The Development of Smart 4D Materials Utilising the Smart Temperature-Sensitive Polymer

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Introduction

There is more that can be done with a 3D structure to make them more flexible and more useful: by utilising structures (Smart Polymers) that can transform in a pre-programmed way in response to a stimulus. Thus, giving them an extra dimension and becoming "4D" objects. The 4D printing is a new concept which was proposed to public in 2013. it is fundamentally the same as 3D printing. The difference is the eventually state of fabricated parts can be changed again. In general, the 4D objects can be created using 3D printer to print stimuli sensitive polymers. The stimuli sensitive polymer is a kind of polymer which shape or properties can be altered while a reaction or trigger acts on it, such as temperature change, PH change, moisture change and magnetic change. Because the 4D printing is still in the early phase of the research. To date, the developed 4D objects are mainly used to make simple actuators, sensors, toys and electronics parts.

Methods

First, as a temperature sensitive polymer, N-vinylcaprolactam (NVCL) was chosen as the base polymer. This polymer was incorporated with different types and concentrations of photoinitiators, crosslinkers, and polymers. UV polymerisation, a process with similar mechanisms to SLA printing, was first employed for the preparation of samples. Then, the cured polymers were characterised by various techniques, such as FTIR, DSC, UV-plate reader and swelling studies etc. Based on the formulations, the sample that demonstrate suitable properties and performances is considered to be candidate resin for 4D printing. However, as a hydrogel-based product, it is only able to expend/contract in water after printing. In order to get more use out this 4D material, the bilayer structures are designed. These bilayer structures are composed of smart + flexible material and are formed by a UV chamber system. This allows hydrogel based materials exhibit various shape shifting behaviours (such as self-curving and self-bending behaviours). Finally, based on the different ways of transformation diverse applications were developed. In this work, a smart temperature sensitive 4D material has been developed. By using this 4D material, the 4D printing has been achieved via stereolithography (SLA). In addition, with the combination of other flexible materials, the shape shifting behaviours have been developed via UV chamber system, which greatly increases the possibilities of applying the 4D material to various field.

