to be perfectly suitable for the patient instead of risking unsuitable donor material. Manufacturing the biomaterial with 4D printing would also reduce the amount of transportation that is now sometimes needed to get a donor organ from the donor to the recipient. Creating biocompatible smart materials is of the utmost importance for biomedicine applications. There have been at least some advancements in creating biocompatible and biodegradable pH responsive SMP materials [11]. 4D printing could also be used to create a number of different body systems such as wearable sensors, artificial muscles, implantable biomedical devices or even contact lenses [40].

This technology could be used in advancing personalized medicine and 4D printed microstructures could be used for drug delivery. This way the smart material microstructures could be responsive to some external stimuli and the SCE be triggered in the correct area that needs the medication thus helping to directly administer the medication to the area that needs it. Direct administering this way instead of injections or oral ingestion for example, would reduce dosage of medication needed and circumvent at least some of the possible side-effects of the more conventional administration, by making the procedure less invasive. In the magnetic field example [7] the magnetic response microgrippers the same procedure could be reversed and the soft microgrippers be used to release something they are holding instead of gripping something as a response to the magnetic field.

4D printing medical devices like stents could have lifesaving effects. Replacing traditional stents with 4D printed stimulus responsive stents could reduce the need for highly invasive surgeries to install them with less invasive surgeries. Getting the smart material stent into the blood circulation and then activating it remotely via some stimulus thus negating the need for difficult and dangerous surgeries to widen clogged arteries. Despite various efforts to manufacture stents, the design has been limited by fabrication methods. These traditional manufacturing methods are complex and time consuming. 4D printing them could enable the manufacturing to be modifiable to be the best possible stent for each use case, make the manufacturing process faster and cheaper. Ge et al. [10] describe and show a printed shape memory stent that can expand to a larger diameter in a narrow artery as a response to heat.

4D printing tissue and organs like heart valves, liver and kidney implants and even muscles, has clear advantages to using donor or other alternative organs. The fact that the end product can be designed and personalized by a professional in each case and that it can be produced locally if the medical facility has the capability of 4D printing and the required materials. This naturally requires smart biomaterials that can be programmed to actuate as they are designed to [19]. This helps shorten the time that finding the suitable organ takes. In addition to shortening the wait time for patients the new organ can be designed specifically for each patient to their specific needs. The possibility to manufacture organs also might help with illegal organ trade as the market for organ donors has no buyers. Kang et al. [18] presented an integrated tissue organ printer (ITOP) that can be used to fabricate stable, human-scale tissue constructs of any shape. ITOP prints cell laden hydrogels together with biodegradable polymers. There are three different approaches to manufacturing organs and tissue with 4D printing [49]. First one is using SMPs and hydrogels to print a stimulus responsive 3D structure [46]. The structure could be an organ, muscle or other tissue structure that is designed to replace an existing biological system. Second one is implanting a polymer medical device which then accommodates the growth of tissue or organ after the surgical period. After the tissue grows and becomes stringer the medical device dissolves. 3D printed objects that change their structure with tissue growth and resorption conditions over time. Morrison et al. [30] described a way to use printing in tracheobronchomalacia (TBM) treatment in infants. In this treatment a 4D printed external airway splints were implanted into three infants. The structures helped and supported the tissue growth for 3 years after which the structures were dissolved leaving stronger and self-sufficient lung tissue behind. The last approach is using on-demand self-assembly or self-organization. Microdroplets of pre-programmed cells self-assemble themselves into a pre-determined pattern creating the desired structure.

6. CONCLUSION

The goal of the thesis was to give an extensive summary about 4D printing, the challenges it faces and the applications that it enables. 4D printing is a recent technology that is ever evolving, so the sources have been mostly from the past few years to give an up-to-date overview. This thesis gave a look at the different stimuli and smart materials that 4D printing can make use of. It also gave a summary of the challenges that need to be overcome so the applications 4D printing enables can be utilized to their full potential

4D printing is a fast-growing industry because it is so promising for many different fields as it is the next step in additive manufacturing. This new technology is like 3D printing where time acts as the 4th dimension. What this means is that it works like 3D printing except that the finished product is not a static 3D object but can change its properties like shape or color as time passes on as a reaction to an external stimulus. This is a desirable trait in a structure as the desired actuation can be built-in to the material itself reducing the need for more difficult methods of achieving the actuation. 4D printed structures require 5 different parts to make: stimulus, smart material, 3D printing facility, mathematical modelling and an interaction mechanism.

Stimuli most used in 4D printing are temperature, water/moisture, light, electric and magnetic fields, chemicals, or pH value. They all work by causing a reaction in the material that causes the structure to then change its physical properties in response. Smart materials can be made responsive to some stimuli by introducing a stimulus responsive molecule group into the material.

There are multiple different smart materials that can be used in 4D printing. The main types of smart material are hydrogels, shape memory polymers, shape memory alloys and composites. Hydrogels are gel like materials that are usually water absorbent. The materials are also relatively biocompatible making them ideal for biomedical applications. Shape memory polymers are polymers that have the shape memory capability. These materials are relatively cheap, lightweight, and easy to print, even working with FDM printers. Disadvantages for them is that they are fairly weak and have limited high-temperature capabilities innate to polymers in general. Shape memory alloys are metal alloys that have the capability for shape memory. However, they have disadvantages that make them not so ideal for 4D printing. These include high cost, limited high temperature capability, metals are hard to 3D print to begin with. Composites are for example SMPs that have strong fibers implanted into the material making them much stronger. There are also so-called multi-materials are a combination of smart materials and conventional materials that are mixed to achieve the desired result. The smart material types themselves can also have a variety of materials that are responsive to different stimuli.

The challenges facing 4D printing are still numerous. There are technological limitations, material limitations and design limitations that must be overcome before 4D printing can be widely commercialized. Software and hardware need to advance considerably in the coming years to make the technology easier and more reliable to use. Some of the challenges that 4D printing faces are the same that AM in general is facing.

Applications for 4D printing are exiting and limitless. 4D printing gets all the environmental and commercial benefits of saving resources with being able to produce useful self-actuating structures. Many different fields of technology and science could benefit from the possibilities that 4D printing will one day enable as the only limitation for the technology will be imagination once the major challenges are worked out.

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