DESIGN OF MECHANICAL METAMATERIALS FABRICATED VIA TWO-PHOTON LITHOGRAPHY AND ATOMIC LAYER DEPOSITION

Doctoral Thesis

Author(s):
Diamantopoulou, Marianna

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DESIgn OF MECHANICAL METAMATERIALS

FABRICATED VIA

TWO-PHOTON LITHOGRAPHY AND ATOMIC LAYER DEPOSITION

A thesis submitted to attain the degree of

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presented by

MARIANNA DIAMANTOPOULOU

MSc  ETH in Process Engineering

born on 19.06.1991
citizen of Greece

accepted on the recommendation of

Prof. Dirk Mohr
Prof. Ralph Spolenak
Prof. Eleftheria Roumeli

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Abstract

Two-photon polymerization has enabled the fabrication of micro- and nanoscale components with high resolution down to a few nanometers. The expansion of that technology has arisen a relatively new field of research at which the length scale effects of different materials combined with complex architectures have been explored for the past twenty years. Micro- and nanolattices consisting of several unit cells have been realized with the emergence of this technology.

A wide variety of materials (photoresists) are utilized for achieving the low resolution feature size of 3D complex structures in the two-photon polymerization process. For modeling the behavior of structures made of various photoresist materials, researchers have investigated till now with a study-specific manner the mechanical properties of the desired photoresist with the aim of extracting information which can be used as inputs for the numerical analysis. However, a photoresist material can have properties which span over a large range and depend primarily the fabrication parameters chosen each time. Thus, in this work an extensive study is conducted by varying the fabrication parameters of the two-photon lithography technique and utilizing this information in order to train a model that can predict the mechanical behavior of different resins.

Additionally, there has been a long discussion regarding the trade-off between different properties that the microlattices exhibit. In specific, there is a sacrifice between recoverable ceramic microlattices and stiffness. It has been shown that ceramic microlattices exhibit shape recoverability upon unloading during an uniaxial compression test. The recoverability, however, deteriorates as the ceramic coating becomes thicker; simultaneously though the stiffness of the lattice is higher. Double-wall tube architecture is proposed as an alternative design to overcome this trade-off between recoverability and enhanced stiffness compared to the most investigated single-wall tube architecture.

Finally, a well-established engineering concept, the sandwich construction is implemented for the purpose of this thesis in order to fabricate microlattices with sandwiched-walls. The sandwiched-wall triply periodic minimal surface microlattices
exhibit high energy absorption with an optimum weight fraction of alumina in the sandwich at 40% when the macroscopic density of the lattice is kept constant and as low as 42 kg m$^{-3}$. At higher densities, it is shown that 10% weight fraction of alumina already outperforms the mechanical response in terms of peak stress and energy absorption compared to sandwich lattices of 20-60% alumina weight fraction. This finding proposes that the sandwich concept when implemented on lattices’ walls has a tremendous benefit on the mechanical attributes as compared to monolithic polymer lattices of equal density.
Zusammenfassung


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1 General Introduction

1.1 Motivation

The development of several additive manufacturing processes in the recent years has made possible the fabrication of complex 3D geometries ranging several length scales from a few nanometers to centimeter feature size [1–6]. The periodic repetition of a unit cell of specific architecture creates lattices with exceptional mechanical properties, the mechanical metamaterials [7]. Especially, microlattices can be fabricated with the two-photon lithography technique, a process able to achieve feature size in the nanometer scale [1,8]. The resulting microlattices, as fabricated through this process, are made out of polymer, as the base material used in this technique is a photosensitive solution of monomers and photoinitiators, the photoresist material [9,10].

Further fabrication steps can result in creating composite [11], ceramic [12] or metal lattices in the micrometer scale [13]. Combining different fabrication processes with optimized topology of the lattices is one major field of research in order to overcome structural weaknesses [7,14] as well as to examine scale effects of specific materials [15]. Researchers have drawn their attention in three different aspects: i. The optimization of the architecture of the 3D lattice in respect to leveraging specific properties [16–18], ii. The investigation of the length scale effects for certain materials [13,15,19], iii. Process-specific research in the field of micro- and nanofabrication [20]. The motivation behind this work is to utilize the developments in the abovementioned three aspects in order to push the limits and expand the up-to-date knowledge of the micro- and nanomechanics both in terms of materials’ and possible architectural designs’ selection.
1.2 Objectives

The objectives of this thesis derive from the: i. Process-, ii. Architecture- and iii. Material-oriented aspects of mechanical metamaterials in the micro- and nanoscale. The following chapters focus on one aspect of each.

Firstly, this thesis targets at expanding the knowledge of how the fabrication parameters in two-photon lithography can affect the mechanical properties of the final polymer structure. Researchers till now conduct studies on characterizing the photoresist material in order to be able to use this information as inputs in numerical analysis [12,21]. The idea behind the first part of this thesis is to fully characterize two commercially-available photoresists (IP-S and IP-Dip) in respect to the laser power used during the two-photon lithography by providing a quantification of the degree of cross-linking achieved, via Raman spectroscopy. Utilizing this information, the goal is to develop a neural network model which provides engineering stress and strain curves for each polymeric structure fabricated under different laser power. Thus, this work can be used as a prediction means of the mechanical properties of the 3D printed polymer for user-specific fabrication parameters.

The objective of the second part of this thesis is to use the architecture in order to overcome a long-lasting problem of sacrificing the stiffness of a structure in order to gain in recoverability (and thus energy absorption) [6,22–24]. The simple cubic hollow truss-architecture is used as the base geometry for creating microlattices via two-photon lithography. Then, the polymer microlattices undergo three further processes [8,11]: a. Atomic layer deposition of a ceramic (alumina in this case), b. Focused ion beam cuts of the cross-sectional areas and c. Oxygen-etching in order to have a final free-standing pure ceramic lattice, the double-wall tube microlattice. These lattices are then tested under uniaxial compression in order to derive their stiffness and validate their shape recoverability. Comparisons are then drawn between counterpart lattices of this new proposed architecture and the most investigated, the single-wall tube one. The goal is to use the double-wall tube architecture and benefit not only on the stiffness but also on the recoverability aspect.

Last but not least, the third part of this thesis has as objective the material-oriented aspect of mechanical metamaterials. The idea is to use the combination of two materials (alumina and the polymer as produced by the IP-S photoresist) in a sandwich
configuration in order to enhance the energy absorption capabilities in the field of micromechanical metamaterials [16,25,26]. Toward this end, another architecture is implemented, the triply periodic minimal surface topology for fabricating the lattices. By varying the alumina content in the sandwich configuration, and for different macroscopic densities of the overall sandwich triply periodic minimal surface lattices, optimal combinations of alumina and polymer weight fractions are discovered for which the energy absorbed by the lattices as well as the peak stress before the first collapse are maximized.

Summing up, all aspects of this thesis have as final aim the creation of design maps or design guidelines by which engineers and researchers can be advised prior to the fabrication of the desired lattices, by identifying the mechanical properties of interest and targeting the fabrication towards maximizing their potential. Additionally, all the abovementioned studies can be extended to several different architectures and the combination of different materials, with the hope to come up in the next few years with universal design maps covering all possible materials’ and architecture’s selection.
1.3 Structure of the Thesis

This thesis is divided into five chapters. Each chapter (Chapter 2 to 4) is self-contained and corresponds to either a study already published or submitted for publication. In Chapter 1, a general introduction including the motivation and objectives of this work is presented.

Chapter 2 introduces the study conducted for the characterization of two negative-tone photoresist materials widely used in two-photon lithography. The materials and the methods are presented, followed by the results and discussion of the experiments covering a wide range of fabrication parameters. The correlation of the mechanical attributes to the degree of conversion for each case is analyzed and finally the neural model developed is presented and discussed.

Chapter 3 presents the double-wall tube microlattices that exhibit high shape recoverability and enhanced stiffness. The fabrication route of this complex lattices is shown, the experimental results are discussed and the numerical analysis presents and compares the double-wall tube architected lattices to the single-wall tube lattices. This study expands the design space of recoverable yet stiff mechanical metamaterials and can be implemented to all geometries.

Chapter 4 provides the study that focuses on utilizing the traditional sandwich construction concept to the cell walls of triple periodic minimal surface lattices. The goal of this study is to vary the weight fraction of the ceramic material in the sandwich lattice and identify optimal fractions at which the energy absorption of the lattices maximizes. Selected fabricated lattices are presented and numerical analysis is conducted to cover a wide range of sandwich lattices’ macroscopic densities.

A summary and possible future research expanding this work are discussed in Chapter 5. At the beginning of each chapter, a coherent and topic related introduction is presented.
2 Stress-Strain Response of Polymers: Micro-scale Experiments and Neural Network Modeling


2.1 Introduction

Two-photon lithography (TPL) is nowadays widely used in the creation of 3D structures with micro- and nano-scale feature sizes down to a few nanometers [27–33]. Due to the low feature size resolution achieved, TPL has made feasible the fabrication of complex nano- and micro-scale structures, such as microrobots [34–36], microactuators [37,38], micro-architected mechanical metamaterials [14,39–42], biomedical components [43–47] and chip-to-chip interconnects [48,49]. The remarkable resolution arises from the simultaneous absorption of two near-infrared photons, which results in a collective energy in the UV spectrum [27].

Many parameters influence the resulting resolution quality such as: laser characteristics (wavelength of laser of the femtosecond pulses), writing parameters (laser power, exposure time, aperture of objective lens, writing speed etc.), as well as the sensitivity of the chosen photoresist [27]. The abovementioned parameters influence the kinetics of the polymerization reaction taking place in the focal voxel, which determines the degree of conversion (DC) of the written structures [50–54]. Especially in acrylate-based resins, the DC is the reflection of the degree of cross-linking between the polymer chains during polymerization [9,55–57]. It has been shown that the DC is the most crucial factor for the mechanical response of micro-fabricated 3D lattices [58], so that a thorough experimental understanding and estimation of the DC is essential for different photoresist materials.

Several methods have been used to experimentally estimate the DC of polymers, such as differential scanning calorimetry (DSC) [59], Fourier transform infrared spectroscopy (FTIR) [60,61], Raman spectroscopy [9,10,56,57,61–63] and coherent anti-
Stokes Raman scattering spectroscopy (CARS) [55,64,65]. For the purposes of the current work, Raman spectroscopy is employed, as it is non-destructive, enables the probing of small volumes and is simultaneously very sensitive to the stretching vibration of the double carbon bond, which is essential for the estimation of the DC [61].

Via Raman spectroscopy, a spectrum is acquired in a desired range which in the case of acrylate-based materials lies approximately between 1600 cm\(^{-1}\) to 1800 cm\(^{-1}\) [9,57,61]. In that range, two peaks are of interest for the characterization of the degree of conversion. The first one at around 1638 cm\(^{-1}\) corresponds to the vibrational mode of the double bond of carbon (C=C) and the second one at around 1720 cm\(^{-1}\) is ascribed to the vibrational mode of the double bond between carbon and oxygen (C=O) of the monomer units [9,64]. During the polymerization process, the intensity of the peak at 1638 cm\(^{-1}\) that corresponds to the double bond of carbon is reduced because this bond opens homolytically and converts to simple bond (C-C) [64]. The DC depends directly on the bell-shaped areas corresponding to the abovementioned peaks, with a reduction of the area at 1638 cm\(^{-1}\) related to a higher degree of conversion [64].

It has been shown that the degree of conversion is influenced significantly by both the laser power and the writing speed in the TPL process [9]. More specifically, the higher the writing speed (from 20 µm s\(^{-1}\) to 80 µm s\(^{-1}\)) the lower is the DC (from 42% to 35% respectively) [30]. However, the laser power in the TPL process is the most crucial factor, as it has been shown that for a constant writing speed there is a two-fold increase in the degree of conversion when the laser power is increased from 8 mW to 15 mW [9,66]. Therefore, in the current work, the writing speed is chosen to be constant and as low as possible in order to thoroughly investigate the influence of the laser power on the resulting DC of the printed materials [67].

In the current work, the relationship between the mechanical properties of negative-tone photoresist materials and the degree of conversion achieved during two-photon polymerization is derived using a hybrid experimental-numerical approach. Firstly, specimens covering a wide combination of design parameters (photoresist material, wall thickness, laser power) are fabricated. Subsequently, uniaxial compression experiments at different strain rates are conducted to determine their stress-strain response up to 30% strain. Raman spectroscopy is employed to estimate the degree of conversion.
as a function of the laser power employed in the fabrication process. Based on the experimental results, neural network models are developed to predict the stress-strain curves as a function of the degree of conversion.

2.2 Materials and methods

2.2.1 Triangular honeycomb preparation

Triangular honeycomb structures of different wall thickness, 5 µm and 10 µm, are fabricated with the use of two-photon lithography in a direct laser writing system (Pho- tonic Professional GT, Nanoscribe GmbH). The excitation source is a femtosecond laser with emission center wavelength at 780 nm, pulse width at approximately 100 fs and repetition rate of 80 MHz. Two negative-tone photoresist materials (resins) are used, IP-S and IP-Dip, commercially available and supplied by Nanoscribe GmbH. A 63× microscope objective lens with a numerical aperture of 1.4 was chosen to focus the laser beam in the resins. The laser power provided by the system during the fabrication is varied for the different structures from 14 mW to 20 mW. The writing speed is set to 10 mm s⁻¹ and the target overall dimensions of the structures are 50 × 43.3 × 70 µm³. Glass substrates of 25 × 25 × 0.7 mm³ are used for the fabrication process, prior cleaned with isopropyl alcohol in ultrasonic bath for 10 min. After the fabrication process is completed, the structures are developed for 15 min (12 min in developer mr-Dev 600 (Micro Resist Technologies GmbH, Berlin, Germany) and 3 min in isopropyl alcohol) and then are dried with a nitrogen gun. A schematic of the fabrication process is shown in Figure 2-1.
2.2.2 Scanning electron microscopy (SEM)

The honeycomb structures are characterized after fabrication with respect to their structural integrity and target dimensions, using scanning electron microscopy (Scios Dual Beam, FEI). The dimensions of the structures were $50 \times 44 \times 69 \, \mu\text{m}^3$ with a maximum error of $\pm 1 \, \mu\text{m}^3$ per dimension for all created specimens. The relative density of honeycomb specimens with 5 $\mu$m and 10 $\mu$m wall thickness is 0.71 and 0.99 respectively.

