공학석사학위논문

사전변형이 인가된 형상기억수지를 이용한 단일재료 4D 프린팅

Single material 4D printing
by pre-strained Shape Memory Polymer

2018 년 2 월

서울대학교 대학원

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이 논문을 공학석사 학위논문으로 제출함

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주형준의 공학석사 학위논문을 인준함

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위 원 장	이 경 수
부위원장	조 규 진
위 원	이 동 준

Abstract

Single Material 4D Printing by Pre-strained Shape Memory Polymer

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4D printing, a technology that makes 3D printed outputs move by themselves, is a 3D printing technology for smart materials. As 3D printing technology did before, 4D printing will also play a major role in achieving the ultimate goals of smart materials such as self-assembly, self-healing, and variable infrastructure by giving new degrees of freedom to existing material design methods. In this research, we have developed a new method to solve the one of the biggest challenges in 4D printing technology: applying pre-strain at the printing stage. This technique is a simple process of pulling out the shape memory polymer while printing it out. It solves the pre-strain-applying problem easily and cheaply. At the same time, it enables to manufacture the shapes that could not be created with previous 4D printing technology. Finally, we succeeded in controlling the degree of pre-strain by manipulating printing variables.

Keywords: 4D printing, Shape memory polymer, Pre-strain, FDM 3D printer, Programming matter

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Contents

Chapter 1. Introduction

1.1. Research Background

4D printing is a technology that allows the shape of 3D printed output to change itself. 4D printed output undergoes shape change when it is exposed to external stimuli (ex. heat, moisture, electricity, time, etc.), while the shape of 3D printed output does not change after the printing process. The name 4D printing was given by S. Tibbits. (Self−Assembly lab, MIT) in 2013, indicating that an additional one−dimension of time is now available when designing three−dimensional objects.(1)

In order to make the 3D printed output to transform on its own, the usage of smart materials which are capable of self−shape change, such as hydrogel, Shape Memory Polymer (SMP), and Electroactive Polymer (EAP), is inevitable.(2) On account of this, 4D printing can be said to be 3D printing of smart materials.

As 3D printing technology enabled the manufacturing of figures that are originally difficult or even impossible to make with the conventional manufacturing method (ex. machining, molding, etc.), 4D printing technology will increase the range of designing smart materials. As a result, it will play a key role at achieving the vision of smart materials including self−assembly, self−healing, and variable infrastructure.(3)(4) Although there is a long way to go to reach the ultimate goal since the technology is at the infantile stage, 4D printing is already a leading innovation in the field of 3D printing in the perspective of saving printing time, materials, and storage space.(5)

Current 4D printing technologies mainly use two types of material.[6] One material group, represented by hydrogel,[7][8] simply undergoes volume change with given external stimuli. From here emerges the contradictory criteria on material stiffness: while the smaller stiffness warrants the larger expansion, the structure cannot withstand itself with too small stiffness. Indeed, hydrogel has low stiffness that is even softer than human skin, which makes it difficult to maintain its shape. Furthermore, its actuation requires immersing in water, which also significantly restricts range of application.

The other material group, on the other hand, represented by shape memory polymer,[9][10] undergoes phase change before volume change. Its stiffness becomes dramatically lower with external stimuli, only when it is in the transforming state. After the transformation, when the external stimuli are vanished, it becomes stiff again to withstand itself. However, it still has a limitation in which a post-printing process is required. Since it is not capable of expand itself unlike hydrogel-group, one has to manually generate strain at the initially printed output before making it transform. When the external stimuli are given, the manually strained output returns to the initially printed shape. Manual post-printing process makes shape control difficult and it also severely damages the design diversity.

1.2. Purpose and Contribution of Research

Giving strain from the printing process became one of the main issues among 4D printing researchers since it was critical for practical 4D printing as mentioned before.[2] In consequence, a few technologies have currently been developed which successfully removed the post-printing manual-strain-giving process.[11] However, UV curing process is essentially required for these technologies, making them more expensive than FDM printing method, and hard to access. Moreover, they only can make sheet−type output with restricted deformed shape due to the way of giving pre−strain.

