Micro-vascular shape-memory polymer actuators with complex geometries obtained by laser stereolithography

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Abstract

In our work we present the complete development process of geometrically complex micro-vascular shape-memory polymer actuators. The complex geometries and three-dimensional networks are designed by means of computer aided design resources. Manufacture is accomplished, in a single step, by means of laser stereolithography, directly from the computer-aided design files with the three dimensional geometries of the different actuators under development. To our knowledge, laser stereolithography is applied here for the first time to the development of shape memory polymer devices with complex geometries and inner micro-vasculatures for their activation using a thermal fluid. Final testing of the developed actuators helps to validate the approach and to put forward some present challenges.

Keywords: shape-memory polymers, micro-vascular shape-memory polymers, additive manufacture, laser stereolithography, smart materials and structures

(Some figures may appear in colour only in the online journal)

1. Introduction

Shape-memory polymers (SMPs) are active or 'smart' materials that present a mechanical response to external stimuli, normally changes in surrounding temperatures. Although other types of stimuli such as light, water or chemicals, can promote shape-memory effects in polymers, we focus here on thermally activated SMPs, as they are the most common ones. When these materials are heated above their 'activation' temperature (T_{act}), typically corresponding to glass (T_g) or melting transitions (T_m), a radical stiffness change takes and the SMPs change from a rigid to an elastic state, which in some cases allows deformations of up to 400%. After being manipulated and deformed, if the material is cooled down with the imposed deformation, this structure is 'frozen' and returns to a rigid but 'unbalanced' state. This process is usually referred to as 'shape-memory training' process. When the material is once again heated above its 'activation temperature' (normally corresponding to glass transitions temperatures) it returns to its initial non-deformed state. The cycle can be repeated numerous times without any degradation to the polymer and most suppliers can formulate different materials with typical values of activation temperatures between –50 °C and 250 °C, according to the desired final applications. Among the polymers developed with remarkable shape-memory properties, the most important are epoxy resins, polyurethane resins, cross-linked polyethylene, diverse styrene-butadiene copolymers, and other formulations described in previous reports [1–4].

They are, therefore, active materials that possess thermo-mechanical coupling and an ability to recover from high deformations, (much greater than that of shape memory metal alloys), which combined with their lower density and cost has encouraged the design of numerous applications. Their properties permit applications in the manufacture of sensing

devices or actuators, particularly for the aeronautic, automobile and medical industries. Their recent proposals for medical use have been examined previously [5, 6]. Nevertheless, if the development of new and more demanding applications is to be encouraged, especially for the medical industry, and if implantable devices for human beings are to be obtained, the synthesis, processing, modeling, prototyping, characterization and environmental response of these materials need to be given a very close examination [1, 2, 4, 7–11].

Another limitation of intelligent devices based on the use of SMPs as actuators, is linked to the widespread use of 'punctual' distributed heating resistances, working via Joule effect heating of small resistors connected in series, as activation method [6, 10]. Joule effect heating using resistors involves several relevant issues needing attention, such as: (a) final device size is importantly increased due to the additional place required for the resistances; (b) the use of resistances limits materials' strength and the obtained devices are normally weaker; (c) the activation process through heating resistances is not homogeneous, thus leading to important temperature differences among the polymeric structure and to undesirable thermal gradients and related stresses, also limiting the application fields of SMPs.

In relation to the progressive improvement of shape memory polymer capabilities and optimization of their activation process (searching for alternatives to punctual heating resistances), it is worth mentioning the use of nickel nanoparticles, carbon black, carbon nanotubes (amongst others), embedded inside the material, in order to obtain electroactive shape memory polymers whose heat-based activation process is faster, more controllable and more efficient, as a result of the homogeneous distribution of the heating particles. Additional information on electroactive shape memory polymers can be found consulting [12, 13] for explaining the use of carbon nanoparticles, [14, 15] for a description on using nickel nanoparticles and [16] for a specific review on the topic. More recently, pioneer research [17, 18] describes the use of nanopapers with embedded nanotubes, as coating for promoting the conductivity of SMPs and enabling their activation by heat transfer from the nanopaper to the SMPs, what opens new activation possibilities, highly linked to the alternatives presented in our current study.