2.2.3 Mechanical characterization

Uniaxial compression experiments were conducted with the use of a custom-made, displacement-controlled microtesting device. The device is described in detail in [14]. The displacement of a flat punch ($1 \, \text{mm} \times 0.5 \, \text{mm}$) that compressed the structures was monitored with the use of an optical microscope (Keyence VHX-5000). Digital image correlation (VIC-2D, Correlated Solutions) was employed to obtain the displacement of the punch. The force that the structures experienced during the compression was measured via a strain-gaged load cell (Omega, LCAE 6N). Different compression speeds were employed to investigate the sensitivity of the mechanical response to small strain-rate variations. The compression speeds were chosen such that the strain-rates
imposed were 0.005 s\(^{-1}\), 0.01 s\(^{-1}\) and 0.02 s\(^{-1}\). The strain-rates investigated correspond to a quasi-static response, with the range primarily dictated by the compression speed limits of the motor controlling the displacement of the punch.

From the experimental force-displacement data, the stress-strain response of the bulk material is determined. Instead of using fully-dense cylindrical specimens (upsetting tests), honeycomb specimens are employed to delay the onset of buckling when testing thin-walled material. It is emphasized that the stress field in the cell walls of a honeycomb is of uniaxial nature when they are subject to out-of-plane compression. The engineering stress acting on the constituent material can thus be conveniently computed when dividing the measured force by the net cross-sectional area, i.e. the cross-sectional area of the fully-dense honeycomb cell walls. For the honeycomb specimens of 5 µm wall thickness, this area is approximately 0.0011 mm\(^2\), while for the case of 10 µm wall thickness the cross-sectional area is around 0.0016 mm\(^2\). The engineering strain is estimated by dividing the displacement with the undeformed height of each specimen. The apparent Young’s modulus is then estimated from the slope of the linear initial part of each engineering stress-strain curve. The terminology “apparent Young’s modulus” is employed to acknowledge possible visco-elastic effects. The tangent modulus is computed from the slope from a linear approximation of the stress-strain curve in the 5% to 25% strain region. The deformation resistance is calculated by averaging the stresses over the same strain interval (5% to 25% strain).

The combination of the fabrication parameters discussed in Section 2.2.1 and of the varying strain-rates result in 48 unique uniaxial compression experiments. With a repeatability of minimum 3 experiments, a minimum total number of 140 experiments is realized. In Table 2-1, the different experimental parameters under investigation are summarized.
Table 2-1. Parameters investigated in this study. Four laser powers, three strain-rates, two photoresist materials and two honeycomb designs are selected. The combination of these parameters results in 48 unique mechanical sets of experiments with a repeatability of minimum 3 experiments for each case.

<table>
<thead>
<tr>
<th>Laser power, [mW]</th>
<th>Strain-rate, [s⁻¹]</th>
<th>Photoresist material</th>
<th>Wall thickness, [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.005</td>
<td>IP-S</td>
<td>5</td>
</tr>
<tr>
<td>16</td>
<td>0.01</td>
<td>IP-Dip</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2.4 Estimation of the degree of conversion (DC)

In order to quantify the DC for each structure, Raman spectroscopy was employed. The honeycomb structures were fabricated onto fused silicon substrates in a horizontal orientation in order to provide a larger area for obtaining spectra at three different positions throughout the surface of the honeycomb (Figure 2-2a). For the acquisition of the spectra, a Raman system (Horiba: LabRAM HR Evolution) equipped with a 785 nm high power signal frequency diode laser (Toptica XTRA II) with maximum laser power of 300 mW was used. Each spot on the surface of the structure during the measurement was exposed to 100% of the laser power twice, with an exposure time of 30 s each. The laser beam was focused on each structure with the use of an upright microscope (Olympus BX) and a 100× objective lens. These measurement conditions were applied to all structures.

A typical spectrum obtained by Raman spectroscopy is shown in Figure 2-2a. A baseline correction is applied to all spectra. Furthermore, the acquired data are normalized for the C=O peak. The areas of the peaks of interest corresponding to the double carbon and double carbon to oxygen bonds are indicated with different color shades in Figure 2-2a. Raman spectra are as well obtained on a droplet of the unpolymerized resin for both materials, IP-S and IP-Dip (Figure 2-2b). For the IP-S material, the peak of the vibrational mode of the C=C bond appears at 1640 cm⁻¹ and of the C=O bond at 1715 cm⁻¹, while for the IP-Dip the corresponding peaks are found at 1636 cm⁻¹ and 1723 cm⁻¹.
Materials and methods

The minor shift in-between the peaks of the liquid resins is in agreement with observations found in the literature [61].

Figure 2-2. (a) Typical Raman spectrum of a triangular honeycomb structure printed in horizontal orientation with indications of the peaks and corresponding areas at 1636 cm$^{-1}$ and 1723 cm$^{-1}$. (b) Raman spectra obtained on droplets (unpolymerized) IP-S and IP-Dip resins. Scale bar is set at 25 µm.

Finally, the $DC$ is calculated with the use of the formula [9,10,57,61,64]:

$$DC\% = 1 - \left[ \frac{(A_{C=C}/A_{C=O})}{(A_{C=C}^{\text{resin}}/A_{C=O}^{\text{resin}})} \right] \times 100 \quad (2-1)$$

where $A_{C=C}$, $A_{C=O}$, $A_{C=C}^{\text{resin}}$, $A_{C=O}^{\text{resin}}$ are the integrated Raman peaks ascribed to the double carbon bond and double carbon-oxygen bond moieties in the polymerized structures and in the unpolymerized resins respectively.

2.2.5 Neural network model

Machine learning algorithms have been successfully utilized in the context of two-photon lithography to automate the evaluation of the printing quality and to identify optimal laser dosage for printing a high quality structure with minor defects [68,69]. Here, neural network (NN) models are developed to predict the stress-strain response of polymers made through two-photon lithography (Section 2.2.1) as a function of the degree of conversion. Using the stress as output variable, two primal parameters are used as inputs of the neural network models: the engineering strain and the degree of
Stress-

Strain Response of Polymers: Micro-scale Experiments and Neural Network Modeling

conversion DC, obtained through the Raman spectroscopy process elaborated in Section 2.2.4. For the training, a minimum of two experimentally obtained stress-strain curves are used at each laser power magnitude, with 20% of the data used for validation and an independent experimental curve used for testing for each case. At a given strain-rate and laser power (Table 2-1), the stress-strain and DC results obtained for the 5 µm and 10 µm wall thickness honeycombs are merged for each base resin material case (IP-S, IP-Dip). Feed-forward network architectures are parsed with n number of hidden layers and m nodes per layer, as schematically depicted in Figure 2-3. For the training process, different activation functions are probed, including the hyperbolic tangent and sigmoid functions [70]. During the training process, the mean squared error function is used, defined as \[ \text{MSE} = \frac{1}{N} \sum_{i=1}^{N} (\bar{\sigma} - \sigma)^2 \] with \( \bar{\sigma} \) and \( \sigma \) to denote the NN predictions and the experimental stress values respectively. For the training, the Levenberg-Marquardt optimization algorithm is employed.

![Figure 2-3. Schematic of the neural network model of the mechanical response using as input parameters the strain and DC to predict the stress through a feed-forward architecture of n layers with m neurons per layer.](image)

2.3 Results and discussion

Scanning electron microscope (SEM) images of the two distinctive triangular honeycomb structures with wall thickness of 5 µm and 10 µm made of IP-S and 20 mW of laser power are shown in Figure 2-4a and Figure 2-4d respectively. For a strain-rate of 0.005 s\(^{-1}\), the corresponding engineering stress and strain curves for the 5 µm and the
10 µm honeycombs made of IP-S and IP-Dip are shown in Figure 2-4(b-c) and Figure 2-4(e-f).

Figure 2-4. Scanning electron microscopy images of a triangular honeycomb with wall thickness of (a) 5 µm (cross-sectional area equals 0.0011 mm²) and (d) 10 µm (cross-sectional area equals 0.0016 mm²) made of IP-S and 20 mW laser power. Engineering stress and strain curves for IP-S (b and e correspond to 5 µm and 10 µm wall thickness) and IP-Dip (c and f correspond to 5 µm and 10 µm wall thickness) at a strain-rate of 0.005 s⁻¹ and increasing laser powers (from 14 mW to 20 mW). Scale bar is set to 25 µm.

On each graph four distinct curves are depicted (Figure 2-4(b-c) and Figure 2-4(e-f)), each corresponding to a different laser power used during the TPL process. More specifically, Figure 2-4b and Figure 2-4e provide the results for the case of 5 µm and 10 µm wall thickness specimens made of IP-S for different laser powers. Changes in laser power have a noticeable quantitative effect on both the low-strain linear part (approximately up to 5% strain) as well as the large deformation part (5% to 25% strain). The higher the laser power, the higher the slope of the linear part, and the higher the stress level of the nonlinear part. The comparison of the respective top and bottom row plots (Figure 2-7) reveals that the effect of the wall thickness on the obtained stress-strain curves is statistically insignificant (within the range of experimental uncertainty).
The quantitative effect of the laser power depends on the base resin. From comparing Figure 2-4b and Figure 2-4c, it becomes evident that the IP-Dip resin yields a substantially higher deformation resistance (for the same laser power) than the IP-S. For example, at an axial strain of 0.1, the yield stress of the IP-S increases from about 75 to more than 100 MPa when increasing the laser power from 14 to 20 mW. In line with the data reported in the open literature (e.g. [9,55,57]), the present results show that the constituent material properties achieved through direct laser writing are highly sensitive to the laser power used. Similar results are found for the stress-strain response of honeycombs for compression strain-rates of 0.01 s\(^{-1}\) (Figure 2-5) and 0.02 s\(^{-1}\) (Figure 2-6).

Figure 2-5. Engineering stress and strain curves for IP-S (a and c correspond to 5 µm and 10 µm wall thickness) and IP-Dip (b and d correspond to 5 µm and 10 µm wall thickness) of the uniaxial compression experiment with strain rates of 0.01 s\(^{-1}\) and increasing laser power (from 14 mW to 20 mW).
Figure 2-6. Engineering stress and strain curves for IP-S (a and c correspond to 5 µm and 10 µm wall thickness) and IP-Dip (b and d correspond to 5 µm and 10 µm wall thickness) of the uniaxial compression experiment with strain rates of 0.02 s⁻¹ and increasing laser power (from 14 mW to 20 mW).
Figure 2-7. Apparent Young’s modulus (in MPa) as calculated from the uniaxial compression experiments for different strain-rates (0.005 s\(^{-1}\) to 0.02 s\(^{-1}\)) and increasing laser power (from 14 mW to 20 mW) for a honeycomb with a wall thickness of 5 µm (a-b) and 10 µm (c-d) respectively for both base resins.

Figure 2-7 provides the estimates of the apparent Young’s modulus for all strain-rates as a function of the laser power for both photoresist materials and honeycomb wall thicknesses. It is observed for all cases that augmenting the laser power results in an increased apparent Young’s modulus, with modulus increase of up to 50% when changing the laser power from 14 to 20 mW. The effect of strain-rate variations (from 0.005 to 0.02 s\(^{-1}\)) on the apparent Young’s modulus is insignificant as compared to the experimental uncertainty of the measurements for a given laser power (see error bars in Figure 2-7). As for the stress-strain curves shown in Figure 2-4, the modulus plots in Figure
Results and discussion

2-7 also show a negligibly effect of the wall thickness on the obtained results. On average, honeycomb specimens of 5 μm and 10 μm thick walls exhibit less than 7.5% difference in the apparent modulus for the same resin and laser power. In Table 2-2 a detailed summary of the experimental results is provided.

Table 2-2. Apparent Young’s modulus as derived from the uniaxial compression experiments for IP-S and IP-Dip for all structural configurations and combinations of parameters (wall thickness, laser power ($LP$) and strain-rates).

<table>
<thead>
<tr>
<th>$\dot{\varepsilon}$ [s$^{-1}$]</th>
<th>IP-S 5 μm</th>
<th>IP-S 10 μm</th>
<th>IP-Dip 5 μm</th>
<th>IP-Dip 10 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$LP$ [mW]</td>
<td>Apparent</td>
<td>Apparent</td>
<td>Apparent</td>
<td>Apparent</td>
</tr>
<tr>
<td>14</td>
<td>1177 ± 163</td>
<td>1301 ± 297</td>
<td>1428 ± 31</td>
<td>1422 ± 120</td>
</tr>
<tr>
<td>16</td>
<td>1342 ± 151</td>
<td>1365 ± 67</td>
<td>1489 ± 379</td>
<td>1556 ± 109</td>
</tr>
<tr>
<td>18</td>
<td>1525 ± 208</td>
<td>1397 ± 5</td>
<td>1676 ± 15</td>
<td>1566 ± 146</td>
</tr>
<tr>
<td>20</td>
<td>1563 ± 127</td>
<td>1501 ± 47</td>
<td>1730 ± 37</td>
<td>1739 ± 16</td>
</tr>
</tbody>
</table>

| 0.01            |           |            |             |             |
| 14              | 1441 ± 207| 1020 ± 1.2 | 1405 ± 17   | 1537 ± 55   |
| 16              | 1471 ± 253| 1366 ± 37  | 1596 ± 29   | 1644 ± 205  |
| 18              | 1566 ± 166| 1374 ± 35  | 1619 ± 71   | 1671 ± 49   |
| 20              | 1641 ± 19 | 1662 ± 54  | 1647 ± 84   | 1761 ± 23   |

| 0.005           |           |            |             |             |
| 14              | 1457 ± 28 | 1281 ± 6   | 1413 ± 123  | 1516 ± 154  |
| 16              | 1507 ± 289| 1296 ± 110 | 1620 ± 194  | 1662 ± 182  |
| 18              | 1523 ± 97 | 1494 ± 105 | 1647 ± 51   | 1716 ± 190  |
| 20              | 1569 ± 95 | 1545 ± 119 | 1687 ± 73   | 1750 ± 69   |

In summary we note that the mechanical response of the IP-S and IP-Dip materials is mainly sensitive to the laser power employed upon fabrication, while possible differences related to strain-rates and wall thicknesses fall within the experimental uncertainty at a given laser power. Thus, a grouping for all mechanical results with respect to the laser power is applied in the sequel. Figure 2-8 displays the mechanical attributes
of the IP-S and IP-Dip resins (Young’s modulus, tangent modulus and deformation resistance) after averaging over all strain-rates and wall thicknesses.