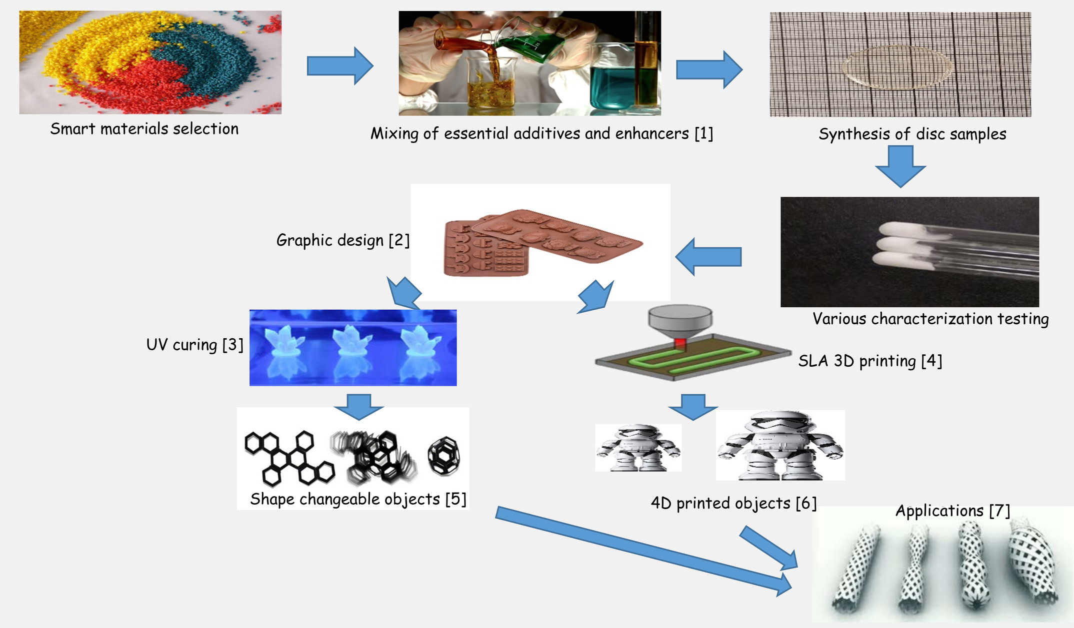

Fig.1 *the scheme of 4D objects implementation.*

Results

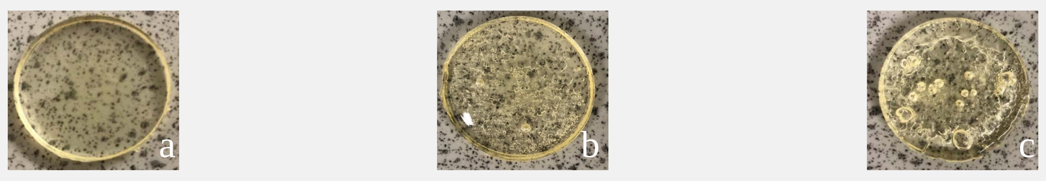

Fig.2 *the appearance of hydrogel disc samples: a) perfect appearance: the samples were cured well. The polymers were transparent and glass-like. Samples maintained shape and integrity, and had a shiny, smooth surface; b) Defective appearance: Plenty of bubbles rose in the sample surface after curing. The surface is also uneven, even with some of them protruding upward; c) Poor appearance: with many cavity and big bubbles inside samples, which affected its weight and shape integrity.*

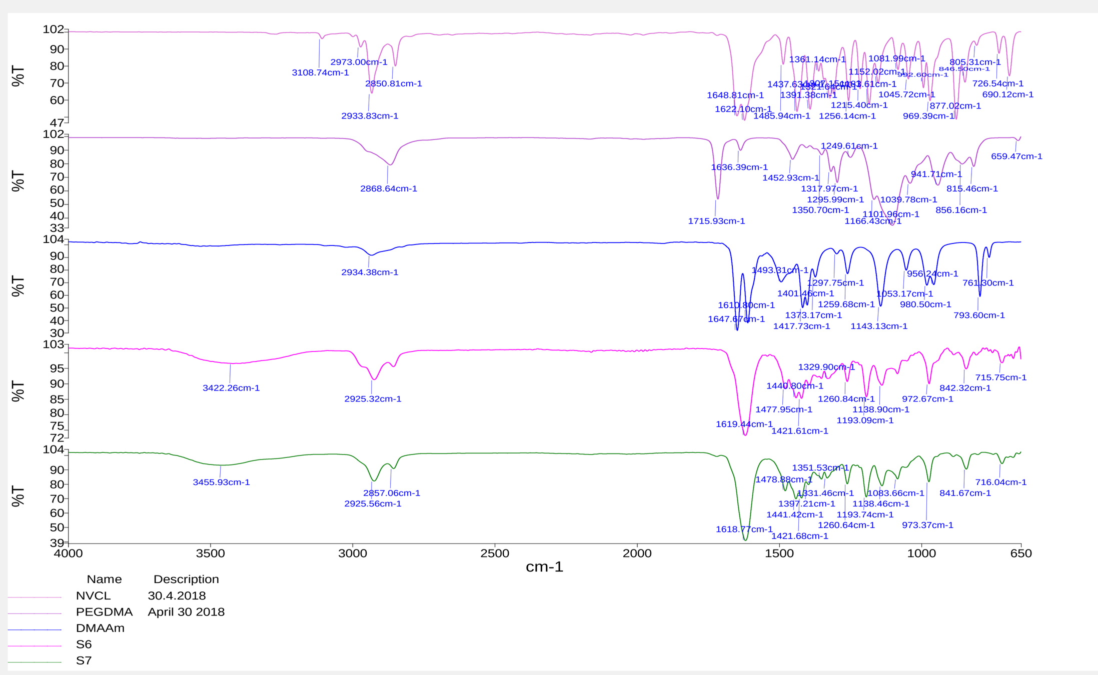

Fig.3 *The FTIR Spectrum shown: on the band range between 1500 cm^{-1} and 1700 cm^{-1}, there are two peaks can be found in monomer NVCL and DMAAm curves. These bands are assigned to the carbonyl group C=O bond stretching vibration and the C=C bond stretching vibration. However, only an intensity peak displayed in copolymer(S6/S7) curves, is attributed to the characteristic absorption of C=O stretching. The disappearance of the C=C peaks in the copolymer (S6/S7) spectra indicate successful polymerisation.*

Gel code	Cloud point (°C)	DSC (°C)	UV-spectrometry (°C)	Rheological analysis (°C)
S1(70NVCL/30NVP)	40.0±0.5	38.0	38	-
S2(70NVCL/30DMAAm)	33.0±0.5	32.3	32	33.7
S3(70NVCL/15NVP/15DMAAm)	35.0±0.5	36.3	35	38.0
S10(15NVCL/20NIPAAm/65NVP)	53.0±0.5	54.1	>50	-
S12(40NVCL/30NIPAAm/30NVP)	43.0±0.5	42.9	>50	-
S13(25NVCL/50NIPAAm/25NVP)	41.0±0.5	45.2	46	-