It is important to remark that in previous devices based on shape memory polymers, typically activated using heating resistances (as well as in recent studies from our group using Peltier heater-coolers [19]) temperature differences around 30 °C–60 °C can usually be found within the core of the polymer, while these novel electroactive shape memory polymers provide temperature differences normally lower than 30 °C among the whole structure. Such homogeneous and more controlled behavior has potential for enabling medical applications, as the references explain in depth. Another interesting possibility is linked to the incorporation of micro and nanoparticles into shape memory polymeric devices or structures for promoting induction heating, thus achieving remote activation of the shape memory effect, with notable prospects in terms of the development of active implantable devices, as wireless devices can be thus developed [20, 21]. In these devices, the impact of nanoparticle inclusion on the mechanical properties is also relevant and should be addressed, as well as the influence of processing on final device cost. It is important to note that these aforementioned solutions, linked mostly to the incorporation of nanoparticles into the polymeric matrix or to the use of nanocomposites, require systematic synthesizing and processing methods, equipments not always available, as well as special security issues linked to working with nanoparticles. A low-cost alternative to the use of nanoparticles, is based on the use of conductive inks and electrotextiles glued to the polymer surface, but the incorporation of such additional materials is not always possible in complex actuators [22].

The recent development of micro-vascular SMPs, also referred to as micro-vascular SMP composites, is opening new horizons in the field of actuators based on SMPs. In short, micro-vascular shape memory polymers composites are a new class of active 'composites' consisting of an embedded micro-vascular network in a SMP matrix. The micro-vascular network can be used to deliver thermal, chemical, electrical, and magnetic stimulation to the SMP matrix thus integrating the activation and deactivation mechanisms, promoting homogeneous activations, simplifying final devices and opening up a new functional space for active polymers [23]. Pioneer studies in the field have dealt with the incorporation of the micro-vascular network, by means of including tubular inserts, during the conventional molding of shape memory (pre-)polymers, which are retired after polymerization and lead to testing probes with inner linear or even branched vasculatures [23, 24]. Such first experiences have also dealt with the analytical modeling [23] and with the simulation using the finite element method (FEM) [25] of such systems, so as to optimize the vascular networks.

However, towards more complex actuators benefiting from the potential of micro-vascular SMP composites, the development of three-dimensional vasculatures is required and alternative manufacturing strategies are needed. In this work we present the complete development process of geometrically complex micro-vascular SMP actuators. The complex geometries and three-dimensional networks are designed, assessed *in silico* and optimized by means of computer aided design and engineering resources (FEM-based simulations). Manufacture is accomplished, directly from the computer-aided design (CAD) files with the three dimensional geometries of the different actuators under development, by means of laser stereolithography. Such additive manufacturing technology is able to construct complex devices, working on a layer-by-layer approach, and currently provides one of the best compromises between part size, manufacturing precision and productivity among all 3D printing resources. It has been previously used by our team for the development of several SMP systems [6, 10, 19, 22] and has been recently highlighted as a key resource for microfluidic systems, due to the possibility of manufacturing labs-on-chips with complex inner channels in a one-step process [26]. To our knowledge, laser stereolithography is applied here for the first time to the development of shape memory polymer devices with complex geometries and with

Table 1. Properties of the materials used for prototype manufacture.

Accura® 60 epoxy resin from 3D Systems	
Density	1.21 g cm^{-3}
Tensile strength	58–68 MPa
Young's modulus	2690–3100 MPa
Activation temperature (T_{act})	58 °C–62 °C
Hardness-Shore D scale	86

inner micro-vasculatures for their activation using a thermal fluid (water in our case). Final testing of the developed actuators helps to validate the approach and to put forward some present challenges. The following section describes the materials and methods used, before presenting and discussing main results of current research and future issues.

2. Materials and methods

2.1. Shape memory epoxy

Proof of concept probes, for assessing the manufacturability of the inner vasculatures, and final application prototypes (spring and micro-claw) for testing their shape-memory properties, are obtained via additive laser stereolithography using a shape memory epoxy sold under the trade name of Accura® 60(3D Systems, 333 Three D Systems Circle, Rock Hill, SC 29730 USA) the properties of which are listed in table 1. In order to obtain more detailed information about material properties, supplier's data sheets can be consulted or they can be directly contacted for more specific questions. Its applicability to the rapid development of SMP based devices has been previously put forward by our team [6, 10, 19, 22]. Additionally some studies have shown the utility of carrying out dynamic mechanical analysis for obtaining full knowledge about the properties of parts manufactured by laser stereolithography. That research has used photo-curable epoxy resins, similar to the one employed in our trials, for evaluating the effects of different influencing factors, such as part geometries, machine precision, processing conditions, post-cure time or the inclusion of different additives and reinforcement fibers [27–30].