![Graphs showing stress-strain response](image)

Figure 2-8. (a) Young’s modulus, (b) tangent modulus, and (c) deformation resistance as a function of the laser power used during TPL (of IP-S and IP-Dip resins). The results are obtained after averaging over all strain-rates and wall thicknesses.

The results of Figure 2-8a indicate that the Young’s modulus for the IP-S material is $1279 \pm 150$ MPa, $1391 \pm 73$ MPa, $1480 \pm 70$ MPa and $1580 \pm 55$ MPa for the 14, 16, 18 and 20 mW laser powers, respectively. The results for the IP-Dip polymerized material yield a Young’s modulus of $1453 \pm 52$ MPa, $1594 \pm 58$ MPa, $1649 \pm 47$ MPa, and $1741 \pm 28$ MPa for the 14, 16, 18 and 20 mW laser powers (Figure 2-8a). These results highlight the conclusions of Figure 2-7, with a 10 to 15% higher Young’s modulus of the IP-Dip material as compared to IP-S.
Results and discussion

Not only the linear, but also the nonlinear stress-strain responses of the two resins exhibit significant differences. More specifically, the tangent modulus of the IP-Dip material is 155-181% higher that the one computed for the IP-S resin (Figure 2-8b), with the difference to depend on the laser power employed. Moreover, higher laser power yields higher tangent moduli for both resins (Figure 2-8b), with the increase in tangent modulus of the IP-Dip material approaching 50% for a laser power increase of 6 mW (from 14 mW to 20 mW). Accordingly, the deformation resistance of the IP-Dip (for a given laser power) is 30-33% higher than that for the IP-S (Figure 2-8c). In Table 2-3, a detailed summary of the tangent moduli and deformation resistances is given.

Table 2-3. Young’s modulus, tangent modulus and deformation resistance as derived from the strain range of 5-25% of the stress-strain curves of the IP-S and IP-Dip honeycombs after averaging over all strain-rates and wall thicknesses for each resin and laser power (LP).

<table>
<thead>
<tr>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1279.72 ± 150.59</td>
<td>160.59 ± 38.41</td>
<td>93.75 ± 7.68</td>
<td>1453.90 ± 52.58</td>
<td>414.83 ± 50.89</td>
<td>122.48 ± 6.13</td>
</tr>
<tr>
<td>16</td>
<td>1391.33 ± 73.66</td>
<td>181.11 ± 31.57</td>
<td>102.24 ± 4.72</td>
<td>1594.80 ± 58.22</td>
<td>474.89 ± 58.99</td>
<td>135.20 ± 3.64</td>
</tr>
<tr>
<td>18</td>
<td>1480.16 ± 70.03</td>
<td>189.02 ± 35.51</td>
<td>107.77 ± 4.42</td>
<td>1649.36 ± 53.20</td>
<td>532.02 ± 45.62</td>
<td>143.16 ± 6.09</td>
</tr>
<tr>
<td>20</td>
<td>1580.33 ± 55.38</td>
<td>204.01 ± 33.25</td>
<td>114.26 ± 4.63</td>
<td>1741.44 ± 57.24</td>
<td>572.46 ± 28.79</td>
<td>150.78 ± 4.96</td>
</tr>
</tbody>
</table>

Subsequently, the material composition arising from the TPL process for each base resin (IP-S, IP-Dip) and laser power is correlated with the above-reported mechanical results, using Raman spectroscopy. The latter is employed to characterize the degree of conversion (DC) of the obtained polymers. Each DC is directly linked to a laser power.
Figure 2-9a provides the Raman spectra as obtained for honeycomb specimens of 5 µm wall thickness, fabricated with IP-S resin and varying laser powers. On the upper part of Figure 2-9a, all spectra are simultaneously depicted, while on the lower part of Figure 2-9a, each spectrum is shifted in the vertical axis, so as to distinguish for the different laser power used. In Figure 2-9b, a magnified view of all spectra is provided.

Figure 2-9. (a) Raman spectroscopy of specimens of 5 µm wall thickness made of IP-S and varying laser power. On the lower section of the graph, the spectra for the different laser powers are shifted vertically for presentation purposes. (b) Magnified view of all spectra with a visible reduction in the area below the peak of the double carbon bond at 1640 cm⁻¹.

The spectra shown in Figure 2-9a exhibit the peaks of the vibrational mode for the double carbon bond and the double carbon-oxygen bond that appear at 1640 cm⁻¹ and 1715 cm⁻¹, respectively. In order to compute the DC corresponding to each spectrum, the areas below the peaks of each bond need to be estimated with the use of Equation 2-1. While the peak of the carbon-oxygen bond remains practically invariant upon varying laser power (Figure 2-9b) (an observation already reported in literature [10,64]), the peak of the double carbon bond decreases as the laser power increases (Figure 2-9b). More specifically, it can be observed that the peak with the highest intensity which corresponds to a honeycomb fabricated with a 14 mW laser power yields a degree of conversion of 29.3% (Figure 2-9b). As the peak intensity (and corresponding bell-shaped area) is decreasing (Figure 2-9b) upon increasing laser power (from 14 mW to 16, 18 and 20 mW), the corresponding DC increases to 32.9%, 37.1% and 39.6% respectively. This suggests that upon increasing laser power for the TPL process, less
Results and discussion

double carbon bonds are found in the structure after fabrication, a reduction which corresponds to an increase in the degree of conversion [64]. In Figure 2-10, we provide a comparison between the DC of honeycombs made of IP-S (Figure 2-10a) and IP-Dip resins (Figure 2-10b) for different laser powers and for both wall thickness values of Table 2-1 (5 μm and 10 μm).

The results of Figure 2-10a and Figure 2-10b indicate an increase in the degree of conversion upon increasing laser power for both resins and honeycomb designs. It can be also noted that the architecture of the honeycomb does not play a significant role for the degree of polymerization, with 5 μm and 10 μm feature honeycombs to have less than 4% difference in the mean DC value for each laser power level, a finding that is in close agreement with the differences observed in the mechanical analysis results of Figure 2-4 and Figure 2-7. However, a clear difference between the DCs of the two resins appears, with the IP-Dip yielding a higher DC (33.5%) for the minimum laser power employed (14 mW), as well as a higher upper limit (42.5%) upon 20 mW of laser power, when comparing to the corresponding results for the IP-S case (28.8% and 40.2% respectively for laser power of 14 mW and 20 mW), as shown in Figure 2-10c. It can be as well observed that for a certain laser power, the DC for the honeycombs made of IP-Dip is 6% to 16% higher than the corresponding results for the IP-S case (Figure 2-10c). Other research groups have also reported DC results as a function of the laser power but a direct comparison cannot be made due to different fabrication parameters chosen (photoresist material, writing speed) [9,10,61,64]. The detailed computations for the DC, for both resins and for all laser powers considered are summarized in Table 2-4.
Table 2-4. Degree of conversion (DC) and mean values as derived from the Raman spectroscopy measurements for IP-S and IP-Dip honeycomb structures fabricated by varying laser power and wall thickness.

<table>
<thead>
<tr>
<th>LP [mW]</th>
<th>IP-S</th>
<th>IP-Dip</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 µm</td>
<td>10 µm</td>
</tr>
<tr>
<td></td>
<td>DC [%]</td>
<td>DC [%]</td>
</tr>
<tr>
<td>14</td>
<td>28.77 ±</td>
<td>28.83 ±</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td>1.32</td>
</tr>
<tr>
<td>16</td>
<td>32.30 ±</td>
<td>33.57 ±</td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>1.23</td>
</tr>
<tr>
<td>18</td>
<td>36.71 ±</td>
<td>37.98 ±</td>
</tr>
<tr>
<td></td>
<td>0.98</td>
<td>1.05</td>
</tr>
<tr>
<td>20</td>
<td>40.45 ±</td>
<td>39.99 ±</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Results and discussion

Figure 2-10. Degree of conversion (DC) as a function of the laser power for (a) IP-S and (b) IP-Dip honeycombs of 5 µm (left section) and 10 µm (right section). (c) Mean degree of conversion as a function of the laser power for both IP-S and IP-Dip honeycomb structures resulting from averaging the DCs for both wall thickness cases for each laser power. (d) Young’s modulus and deformation resistance as a function of the mean degree of conversion for both IP-S and IP-Dip polymers. Full symbols correspond to the deformation resistance values (secondary axis).

The Young’s modulus and the deformation resistance are plotted as a function of the mean degree of conversion in Figure 2-10d for the IP-S and IP-Dip resins. For both photoresists, achieving a higher degree of cross-linking during photopolymerization results in a higher Young’s modulus and deformation resistance. The observed relationship is of linear nature which is in qualitative agreement with the findings of Bauer et al. [57]. For selected experiments, a quantitative agreement with results from literature is observed. Bauer et al. [57] show that a multi-voxel line specimen made of IP-Dip
with DC=44% exhibits a compressive stress of approximately 145 MPa at a strain of 0.1. In this work, the honeycomb structure with 5 µm wall thickness and similar degree of conversion (DC=42.1%) made of IP-Dip (Figure 2-10b) exhibits an engineering stress of 137 MPa for the same strain (Figure 2-4c). The experiment on a honeycomb specimen (10 µm wall thickness, IP-Dip, DC=43.0%, Figure 2-10b) exhibits an engineering stress of 108 MPa at 0.07 strain (Figure 2-4f), while Bauer et al. [57] report a compressive stress of around 100 MPa at the same strain. Aside from experimental uncertainty, differences in the measured mechanical properties may be attributed to differences in the curing techniques, writing speeds, strain-rates and stress states.

The degree of conversion obtained from Raman spectroscopy for each laser power is used along with the corresponding stress-strain response of the specimens of 5 µm and 10 µm wall thickness for a strain-rate of 0.005 s⁻¹ to train feed-forward neural network architectures (Section 2.2.5). Figure 2-11, the NN based prediction of the constitutive response is provided for the IP-S (Figure 2-11a) and IP-Dip (Figure 2-11b) resins. In both figures, the limiting cases of DC=29% and DC=40% as well as DC=35% and DC=42.5% corresponding to 14 mW and 20 mW power during the fabrication process of the IP-S and IP-Dip honeycombs are provided (Figure 2-11a and Figure 2-11b). Moreover, the constitutive response is given for an intermediate DC value within the limits of the experimentally available information (35% and 39% respectively) and for a higher DC value of 43% and 45% (Figure 2-11). Two representative experimental results for the specimens fabricated with 14 mW and 20 mW laser powers have been added, both for the IP-S (Figure 2-11a) and IP-Dip (Figure 2-11b) photoresist materials, to allow for the comparison of experimental data and predictions over the entire range of strain values investigated and for considerably different DC values. The recorded model inaccuracies are within the range of the experimentally observed uncertainty for all DC values and strain magnitudes investigated.

The curves of Figure 2-11 highlight the robustness of the developed NN model in the prediction of the constitutive response for different degrees of conversion corresponding to different laser powers (Figure 2-10) over the entire strain-rate range, for both photoresist materials investigated. More specifically, the NN-based stress predictions for the limiting laser power cases (14 mW and 20 mW) lie in well accordance with the experimental constitutive response (Figure 2-4), with the stress magnitude at each strain level to be within the variance recorded for each experimentally obtained
stress-strain curve (Figure 2-7 and Figure 2-8) at a given laser power (or accordingly $DC$ value, Figure 2-10) for both materials. Moreover, the NN model provides high fidelity stress-strain estimates for $DC$s within the range of the experimentally investigated laser power values (Figure 2-11), while extrapolated curves retain the primal constitutive response characteristics, highlighting the robustness of the elaborated machine learning approach.

Figure 2-11. NN-based prediction of the constitutive response for the (a) IP-S and (b) IP-Dip material case for different degree of conversion ($DC$). The lowest and highest laser power (14 mW and 20 mW) cases are depicted in black and green color (with lower pointing triangle and square markers respectively) along with an intermediate and higher $DC$ value case. For the case of 14 mW and 20 mW laser power for both IP-S and IP-Dip, the experimentally-measured engineering stress-strain curves are superimposed with dashed lines for comparison purposes (barely visible due to good agreement with the dotted model predictions).

