

REACTIVE INKJET PRINTING APPROACH TOWARDS 3D SILICONE ELASTOMERIC STRUCTURES FABRICATION

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Abstract

Production of 3D silicone structures with tailored architectures has a wide number of applications including soft robotics and stretchable electronics. This work investigates a method based on a reactive inkjet printing approach to produce 3D silicone structures. Printing parameters including pressure and temperature for jetting SE1700 ink to produce silicone structures were optimised. Additives, silicone oil and vinyl terminated polydimethylsiloxane were added to the main SE1700 formula to evaluate mechanical properties of the final parts. Characterisation was performed to understand the change in a sample's properties in relation to different formulations. Silicone structures with different porosities were printed and the mechanical properties were investigated. It has been demonstrated that 3D silicone structures can be produced using reactive inkjet printing approach. The presented method allowed tailoring of the mechanical properties of silicones without increasing the viscosity properties of the base material by adjusting the silicone formula and using different structures.

Introduction

Production of tailored and porous elastomeric structures has a wide number of industrial applications but at the same time due to the nature of the material can be very challenging [1]. Additive manufacturing creates final parts using a layer by layer approach allowing fabrication of a wide range of 3D shapes. It offers many advantages over traditional fabrication techniques such as personalisation, reduced material consumption and waste products and unparalleled design freedom including complexity of the structures. Using soft materials and the desired 3D structures, additive manufacturing technique can be used in the fabrication of components used for shock absorbents [2], stretchable electronics [3], or soft robotics [4]. Additive manufacturing of cellular structures has a potential to replace traditional methods for producing foams. Having a fabrication method that allows controlling size, shape, and distribution of the pores hence mechanical properties of the silicone features is essential for expanding their application.

Polydimethylsiloxane (PDMS) belongs to organosilicon compounds. Silicone elastomers are obtained by crosslinking functionalised polydimethylsiloxane in the presence of catalyst using free radical or addition mechanism. SE1700 is two-part polymer which when exposed to temperatures of 120°C cures into an elastomeric film. Due to the presence of highly stable siloxane bonds (-Si-O-Si) in the backbone of the silicone, crosslinked PDMS are resistant to high temperatures, UV, oxidation, and possess good insulative electrical properties. Due to the low intermolecular forces and high capability of coil formation crosslinked PDMS are flexible, elastic, and highly compressible. PDMS is often used for encapsulation of fluidic chips, flexible scaffolds [5] or thermal insulation for delicate electrical components in high vibration environments.

The reactive inkjet printing approach (RIJ) in 3D printing is particularly suited for polymers since one reactive component can be deposited on top of or adjacent to one another in a controlled manner and then polymerise on the substrate [6]. Nonetheless, a challenge in this approach is to jet a drop of highly viscous polymer rather than one of low viscosity. The presence of high molecular weight (above 500 000 Mw) hence high viscosity polymers in ink formulations introduces the viscoelastic properties which influence the droplet formation during printing [7, 8]. Having a fabrication method that supports printing of high viscosity fluids and allows control of the polymeric structure and hence mechanical properties of the silicone elastomeric features is essential for expanding their application.

This work investigates a method based on the reactive inkjet printing approach to produce 3D silicone structures of which mechanical properties can be tailored by varying the process parameters and structure's design. Printing parameters such as pressure and temperature were investigated to optimize the process for SE1700 silicone material. The vinyl terminated part of SE1700 silicone with additive vinyl terminated polydimethylsiloxane (100cP) and silicone oil (100cP) were evaluated for their printability using rheological characterization. Whilst the mechanical properties of printed films and silicone structures with different porosities were investigated with dynamic mechanical analysis (DMA). The results showed that despite the high viscosity of silicone fluids, it is possible to employ a reactive inkjet printing approach to obtain silicone structures. It was also demonstrated that the capability to alter mechanical properties of printed silicone structures could be achieved using different process parameters and by different structure design.