It would be also important to study in depth how several aspects can modify the properties of these materials, especially their activation temperature. For example environmental humidity or physical ageing have proven to be of importance and should be carefully taken into account, as previous research has shown for different polymers [9, 31]. We would also like to note that very recent advances have led to the development of new photo-sensitive materials for stereolithography, especially focused on the medical industry, whose shape memory properties should be thoroughly analyzed, in order to promote the design of active implantable medical devices [32–35]. Anyway the Accura® 60 expoy resin used helps us to study the possibilities of activating

shape memory polymer structures and devices, by heating through inner complex vasculatures incorporated to the CADs of the different sample actuators developed, as detailed in the following sections.

2.2. Computer-aided designs

Several CAD and engineering programs help with the development process of novel products. In our case, the different geometries of the active devices under study (active spring and active micro-claw) are designed with the help of NX-8.5 (Siemens PLM Solutions). We study three different configurations for each prototype, corresponding to inner vasculatures with cross-section diameters of 0.6, 0.8 and 1.2 mm, according to the manufacturing capabilities of our stereolithography system. Such design variations can be rapidly obtained thanks to the parametric design features of the NX-8.5 software. Figures 1(a) and (b) shows the CADs and the variations included to the inner vasculatures of the active spring and active micro-claw envisioned as conceptual cases of study. We also carry out the CAD of a couple of probes with 8 inner tubular holes with cross-section diameters varying linearly in the range of 0.4–1.2 mm. The probe is just aimed at helping with the assessment of the manufacturability of micro-channels via laser stereolithography and with the evaluation of the minimal micro-channel diameter and of the minimal wall-thicknesses attainable.

2.3. Prototypes and trials

Rapid epoxy prototypes (see figure 2) have been manufactured using our SLA-3500 laser stereolithography machine from 3D Systems, capable of reading the information about part geometries from the original CAD files and subsequently manufacturing them using a layer-by-layer approach. The possibility of using laser stereolithography and the typical shape memory properties of epoxy resins has been previously highlighted as a rapid way of conceptually validating intelligent devices based on these stimuli responsive materials [6, 10, 19, 22], although it is not the unique possible additive manufacturing (or 3D printing) resource capable of working with SMPs, as discussed in section 3.2. The advantages and limitations of alternative additive and conventional, typically casting-based, procedures are also analyzed towards the end of the study.

The training process of the shape-memory effect has been carried out by heating the prototypes in water at 80 °C and by forcing against a planar surface towards full compression, in the case of the spring, and against a rapid prototyped green cone obtained by fused deposition modeling, in the case of the micro-claw (see figure 2(c)). The shape recovery trials are carried out by connecting the prototypes to a hollow needle with an external diameter of 0.8 mm and by injecting water at 80 °C with the help of a 10 ml syringe during a period of 30 s (which lasts longer than the whole shape-memory recovery process) for promoting the recovery of the original shapes.
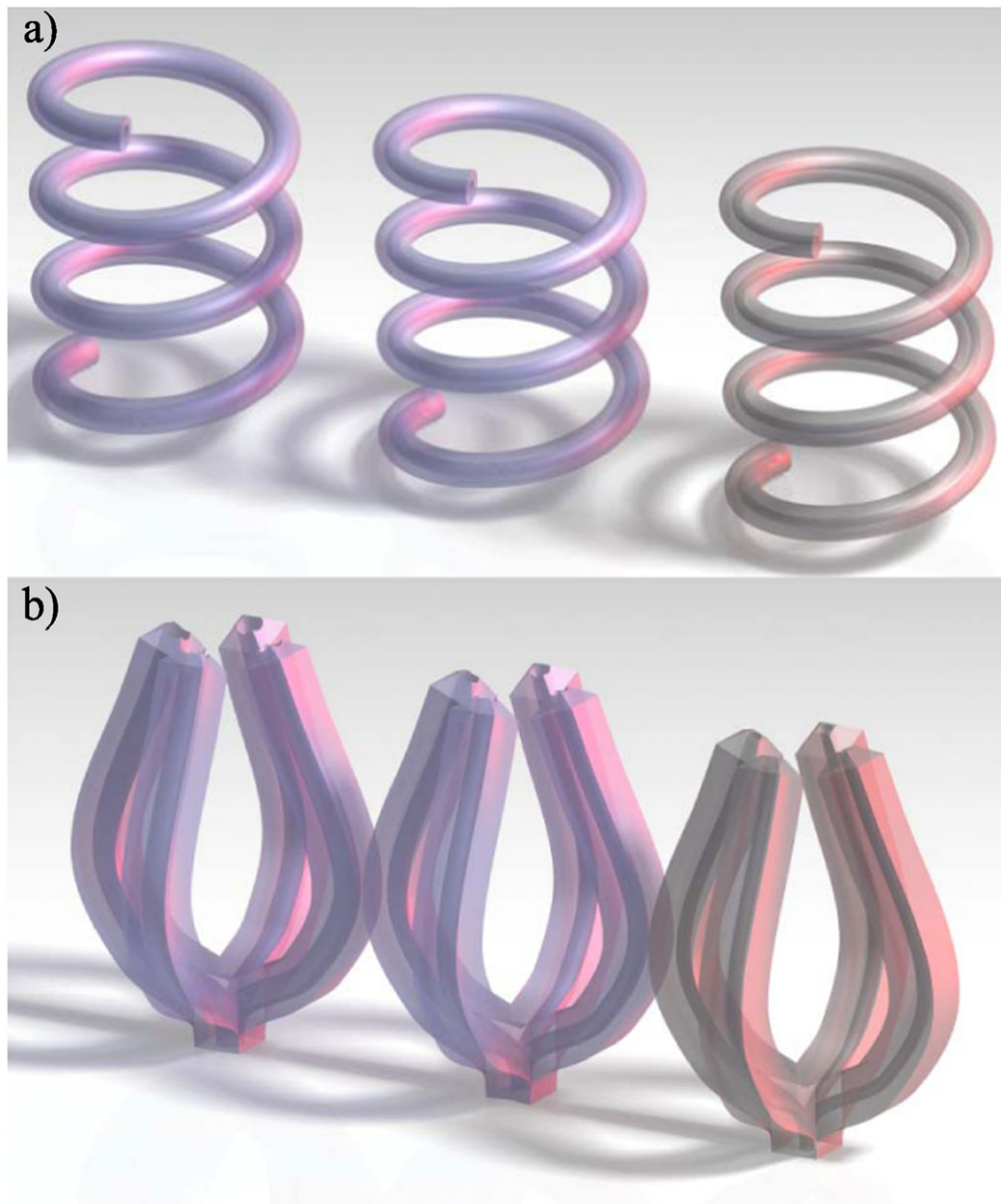
Figure 1. Comptuer-aided designs of micro-vascular shape-memory polymer devices. (a) Active spring with inner vasculatures of different cross-sections. (b) Active micro-claw with inner vasculatures of different cross-sections.