It should be noted that a small number of layers and neurons per layer is sufficient for the results of Figure 2-11 to be obtained, with a total of two layers (with 3 × 1 and 2 × 1 neurons) to be used both in the IP-S and IP-Dip case. It has been observed that a minimum of three distinct $DC$ values is required for the model to well perform, not only within but also outside the range of the curated data. The model could be extended to account for the effects of other parameters (such as strain-rate, temperature and writing speed) once the experimental data becomes available. The rather small network size allows for a data-based identification of analytical expressions characterizing the constitutive response of both base materials. The corresponding formulas for the IP-S are given in Equations (2-2 to 2-4):
\[ \text{Inp}^{\text{IP-S}} = \begin{bmatrix} \varepsilon \\ DC \end{bmatrix} \odot \begin{bmatrix} -0.0003 \\ 3.633 \end{bmatrix} - \begin{bmatrix} 1 \\ 1 \end{bmatrix} \] (2-2)

\[ L_1 = \log \text{sig} \left( \begin{bmatrix} -1.63 & -1.29 \\ 0.145 & 0.17 \end{bmatrix} \odot \text{Inp}^{\text{IP-S}} + \begin{bmatrix} 2.1 \\ 3.03 \end{bmatrix} \right)^T \] (2-3)

\[ \sigma^{\text{IP-S}} = \log \text{sig} \left( \begin{bmatrix} -105.7 \\ 263.87 \\ 57.1 \end{bmatrix}^T L_1 - 213.7 \right) / 0.00606 \] (2-4)

The corresponding analytical formulas for the IP-Dip material case are given in Equations (2-5 to 2-7):

\[ \text{Inp}^{\text{IP-Dip}} = \begin{bmatrix} \varepsilon \\ DC \end{bmatrix} \odot \begin{bmatrix} -0.00002 \\ 0.026 \end{bmatrix} - \begin{bmatrix} 1 \\ 1 \end{bmatrix} \] (2-5)

\[ L_1 = \log \text{sig} \left( \begin{bmatrix} -9.86 \\ -0.0297 \end{bmatrix} \odot \text{Inp}^{\text{IP-Dip}} + \begin{bmatrix} 1.68 \\ 0.253 \end{bmatrix} \right)^T \] (2-6)

\[ \sigma^{\text{IP-Dip}} = \log \text{sig} \left( \begin{bmatrix} -37.56 \\ 252.95 \end{bmatrix}^T L_1 - 1.08 \right) / 0.00269 \] (2-7)

Where in Eqs. (2-2) to (2-7), \( \sigma^{\text{IP-S}} \) and \( \sigma^{\text{IP-Dip}} \) stand for the stress developed in the IP-S and IP-Dip material, while \( \varepsilon \) and \( DC \) for the strain and degree of conversion respectively. The operator (\( \odot \)) denotes the Hadamard product.

The reported results are expected to be independent of the specific structural choice (honeycomb). As mentioned in Section 2.2.3, the stress state is of uniaxial nature in the honeycombs and hence the bulk material properties are extracted (provided that the stresses are calculated using the net cross-sectional area excluding porosity). From this perspective, the results are thus applicable to other structures. The methodology (testing and neural network modeling) has been applied to two distinct resins and there is no restriction as far as its application to other chemistries is concerned. Due to the focus on the identification of constituent material properties, the results and models are also relevant to the design of larger mesoscale parts. The machine learning algorithm is able to provide the basic stress-strain relationship (at the constituent material level). A finite element model can then make use of this information to predict the effective response of other structures made from a given photoresist. In the present work, the degree of
conversion is considered as the main characterizing feature. In case more comprehensive experimental results become available on the effects of other parameters such as the writing speed, it will be straightforward to extend and retrain the proposed neural network model.

2.4 Conclusion

Two negative-tone photoresist materials (IP-S and IP-Dip) for additive manufacturing through two-photon lithography were investigated via mechanical testing and spectroscopic techniques. A direct relation between the measured degree of conversion and the linear and nonlinear mechanical attributes was derived, correlating the structural performance with the chemical composition of the materials after the TPL process.

It is observed that the laser power used in the direct laser writing process controls to a great extent the Young’s modulus and deformation resistance of the resulting polymers. More specifically, an increase in the laser power by 6 mW during polymerization (from 14 mW to 20 mW) results in an increase in the Young’s modulus by more than 200 MPa for both base resin materials. Similar observations are made for the deformation resistance at large strains. It shows an increase of 150 MPa and 50 MPa for the IP-Dip and IP-S resins, respectively. In addition, for all IP-Dip polymers the Young’s modulus and deformation resistance are 10-15% and 150-180% higher than those achieved for the IP-S.

Via Raman spectroscopy, the degree of conversion upon polymerization was determined for each specimen in order to establish a link between the observed mechanical response and the degree of conversion. For a given laser power, the degree of conversion achieved for the IP-Dip resin is 6-16% higher than the one achieved for the IP-S resin. Finally, a neural network model was developed, predicting the Young’s moduli and nonlinear stress-strain curves of the IP-S and IP-Dip materials as a function of the degree of conversion.

The reported results may serve as a reference for the mechanical performance and modeling of the IP-S and IP-Dip resin materials. Furthermore, the machine learning approach provides a general framework for predicting the bulk material properties of materials obtained through two-photon lithography. The framework is developed accounting for one process related parameter only. However, it is sufficiently universal
to be extended to account for additional process characteristics. Moreover, an extension to the current study could provide the constitutive response of a wider variety of photoresist materials, not only those used in TPL but also in other polymerization-based additive manufacturing processes.
3 Double-Wall Ceramic Nanolattices: Increased Stiffness and Recoverability by Design


3.1 Introduction

The properties of metamaterials are largely controlled by a man-made internal structure [71]. By carefully choosing the geometry of the internal structure as well as the governing length scale, metamaterials can be optimally designed for a wide range of applications including vibration absorption [72], acoustics [73,74], microrobotics and scaffolds for cell growth [75]. When used for load carrying structures of vehicles, it is desirable to come up with metamaterials that combine light weight with high stiffness and recoverability [6,22–24].

Additive manufacturing along with special post-processing techniques has enabled the fabrication of metamaterials from pure metals [13,16,76–78], alloys [22,79], polymers [80,81] and composites [21,82,83]. When fabricating metamaterials with structural features at the micro- and nanoscale (i.e. nanolattices) [15,84–89], two-photon polymerization [1,8] is often the prime choice as it guarantees a feature resolution as fine as 150 nm. Further post processing of nanolattices can be performed using techniques such as atomic layer deposition (ALD) [90,91], electroplating, electroless plating, magnetron sputtering and pyrolysis [6,13,92,93]. With the help of ALD, thin ceramic coatings may be applied onto polymer scaffolds in a conformal manner with high accuracy in terms of coating thickness (down to few nanometers), creating polymer-ceramic composites [12,82]. Furthermore, free-standing ceramic hollow-tube structures can be obtained by additional processing steps such as oxygen-plasma etching [11,94,95].

Electroplating hollow templates fabricated by two-photon polymerization allows for creating truss lattices with metals like copper [13] and nickel [6]. While electroplat-
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ing is also suitable for the fabrication of metallic nanolattices with high specific stiffness, the resulting structures often lack recoverability upon removal of the applied loads. Electroless plating provides an alternative to electroplating, i.e. coating polymer structures with metallic films without applying an electric potential [6,92]. However, nickel-based microlattices made via electroless plating exhibit lower yield strength than similar structures fabricated by electroplating [6].

Extensive research has been carried out on the optimization of truss lattices [96–99] and honeycomb [100] architectures with a focus on the relationships between internal structure, the microstructural deformation mechanisms and their effective mechanical properties. New architectures such as 3D plate-lattices have recently been proposed [14,101] and manufactured [14] whose moduli attain the theoretical upper bound of isotropic elastic stiffness (Hashin-Shtrikman limit). Another emerging class of metamaterial architectures with interesting energy absorption capabilities are shell-lattices [7,96,102], which include the hollow-truss lattices as special sub-class [103,104].

Experimental studies report a trade-off between strength and shape recoverability for micro- and nano-architected mechanical metamaterials [6,22–24,92]. Shape recoverability is defined for quantitative purposes as the ratio of the recovered to the total applied strain during a uniaxial compression experiment [6]. Schaedler et al. [92] fabricated ultralight hollow-tube microlattices made of nickel-phosphorous via a self-propagating photopolymer waveguide technique followed by electroless plating. It has been shown that for a density of 0.9 kg m\(^{-3}\) the microlattices exhibit full recoverability after compression to a strain above 50% coupled with a strength of only approximately 10 kPa [92]. Using the same fabrication technique, Torrents et al. [6] fabricated similar microlattices spanning from 120 nm to 3 \(\mu\)m deposited nickel-phosphorous films. For a strut diameter of approximately 500 \(\mu\)m, increasing the thickness of the deposited film from 500 to 800 nm would result in enhanced compressive modulus results (from 14 to 330 kPa respectively) but also in a larger residual strain (from 0.001 to 0.006) [6]. A large residual strain is typical of a microlattice which lacks in recoverability as shown by Torrents et al., which illustrates the trade-off between recoverability and enhanced mechanical stability [6]. Meza et al. [23] utilized the two-photon lithography technique followed by atomic layer deposition of a ceramic material to fabricate octet-truss nanolattices of varying unit cell size and ceramic thickness (from 5 to 60 nm). It was shown that by optimizing the ratio of the wall thickness to tube radius, brittle fracture
could be suppressed resulting in fully recoverable lattices. The transition between recoverable to non-recoverable nanolattices takes place as the ceramic wall thickness increases from very thin walls (5 to 10 nm) to thicker walls (above 20 to 30 nm). The same transition from brittle behavior (no recoverability) to ductile-like behavior (full shape recovery) is also discussed by Zheng et al. [24]. Overcoming the challenge of this trade-off between mechanical robustness and shape recoverability will make such mechanical metamaterials attractive for various applications such as in the energy absorption and mechanical actuation field [22].

The goal of the present work is to expand the design space of hollow-truss lattices to overcome the trade-off between stiffness and recoverability after large deformation. The central idea is to introduce Double-Wall Tube (DWT) architectures in an attempt to outperform Single-Wall Tube (SWT) lattices. Conceptually, a DWT lattice is obtained by nesting two SWT lattices. Therefore, for the same density, the wall thickness of the DWT will be about two times less than the wall thickness of the counterpart SWT lattice. Since the recoverability of a lattice increases with thinner ceramic coatings, the DWT architecture is expected to exhibit enhanced recoverability compared to the SWT architecture of equal density without sacrificing its stiffness. The DWT architecture is also characterized by a small manufacturing time due to reduced coating and scaffold fabrication time. The challenge lies in devising DWT lattice geometries that provide higher stiffness than their SWT counterparts of equal density. In the following, a possible fabrication route is validated for ceramic DWT nanolattices. Subsequently, it is shown through experiments that their recoverability correlates with the wall thickness, before demonstrating that the stiffness of DWT lattices surpasses that of SWT lattices of equal density.

3.2 Materials and methods

3.2.1 Two-photon polymerization

A two-photon polymerization system (Photonic Professional GT, Nanoscribe GmbH) is used to fabricate the sacrificial polymeric template of the simple cubic hollow-truss lattices. The negative photoresist, IP-S, is used in the dip-in mode with a laser power of 20 mW and a scan speed of 10 mm s⁻¹ to fabricate structures with approximate
dimensions of $200 \times 200 \times 200 \, \mu m^3$. The structures are adhered onto a glass substrate which is cleaned prior to the fabrication process by immersion in isopropyl alcohol in an ultrasonic bath for approximately 10 min. After fabrication, the structures undergo a development step to ensure that the non-polymerized photoresist is dissolved completely from the glass substrate.

### 3.2.2 Alumina deposition via ALD

An alumina coating of uniform thickness is deposited onto the polymer hollow-truss lattices via atomic layer deposition (ALD) using a Picosun Sunale R-150B system. The polymer lattices are inserted into the ALD system and purged in consecutive steps with trimethylaluminium (TMA, precursor of Al for the formation of alumina) and water ($H_2O$, precursor of oxygen in the formation of alumina) in order to form the alumina coating. The process is performed inside a chamber under vacuum at 110 °C for 2, 5 and 10 h. The alumina coating thickness is measured with a surface profilometer (DektakXT, Bruker). Three measurements of each coating were made and respectively correspond to the reported 27 nm, 52 nm and 110 nm.

### 3.2.3 Oxygen-plasma etching

To obtain alumina-only structures, the polymer template must be removed from the inner part of the composite structure. The ion beam of a SEM-FIB (Scios Dual Beam, FEI) is focused on a thin cross-sectional area of the polymer-alumina composite to remove a section of alumina and expose the polymer template. Then the composite structure is subjected to oxygen-plasma etching ($O_2$ Plasma Asher, Technics Plasma 100-E) for 120 min at 200 W and 1 mbar $O_2$ gas flow to extract the polymer through the FIB-sectioned areas.

### 3.2.4 Uniaxial compression experiments

The DWT alumina nanolattices were tested under uniaxial compression using an intrinsically displacement-controlled SEM indenter (Alemnis AG, Thun, Switzerland) at room temperature under high vacuum ($\sim 10^{-6}$ Pa) with a 500 $\mu$m diameter diamond flat punch (Synton-MDP, Switzerland) and a 1.5 N load cell in situ in a Vega 3 scanning electron microscope (Tescan, Brno, Czechia). The in situ observation enables precise
positioning of the flat punch above the nanolattice with a small offset. The nanolattices were compressed up to a strain of approximately 0.5 at a constant speed of 1 µm s⁻¹ in a series of three complete cycles of compression and unloading. The resulting force-displacement data was corrected for the system’s compliance, and the contact point was determined for each curve using custom software. Engineering stress and strain were obtained from the force-displacement data by dividing the force by the cross-sectional area and the displacement by the height of each nanolattice, respectively.

3.2.5 Finite element simulations

SWT and DWT unit cell models are created in Abaqus/CAE using first-order reduced integration quadrangular shell elements (S4R in Abaqus library). Periodic boundary conditions are defined using master nodes. The simulations are performed using the implicit solver Abaqus/Standard with a compressive displacement along one of the unit cell axis while the other unit cell surfaces are kept traction-free. The results are reported with the base material density $\rho = 2900$ kg m⁻³, the Young’s modulus $E=164$ GPa and Poisson’s ratio $\nu = 0.25$.

