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POLYMER AS A SMART MATERIAL FOR 4D PRINTING: A REVIEW

Khodadad Mostakim [1*], Md. Fahim Shahriar [1], Md. Arman Arefin [1], Humaira Rafi Zinnurain [1]
Md Sabbir Ahmed [1]
[1]Department of Mechanical Engineering, Rajshahi University of Engineering & Technology, Rajshahi, Bangladesh.

khodadadmostakim@gmail.com* , fahimshahriar9873@gmail.com , arefinarman@gmail.com , humaira.rafi.zinnurain95@gmail.com , Sabbir.ruet13me@gmail.com

Abstract*- Investigation into 4D printing has pulled in phenomenal enthusiasm since 2013 when the thought was first presented. 4D printing is an expansion of 3D imprinting wherein upgrades responsive dynamic smart materials are utilized to deliver the static structure. This static structure at that point changes over into another structure when it is presented to the stimulus. In addition, metals and ceramics, polymers have turned into a broadly inquired about the class of materials for applications in AM (Additive Manufacturing). This paper presents a comprehensive review of the basic principles, considering the 4D printing mechanism as well as the advantages and disadvantages, of the most relevant polymer AM technologies, properties and limitations and applications are described. In recent advances, these dynamic structures developed by the 3D printing process are used for actuators, smart devices, smart textiles, and also in biomedical applications.*

Keywords: 4D printer, Polymer, Additive manufacturing, and Smart Materials.

1. INTRODUCTION

In the late 1980s, great achievements were made in the field of what has later been known as additive manufacturing. Many of the first additive manufacturing processes were introduced commercially during that time period [1-3]. A simple illustration of the concept of 4D printing can be seen in Figure 1.

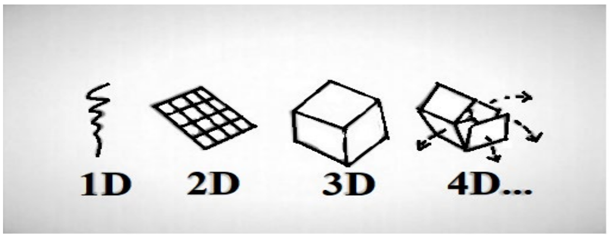


Fig. 1: A simple illustration of the concept of 4D printing [4]

4D printing was firstly introduced by a research group of Massachusetts Institute of Technology (MIT) and defined as the fabrication of 3D printed structures with adaptable and programmable shapes, properties or functionality as a function of time [5]. This term '4D printing was first familiarized by Skylar Tibbits in the TED conference (2013). This approach is similar to 3D printing except it embraces the fourth dimension of time besides 3D coordinates after printing [6]. Additive manufacturing or conventional 3D printing has one major problem that the majority of fabricated components are static and inanimate with the exclusion of moving assemblies [7]. Proper use of smart materials will mitigate the problem to a greater extent. Smart polymers are widespread due to their inherent stimuli-responsive properties and can be used for specialized applications in 4D printing technology. The more comprehensive definition of 4D is a predefined continuous changing of the 3D printed structure regarding shape, functionality, and property. 4D printed parts having dynamics in shapes, properties, and functionality on the exposure of stimuli [8, 9]. There are two stable states in a 4D printed object, and the object can shift from one state to another under the exposure of stimuli [10]

Smart material and smart design can differ the 4D printer from other printers, just because of the material flexibility. The smart material can be changed by exposure to various stimuli. The stimuli which are generally used in 4D printing thus include water(chemo-responsive), heat(thermo-responsive), and light(photo-responsive) [8].

Three key aspects must be fulfilled for 4D printing to take place. The first is the use of stimuli-responsive composite materials that are blended or incorporate multi-materials with varying properties being sandwiched layer upon layer. The second is the stimuli that will act on the object causing it to animate. Examples of these stimuli include heating, cooling, gravity, ultraviolet (UV) light, magnetic energy, and even humidity. The last aspect is time for the simulation to occur, and the final result is the change of state of the object [11]. Shape memory polymers (SMP) are a class of intelligent polymers able to change their shape by means of a stimulus. Indeed, SMPs can be deformed and fixed into a temporary shape that can be turned into the permanent one by applying a stimulus [12]. Compared to the well-known shape memory alloys (SMAs), SMPs present some important advantages, such as a high strain recovery, low density, cheapness, potential chemical stability, easier processability, potential recyclability, biocompatibility, and biodegradability [13]. Moreover, the recovery of the original shape is faster than SMAs, due to the higher permeability to air [14].