During the training and recovery processes, we have used a 'Flyr Systems Thermacam E300', together with the analysis software 'Thermacam Reporter 8.0'. It is important to note that infrared thermography tools have already proved their usefulness for designing, testing and characterizing shape memory polymer-based devices, improving both control over the trials, results assessment and overall process security [36]. They have been also used once again, as an aid to testing the devices produced, for controlling the temperature at every instant in the different zones of the prototypes and for easily following the geometric changes, once the activation temperature of the zones of interest is exceeded. Main results from the prototyping process and from the shape-memory trials are included and discussed in the following results section.

3. Results and discussion

3.1. Results from prototyping and shape-memory effect activation trials

The laser stereolithography system used, working upon the designed test probe, has helped us to check that inner channels down to 0.6 mm can be obtained. Furthermore, wall thicknesses down to 0.5 mm are also attainable. In addition, as shown in figures 2 and 3, prototypes are manufactured with remarkable precision; all designed vasculatures for the micro-claw and spring actuators can be obtained, according to the expected results with the test probes. It is interesting to note that even curved and complex-shaped micro-vasculatures with hollow cross-section diameters down to 0.6 mm can be
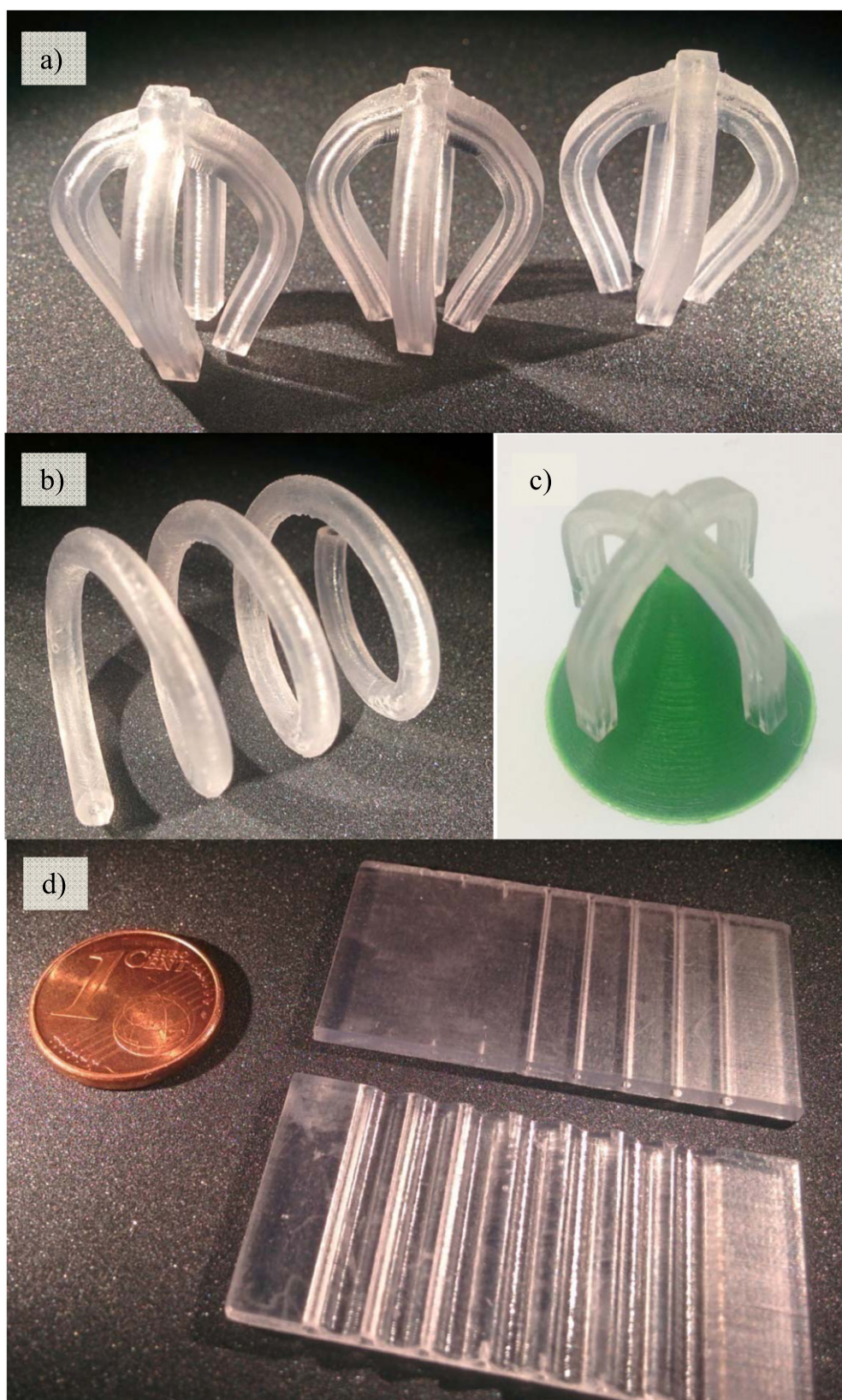
Figure 2. Rapid prototypes of the micro-vascular shape-memory polymer devices and probes under study, obtained by laser stereolithography via additive photo-polymerization of epoxy resin: (a) Micro-claw with inner vasculatures of different sections. (b) Active spring with inner vasculature. (c) Example of geometry obtained after the training process of the shape-memory effect. (d) Test probes for assessing the limits of the laser stereolithography additive manufacturing technology used for obtaining micro-channels.
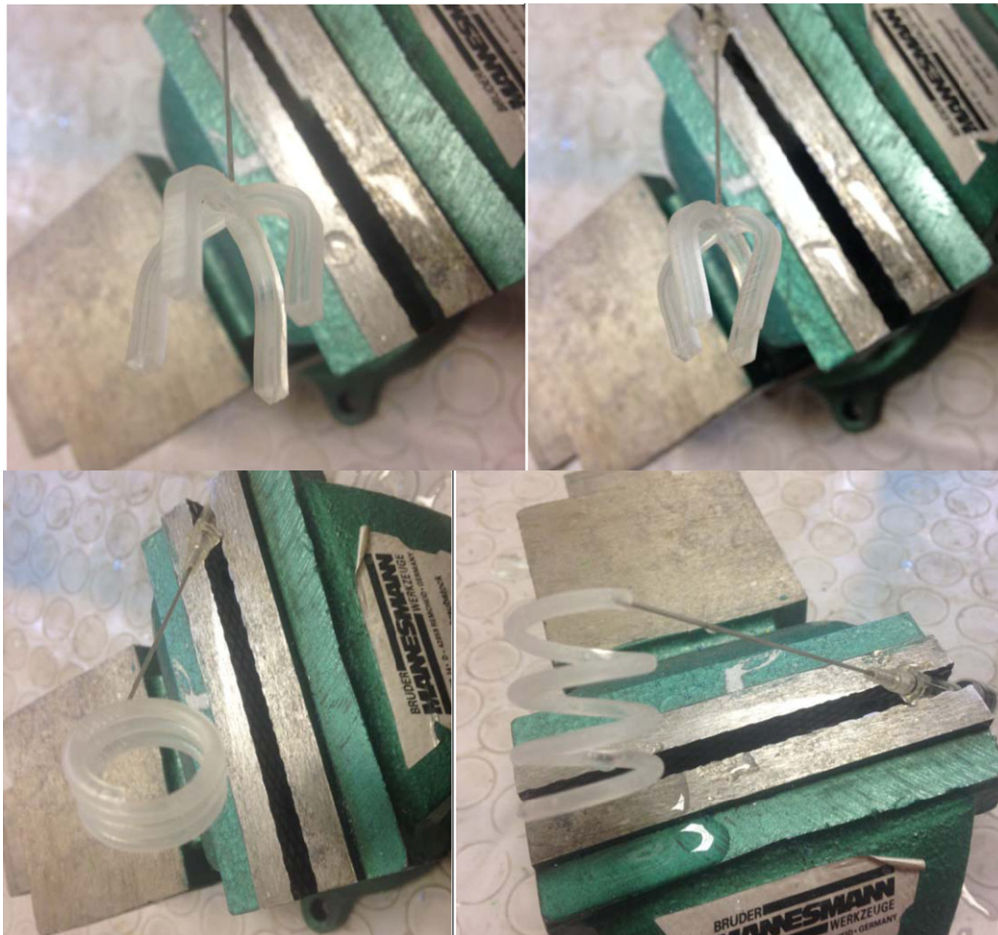
Figure 3. Results from shape-memory effect activation: the micro-claw closes and the spring expands due to the heating effect of the injected water running through the micro-vasculatures.