3.3 Results and discussion

The first step in the fabrication of DWT alumina nanolattices is the additive manufacturing of a sacrificial polymer template (Figure 3-1a) using a two-photon polymerization system (Photonic Professional GT, Nanoscribe GmbH). Simple-cubic, hollow-truss lattice structures composed of $3 \times 3 \times 3$ unit cells with the approximate outer dimensions of $200 \times 200 \times 200$ µm³ are fabricated with an inner radius $R_{in}=18.5$ µm and an outer radius $R_{out}=30.3$ µm. Subsequently, three different alumina coating thickness, respectively 27, 52 and 110 nm are deposited via atomic layer deposition (ALD) (Figure 3-1a). To remove the sacrificial polymer template, two focused ion beam (FIB) cuts are made on opposite sides of the nanolattices (Figure 3-1(b-c)), exposing the ‘trapped’ sacrificial polymeric template, which is further removed via oxygen-plasma etching revealing a double wall architecture (Figure 3-1d). In total, three different DWT nanolattices are realized, with relative densities of 0.17%, 0.36% and 0.76% by increasing their wall thickness from 27 to 110 nm.
Figure 3-1. Double wall lattices architecture. (a) Fabrication route involving three consecutive steps of two-photon polymerization, ALD and oxygen-plasma etching to synthesize DWT alumina nanolattices with specified inner radius (Rin) and outer radius (Rout). (b) Scanning electron microscope (SEM) image showing a focused ion beam (FIB) cut along the height of the alumina-polymer composite lattice. (c) Magnified SEM image of the region where the FIB cut was conducted. The darker region between the outer and inner walls of the composite lattice is the exposed sacrificial polymer template. The brighter regions all over the composite lattice is the alumina coating. (d) Magnified SEM image of the DWT alumina nanolattice after the oxygen-plasma etching. The outer and inner alumina walls are concentric and free-standing (no polymer in between). The scale bars in (b), (c) and (d) correspond to 50, 5 and 0.5 µm respectively as indicated with the yellow arrow below the SEM images.

Figure 3-2 provides snapshots before compression (initial configuration), at maximum strain (deformed configuration) and after unloading for the DWT nanolattices with wall thickness of 27 nm (Figure 3-2(a-c)), 52 nm (Figure 3-2(e-g)) and 110 nm (Figure 3-2(i-k)). It is observed in situ that with increasing alumina wall thickness, the visible damage during and after straining on the lattice structure increases. When the walls are very thin (27 nm), the shape-recoverability of the nanolattice is high and the structure exhibits no visible damage (Figure 3-2c). When the alumina thickness is increased to 52 nm, some cracks are observed on the outer surfaces of the nanolattice.
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(Figure 3-2(f-g)). Finally, in the case of the thickest walls, the DWT alumina nanolattice is heavily damaged (Figure 3-2(j-k)). The aforementioned findings validate the idea that thinner ceramic walls increase recoverability. Three mechanisms can explain this increase: (i) the reduction of imperfections in the nanoscale-deposited ceramic walls, (ii) the local buckling induced by the high strut length to thickness aspect ratio and (iii) the reduced bending stiffness due to the nanoscale alumina wall thickness [105].

Three loading cycles are applied on each specimen. Figure 3-2d, Figure 3-2h and Figure 3-2l show the engineering stress as a function of the engineering strain for the 27 nm, 52 nm and 110 nm DWT nanolattice respectively. For the thinnest nanolattices (27 nm wall thickness), the first loading is characterized by an initial linear part followed by oscillations of the stress towards a maximum value of $6.5 \times 10^{-3}$ MPa at a strain of 0.5 (Figure 3-2d). From the slope of the linear part, the Young’s modulus value is estimated at 0.25 MPa. Upon unloading the stress reaches a plateau corresponding to 17% of the loading plateau stress and no permanent deformation is visible upon full unloading. The second and third cycles exhibit similar features with a lower loading plateau and higher unloading plateau. The energy dissipated on the second and third cycle are respectively 49% and 56% of the energy dissipated during the first cycle. This slight increase in the energy dissipation observed between the second and third cycle is tentatively attributed to buckling-induced contact between the walls of the DWT nanolattice. For the two thicker lattices (Figure 3-2h and Figure 3-2l), the first loading features initially a peak stress at $35 \times 10^{-3}$ MPa and $140 \times 10^{-3}$ MPa respectively for the 52 nm and 110 nm DWT nanolattices followed by a plateau with a 50% lower stress, highlighting the mechanical damage of the nanolattices. The Young’s moduli for the 52 nm and 110 nm DWT nanolattices are 3.46 MPa and 11.7 MPa respectively. The second and third loading exhibit a non-linear stress increase up to a lower maximum stress. The energy dissipated during the second and third loading for the 52 nm wall thickness nanolattice (resp. 110 nm) only corresponds to 27% and 22% (resp. 15% and 8%) of the energy dissipated during the first loading. In the case of the 52 nm and 110 nm lattices, full unloading (zero stress) is observed at residual strains of 0.3 and 0.4 respectively.

Similar results are shown in Figure 3-3 and Figure 3-4 for a second polymer template with inner radius $R_{in} = 22.4 \mu m$, outer radius $R_{out} = 26.3 \mu m$ and the same three wall thickness, demonstrating that the shape recoverability is mainly dependent on the
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wall thickness. SWT nanolattices with similar alumina coating thickness are also fabricated and tested for comparison purposes to DWT nanolattices and the results are shown in Figure 3-5.

Figure 3-2. *In situ* uniaxial compression experiments of the DWT alumina nanolattices: (a-d) 27 nm, (e-h) 52 nm and (i-l) 110 nm alumina coating thickness and the corresponding engineering stress and strain curves for each case. The three different snapshots (from left to right) for each alumina thickness correspond to no compression, compression at maximum strain and the end of unloading. With increasing alumina coating thickness, the damage after unloading the DWT alumina nanolattices is also increased with 27 nm exhibiting full recovery (c), 52 nm a slight damage mainly on the edges (g) and 110 nm heavy damage all over the deformed part of the nanolattice (k) confirming that thinner ceramic coatings provide enhanced recoverability. The scale bars are all set to 50 µm.
Figure 3-3. In situ uniaxial compression experiments on DWT alumina nanolattices with $R_{in}=22.4 \, \mu m$ and $R_{out}=26.3 \, \mu m$ and alumina wall thickness of (a-c) 27 nm, (d-f) 52 nm and (g-i) 110 nm. With increasing alumina coating thickness, the damage after unloading the DWT alumina nanolattices is also increased with 27 nm exhibiting full recovery (c), 52 nm a slight damage mainly on the edges (f) and 110 nm heavy damage all over the upper part of the nanolattice (i). The scale bars are all set to 50 $\mu m$. 
Figure 3-4. Engineering stress and strain curves for two consecutive loading cycles (loading to maximum strain and unloading to zero strain) for a DWT alumina nanolattice with $R_{in}=22.4$ μm and $R_{out}=26.3$ μm and increasing alumina wall thickness (a) 27 nm, (b) 52 nm and (c) 110 nm. Enhanced recoverability is coupled to thinner alumina coating thickness. The energy dissipated on the second cycle is 50%, 19% and 8% of the energy dissipated during the first cycle respectively for the cases of 27 (a), 52 (b) and 110 nm (c) DWT nanolattices.

Figure 3-5. In situ uniaxial compression experiments of the SWT alumina nanolattices with $R=12$ μm: (a-d) 27 nm, (e-h) 52 nm and (i-l) 110 nm alumina coating thickness and the corresponding engineering stress and strain curves for each case. The three different snapshots (from
left to right) for each alumina thickness correspond to no compression, compression at maximum strain and the end of unloading. With increasing alumina coating thickness, the damage after unloading the SWT alumina nanolattices is also increased with 27 nm exhibiting almost full recovery (with minor damage induced by the fabrication process) (c), 52 nm a slight damage mainly on the edges (g) and 110 nm heavy damage all over the deformed part of the nanolattice (k) confirming that thinner ceramic coatings provide enhanced recoverability. The scale bars are all set to 50 µm.

Finite element simulations are used to compare the stiffness of DWT and SWT lattices of equal density. Using unit cell models with periodic boundary conditions, the compressive modulus along the [100] direction is obtained for both architectures over a wide range of geometrical configurations (Figure 3-6(a-b)). Here, the attention is limited on nanolattices with a unit cell size of 66 µm which can be fabricated using the aforementioned processing route, i.e. with a minimum polymer template feature size of 2 µm, and alumina wall thicknesses varying from 10 to 100 nm. The resulting nanolattices belong to the category of ultra-low density materials with densities ranging from ~0.3 to 30 kg m$^{-3}$. Results from more than 1000 finite element simulations are depicted in Figure 3-6c, which shows the compressive modulus $E$ as a function of the density $\rho$. For both architectures, the stiffness increases with the wall thickness, even at constant density. For example, for a density of 4.5 kg m$^{-3}$, a SWT lattice with 70 nm thick walls is about three times stiffer ($E = 23$ MPa vs. $E = 7$ MPa) than a SWT lattice with 30 nm walls (Figure 3-6c). The same trend is observed for the DWT lattices; a DWT lattice with 70 nm walls is three times stiffer ($E = 41$ MPa vs. $E = 14$ MPa) than a DWT lattice with 30 nm walls (Figure 3-6c).
Figure 3-6. (a) Resulting geometrical configurations of the DWT nanolattices for varying ceramic coating thickness (20-50 nm) and constant density $\rho = 4.5 \text{ kg m}^{-3}$. (b) Geometrical configurations of the SWT nanolattices for varying ceramic coating thickness (30-60 nm) and constant density $\rho = 4.5 \text{ kg m}^{-3}$. (c) Ashby chart showing the numerical results of the Young’s modulus versus the density of the DWT (orange circles) and SWT (blue circles) ceramic
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nanolattices with varying ceramic coating thickness (from 10 nm to 100 nm). The dash gray line corresponds to density of 4.5 kg m$^{-3}$ used as reference. The corresponding DWT and SWT experimental results are shown with the orange and blue stars for alumina thickness of 27 nm, 52 nm and 110 nm.

Aside from reconfirming the dependency of the stiffness on the wall thickness, the finite element simulations demonstrate that for the same density and wall thickness, the stiffness of the DWT lattices is always higher than that of the SWT lattices. For example, for a density of 4.5 kg m$^{-3}$ and a wall thickness of 30 nm, the compressive modulus for the DWT lattices is $E= 14$ MPa, twice higher than the corresponding SWT lattice ($E= 7$ MPa). Alumina DWT lattices with 40 nm wall thickness cover a density range from 2.5 to 12 kg m$^{-3}$. The DWT configurations outperform (in terms of compressive modulus) all SWT lattices with equal densities and with wall thicknesses ranging from 10 to 60 nm.

Thus, one may argue that for the same stiffness and density, a DWT lattice configuration exists providing a superior recoverability than its SWT counterpart. At a density of 4.5 kg m$^{-3}$, a SWT lattice (Figure 3-6c) with 50 nm thick walls exhibits a modulus of 14 MPa. A DWT lattice (Figure 3-6c) provides the same stiffness with a wall thickness of only 30 nm, whose recoverability is expected to be higher.

By evaluating and discussing the experimental results shown in this work (Figure 3-6c) another comparison can be drawn between the DWT and the SWT nanolattices of equal unit cell size and alumina thickness. For the case of the 27 nm DWT and SWT nanolattices, the resulting lattice densities are 4.93 kg m$^{-3}$ and 2.69 kg m$^{-3}$ respectively. The Young’s modulus is estimated at 0.25 and 0.18 MPa, respectively, showing that DWT nanolattices are always stiffer than their SWT counterpart of identical wall thickness. Similar findings are shown for the DWT and SWT nanolattices of 52 nm and 110 nm alumina thickness. This is in agreement with the numerical results for all alumina thickness. The numerical simulations are overestimating the resulting stiffness of both the DWT and SWT nanolattices by one to two orders of magnitude compared to the experimental results. This is attributed to the inherent wall waviness and imperfections of the fabricated nanolattices which are not considered in the simulations, as shown by Meza et al. [12]. In addition, the experimentally measured Young’s modulus of the DWT nanolattices is up to two times higher than the corresponding SWT nanolattices of the same alumina thickness, also in agreement with the numerical results.
To gain insight into the relative ranking of alumina DWT lattices with respect to existing architectures, experimental data from the literature are included in Figure 3-6c. The experimentally measured stiffness for the alumina hollow octet-truss evolves with an exponent 1.6 in [23] and with an exponent of 1.1 in [24]. Both studies used the same fabrication technique to create their single-wall lattices with similar wall thickness. In the present study, an exponent of 1.2 is obtained numerically for both the SWT and the DWT nanolattices. The experimentally measured values are 2.9 and 2.7, respectively. It is noteworthy that both scaling laws are very similar for both the numerical and experimental values with the DWT providing a two-fold increase in stiffness. A linear scaling (exponent of 1) should be obtained for stretching dominated lattices, e.g. a simple cubic truss. SWT and DWT nanolattices with a perfect geometry have a higher scaling exponent due to the absence of material at the nodes. When comparing numerical to experimental results, differences arise from the fact that numerical simulations do not take into account parameters like the fabrication complexities and imperfections of the nanolattices such as the resulting wall waviness [12] or the FIB and oxygen-etching fabrication steps, where the nanolattices undergo an intense synthesis process. Moreover, the uneven contact of the surface of the nanolattice with the punch at the beginning of the uniaxial compression experiment is an additional factor which can contribute to experimental errors.

Meza et al. [23] reported a transition from recoverable to non-recoverable lattices for wall thickness above approximately 30 nm. In this work, it is observed that DWT nanolattices of 50 to 60 nm are still recoverable in shape (Figure 3-2(e-h)) with maximum stress during compression at 35 kPa, while the SWT nanolattices of similar wall thickness exhibit less recoverability and lower maximum stress (of around 14 kPa), as shown in Figure 3-5. Thus, the trade-off between enhanced recoverability and high stiffness is reduced with the introduction of the DWT architecture. The detailed results of the experimentally-derived and numerically-predicted Young’s modulus for both DWT and SWT lattices are found in Table 3-1.
Table 3-1. Summary of the resulting Young’s modulus as calculated from the experimental ($E_{exp}$) and numerical ($E_{sim}$) analysis for the DWT and SWT lattices of 27 nm, 52 nm and 110 nm alumina thickness. DWT$^1$ refers to nanolattices with $R_{in}=18.5$ µm and $R_{out}=30.3$ µm, while DWT$^2$ to nanolattices with $R_{in}=22.4$ µm and $R_{out}=26.3$ µm. The SWT nanolattices have a constant radius of $R=12$ µm.