Materials and Methods

Reactive Jetting setup

The Reactive Jetting setup consists of three-dimensional stage (Aerotech) synchronised with Nordson EFD jetting valves. The software used in the system is based on a combination of python and G code and controls printing parameters such as printing speed and drop spacing as well as enabling communication between the stage and the jetting valves. Figure 1 presents a schematic illustration of the jetting system together with a description of the work flow. The ejection and position of the valves are controlled by the stage while the jetting time and temperature are controlled by a PicoTouch controller (Nordson EFD). The jetting valves move along the substrate across X and Y axes building up the depth and width of the sample and moves vertically in the Z axes to build the height. A close-up view of the jetting valves can be seen in Figure 1 (c). The build material is placed in the fluid container into which compressed air is connected. Once the material from the fluid container is pushed towards the nozzle, a piezoelectric actuator drives a ceramic rod located above the nozzle consequently causing its opening and closing. The closing and opening time of the nozzle, as well as pulse and cycle time can be controlled through a digital controller. The maximum jetting frequency that can be achieved is 500 Hz.

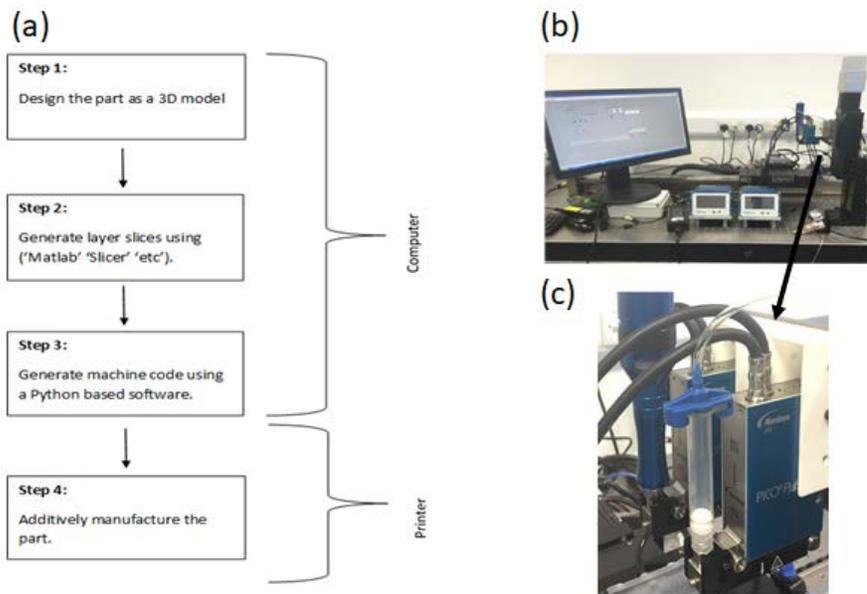


Fig.1 Schematic image of workflow (a) and image of jetting setup (b) and close view on jetting valve (c)

Materials

The material that has been used for the study is an organosilicon compound, polydimethylsiloxane, 2 parts (inks) SE1700 (Dow Corning). Ink A consists of vinyl groups and silica fillers, ink B consists of hydride groups and a platinum catalyst. It is an addition reaction taking place at 120°C. This type of reaction is perfect for reactive inkjet printing, where ink A is loaded into print head 1 and ink B is loaded into print head 2, followed by printing ink B on the top of ink A and reacting on the substrate, the final product is obtained. Figure 2 shows a schematic illustration of the reaction that takes place when ink A and ink B is mixed together.

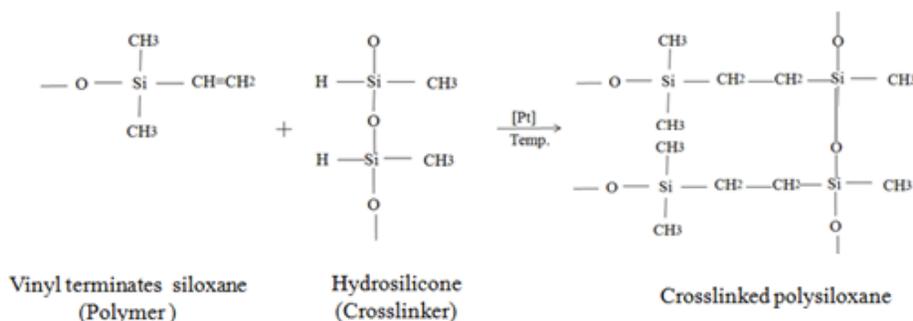


Fig.2 Schematic illustration of the reaction between vinyl groups present in ink A and hydride groups in ink B. The final product is crosslinked polydimethylsiloxane (SE1700)

To modify an original formula of SE1700, low viscosity (~100mPa) additives were added. Vinyl terminated dimethylpolysiloxane (PDMS_V) supplied by Gelest Inc., and silicone oil (SO-100) purchased from Sigma Aldrich.