manufactured. However, in order to benefit from such degree of precision, it is important to inject compressed air, water or (even better) acetone into the inner channels, just after extraction of the prototypes from the stereolithography machine, immediately after photo-polymerization is accomplished, in order to avoid the drying and subsequent polymerization or eventual pre-polymer rests, which may block the micro-vasculatures.

After manufacture, elimination of support structures, eventual manual polishing, cleaning with acetone and shape-memory effect training, the prototypes are connected to a syringe and mounted in a work bench for injecting hot water and analyzing the activation process. For validation purposes we have carried out the study of the whole shape-memory process using the prototypes with the smaller micro-vasculatures (with 0.6 mm of cross-section diameter). The selection is based on criteria including: the availability of standardized syringes with such outer diameter; the additional mechanical endurance of the prototypes, which due to having a thinner vasculature have thicker walls and the lower volume of thermal fluid used. Even more relevant is our wish to evaluate the performance in the more complex conditions, as thicker walls lead to larger gradients of temperature from the inside to the outside, which complicates the process of heating the whole body above the activation temperature. This also proves more fair for

comparative purposes with previously assessed activation alternatives for SMP based devices, as the wall thicknesses of around 2–3 mm of the prototypes used here are similar to those of previous approaches discussed in section 3.2. The training of the shape-memory effect is carried out by heating the prototypes in water at 80 °C (sufficiently above the activation temperature of the epoxy which lays between 58 °C and 62 °C) and by forcing against a planar surface towards full compression, in the case of the spring, and against a rapid prototyped green cone obtained by fused deposition modeling, as shown in figure 2(c), in the case of the micro-claw.

Figure 3 shows the results from shape-memory effect activation: the micro-claw closes and the spring expands due to the heating effect of the injected water running through the micro-vasculatures. The process lasts between 15 and 18 for the active pincer and between 17 and 20 s for the active spring, and leads to almost complete recovery of the original geometries in both cases, as described further on in section 3.2, when dealing with the discussion and future directions.

3.2. Discussion and future directions

The prototypes obtained help to validate the use of laser stereolithography for the development of 3D micro-

Table 2. Comparative summary of the typical temperature variation ranges, obtained in shape memory polymeric devices during their activation process, by using different heating strategies.