<table>
<thead>
<tr>
<th>Type of lattice</th>
<th>Alumina thickness, [nm]</th>
<th>Density, $\rho$ [kg m$^{-3}$]</th>
<th># of lattice</th>
<th>Young’s modulus, $E_{exp}$ [MPa]</th>
<th>Average Young’s modulus, $E_{exp}$ [MPa]</th>
<th>Young’s modulus, $E_{sim}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWT$^1$</td>
<td>27</td>
<td>4.93</td>
<td>1</td>
<td>0.17</td>
<td>0.25 ± 0.07</td>
<td>7.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>10.44</td>
<td>1</td>
<td>4.01</td>
<td>3.46 ± 0.55</td>
<td>20.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>2.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>22.04</td>
<td>1</td>
<td>11.51</td>
<td>11.70 ± 0.19</td>
<td>58.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DWT$^2$</td>
<td>27</td>
<td>5.46</td>
<td>1</td>
<td>0.24</td>
<td>0.20 ± 0.03</td>
<td>7.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.16</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>0.21</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>52</td>
<td>10.52</td>
<td>1</td>
<td>1.83</td>
<td>1.89 ± 0.06</td>
<td>20.17</td>
</tr>
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<td></td>
<td></td>
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<td>2</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>22.26</td>
<td>1</td>
<td>9.11</td>
<td>10.54 ± 1.43</td>
<td>58.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWT</td>
<td>27</td>
<td>2.69</td>
<td>1</td>
<td>0.18</td>
<td>0.18 ± 0.01</td>
<td>3.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.19</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td>3</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>5.19</td>
<td>1</td>
<td>1.74</td>
<td>1.80 ± 0.14</td>
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</tr>
<tr>
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<td>2</td>
<td>1.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>10.99</td>
<td>1</td>
<td>10.18</td>
<td>10.45 ± 0.22</td>
<td>30.39</td>
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<td>2</td>
<td>10.74</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>10.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Conclusion

In summary, the double wall tube (DWT) lattice is proposed as new metamaterial architecture to extend the design capabilities for nanolattices. When applied to brittle nanolattices made out of alumina, metamaterials of double-wall architecture exhibit higher stiffness and shape recoverability than their single-wall counterparts of the equal mass. Large strain in situ SEM compression experiments are performed for both DWT and SWT architectures. The experimental results support the assumption that recoverability increases as the wall thickness decreases. It is also shown both experimentally and numerically that a DWT lattice always outperforms the corresponding SWT lattice.
not only when they are both of equal mass but also of identical alumina thickness. Through numerical simulations, design maps for DWT architectures are established. The design maps include information on the simulations and the experiments on both DWT and SWT lattices. It is evident that the simulations overestimate the Young’s modulus values for both architectures as the wall waviness and experimental defects are not taken into account. With the use of the DWT architecture, shape recoverability is no longer sacrificed for enhanced stiffness. The proposed fabrication route and the double wall lattice concept is readily extendable to any metamaterial which can initially be produce as an open cell with shell components, such as hollow truss or smooth shell lattices [14]. This suggests that the proposed architecture provides a promising engineering solution to overcome the trade-off between recoverability and stiffness for the case of brittle nanolattices.
4 Ceramic/Polymer Microlattices: Increasing Specific Energy Absorption Through Sandwich Construction

This chapter has been submitted for publication: M. Diamantopoulou, C. C. Roth, T. Tancogne-Dejean, C. M. Lauener, D. Mohr, Ceramic/Polymer microlattices: Increasing specific energy absorption through sandwich construction.

4.1 Introduction

The advance of additive manufacturing has enabled the fabrication of complex architectures with a variety of materials from polymer to metals [4,6,106–110]. Truss, shell and plate lattices are among the base designs for investigating the mechanical behavior of periodic structures [14,25,101,111]. Specifically, triply periodic minimal surface (TPMS) topologies are mathematically derived topologies with near-zero mean curvature that have attracted a lot of attention in the field of mechanical metamaterials as they possess high specific energy and strength compared to strut-based architectures [25,26,112–120]. Their open-cell nature makes them excellent candidates for the fabrication of lattices by various additive manufacturing processes, such as powder-bed [2–4,121], liquid-based processes [122] and multi-photon lithography [19,106]. As a result, TPMS lattices are investigated for potential applications in a wide range of fields such as in mechanics [26,114,123], biomedical engineering [18,124] and as photonic crystals [125–127].

The two-photon lithography technique has only recently been used for the fabrication of polymer TPMS topologies in the microscale [116,128]. Possible further fabrication steps could create ceramic or metallic TPMS microlattices, following processes well-established and utilized in previous studies with the use of various other topologies [12,92,129,130]. Meza et al. [12] as well as Bauer et al. [82] used this fabrication route to create composite hierarchical designs and analyze their compressive strength and stiffness. Moreover, Bauer et al. [21] have conducted tensile tests on ceramic-polymer composites with the aim of evaluating the influence of the ceramic thickness on the tensile strength. The goal of this work is to utilize the two-photon lithography and the atomic layer deposition techniques to create nanometer-thick sandwiched-wall TPMS
Ceramic/Polymer Microlattices: Increasing Specific Energy Absorption Through Sandwich Construction

In microscale, identify a specific weight fraction of the materials so as to achieve the highest energy absorption capabilities of the lattices.

The sandwich construction is a well-established design concept in lightweight engineering [131,132]. The main idea is to increase the weight-specific bending stiffness of thin-walled structures (such as beams, plates, and shells) by separating two thin layers (so-called skins) by a lightweight core layer [133]. Augmenting the core thickness is expected to increase the bending stiffness while the structure’s membrane stiffness remains unchanged. The application of this concept is beneficial in weight-critical applications where thin-walled structures are subject to bending-loading. In the context of mechanical metamaterials, it is common to differentiate between stretching-dominated and bending-dominated architectures [116,134,135]. In view of optimizing the weight-specific stiffness (i.e., achieving the highest macroscopic Young’s modulus for a given density), stretching-dominated have demonstrated clear performance advantages over bending-dominated architectures [14,101]. Consequently, the metamaterial architectures that attain the theoretical limits for stiffness are stretching-dominated plate-lattices [14,101].

While even the stiffest truss-lattices provide significantly lower stiffness than plate-lattices of equal weight, the performance of shell-lattices is positioned between these two extremes [14,25,102]. By construction, the cell walls of shell-lattices are also exposed to local bending [25]. The fabrication of shell-lattices with cell walls that are constructed as sandwich shell is thus considered as a possible design option to reduce the stiffness gap between shell-lattices and plate-lattices.

Assume the sandwich wall to be composed of a central core layer (thickness $t_c$, Young’s modulus $E_c$ and density $\rho_c$) and skins (single skin thickness $t_s$, Young’s modulus $E_s$ and density $\rho_s$) where $\rho_c < \rho_s$, as shown schematically in Figure 4-1a. The cross-sectional mass is then given by

$$m = t_c \rho_c + 2t_s \rho_s$$

(4-1)

while the beam bending stiffness $EI$ and the beam membrane stiffness $EA$ (per unit width) of that cell wall read
Introduction

\[
EI = E_c \frac{t_c^3}{12} + 2E_s \left[ \frac{t_s^3}{12} + \frac{t_c(t_s + t_c)^2}{4} \right]
\]

(4-2)

\[
EA = E_c t_c + 2E_s t_s
\]

(4-3)

For a given cross-sectional mass \( m_0 = \text{const.} \), the core thickness \( t_c \) may be expressed as a function of \( t_s \) with \( 0 \leq t_s \leq m_0 / (2 \rho_s) \). Furthermore, the bending stiffness may be expressed as a function of \( t_s \) only.

Figure 4-1. (a) Schematic cross-section cut of unit cell sandwich-wall configuration. (b) A meshed Schwarz Primitive unit cell (for clear visualization of the sandwich wall construction the shell mesh is extruded in the thickness direction) and (c) the \( 3 \times 3 \times 3 \) TPMS sandwich lattice structure. (d) Dependence of the alumina volume fraction as a function of the alumina weight fraction (black solid line). In addition, the normalized bending (solid blue line) and membrane (dashed blue curve) beam stiffness are shown. (e) Numerically investigated TPMS sandwich lattice structures of constant macroscopic density (solid symbols). Normalized polymer (core) thickness as a function of the corresponding normalized alumina skin thickness (skin) for different constant macroscopic densities (\( \rho \)). The experimentally tested lattice structures are denoted by colored circles.
Figure 4-1d presents the bending and membrane stiffness as a function of weight fraction of alumina after evaluation for a polymer core and alumina skins (material properties shown in Table 4-1). The weight equivalent monolithic cases correspond to 1µm thick polymer walls \( t_c = 1 \) µm, \( t_s = 0 \) or 0.3 µm thick alumina walls \( t_c = 0, t_s = 0.15 \) µm. Due to the non-negligible density of the core structure (as compared to the skin material), the bending stiffness versus skin thickness plot exhibits a non-monotonic dependency (Figure 4-1d). Denoting the bending stiffness for \( t_s = 0 \) (polymer only) as \((EI)_0\), we have a bending stiffness of 3.05\((EI)_0\) for the monolithic alumina cell wall and 17.6\((EI)_0\) for the stiffest sandwich configuration of equal weight \( t_c = 0.62 \) µm, \( t_s = 57 \) nm.

It transpires from our basic analysis for the polymer-alumina sandwich that the standard assumptions of sandwich construction of Equation 4-3 a core thickness-independent membrane stiffness, and Equation 4-2 a monotonically-increasing bending stiffness in core height do not hold true. This is due to the fact that skin-to-core density ratio for the alumina/polymer sandwich is only \( \rho_s / \rho_c = 3.29 \) while it is often more than one order of magnitude higher in traditional sandwich construction (e.g. metallic skins with a Nomex honeycomb core) [136]. However, our basic analysis also shows that an optimal core-to-skin thickness ratio may exist that provides the highest stiffness (and/or energy absorption) of a shell-lattice structure for a given macroscopic density target.

4.2 Materials and methods

The goal of this study is to explore configurations of sandwich cell wall designs for shell-lattices that outperform their monolithic counterparts with respect to stiffness, strength and energy absorption. Based on a Schwarz Primitive unit cell [137] with a size of \( l_{UC} = 66.6 \) µm (Figure 4-1b), triply periodic minimal surface (TPMS) shell lattice structures consisting of 3 \( \times \) 3 \( \times \) 3 Schwarz Primitive unit cells and dimensions 200 \( \times \) 200 \( \times \) 200 \( \mu m^3 \) are constructed (Figure 4-1c). The structures are subjected to compressive loading under quasi-static conditions.

Our attention is limited to cell walls comprising a combination of a polymer core with alumina skins (Figure 4-1a), as these are within the fabrication capabilities using
standard fabrication routes [1,82]. Different from studies that are concerned with the properties of monolithic lattice materials, the results are not represented in terms of relative density. Instead, the macroscopic density $\rho$ of the shell-lattice is reported. This is due to the fact that sandwich materials feature two solid phases. If the shell-lattice was made with the same geometrical features from a single material, the solid volume fraction would correspond to the relative density.

For the parametric study, ten macroscopic reference densities are chosen (detailed values can be found in Table 4-1), which correspond to monolithic polymer designs with cell walls of thickness $t_{sw} = 1, 2, 3, \ldots, 10 \mu m$ (Figure 4-1e) for the given unit cell size and solid phase volume fraction $\rho^* = \{4\%, 7\%, 11\%, 14\%, 18\%, 21\%, 25\%, 28\%, 32\%\}$ and $35\%$ (see also Table 4-1). Maintaining the macroscopic density $\rho$ of the overall structure constant for each case, the thicknesses of the alumina skins ($t_s$) and the polymer core ($t_c$) sandwich components are then varied from pure polymer (0% weight fraction of alumina) to pure alumina (100%wt) (Figure 4-1e).

Assuming the cell wall volume is linearly related to the shell wall thickness $t_{sw} = 2t_s + t_c$ (compare Equation 4-1), for a given weight fraction of alumina $\eta$ (with $\eta = V_s/V_{tot}$), the skin and core thicknesses read

$$t_c = \frac{m}{\rho_c} (1 - \eta)$$

(4-4)

$$t_s = \frac{m}{2\rho_s} \eta$$

(4-5)

The overall cell wall volume fraction of alumina $\lambda$ can then be approximated as

$$\lambda = \frac{2t_s}{2t_s + t_c} = \frac{\eta}{\eta + \rho_s (1 - \eta) + \rho_c (1 - \eta)}$$

(4-6)

and is shown as a function of the weight fraction of alumina $\eta$ in Figure 4-1e. It underlines that the difference in the densities of the two sandwich components has the effect on the appearance of a non-linear relation between volume and weight fractions.

Table 4-1. Resulting solid phase volume fraction, Young’s modulus, peak stress and specific energy absorption of the monolithic polymer lattices (0% alumina weight fraction) for each
density under investigation. These values are the reference data for all normalization results presented in this work.

<table>
<thead>
<tr>
<th>Monolithic polymer lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$ [kg m$^{-3}$]</td>
</tr>
<tr>
<td>42.38</td>
</tr>
<tr>
<td>84.76</td>
</tr>
<tr>
<td>127.14</td>
</tr>
<tr>
<td>169.52</td>
</tr>
<tr>
<td>211.90</td>
</tr>
<tr>
<td>254.28</td>
</tr>
<tr>
<td>296.66</td>
</tr>
<tr>
<td>339.04</td>
</tr>
<tr>
<td>381.42</td>
</tr>
<tr>
<td>423.80</td>
</tr>
</tbody>
</table>

4.2.1 Finite element modeling

A finite element model of a Schwarz Primitive shell lattice structure consisting of $3 \times 3 \times 3$ unit cells is created (Figure 4-1c) for use in Abaqus/Explicit. It is meshed with first-order reduced integration quadrangular shell elements (S4R, Abaqus library) with an approximate element edge length of 2.6 μm. The sandwich design of the lattice walls is modeled using a composite shell section. The polymer is modeled as an elasto-plastic von Mises material based on preliminary compression experiments [138] (Figure 4-2), while the alumina is described as purely elastic. All material properties and the corresponding references are given in Table 4-2. To account for the brittle nature of the alumina, a Rankine criterion [139] is used to detect crack initiation once the maximum principal tensile stress exceeds the critical tensile strength of the material $\sigma_T > \sigma_{T,c} = 6 \text{ GPa}$, in close analogy to [12,140,141]. To account for post crack tension softening (observed softening behavior prior to brittle failure) the brittle failure concept as shown in [142] is chosen, with a critical strain of 0.001. The lattice is subjected to uniaxial compressive loading with a velocity of 1 μm s$^{-1}$ between two analytical rigid surfaces. General contact is established with a friction coefficient of $\mu = 0.1$. The simulation is stopped once a displacement of 66.6 μm is reached, corresponding to a third of the
structure height. Uniform mass scaling is applied so that at least 100’000 time increments are reached. Overall 100 numerical simulations are performed (solid symbols, Figure 4-1e).