Thus, this research suggests a novel 4D printing method, which succeeded in solving the pre−straining problem while keeping the printing cost low and thereby achieving enhanced accessibility. It was possible by using Fused Decomposition Modeling (FDM) printing method rather than using UV curing method since FDM printers and their materials are easily available and extremely cheaper. By using FDM, the constraints on the shape of the output are also overcome. As a result, multi−directional bending, which is not possible when UV curing method was used, became possible.

1.3. Research Overview

In this paper, principle of the novel 4D printing method is described. Experiments for estimation of effect of main printing variables on controlling the rate of pre−strain are followed. Finally, available shape samples are suggested.

Chapter2. Methods

2.1. Principle

2.1.1. Principle of Shape Memory Polymer

Shape memory polymer is a polymer having a property of storing a specific initial shape and returning to its original state when an appropriate external stimulus such as heat is given. Shape memory polymers have the property of retaining the reticular microstructure formed in the permanent shape. This property causes a shape memory effect to return to the memorized permanent shape even when external force is applied and the shape is deformed to the temporary shape.[12] The process of deforming from permanent shape to the temporary shape takes place above the glass transition temperature of the shape memory polymer. (cf. $T_g = 55$℃ in the case of DiaPLEX) This is because the shape memory polymer is in a solid state at a temperature below the glass transition temperature, and its rigidity steeply decreases due to a phase change to a rubbery state through the glass transition temperature.

2.1.2. Principle of FDM 3D Printer

When the filament type material is heated close to the melting point and extruded through the nozzle by the force of the extruding motor, the FDM printer stacks the extruded material from the nozzle attached to the three-axis feed device along the preset print path and generates the desired shape. In this conventional 3D printing method, the ratio of the filament extrusion speed and the nozzle moving speed is precisely controlled so that the length of the extruded material extruded from the nozzle is made equal to the length of the actual formed product, thereby preventing unnecessary elongation or aggregation of the output. When the ratio of the two speeds is improperly set, the following will occur. If the length of the output to be actually formed is longer than the length of the extruded material extruded from the nozzle due to the nozzle moving speed being excessively faster than the filament extruding speed, the shape of the output product will become longer and thinner than that of the output at an appropriate speed ratio. On the contrary, if the nozzle moving speed is excessively slower than the filament extrusion speed, the extrudate will be continuously pushed out from the nozzle before the nozzle is moved to form a new shape.

2.1.3. Principle of Single Material 4D Printing by Pre-strained Shape Memory Polymer

In this research, the FDM 3D printed output is stretched at the printing process due to the intentionally lowered ratio of the filament extrusion speed to the nozzle moving speed used in typical 3D printing. When the output is stretched, the reticular microstructure formed in the shape memory polymer is elongated together, and the elongated reticular structure generates a stress to return to the original shape. However, the output remains in the stretched state since it cannot go back to its original shape due to the already generated adhesion between the output and the bed or the output printed earlier. Moreover, the output temperature is gradually cooled down below the glass transition temperature, and keeps the output shape as it is. (Printed shape= Temporary shape) However, if the output removed from the bed is heated again above the glass transition temperature, the stress of the stretched reticular structure is activated and the structure shrinks since there is no force to prevent contraction, unlike the output bonded to the bed. (Activated shape= Permanent shape)

The lower the temperature of the printed output, the more pre-strain can be applied. Since the new stretched reticular structure will be memorized if the output is exposed to a high temperature for long time. Therefore, in this research, the printing will take place at a lower temperature than conventional FDM 3D printing.