Heating element	Typical temperature variation range within the polymer (according to real trials)	Recovery ratio (*)	Reference
Heating resistors	50 °C–60 °C	>80%	[10], [36], [37]
Peltier devices	40 °C–50 °C (in the heated zone)	>85%	[19]
Induction heating (coil core)	35 °C–45 °C	>80%	[10]
Induction heating (nanoparticles)	<15 °C	≈100%	[16], [20]
Light activation (laser heating)	<10 °C (very thin device)	≈100%	[21]
Electrotextiles	33 °C–37 °C	>95%	[22]
Conductive threads	25 °C–29 °C	≈100%	[22]
Conductive inks	18 °C–24 °C	>85%	[22]
Fluid through micro-vasculature	3 °C–7 °C	>85%** >85%***	Present study

Note: *We have used a recovery ratio for the micro-claw** according to: $R_r = (\theta_t - \theta_r)/(\theta_t - \theta_0)$; being θ the angle formed among the tangents to the prototypes on their extremes: θ_0 before training, θ_t after training and θ_r after recovery. For the spring*** we use the expression: $R_r = (L_t - L_r)/(L_t - L_0)$; being L the length of the spring in the different moments (before and after training and final state).

vasculatures aimed at finally obtaining micro-vascular SMPs with pre-defined and complex three-dimensional geometries. The test probe also helps us to assess the potential of laser stereolithography for the manufacture of micro-vasculatures and to check that, with our SLA-3500 machine by 3D Systems, hollow structures down to 500 microns of cross-section diameter can be obtained. Other additive manufacturing resources, also based on photo-polymerization, such as Object or 2PP, may go down beyond such limit, allowing for the manufacture of hollow structures with details in the range of 50–250 μm, although typically for much smaller devices. Currently laser stereolithography is still one of the most remarkable technologies for obtaining an adequate compromise between attainable final part sizes and manufacturing precision.

Regarding the benefits of the micro-vasculature for activating SMPs and related devices, table 2 includes a quantitative summary of the typical temperature variation ranges, obtained in shape memory polymeric devices during their activation process, by using different heating strategies. Main results from present study are also included, together with some data from previous experiences by our team (linked to using heating resistors [10, 35, 36], Peltier devices [19] and surface coatings and textiles [22] as activation elements) and with information taken from ground breaking research in the field of shape memory polymers.

While in solutions using single or multiple heating resistors, among devices with typical dimensions similar to the ones studied here, typical temperature variation ranges reach values of 50 °C–60 °C during the heating process, the solutions analyzed here lead to more homogeneous heating processes [10, 31, 32], especially those based on the use of conductive thread with Ag nanoparticles and ink with carbon particles. The use of Peltier devices also leads to variation ranges around 40 °C–50 °C in the heated zone, although differences of more than 70 °C between both sides of the Peltier device have been registered, what has proved to be useful for sequential activations [19]. Resistive and inductive heating, using coils embedded into the devices, also leads to

important variation ranges [10] and the mechanical influence of the embedded coils can be problematic for the training and recovery stages. In any case, currently induction heating is probably the best strategy for a homogeneous heating, when using shape memory polymers with embedded nanoparticles; with the advantage of being contact-less, what can promote the activation of implantable devices from outside patient's body [37–39]. Although some of the references [20, 39] do not provide a quantitative evaluation of temperature differences among the polymer during the heating process, the process is highlighted as homogeneous.

In addition, the excellent review by Leng and colleagues [16] includes thermographs, in which such typical variation ranges, for solutions based on nanoparticles, can be clearly appreciated. The use of low-cost electrotextiles and conductive coatings is also of interest, although the homogeneity is not as remarkable as using nanoparticles [22]. Another interesting alternative, for promoting homogeneous and effective heating, is the use of the shape memory polymer as a wave guide for a laser that heats the polymer, typically referred to as light activation [21]. The heating process seems to be very uniform, although quantification is not included and the prototypes shown in the mentioned reference are very thin, which may promote uniformity.

In the experiments presented here, the low 2–3 mm thicknesses of the prototypes have helped to limit the cross-sectional temperature gradients below 5 °C, but the mentioned limitation has to be taken into account when trying to use micro-vasculatures to activate shape-changes of thicker parts. To that purpose, resorting to analytical methods [23] and to FEM based simulations [25] may provide designers with relevant information, towards further improvements. It will be interesting to follow progresses in the different strategies, as well as combinations among them, especially due to the continuously evolving families of shape memory polymers [37, 38], to novel approaches enabling tunable multi-shape memory effects [40] and to recent advances in self-healing applications [41–44], where homogeneous heating is a critical

aspect. The use of micro-vasculatures is for sure an option with remarkable potential.

Summarizing, the proposed development process of micro-vascular SMPs provides interesting advantages, when compared to more traditional process, mainly linked to: (a) the possibility of obtaining CAD controlled geometries of complex SMP actuators, which in many cases may provide improved functionalities; (b) the capability of generating intricate inner vasculatures, capable of providing a quite homogeneous activation process thanks to the use of a thermal fluid; and (c) the potentials of rapid prototyping, thanks to directly linking the CAD with the final devices in a single manufacturing step. Furthermore, the use of CADs may even help to incorporate the shape-memory actuator to a certain zone of a predesigned component, in order to incorporate some functionality to a concrete region of a device. Such knowledge-based designs, which may include gradients of mechanical, thermal, electrical and even optical properties, can be then obtained in a just a single step thanks to additive manufacturing resources.