Figure 4-2. True stress as a function of the plastic strain for the polymer [138]. The fitted results (Voce function) were used as inputs for modeling the plastic behavior of the polymer material.

Table 4-2. Properties of base materials. The stress-strain curves for the polymer are shown in Figure 4-2 on which the plasticity input data are based.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus</th>
<th>Density</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ [GPa]</td>
<td>$\rho_x$ [kg/m$^3$]</td>
<td>$\nu$ [-]</td>
</tr>
<tr>
<td>Alumina (Al$_2$O$_3$)</td>
<td>172 [12,21,143]</td>
<td>3950</td>
<td>0.24</td>
</tr>
<tr>
<td>Polymer (base material: IP-S photoresist)</td>
<td>1.58 [138]</td>
<td>1200 [82]</td>
<td>0.40</td>
</tr>
</tbody>
</table>

For each simulation a force-displacement curve is obtained from the platens which is then translated to engineering stress and engineering strain according to $\sigma_{eng} = F/A_o$ and $\varepsilon_{eng} = \Delta l/l_o$ with $l_o = 3l_o=200 \mu$m and $A_o=I_o^2 = 0.04 \text{ mm}^2$. The Young’s
modulus for each lattice structure is calculated from the slope of the elastic part of each engineering stress-strain curve, i.e. up to an engineering strain of 0.018. The peak stress $\sigma_{\text{eng},P}$ is defined as the maximum stress the TPMS lattice endures before the first drop in force. We define a post-peak stress and strain as the location on the engineering stress-strain curve where 90% of the peak stress is reached on the first drop in load, i.e. $\sigma_{\text{eng},PP} = 0.9 \sigma_{\text{eng},P}$ and $\varepsilon_{\text{eng},PP} = \varepsilon_{\text{eng}} (0.9 \sigma_{\text{eng},P})$. It is used for the calculation of the specific energy absorption as follows

$$\psi = \rho \int_0^{\varepsilon_{\text{eng},PP}} \sigma_{\text{eng},PP} d\varepsilon$$

(4-7)

4.2.2 Experimental techniques

4.2.2.1 Specimen fabrication

Selected TPMS lattices with a constant density of 127 kg m$^{-3}$ and alumina weight fraction of 10%wt, 30%wt and 40%wt, corresponding to alumina and polymer thickness of $t_s = [0.045; 0.135; 0.2] \mu m$ and $t_c = [2.65; 2.06; 2.00] \mu m$ are fabricated. In a first step, the structures are built onto glass substrates using two-photon lithography (TPL). The IP-S photoresist material is drop-casted onto the substrates and the dip-in mode [1] is used with a 63× objective lens in a direct laser writing system (Photonic Professional GT, Nanoscribe GmbH). The writing speed is selected at a constant 10 mm s$^{-1}$ and the total laser capacity of the system (100%) is used. The fabricated lattices are developed upon termination of the fabrication process for 12 min in an organic developer (Mr-Dev 600, micro resist technology GmbH) and for another 3 min in isopropyl alcohol (VWR International GmbH).

In a second step, alumina is deposited onto the open 3D polymer microlattices via atomic layer deposition (ALD), thereby creating the final sandwich-walled configuration of alumina-polymer-alumina. The deposition temperature is 110°C, with a pulse duration of 10 s and 3 s for the alumina and oxygen precursor, respectively. Purge time is set to 3 s for both precursors. The deposition time varies depending on the targeted weight fraction of alumina, i.e. alumina thickness in the sandwich configuration. The fabrication quality of the sandwich lattice structures is verified in three steps: i. Scanning electron microscopy (SEM, Scios Dual beam, FEI) is used to check the overall...
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build quality of the structures and take visualization images. ii. Transmission electron microscopy preparation (TEM, Talos F200X, Thermo Fischer Scientific) is conducted in order to measure and validate the alumina thickness and iii. Energy dispersive x-ray analysis (EDX, Super-X, Thermo Fischer Scientific) is used to evaluate the elemental composition and uniformity of the deposited alumina as shown in Figure 4-3 for the case of 10%wt alumina. A silicon wafer is used (for the purpose of the TEM sample preparation) onto which the targeted thickness of the alumina is deposited. In the case of 10% weight fraction of TPMS lattices, the targeted alumina thickness is 45 nm. Figure 4-3a shows the total deposited thickness (~68 nm). However, there is a gap of alumina material which is roughly calculated to be approximately 20 nm. Thus, the actual deposited alumina is approximately 48 nm. Figure 4-3(b-d) also provides information of the elemental composition either by detecting the aluminium and oxygen compounds simultaneously as shown in (b), as well as by limiting the detection of one compound at time (c and d). It can be observed that apart from the discontinuous material regions, the rest of the deposited alumina material has a uniform distribution of the aluminium and oxygen compounds. In Figure 4-3b, the silicon substrate is also distinguished from the alumina with yellow color.
Figure 4-3. (a) Image of the deposited alumina as prepared for TEM onto a silicon wafer. (b) EDX analysis detecting the aluminium and oxygen elements of the deposited alumina. (c) EDX analysis selected to detect only the aluminium in the material. (d) EDX analysis selected to detect only the oxygen in the material.

### 4.2.2.2 Mechanical characterization

The fabricated TPMS lattices are tested under uniaxial compression with the use of a displacement-controlled *in situ* SEM indenter (Alemnis AG, Thun, Switzerland) at room temperature and under vacuum conditions (~10⁻⁶ Pa). A diamond flat punch with a diameter of 350 μm (Synton-MDP, Switzerland) is used to compress the structures to an engineering strain of approximately 0.30 and at a constant speed of 1 μm s⁻¹. A load cell of 1.5 N is mounted on the indenter, which is placed in situ in a Vega 3 SEM (Tescan, Brno, Czechia). From the experiments, the force and indenter displacement
are recorded and used to obtain engineering stress and engineering strain. Three experimental repeats on each type of lattice structure are conducted to assess repeatability (Figure 4-4). The Young’s modulus for each lattice structure is calculated from the slope of the elastic part of the experimentally-derived engineering stress-strain curve, i.e. starting from an engineering strain of 0.005 up to approximately 0.02.

![Graphs showing engineering stress and strain curves for 10%, 30%, and 40% wt alumina](image)

Figure 4-4. Engineering stress and strain curves of the three repeats of each case of fabricated lattices for (a) 10%wt, (b) 30%wt and (c) 40%wt of alumina and constant density of $\rho = 127$ kg m$^{-3}$. 
4.3 Results and discussion

4.3.1 Experiments

The results of in situ compression tests on TPMS lattice structures with $\rho = 127 \text{ kg m}^{-3}$ and varying weight fractions of alumina (10%wt, 30%wt and 40%wt) are shown in Figure 4-5. All engineering stress–strain responses (dotted lines, Figure 4-5a) show an alumina weight fraction dependent increase in the Young’s modulus from $147.41 \pm 45.76 \text{ MPa (10%wt)}$ to $148.85 \pm 14.31 \text{ MPa (30%wt)}$ to $310.52 \pm 33.51 \text{ MPa (40%wt)}$, which is in agreement with the expected increased stiffness of the base material. For the 40%wt and 10%wt structures a peak stress is reached at $11.02 \pm 0.11 \text{ MPa}$ and $6.99 \pm 0.11 \text{ MPa}$ respectively, while a peak stress is observed at $8.16 \pm 0.23 \text{ MPa}$ for the 30%wt. The two structures with the highest weight fractions of alumina show a steep drop in force after the peak load, while for the 10%wt case the load decreases much slower with a slope comparable to its corresponding negative Young’s modulus. For the 40%wt case, the load drops to zero indicating complete brittle failure of the structure, while the other two cases maintain some residual load carrying capacity. The experimentally measured specific energy absorption $\psi$ shows a non-monotonic evolution from $3.70 \pm 0.23 \text{ kJ kg}^{-1}$ (10%wt) to $2.46 \pm 0.25 \text{ kJ kg}^{-1}$ (30%wt) to $3.36 \pm 0.22 \text{ kJ kg}^{-1}$ (40%wt). It is noteworthy that the structure with the lowest alumina content in the sandwich wall absorbs the highest amount of energy, outperforming the other two structures by about 30% and 10%, respectively.

Figure 4-5(c-e) shows images of the structures at selected strain levels, which reveal the brittle to ductile transition in the behavior of the structures when reducing the alumina weight fraction in the sandwich wall. Initially all structures deform uniformly. At peak stress ($\varepsilon_{\text{eng}} = 0.049$) the 40%wt alumina structure exhibits visible vertical marks in the horizontal ligaments connecting the unit cells. These are attributed to a concentration of the maximum principal stress (as observed in contour plots of the numerical analysis in Figure 4-6) and it is speculated that they are precursors for initiating fracture of the alumina. In the subsequent deformation steps, a macroscopic crack originates at these locations along the \{1,0,1\}-direction of the lattice structure and leads to catastrophic failure. For the 30%wt structure these marks are not at all visible at peak stress ($\varepsilon_{\text{eng}} = 0.056$), while the 10%wt alumina structure shows barely visible marks at
peak stress, which occur at about twice the engineering strain ($\varepsilon_{\text{eng}} = 0.09$) than for the other two structures. In the subsequent deformation steps, the 30%wt structure collapses from its bottom layer as individual unit cells are split open along their vertical symmetry axis. In contrast, the 10%wt alumina structure deforms uniformly up to $\varepsilon_{\text{eng}} = 0.15$, thereby showing slight barreling. At this strain level, the vertical marks become more prominent and minor cracks are already visible in the bottom layer, however only at a strain level of $\varepsilon_{\text{eng}} = 0.2$ the bottom layer has collapsed and a unit cell in the mid plane has split on its free face along its vertical axis. All experimental results (10%wt, 30%wt and 40%wt of alumina) are shown Table 4-3.
Figure 4-5. (a) Engineering stress - engineering strain curves from the experiments (dotted lines) and numerical simulations (solid lines) for fabricated TPMS lattice structures with $\rho = 127.14$ kg m$^{-3}$. The post-peak point is indicated with crosses for the numerical results and with filled circles for the experimental results. (b) SEM image of a structure with 10%wt of alumina. (c) Images from the in situ compression experiments with (c) 40%, (d) 30% and (e) 10%wt of alumina at various strains.
Figure 4-6. (a) SEM screenshot of the compression experiment at an engineering strain of 0.049 (strain at peak stress) of the 40% wt fraction of alumina TPMS lattice ($\rho = 127$ kg m$^{-3}$) with indications of the initial locations of alumina failure. (b) Corresponding contour plot of the maximum principle stress with similar predicted precursor locations as the ones exhibited during the uniaxial compression experiment.
Table 4.3. Young’s modulus, peak stress and specific energy absorption of TPMS lattices fabricated with different alumina weight fractions and constant density of \( \rho = 127 \text{ kg m}^{-3} \). A minimum number of three repeats for each case of lattice is conducted to ensure repeatability.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>TPMS lattices of ( \rho = 127 \text{ kg m}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta, % )</td>
<td>#</td>
</tr>
<tr>
<td>10%</td>
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<td>3</td>
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<td>Mean</td>
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<tr>
<td></td>
<td>St. Deviation</td>
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<tr>
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<td>1</td>
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<td>Mean</td>
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<td>St. Deviation</td>
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4.3.2 Finite element simulations

Figure 4-7a shows the engineering stress - engineering strain responses from the numerical simulation of TPMS sandwich lattices of constant density \( \rho = 127 \text{ kg m}^{-3} \), while the results for \( \rho = 42 \text{ kg m}^{-3} \) are shown in Figure 4-8. The monolithic polymer and alumina TPMS lattices (0\%-wt and 100\%wt of alumina, respectively) as well as selected weight fractions of alumina (20\%-wt, 50\%wt and 80\%wt) are shown. All curves increase until the first stress maximum, the peak load \( \sigma_{\text{eng P}} \), is reached. Thereafter, a first load drop occurs, which corresponds to the first unstable collapse (i.e. the load drops abruptly) of a layer of unit cells, i.e. the instant at which the structure loses its load bearing capacity for the first time (Figure 4-7c and Figure 4-7d). After this first collapse, all structures show a significantly lower and stagnating stress response, which is
either followed by an increase before the second drop in load (e.g. 100%wt alumina) or directly a second drop in load (e.g. 20%wt alumina). It is observed that a higher alumina weight fraction results in a stiffer response. More specific, for a sandwich lattice with 20% weight fraction of alumina, the Young’s modulus (169.91 MPa) is almost 8 times higher than for monolithic polymer (22.69 MPa). At the same time, the peak stress $\sigma_{\text{eng},P}$ does not evolve monotonically when increasing the weight fraction of alumina. For monolithic polymer and alumina it is 1.73 MPa and 14.08 MPa, while for the cases of 20%wt, 50%wt and 80%wt alumina it increases to 7.00, 11.30 and 10.51 MPa, respectively. It is noteworthy that despite the significantly lower alumina content, the 50%wt lattice is about 7.5% stronger than the 80%wt alumina lattice structure. A non-monotonic evolution is also observed in the post-peak strain $\varepsilon_{\text{eng},PP}$ for different weight fractions of alumina. While monolithic polymer and alumina mark the highest (0.16) and lowest (0.047) values respectively, the value changes for the 20%wt (0.052), 50%wt (0.059) and 80%wt (0.085) alumina weight fractions. Combining these findings, the specific energy absorption $\psi$ is calculated to 1.50 kJ kg$^{-1}$ and 3.37 kJ kg$^{-1}$ for the monolithic polymer and alumina structures, respectively and 1.57, 3.36 and 5.54 kJ kg$^{-1}$ for the 20%wt, 50%wt and 80%wt of alumina. It is noteworthy that a maximum is not obtained for the monolithic alumina or polymer structure, but exists in the vicinity of the 80%wt fraction of alumina. This underlines that a higher weight percentage of alumina in the sandwich lattice does not necessarily result in better mechanical properties, i.e. a higher peak stress, post-peak strain or specific energy absorption, but an optimum exists at which each property is maximized.
Ceramic/Polymer Microlattices: Increasing Specific Energy Absorption Through Sandwich Construction