Characterization of Silicone before printing

The viscosity of the materials was measured with a Kinexus Pro rheometer (Malvern Instruments Ltd.) with a cone-plate configuration. A shear rate of $1 - 1000 \text{ s}^{-1}$ was used for the ink A of SE1700 while shear rates of $1-100 \text{ s}^{-1}$ was tested for ink B of SE1700 and Pluronic F-127 (PF127). The tests were carried out for the range of temperatures from 25 to 80 °C.

Jetting parameters investigation and sample preparation

Silicone films were fabricated by printing two separated inks, ink B on top of ink A and cured on the substrate at 120 °C for 1 h. The shape of the printed structures was retained through the whole time of curing due to the high viscosity of ink A. Printing parameters were as follow: temperature of ink A was 80°C, air pressure 14 bar, temperature of ink B was 25°C, and air pressure 2 bar. For ink A, close time was 0.2ms and open time 0.25ms. For ink B, close time was 0.4ms, open time 0.25ms. For both inks, the pulse time was 0.3ms, stroke was 75%, close voltage 120V and drop spacing was 300 μm . Nozzle size for ink A was 150 μm while for ink B it was 50 μm . Modified silicone samples were prepared by mixing 15 wt% of silicon oils (SO-100cP) and vinyl terminated PDMS (PDMS_V) with ink A of SE1700. Printing parameters were used as above.

Printed samples resulted in no spreading of the inks and relatively sharp edges for all the samples. Example of the printed sample can be seen in Figure 3.

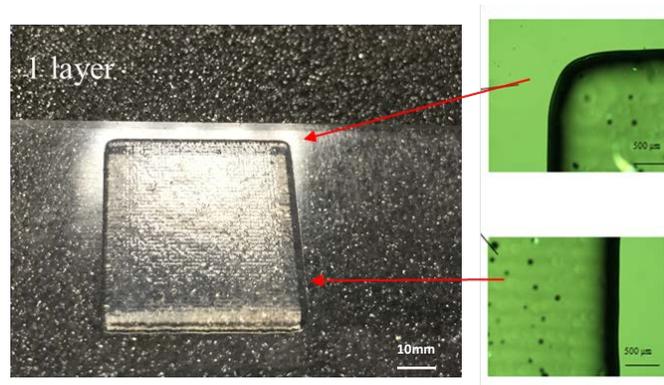


Fig.3 Printed silicone SE1700 square 50 x 50 mm

Structural investigations and mechanical properties of printed samples

To identify the functional groups in ink A and ink B of SE1700, as well as the bond formation in crosslinked polymer, Fourier transform infrared spectroscopy (FTIR) analysis was performed. The experiments were carried out using a Frontier Fourier Transform Spectrometer (Perkin Elmer). Absorption spectra of the samples were recorded at a constant temperature (25°C) in a range: $3500-500 \text{ cm}^{-1}$, at a resolution of 4 cm^{-1} .

The influence of additives in silicone formulation and different cellular structures on the mechanical properties was studied by determining the shear storage and shear loss modulus of the printed samples using DMA 8000 (Perkin Elmer). Printed samples structures were

observed with optical microscope (Eclipse LV100 ND, Nikon) and scanning electron microscope (JEOL 7100F FEG-SEM).

Fabrication of 3D cellular structures

Figure 4 presents schematic illustration of strategy undertaken to print 3D cellular structures using a support material. A support material is jetted from the nozzle to fill the space between the build material deposited from the other nozzles. After the final structure is completed, the support material is removed by immersion in water. The water based support material is dissolved without damaging the surface of the elements of the final structures.

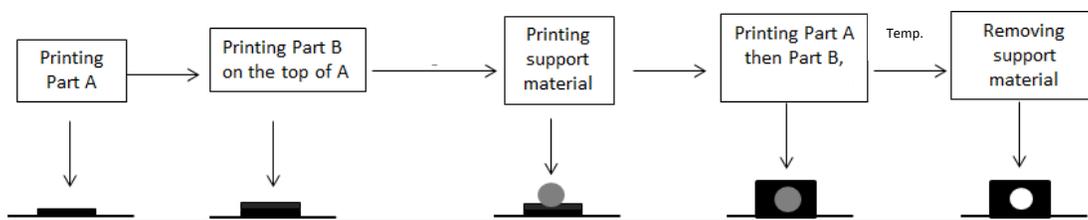


Fig.4 Schematic representation of printing strategy for obtaining 3D cellular structures