However, apart from referring to the benefits of the proposed approach, it is also important to cite some drawbacks and present challenges and to mention potential research strategies towards improved results:

A relevant limitation of using laser stereolithography for developing SMP based actuators is linked to the fact that the available materials are mainly limited to epoxy or acrylic photopolymers. Only two providers (3D Systems and Somos) supply materials verified for our SLA-3500 manufacturing system and, even their resins approved for the medical device industry under ISO 10993 (i.e. Somos' WaterShed®XC 11122 and Somos' ProtoGen™ 18420), checked for irritation, sensitization and cytotoxicity, can just be used for devices used as supporting tools for surgical, for anatomical modeling and for temporary contacts with skin, but clearly not for implantable devices. In addition, the activation temperatures of these polymers are typically in the range of 50 °C–70 °C, as we have previously detailed for our 3D Systems' Accura60®, which constitutes an additional drawback for the development of devices aimed at interacting with the human body.

In consequence, medical applications, which constitute one of the more relevant fields of application of SMPs [3], are currently very limited. Fortunately, advances in materials science applied to additive manufacturing via photo-polymerization are providing new materials for stereolithography with enhanced biological response and great potential for the development of medical applications [32–34, 45], although their eventual shape-memory properties still need to be assessed.

Alternative 3D printing processes, such as fused deposition modeling, are currently more adequate for working with thermoplastic polymers with verified shape-memory properties and remarkable biological response, being in some cases even biodegradable, which may clearly promote the development of active implantable medical devices. For instance, filaments of poly(caprolactone), poly(L-lactide) and poly(lactide-co-glycolide) have been printed, using image based design and indirect solid freeform fabrication, and verified as biodegradable tissue engineering scaffolds [46].

The typical shape-memory properties of these materials may add up to the functionalities of such devices and of novel medical actuators. However, the prototypes obtained by low-cost 3D printing technologies, including fused deposition modeling, lead to porous surfaces and have therefore reduced applicability to the development of micro-vascular SMP actuators, which require inner vasculature with well defined surfaces for allowing flow and preventing leakage. In addition, the precision of additive manufacturing processes based on photo-polymerization is still unmatched by other 3D printing process, which may clearly contribute to the application of the procedure presented here to the development of minimally invasive surgical actuators, once the challenges linked to materials' biological response are solved.

Regarding stress recovery, the SMP based actuators attainable by laser stereolithography are able to generate stresses during their recovery in a typical range of 5–8 MPa, according to previous research [10]. The value, even though being in the same order of magnitude of many commercially available SMPs, is quite low when compared with more recent SMP composites. For instance, the maximal stress generated by a CNT/polyvinyl alcohol shape-memory fiber reached 150 MPa, which is a value two orders of magnitude higher than that of neat SMPs and more than one order of magnitude higher than that of photo-polymerized actuators [47], as recently reviewed in the comprehensive work by Meng and Li [38]. However, the incorporation of (nano-) fibers or (nano-)particles to the pre-polymer vat is not yet a possible technological solution for the three-dimensional additive manufacture of SMP composites, as the fibers and particles scatter the laser beam and affect the manufacturing process in a negative way. We hope that the limitations detailed will serve as motivation towards future research aimed at improving the capabilities of micro-vascular SMP actuators obtained via additive photo-polymerization.

4. Conclusions

Present study has focused on and presented the complete development process of geometrically complex micro-vascular SMP actuators. The complex geometries and three-dimensional networks have been designed, assessed *in silico* and optimized by means of computer aided design and engineering resources (FEM-based simulations). Manufacture has been accomplished, directly from the CAD files with the three dimensional geometries of the different actuators under development, by means of laser stereolithography, which has provided an excellent compromise between part size and precision and which has proved to be very adequate for the manufacture of inner micro-vasculatures. The proposed approach can be applied to the development of very complex micro-vascular SMP composites and related actuators, based on the remarkable properties of this novel sub-family of SMPs, towards improved functionalities and versatility. Challenges regarding the use of the micro-vasculatures for

promoting the activation using other physical principles and linked to the combination of heating/cooling strategies for an improved control of actuator response will be issues of study for the future. We truly hope that the presented results may be of interest for colleagues carrying out research in these areas.

Acknowledgments

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