Fig.4 *the lower critical solution temperature (LCST) detected by four techniques: cloud point measurement, DSC, UV-spectrometry and Rheology. The LCST in this study can be tuned from 33°C to 54 °C. This gives more possibilities to develop applications for different temperatures.*

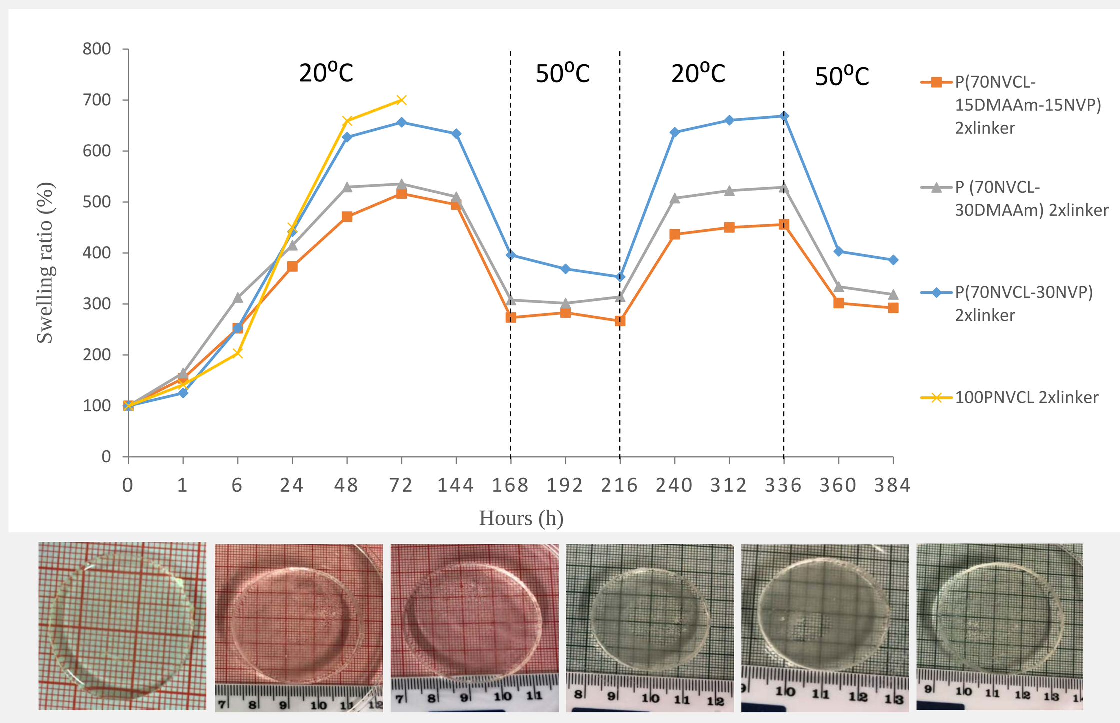

Fig.5 *the pulsatile swelling studies for specific samples. The time of photograph for S7 discs from left to right: 0 h, 6 h, 72 h, 216 h, 336 h, 384 h. For all copolymer samples below LCST, the maximum swollen weight had been reached after 72h. Subsequent to the maximum swollen weight being achieved, when the temperature was above LCST, the samples started to shrink and exhibit reversible shape change behaviour as each temperature rose and fell. All samples exhibited reversible swellability, but only S7 showed suitable swelling and mechanical properties at both low and high temperatures.*