A programming process defines the fixing of a temporary shape. In the case of a thermally induced shape memory effect (SME), the material is heated up to a $T > T_{trans}$, where the T_{trans} is the temperature at which the switching segments melt or become viscous. The nature of the T_{trans} is determined by the type of the switching segments: glassy domains will become viscous at $T > T_g$ ($T_{trans} = T_g$); crystallites can be melted at $T > T_m$ ($T_{trans} = T_m$). In this state, the material can be transformed into a temporary shape, which can be fixed by cooling down to a $T < T_{trans}$, due to the presence of net points and to the crystallization/vitrification of the switching segments. By reheating, either crystallites or glassy domains respectively melt or return to the viscous state, leading to the regain of the original permanent shape [12,13,15]. This review provides an in-depth insight into the huge potential of using smart polymer for 4D printing technology. However, further research work will be vital for the future success of this technology.

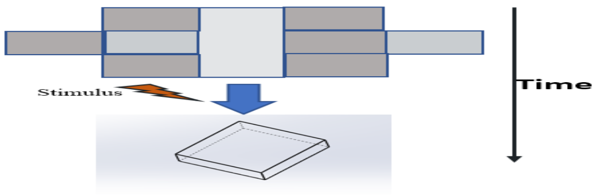
2. DEFINITION OF 4D PRINTING

"3D printing", also known as "Additive Manufacturing", turns digital blueprints to physical objects by building them layer by layer. 4D printing is based on this technology with one big modification. It uses smart materials and sophisticated designs that are "programmed" to rapid 3D print to change its shape post-production. Although smarts materials are used in many research areas, it is difficult to describe an exact catch-all introduction for smart materials [16]. Leo [17] defines them as "smart materials are those materials which convert thermal energy into mechanical work". According to Varadan et al. [18], smart materials are those materials that can change material properties or shape in response to the external environment. The use of smart materials in 3D printing technology has given rise to the introduction of 4D Printing, attracting much interest since 2013 when the idea was first presented [19, 20]. At its core, 4D printing is dependent upon the smart material, additive manufacturing technologies and design [21]. 4D printing has many benefits over 3D printing in several features [22]. The earliest definition of 4D printing was that it was equal to "3D printing" plus "time" [23, 24, 19, 25-28]. Anna Balazs made research on 4D printing, describing the use of 4D printing materials that can transform themselves due to external stimuli [28].

3. DEFINITION OF STIMULI

Stimuli is a distinguishable change in the physical or chemical structure of an object inside or outer condition. As shown in Figure 2, some typical stimuli are being applied to activate the shift of materials in either reversible or irreversible process, such as pressure, temperature (heating or cooling), water, moisture, light, magnetic field, gravity, the combination of heat and light, and the combination of water and heat [29, 30, 31–36]. Recent research shows that water and temperature are the best media to change the shape of smart material.

Fig. 2: The transition of 4D printed material through



stimulus

4. CLASSIFICATION OF MATERIALS USED FOR 4D PRINTING

According to the definition of 4D printing, stimulus-responsive materials are a kind of smart material that is the most commonly used material for 4D printing at present.

A simple classification of smart materials can be seen in

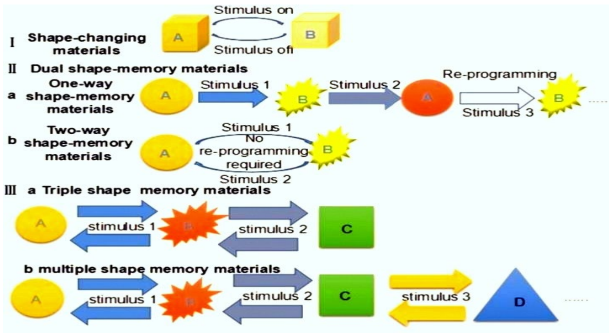


Fig. 3: Classification of smart materials [64]

Figure 3 [64]. Smart materials used for 4D printing can be categorized into the following two types

a. The stimulus-responsive materials,

b. Triple and multiple shape-memory materials.