2.2. Process

A FDM 3D printer (CORE200, Making tool Co., Ltd.) available on the market is used, and shape memory polymer filaments (DiaPLEX, SMP Technologies Inc., glass transition temperature T_g = 55℃), which are also commercially available, are used. The printer prints at a lower temperature (150℃ ~ 190℃) than the typical printing temperature in 3D printing (220℃ ~ 230℃). Since it is difficult to extrude at low temperatures, the printer uses large diameter nozzle (diameter 3.0mm) instead of general nozzle (diameter 0.4 ~ 2.0mm). Users can choose whether to apply pre-strain or not by setting printing variables. In the case of printing with pre-strain, they need to set the printing temperature and the ratio of the extrusion speed to the nozzle moving speed both lower than the conventional setting. In the case of printing without pre-strain, on the other hand, they simply have to set the parameters as conventional ones. After the printing is completed, the solid output adhered to the bed is removed. The printed output is activated by applying heat.

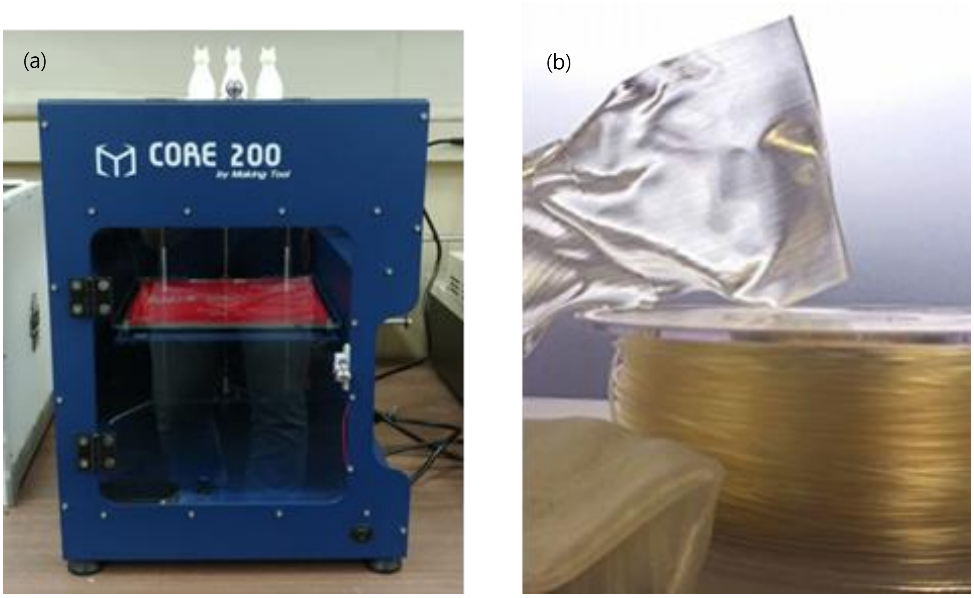

Figure 1 (a) Commercial FDM 3D printer CORE200 (Making tool Co., Ltd.) (b) Commercial shape memory polymer filament DiaPLEX (SMP Technologies Inc.)

Chapter3. Experiments

When 3D printing with a conventional 3D printer, there are approximately eleven important printing variables: power of the extruding motor, filament diameter, nozzle diameter, ambient temperature and humidity, printing temperature, use of cooling fan, z axis offset, bed temperature, bed condition, extrusion speed, nozzle moving speed, and so on. Among them, the parameters which have a major influence on the pre−strain degree in 4D printing are reduced to the two: printing temperature, extrusion speed/ nozzle moving speed ≡ speed ratio). The following experiment was conducted to investigate the effect of these two variables on the degree of pre−strain. The test specimens with a length of 100mm were varied (the thickness and width of specimens vary depending on the printing variables), while the printing variables were fixed and only the printing variables to be tested were changed. Longitudinal strain was measured after inducing shrinkage by applying the same amount of heat. In order to apply the same amount of heat, every specimen was heated in an 80°C natural convection oven for 10 minutes.