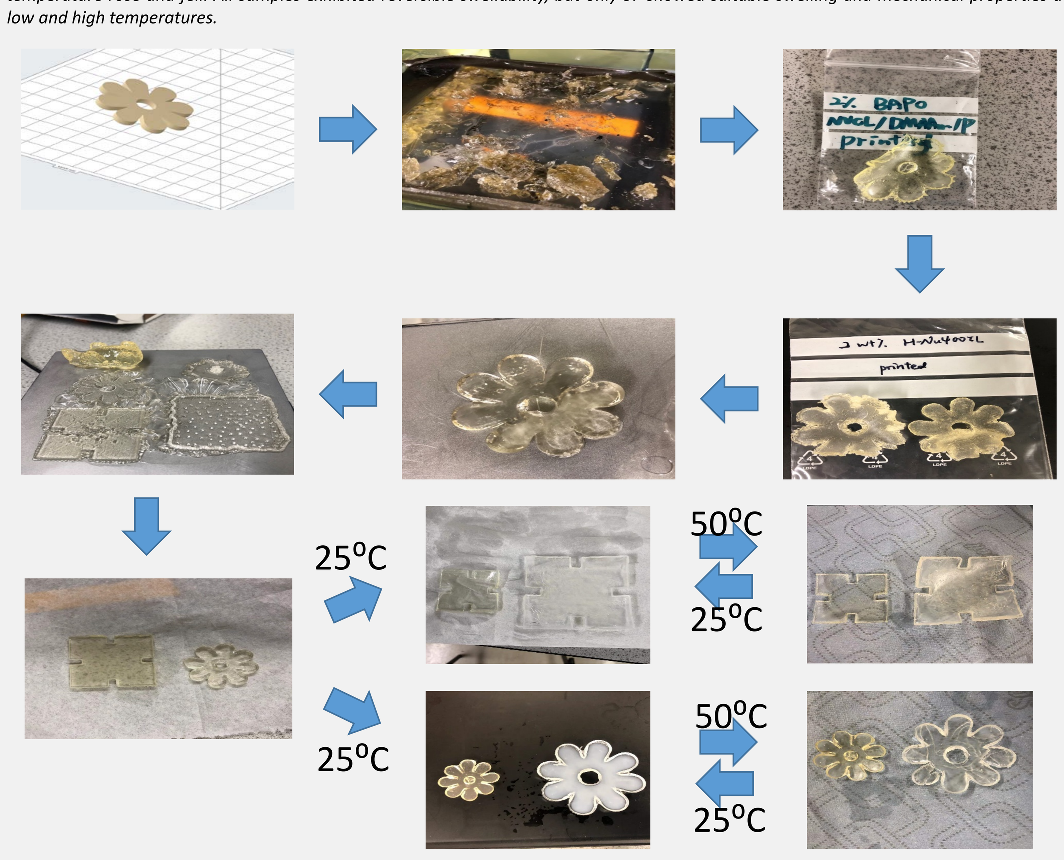

Fig.6 *4D printing trials. At first nothing was printed. By modifying the type and concentration of the photoinitiator, adjusting the print orientation and increasing the resin content, the quality of the prints was improved. The 4D printed objects in the final stage were able to show cyclic expansion/shrinkage behaviour with temperature changes.*