Results and discussion

Rheological behavior of materials

The viscosity of ink A of SE1700 was studied at different shear rates and temperatures, the results of these measurements are presented in Figure 5. The data indicate that ink A shows non-Newtonian flow behaviour, where the viscosity decreases with increasing shear rate, consequently allowing the ink to flow out of the nozzles during jetting. Also, the viscosity of ink A reduces as the temperature increases and it reaches 16.3 mPa s at shear rate 100/s at 80°C. This temperature was chosen to be used during printing of ink A.

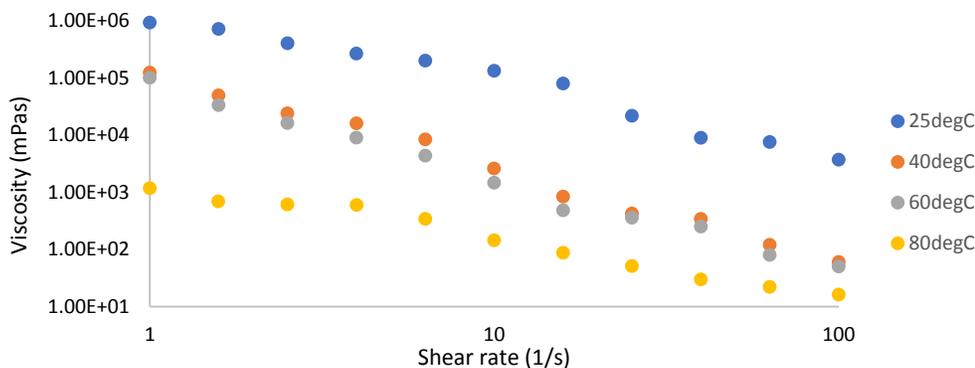


Fig.5 Viscosity vs share rate for ink A at 25, 40, 60, and 80 °C

The viscosity of the ink B of SE1700 was also studied (Figure 6). It can be observed that the viscosity stays constant over the share rate range. The rheology study indicates that ink B is a Newtonian fluid with viscosity of 0.12 Pa s at 25°C. Ink B of SE1700 showed completely different behaviour when compared to ink A as the polydimethylsiloxanes present in this ink have lower molecular weight and in ink B there is no presence of fillers, hence much lower viscosity is observed. At this value of viscosity for ink B there was no need to carry the viscosity measurement for higher temperatures. The rheological properties of ink B at 25 °C was satisfactory for its printability.

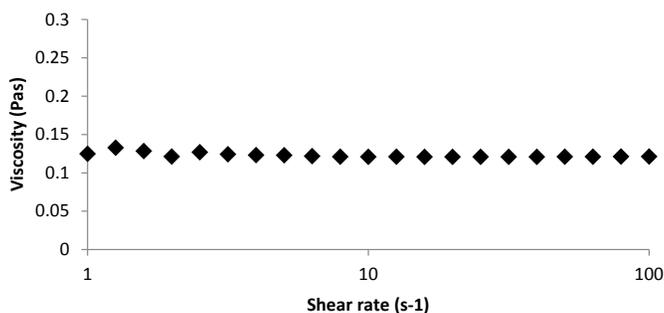


Fig.6 Viscosity vs shear rate for Ink B (viscosity = 0.12 Pas)

The viscosity measurement was also conducted for the support material used to create 3D cellular structures. The support material consists of aqueous solution PF127 (PF127) triblock copolymer mixed with 10 wt% addition of carbon paste. PF127 is thermoreversible polymer which undergoes phase transition depending on temperature and concentration [9-11]. An aqueous solution of PF127 used in this study was 20wt% which at this concentration at room temperature behaved like a gel. However, as seen in Figure 7 where viscosity vs shear rate is presented, PF127 with and without addition of carbon paste shows shear thinning behaviour which enables the ink to flow out of nozzles during jetting. Once the fluid exits the nozzle, it quickly stiffens on the substrate serving as a support material for ink A and B. In Figure 7 image of printed lines, well-shaped with no satellites can be observed