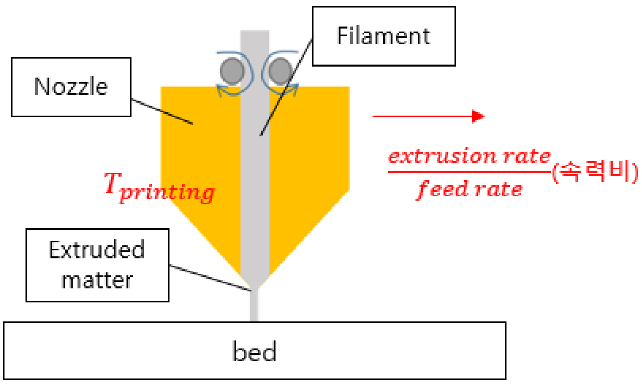

Figure 2 Two critical variables that affects the degree of pre-strain

3.1. Printing Temperature

It was confirmed that the strain increases as the printing temperature decreases. This is because the timing of each process is affected by the printing temperature, which determines the degree of pre−strain. In order to apply pre−strain, stretching process needs to occur after the shape memory process. Meanwhile, the process of forming the reticular structure of the shape memory polymer is a gradual process that occurs above a certain temperature, which is difficult to specify. In other words, although it is necessary to stretch the output after the temperature of the output is dropped enough and the shape memory process is finished, if the printing temperature is too high, the output temperature will not be sufficiently cooled down before the stretching process. In addition, the stretching process will take place during the formation of the reticular structure. As a result, the stretched new shape will be overridden, and the pre−strain will be decreased. Therefore, the lower the printing temperature is, the smaller the effect due to the shape memory in the new stretched shape is, and the higher the pre−strain is.

Although it is proven that the lower printing temperature promises the larger pre−strain, the temperature cannot be lowered indefinitely because the force required for extruding becomes larger as the printing temperature is lowered. Extrusion failure occurs at around the printing temperature of 140℃, and 180℃ when using a large nozzle (diameter 3.0mm), and a standard nozzle (diameter 0.4mm), respectively.

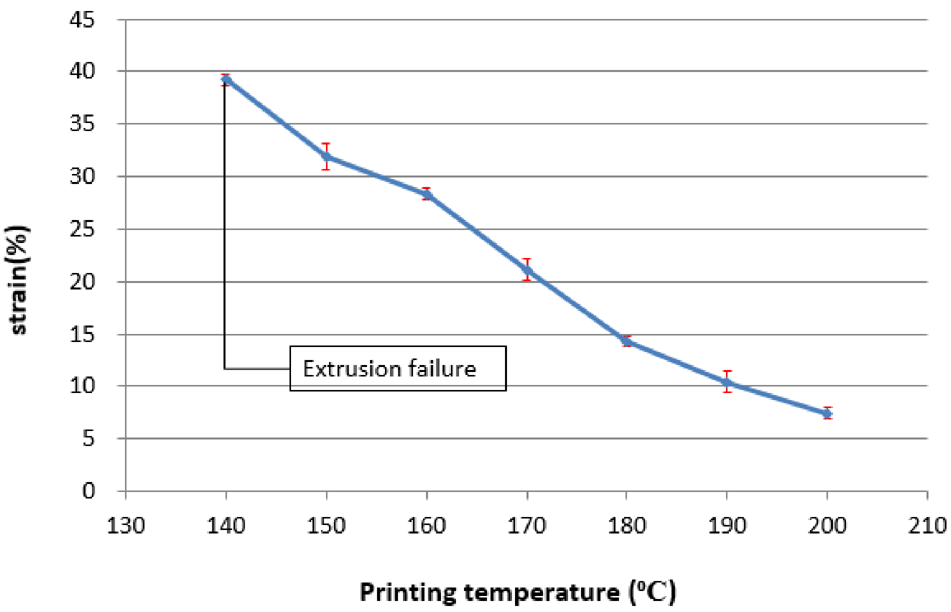

Figure 3 Strain graph for printing temperature (with 3.0mm diameter nozzle)

3.2. Extrusion Speed ratio

Since the pre-strain is applied by intentionally setting the filament extrusion speed lower than the nozzle moving speed, the ratio of the two speeds is inevitably important printing parameter. Through experiments, it was confirmed that as the speed ratio is lower (as the filament extrusion speed is slower than the nozzle moving speed), more pre-strain is applied and the strain increases. As with the printing temperature variable, the speed ratio variable also has a second criteria. If the speed ratio is too low, the thickness of the extrudate becomes too thin and the printing becomes unstable.