5. SHAPE CHANGING MATERIAL VS SHAPE MEMORY MATERIAL

A shape-changing material changes its shape immediately when a stimulus is applied and returns to its original shape immediately when the stimulus is removed. This type of transformation is limited to simple affine alterations such as linear volume expansion and shrinkage [37]. On the other hand, the shape-memory effect (SME) involves a two-step cycle. Step 1 is the programming step in which a structure is deformed from its primary shape then held in a metastable temporary shape, and Step 2 is the recovery step in which the original shape can be recovered with an appropriate stimulus [38, 37, 39]. One issue with classical one-way

SME is irreversibility [40]. After the original shape is recovered, a new programming step is needed to re-create the temporary shape. This issue can be avoided with two- way SME, which can alter the shape in a reversible manner [40]. This concept is illustrated in figure 4.

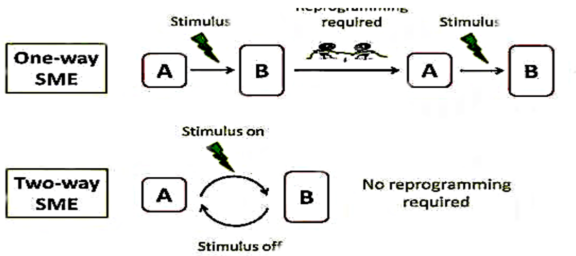


Fig. 4: The difference between one-way and two-way shape-memory materials [40].

6. MATERIAL PROPERTY OF SMART POLYMER

While talking about smart polymer, it becomes imperative to mention its property. The property of smart polymers is shown in Table 1.

Table 1: Material Property of smart polymer [41]

The extent of deformation (%)	Up to 800%
Density / g cm-3	0.9 - 1.1
Critical temperature (°c)	-10°C - 100°C
Recovery speed (minutes)	<1second to several mins
Corrosion performance	Excellent
Processing conditions	< 200°C, low pressure

7. ADVANTAGES OF SMART MATERIAL IN 4D PRINTING

4D printing technology and its application in the intelligent material structure are still in its initial stage. However, its research and development applications will have a profound impact on traditional mechanical structure design and manufacturing [65]. This trend is reflected in the following aspects:

1. 4D printed materials will no longer be restricted by the degree of freedom for mechanical structure, thus the weight will be significantly reduced.
2. Proper use of stimuli-responsive materials based on ambient conditions will result in better monitoring of environmental conditions. In this case, deformation can be correlated with a change in ambient conditions.
3. With 4D printing technology, intelligent material structures integrated with drivers and sensors can be produced [65].
4. 4D printed materials can change their shape when external stimuli are applied; consequently, 4D printed materials can simplify the intricacies related to the complex model.
5. Self-assembly is possible through the proper use of smart material in 4d printing.

8. APPLICATIONS

Many applications have been found for smart material. Besides traditional applications such as heat shrinkable tapes and tubes made with radiation-cross-linked polyethylene, these materials have also been used for information storage that can allow thermally reversible recording, [42–45] temperature sensors, [46–49] and actuators. However, our literature search found that recent applications are mainly focused on medical areas, such as biodegradable sutures, [50,51] actuators, [52,53,54,55,56] catheters, and smart stents [57,58].

Shape Memory Fabric: Shape memory polymers find their application in various fields due to its special and unique properties [59]. The shirt with long sleeves could be programmed so that the sleeves shorten as room temperature becomes hotter. The fabric can be rolled up, pleated, creased and returned to its former shape by applying heat. Ex: blowing air through the hairdryer.

Ergonomic: The violin is made from the combination of shape memory polymer and carbon fibers. The shape memory polymer used here is "Veriflex". It designed to help to reduce the neck and shoulder pain of the player, as it can be reshaped as desired by the player.