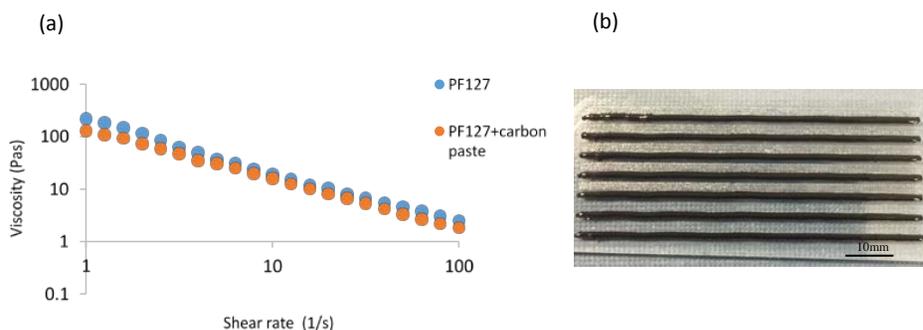


Fig. 7 Viscosity vs shear rate for 20wt% PF127 mixed with 10wt% carbon paste (a). Picture of printed line of support material (b)

Jetting parameter optimization and sample preparation

The jetting parameters for the silicone materials were investigated. The influence of temperature, pressure and nozzle size on the drop volume are presented in Figure 8. The results show that the jetting volume increases with the increase of temperature and pressure. This is because the viscosity of the material decreases with the temperature and since the drop volume is decided by mechanical force applied to the ink [12], it is much easier for the material with lower viscosity to flow through the nozzle.

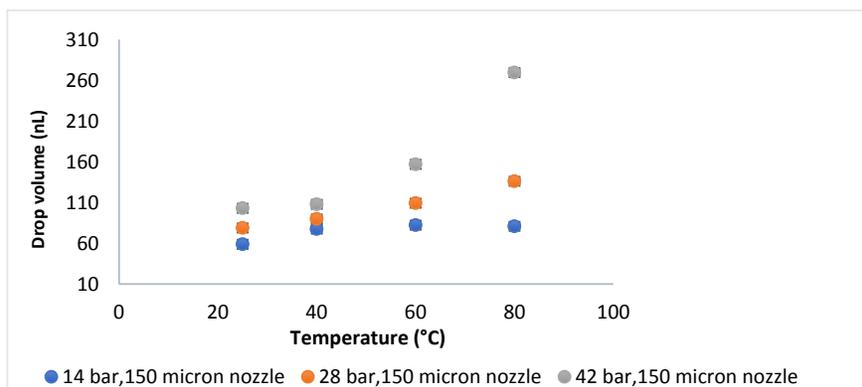


Fig.8 Drop volume vs temperatures at various air pressure. Drops jetted using 150µm nozzle

FTIR analysis

FTIR technique was used to characterize SE1700 before and after printing to ensure that the reaction took place. The FTIR spectra of ink A and B before and after reaction are presented in Figure 9. The FTIR spectrum of ink A (blue line) reveals the presence of Si-CH₃ groups (absorption bands at 1260 cm⁻¹ together with bands in the range 865-750 cm⁻¹), presence of vinyl groups (absorption bands at 1410 cm⁻¹ and 1010 cm⁻¹) and Si-O-Si (1070 cm⁻¹). The FTIR spectrum of ink B (red line) reveals the presence of characteristic functional Si-H group (2164 cm⁻¹) which takes part in the reaction with vinyl groups present in ink A. The FTIR spectrum for ink B also shows the presence of groups Si-CH₃ (1260 cm⁻¹, 840 cm⁻¹, and 756 cm⁻¹). Crosslinked polydimethylsiloxane is represented by the green line on the FTIR spectrum. It shows reduced intensity of the Si-H absorption (2170 cm⁻¹) when compare to starting precursors (blue and red line). This spectral change indicates the addition reaction between vinyl group in ink A (Polymer) and the Si-H group in ink B (cross-linker) successfully proceeded.