It should be noted here that the filament extrusion speed is not the speed of the extrusion motor but the speed of the extrudate being extruded through the nozzle. Therefore, the extrusion speed at which the extruding motor pushes the filaments should be multiplied by a constant ($filament\ diameter^2/nozzle\ diameter^2$) to compare with the nozzle moving speed.

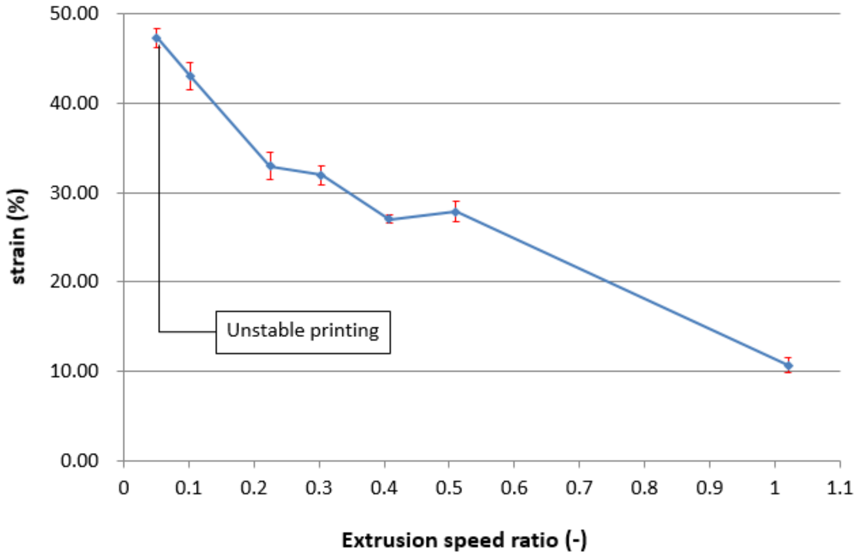

Figure 4 Strain graph for extrusion speed ratio

Chapter4. Results

When using this technique to construct a 4D structure, bending movements are used instead of linear movements to promote stable printing. In order to achieve a stable printing, the first layer must adhere well to the bed, and from the second layer thereafter, it must adhere well to the layer which is printed immediately before. Within the printing temperature range used in this research, the adhesion of the shape memory polymer to one another is comparatively satisfactory. However, the problem arises at the first layer in which the adhesion between the shape memory polymer and the bed occurs. Unlike normal 3D printing, it prints at a low temperature and even pulls the output, which does not stick to the bed properly. For this reason, the first layer should be printed at a high temperature (over 190ºC) without pre−strain so that the output can stably bond to the bed. Likewise, if pre−strain is not applied to the first layer and is applied to the next layers, bending motion which resembles bimetal, occurs when heat is applied to deform the shape. Therefore, the 4D structure in this study necessarily becomes a structure based on the bending motion.

4.1. Curvature control

The curvature can be controlled by controlling the speed ratio and adjusting the amount of pre−strain. As a result, the following rib shapes and petal shapes could be created.