SI Suits: The suit was developed to help the sailors on the oceans and sea. It adapts to the temperature variations and maintains a persons body temperature constant. The membrane gives optimal breathability in any given atmospheric condition.

Morphing aircraft: Developing and demonstrating morphing materials and technologies that are necessary to construct deployable morphing aircraft and other innovative adaptive structures critical to air force are taking place.

Medical field: In many operations that involve stitches inside the human body, a second operation is done to remove the internal stitches. In such cases when biodegradable SMPs are used they dissolve gradually and need not be removed as their composition is harmless. An example of a biomedical application is a

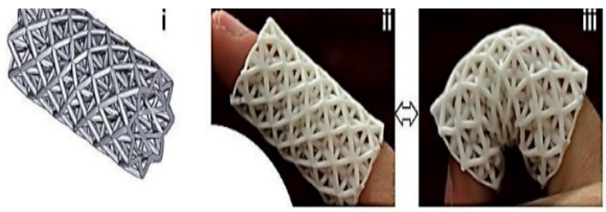


Fig. 5: Elastomer metamaterials (Jiang & Wang, 2016) [60]

microactuator made from an injection-molded shape-memory thermoset polyurethane that was used to remove blood vessel clots [55]. Jiang and Wang [60] fabricated and analyzed elastomer metamaterials (figure 5) that can be used as reversible shape-shifting connectors. The shape-shifting action is enabled by external mechanical loadings. These materials can be applied through the 4D printing process to bridge components for flexible twisting or bending [60].SMP-based thermo-responsive multi-material gripper was developed in 2016 [61]. Bakarich et al. [62] fabricated a skeletal muscle-like actuator with high response speed and reversibility based on the principle. They merged it into a smart valve (figure 7) and measured the water flow by opening closing the valve.

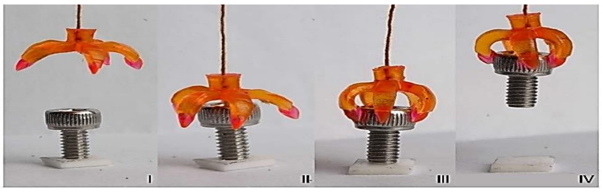


Fig. 6: 4D-printed shape memory gripper that can reversibly grab and release the objects by heat (Ge et al., 2016) [61].

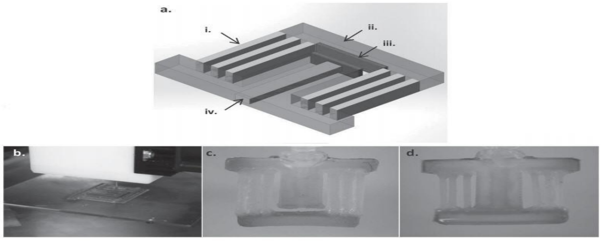


Fig. 7: a) Design model of the smart valve, b) Printing of the CAD model of the valve, c) The 4D printed valve in cold water, and d) The 4D-printed valve in hot water [62]

9. CURRENT TRENDS AND FUTURE

Future applications of 4D printing will depend on how better smart materials can be utilized. At different temperature stages, Shape memory polymer (SMP) can recover in a tandem manner from one shape to another and finally to its original shape. This class of SMP, called ‘‘tandem shape-memory polymer [66] or ‘‘polymeric triple-shape materials [67] are expected to be capable of providing more complex actuation events and potential for application in biomedical devices or deployable structures. For its better flexibility and shape-changing character, it will be a great material for making an industrial robot and plastic industry. The construction of the ship, satellite in space and air-craft will be the next concern. A 4D printed water pipe can change its size to control the water flow rate. Through proper mass production, 4D printing technology can also be used to enhance the quality of daily products in the near future.

10. CONCLUSION

Through the advancement of science and technology, 4D printing technology will take printing technology to a whole new level. Existing printers are needed to be developed to initiate mass production. Smart material development is also essential as it has enough potential to control a surfeit of industrial issues. This review paper provides a brief insight into the world of 4D printing technology. This will help the researcher to develop 4D printing technology further. For a better manufacturing process, 4D printing is surely the way forward.

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