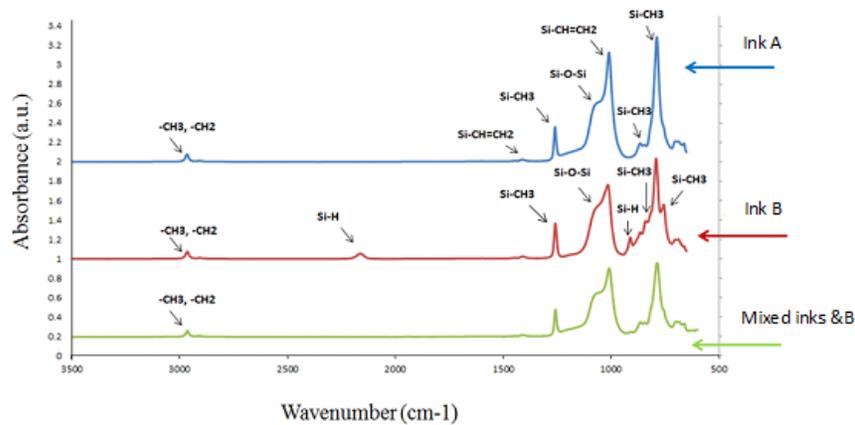


Fig.9 FTIR analysis of ink A, ink B, and mixed ink A&B at 120°C for 1 hour

Influence of additives on mechanical properties

Dynamic mechanical analysis (DMA) was employed to characterize the effect of additives on the mechanical properties. The effect of addition of silicone oil (SO-100cP) and vinyl terminated polydimethylsiloxane (PDMS_V) into ink A on storage modulus was investigated. Figure 10 presents the storage modulus vs temperature for all the samples. The storage modulus for SE1700 was 0.68 MPa. After addition of SO-100cP into ink A the storage modulus decreased down to 0.37 MPa. However, after addition of PDMS_V into ink A, the storage modulus increased up to 1.3 MPa indicating the highest crosslinking density within the sample.

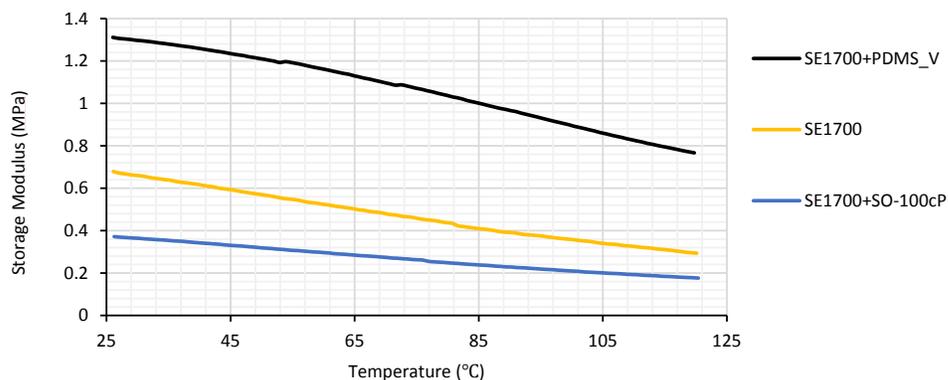


Fig.10 Plot of storage modulus against temperature for SE1700 without solvent, and with addition of 15 wt% silicon oil (SO-100cP) and vinyl terminated polydimethylsiloxane (PDMS_V).

Fabrication of 3D cellular structures

Two different 3D porous structures of SE1700 were created using reactive inkjet printing approach. The structures differ between each other through modification of the cell

width between the build material. The first structure was printed using a 0.35 mm space between the build material while the second one used 2.5 mm. The results shown in Figure 11 indicates that the structure 1 (a) and structure 2 (b) were successfully printed and the support material was removed without causing any damages to the final structures for both structures.

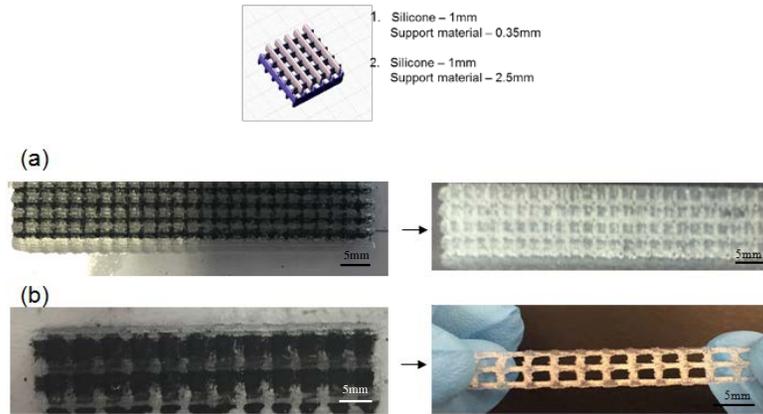


Fig. 11 3D printed cellular samples (a) structure 1 and (b) structure 2

Figure 12 shows closer views on the top and cross section of the structure 1 where the holes created after removal of the support material can be seen.