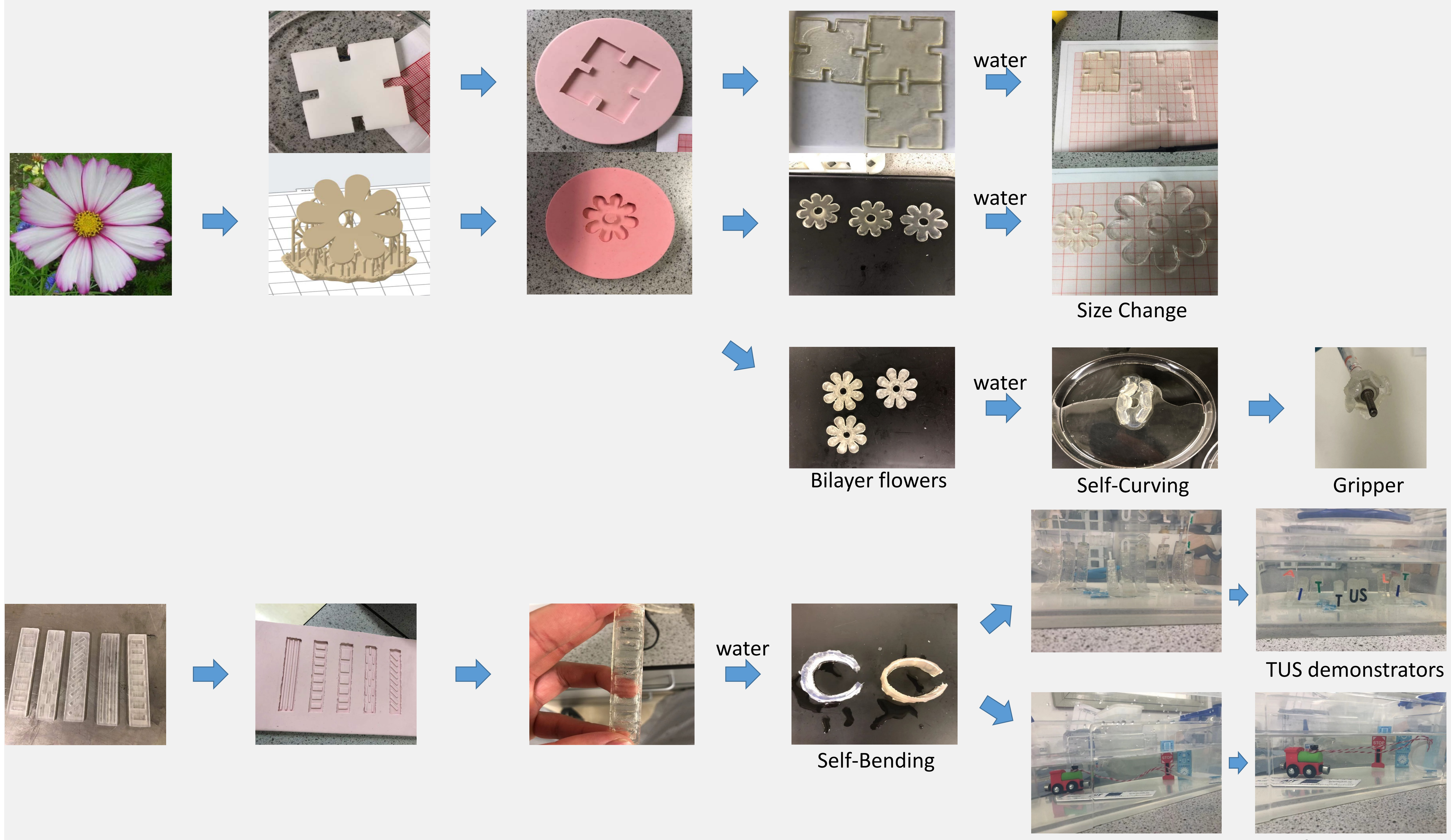

Fig.6 *UV-chamber system curing trials: the process of jigsaw and flower models made with S7 formulation. And the swelling tests in room temperature, both xerogels have the same swelling ratio as round samples that could expand 5 times bigger than their original size. On the other routes, the bilayer flowers have been fabricates. The self-Curving behaviour was exhibited and used as a gripper. In addition, dual tapes have been designed and created to achieve self-bending behaviour. And application demonstrators and tractors have been prepared.*

Discussion

The materials most commonly used for 4D printing are shape memory polymers due to their outstanding flexibility and simple operability. This project not only develops a new material that can be used for 4D printing, but also provides a new method for fabricating the shape shifting objects for hydrogels-based materials.

- The first part of this study was to synthesise and characterise the temperature sensitive Poly (N-vinylcaprolactam) (PNVCL) homopolymer. The NVCL monomer was blended with different types of photoinitiators and crosslinkers at different concentrations. As a result, the sample formulation combined with 0.1 wt% Irgacure 2959, and 2 wt% PEGDMA exhibited a great appearance and reasonable swelling capacity.
- The general concept of second part research was to copolymerise and characterise the NVCL with N-isopropylacrylamide (NIPAAm), N-vinylpyrrolidone (NVP) and N,N-dimethylacrylamide (DMAAm). These crosslinked hydrogels were prepared with the purposes of adjusting PNVCL's LCST and swelling performance, and enhancing the mechanical properties of the hydrogels. The sample mixed with 0.1 wt% Irgacure 2959, 2 wt% PEGDMA, 70 wt% NVCL and 30% DMAAm have great quality and properties that guarantee the feasibility of 4D printing.
- The third aspect of this research was to implement 4D printing using the candidate formulation developed in the second part. To date, 4D printing was initially considered as a methodology that connects rapid manufacturing with time and very little research has been conducted on the development of 4D materials using NVCL copolymers. As a result, By modifying the type and concentration of the photoinitiator, adjusting the print orientation and increasing the resin content, The 4D printed objects are successfully developed.
- The final part of this research involved combining NVCL copolymer with commercially available flexible materials to form the bilayer structures. The shape-shifting behaviour (such as self-curving and self-bending) have been achieve in a UV curing system. And the applications have also been developed in this section.

Conclusion

This research have successfully developed a 4D material that is capable to used as the resin in a cheap SLA 3D printer, and the prints possess excellent quality and behaviour, which could exhibit cyclic expansion/shrinkage behaviour with temperature changes in water. In addition, the 4D materials can also be used as a smart material to force the flexible material to change their shape in a bilayer structure, and the bilayer structures can be easily manufactured in a UV chamber system.

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