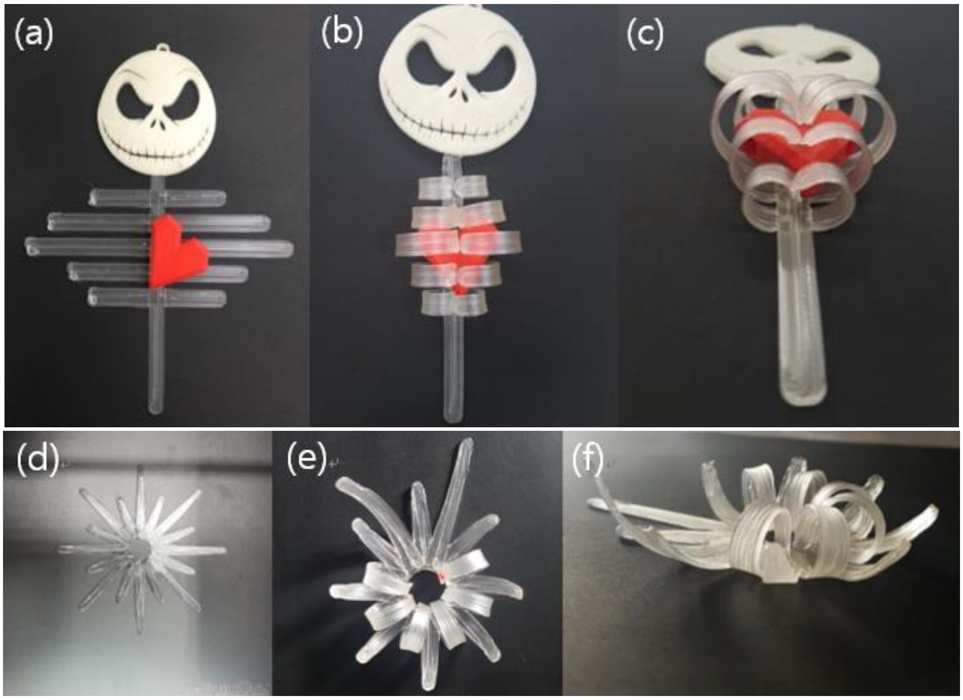

Figure 5 (a) Temporary shape right after the printing (b) Permanent shape after the actuation (Top view) (c) Permanent shape after the actuation (Front view) (d) Temporary shape right after the printing (e) Permanent shape after the actuation (Top view) (f) Permanent shape after the actuation (Front view), different curvatures can be identified.

4.2. Multi-directional Bending

By partially applying the pre−strain in the entire structure, bending in the x/y –axis direction (bending in a direction perpendicular to the sheet) and bending in the z−axis direction (bending in a direction parallel to the sheet) occurs simultaneously.

Chapter5. Conclusion

In this research, a novel method in solving the immediate problem of 4D printing – applying pre−strain at the printing process− is suggested. By intentionally decreasing the ratio of the filament extrusion speed to the nozzle moving speed of the FDM 3D printer lower than the conventional level as well as lowering the printing temperature than the conventional level. In recent years, the world leading research group has succeeded in preliminarily applying the pre−strain in the printing process. However, in principle it is necessary to use the ultraviolet curing process and it is necessary to use expensive and inaccessible equipment and materials to significantly inhibit the accessibility and efficiency of the technology. On the other hand, despite the use of cheap and accessible equipment and materials using FDM 3D printing method, this technology can control the degree of pre−strain by simply manipulating printing variables while solving all of the above problems. Furthermore, with the proper structure design, the 4D structures which could not be manufactured with existing technology, were enabled.

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국문 초록

사전변형이 인가된 형상기억수지를 이용한 단일재료 4D프린팅

3D프린팅 출력물이 스스로 움직이게 만드는 기술인 4D프린팅 기술은 스마트 재료의 3D프린팅 기술이라 할 수 있다. 3D프린팅 기술이 그러하였듯 4D프린팅 또한 기존의 스마트 재료 디자인 방식에 새로운 자유도를 부여하여 자가조립, 자가치유, 가변인프라 등 스마트 재료가 달성하고자 하는 궁극적인 목표를 달성하는 것에 큰 역할을 할 것이다. 이 연구에서는 4D프린팅 기술의 가장 큰 당면과제인 사전변형인가 문제를 해결하는 새로운 방법을 개발하였다. 이 기술은 형상기억수지를 잡아당기며 출력한다는 간단한 과정으로 간편하고 값싸게 4D프린팅의 핵심적인 문제를 해결하였으며, 앞선 4D프린팅 기술로는 출력하기 힘들던 형상을 쉽게 출력 가능케 하였고, 출력변수들을 조작하여 사전변형의 정도를 제어하는 것에 성공하였다.

주요어: 4D프린팅, 형상기억수지, 사전변형, FDM 3D프린터, 프로그래밍 가능한 물질