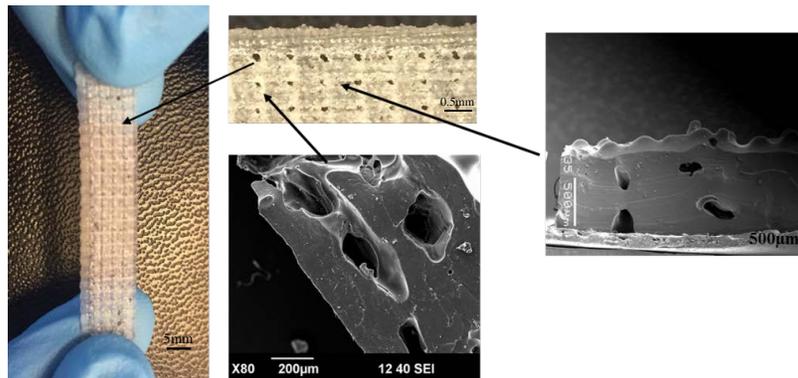


Fig. 12 Optical microscope of top view and SEM image of cross section of printed SE1700 cellular structure no 1

Characterisation of 3D cellular structures

The influence of the different cellular structures on the mechanical properties of SE1700 was studied by obtaining the shear storage and shear loss modulus of the printed samples using dynamic mechanical analysis. The storage modulus measures the ability of the material to store energy and represents the elastic portion, it can also be associated with stiffness of a material. The loss modulus describes the energy dissipated as heat and relates to

the viscous portion [13]. The two 3D structures have been tested and the results are shown in Figure 13. For both samples, the storage modulus was almost one order of magnitude higher than loss modulus at 1 Hz indicating dominant elastic response. Lower storage and loss modulus were obtained for structure 2 than for structure 1. This is due to an increased material density which forms stiffer films. It can also be seen that samples printed with structure 2 were more stable over the temperature range compared to samples with structure number 1. The storage and loss modulus for structure number 1 reduced from 0.57 to 0.3 and from 0.062 to 0.015 respectively when the temperature decreased from 25°C to 120°C. For structure number 2 the difference was only 0.03 MPa for storage modulus and 0.01MPa for loss modulus.

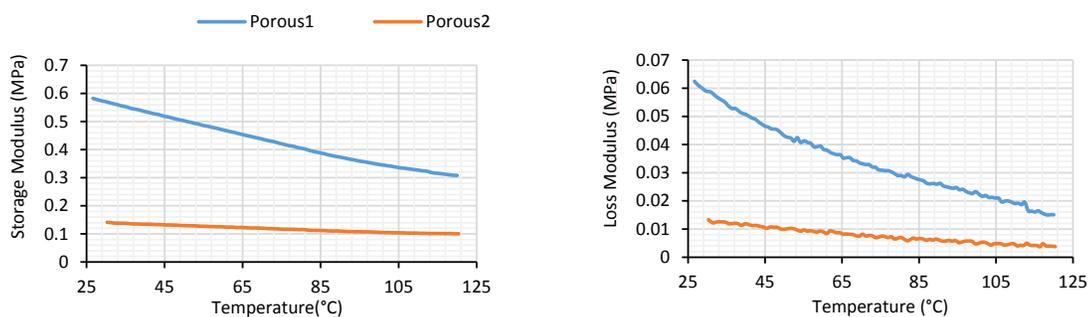


Fig.13 Plot of storage modulus and loss modulus vs temperature for SE1700, porous 1 and porous 2 samples measured at mechanical vibration frequency of 1Hz

Conclusion

This work investigated a method based on reactive inkjet printing to produce 3D silicone structures of which mechanical properties can be tailored by varying the process parameters and structure's design. The proposed jetting setup was shown to be suitable for printing high viscosity polydimethylsiloxane exhibiting the high potential of reactive inkjet printing approach in producing 3D polymer structures. The parameters for jetting highly viscous SE1700 have been investigated, the best results have been achieved using 14 bar and 80°C. Addition of low molecular weight, vinyl terminated PDMS into part A of SE1700 increased the storage modulus up to 1.3 MPa. It has been demonstrated that 3D porous silicone structures can be produced using reactive inkjet printing approach and support material although it is still in the preliminary stages.

References

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