Figure 4-7. (a) Engineering stress - engineering strain curves of the TPMS sandwich lattices of constant density ($\rho = 127.14 \text{ kg m}^{-3}$) and varying weight fractions of alumina (0%, 20%, 50%, 80% and 100%). Contour plots of the TPMS lattice characterized by weight fractions of alumina at selected strains: (b) 20%wt, (c) 50%wt and (d) 80%wt. The dashed lines correspond to the initial height $l_0$ of the TPMS lattice structure.
Figure 4-7b and Figure 4-7d provide contour plots of the maximal principal stress at peak strain and selected engineering strains for the 20%, 50% and 80%wt alumina TPMS structures, respectively. With increasing the alumina weight fraction from 20%wt to 50%wt and 80%wt, the post-peak strain increases from 0.052 to 0.059 and 0.085, with the instabilities to be more profound for the case of 80%wt, while for the 20%wt the stress concentration is uniformly distributed (comparison between Figure 4-7b and Figure 4-7d at post-peak strain). The deformation response changes significantly with decreasing amount of alumina also for the rest of engineering strains. Specifically, at $\epsilon_{\text{eng}} = 0.15$ the 80%wt structure exposes a fully collapsed middle unit cell layer, while the 50%wt structure shows instabilities in sections of the middle and the bottom layer. In contrast, no clear collapse is visible for the 20%wt structure. Subsequently, at $\epsilon_{\text{eng}} = 0.3$ the 80%wt and 50%wt structures have collapsed and crumpled in the previously triggered layers, while the 20%wt structure shows a cleanly collapsed upper unit cell layer.

Comparing the numerical to the experimental results for a density of $\rho = 127 \text{ kg m}^{-3}$ (Figure 4-5) the overall trends agree acceptably. The numerically determined Young’s modulus for the 10% (102.62 MPa), 30% (224.33 MPa) and 40%wt alumina (282.53 MPa) are within 33% of their experimental counterparts. While the peak stresses agree well for the 30 and 40%wt cases with an error of less than 9%, in the 10%wt case the numerical simulation underestimates the experimental value by more than 1/3. Slight discrepancies are also observed in the post-peak strain, however the specific energy absorption is in acceptable agreement for the 10% (3.21 kJ kg$^{-1}$) and 30% (2.11 kJ kg$^{-1}$) cases (compared to the experimental results of 3.70 ± 0.23 kJ kg$^{-1}$ and 2.46 ± 0.25 kJ kg$^{-1}$ respectively) while the 40%wt alumina case (2.65 kJ kg$^{-1}$) is significantly underestimated (experimentally derived energy absorption at 3.36 ± 0.22 kJ kg$^{-1}$).
Figure 4-8. (a) Engineering stress - engineering strain curves of the TPMS sandwich lattices of constant density ($\rho = 42$ kg m$^{-3}$) and varying weight fractions of alumina (0%, 20%, 50%, 80% and 100%). Contour plots of the TPMS lattice characterized by weight fractions of alumina at selected strains: (b) 20%wt, (c) 50%wt and (d) 80%wt. The dashed lines correspond to the initial height $l_0$ of the TPMS lattice structure.
Results and discussion

Figure 4-9 shows the results from the numerical simulations for all macroscopic densities as well as for the varying weight fractions of alumina as denoted in Figure 4-1(d-e). All values of the monolithic polymer used for normalization are shown in Table 4-1.

The structure’s Young’s modulus normalized by the respective value for a monolithic polymer lattice $\hat{E}(\eta) = E(\eta)/E(\eta = 0)$, shows an almost linear dependence on the weight fraction of alumina (Figure 4-9a). It is noteworthy that a monotonic increase in the normalized Young’s modulus is observed for decreasing macroscopic densities. In other words, for any given weight fraction of alumina, a lower macroscopic density will yield a higher normalized Young’s modulus, with up to 24 times the stiffness of the corresponding monolithic polymer lattice for the case of 85 kg m$^{-3}$.

Figure 4-9b shows the evolution of the normalized peak stress $\hat{\sigma}_{\text{eng},p}(\eta) = \sigma_{\text{eng},p}(\eta)/\sigma_{\text{eng},p}(\eta = 0)$ as a function of the alumina weight fraction. With the exception of the two highest alumina weight fractions, a maximum in the normalized peak stress exists for all assessed configurations between 40%wt and 60%wt alumina. It is noteworthy that for lower macroscopic densities (<127 kg m$^{-3}$) the normalized peak stress exhibits a global maximum within this weight fraction range, exceeding the values of the monolithic polymer structure by a factor of up to 12.

The normalized specific energy absorption $\hat{\psi}(\eta) = \psi(\eta)/\psi(\eta = 0)$ as a function of the weight fraction of alumina is shown in Figure 4-9c. With the exception of the lowest macroscopic density (42 kg m$^{-3}$), all assessed cases exhibit two maxima in $\hat{\psi}$ - one around 10%wt and one at 80%wt of alumina each of which outperforms the monolithic polymer case by a factor of about 2. It is noteworthy that structures with lower macroscopic density see a significant increase in energy absorption when using sandwich walls. While for the 85 kg m$^{-3}$ case a factor of 5 is gained, for the lowest macroscopic density of 42 kg m$^{-3}$ the specific energy absorption of the structures with 40% and 50%wt alumina exceeds the monolithic polymer case by a factor of 9.

A set of configurations exists between 20% and 40%wt alumina which expose a lower normalized specific energy absorption than their corresponding monolithic polymer cases, which is explained by the significant drop in post-peak strain $\varepsilon_{\text{eng},PP}$ for
these structures. Figure 4-9d shows the post-peak strain $\varepsilon_{\text{eng, pp}}$ as a function of the weight fraction of alumina. With the exception of the lowest macroscopic density, all curves follow the same trend – the global maximum in $\varepsilon_{\text{eng, pp}}$ is obtained for the monolithic polymer cases between 0.13 and 0.25, while the global minimum is obtained for all macroscopic densities in the case of the monolithic alumina lattice at around 0.04. It is noteworthy that at 10%wt of alumina the post-peak strain is about 1.5 times higher than for the value at 80%wt alumina. For the lowest global density (42 kg m$^{-3}$) the post-peak strain varies around 0.06 ± 0.009 with maxima for monolithic alumina (0.067) and polymer (0.079) and a minimum at 80%wt alumina (0.051).

Figure 4-9. (a) Normalized Young’s modulus, (b) normalized peak stress, (c) normalized specific energy absorption and (d) post-peak strain as a function of weight fraction of alumina in the sandwich lattice structure for varying densities ($\rho$). The reference for the normalization data
is the Young’s modulus, peak stress and specific energy absorption of monolithic polymer lattice (0%wt fraction of alumina) at each macroscopic density. The detailed reference data can be found in Table 4-1.

Design maps of the numerical results for the Young’s modulus, the peak stress and the specific energy absorption as a function of the macroscopic density are shown in Figure 4-10. It is apparent that the linear dependence of the Young’s modulus on the macroscopic density becomes stronger the higher the weight fraction of alumina in the sandwich walls (Figure 4-10a). For the evolution of the peak stress, at low macroscopic densities (<127 kg m\(^{-3}\)) maxima can be obtained for weight fractions of alumina around 40%wt (Figure 4-10b). For higher densities these sandwich structures are only marginally outperformed by the 90%wt alumina cases, with the highest peak stress obtained for monolithic alumina structures. The specific energy absorption increases only up to a given level for monolithic polymer (2.98 kJ kg\(^{-1}\) for \(\rho= 212 \) kg m\(^{-3}\)) and alumina structures (4.56 kJ kg\(^{-1}\) for \(\rho= 212 \) kg m\(^{-3}\)) before a plateau is reached. This can be attributed to the brittle material behavior in the case of the alumina. It is noteworthy that for all densities >42 kg m\(^{-3}\), a maximum in specific energy absorption is obtained for structures with a weight fraction in alumina around 80%wt. However, a significant improvement is already obtained for all the 10%wt alumina sandwich structures which is a relevant configuration under building time aspects and cost-effective selection of materials compared to a higher alumina weight fraction TPMS lattice (of 80%wt) or a monolithic alumina TPMS lattice of equal density.
Figure 4-10. Design maps of (a) the Young’s modulus, (b) the peak stress and (c) the specific energy absorption as a function of the density for varying weight fractions of alumina in the sandwich lattices. Filled symbols represent the numerical results while crosses denote the corresponding experimental results.
4.4 Conclusions

The effect of sandwich walls made from alumina skins and polymer cores on the mechanical properties of a $3 \times 3 \times 3$ Schwarz Primitive lattice structure is investigated. The main conclusions drawn from this numerical and experimental study are:

1. The absolute Young’s modulus of the lattice structure increases monotonically with increasing macroscopic density and increasing weight fraction of alumina. However, the relative increase, i.e. the effect on the Young’s modulus normalized by the monolithic polymer structure’s Young’s modulus, is highest for the least dense structures.

2. For low macroscopic densities, sandwich walled lattices exist that outperform in terms of obtainable peak load the corresponding monolithic alumina and monolithic polymer structures by a factor of up to 3 and 12, respectively. For these cases, the energy absorption can be increased to up to 9 times over the corresponding monolithic polymer structures when using sandwich walls.

3. For higher macroscopic densities local maxima in the peak load exist around 40-60%wt alumina, however the monolithic alumina outperforms all other structures. In contrast, the specific energy absorption can be maximized for sandwich walled lattices with either a low (~10%wt) or a high (~80%wt) weight fraction in alumina, i.e. very thin or thick skin layers. In these cases the energy absorption can be increased to up to 5 times over the corresponding monolithic polymer structures.

Overall, the sandwich construction on the walls of TPMS lattices is proposed as an advantageous structural design for lightweight engineering applications at which the maximization of the energy absorption capabilities of the lattices is the crucial design component. However, in terms of stiffness, monolithic alumina lattices still outperform the TPMS sandwiched-wall lattices.
5 Summary and Outlook

5.1 Summary of the contributions

The work described in this thesis may be divided into four main research tasks that all contribute to the understanding of the mechanical behavior and optimal design of mechanical metamaterials with characteristic features at the micro- or nanometer level.

The first research task dealt with the development of an experimental protocol to characterize the mechanical and chemical properties of two widely used (in two-photon lithography) negative-tone photoresists. The laser power during the fabrication process of the structures was varied between 70% to 100% of the full capacity of the system. The characterization method involved Raman spectroscopy with the aim of quantifying the degree of polymerization achieved, which is directly connected to the laser power of the 3D printer. It was found that increasing laser power results in achieving higher degrees of conversion (degrees of polymerization) which had an effect on the stiffness and deformation resistance of the final polymer structures. Via this study, a link between a chemical reaction (degree of cross-linking during polymerization) to the mechanical response (stiffness, deformation resistance) is established.

Subsequently, a machine-learning based model is proposed to describe the relationship between the degree of polymerization and the stress-strain response of polymers fabricated via two-photon lithography. The results of more than 140 experiments were used as training data and/or inputs of a neural network model. This model uses the strain and degree of conversion as inputs in order to predict the stress that a polymer structure will experience when compressed within the quasi-static strain-rate range. The model can be used as a prediction tool of the mechanical response of polymer structures without the necessity of conducting mechanical experiments, but only by knowing the fabrication parameters used (laser power in 3D printer).

A third major research task is concerned with the proof of a new design concept for mechanical metamaterials. In the field of ceramic nanolattices, there is often trade-off between recoverability and stiffness. Here, a new design is proposed that achieves high recoverability while increasing stiffness at the same time (as compared to lattices of equal density and traditional design). Specifically, it was shown that the double wall tube lattices of similar shape recoverability (identical ceramic wall thickness) are
always stiffer compared to their single wall counterparts. Additionally, for double wall and single wall tube lattices of equal density (as well as identical shape recoverability), the stiffness of the double wall lattices is twice higher than the one of the single wall lattices. The findings suggest that the double wall tube architecture can be universally applied to various base geometries (such as truss or shell designs) with the aim of pushing the limits of recoverable and stiff ceramic nanolattices.

A forth (and last) research task then explored the potential of sandwich construction to increase the specific stiffness of mechanical metamaterials. Specifically, the walls of shell lattices are built in sandwich construction with ceramic skins and a polymer core layer. The base design of lattices selected for investigating the impact of the sandwich wall on the stiffness, peak stress and energy absorption capabilities of these lattices is the Triply Periodic Minimal Surface (TPMS) topology. Sandwiched-wall TPMS lattices are fabricated for different alumina weight fractions and tested under uniaxial compression. Numerical analysis over a wide range of macroscopic densities is conducted with the aim of revealing any density-related effect. It is found, from the experimental and numerical analysis, that the higher the alumina weight fraction, the stiffer is the lattice for all densities investigated. However, it is found that the lattices with 10\% wt of alumina outperform the energy absorption of lattices with 20-60\% wt and provide similar results to the 70\% or 80\% wt lattices. In terms of peak stress, it is found that there is an optimum alumina weight fraction (40\% wt) for which the peak stress (stress reached prior to a first drop) maximizes for all densities studied with the effect being more profound for the lighter structures. The findings of this task suggest that the sandwich concept is beneficial in terms of energy absorption and peak stress especially for lightweight engineering applications with the decision of the optimal alumina weight fraction to depend on the specific requirements of each application.

5.2 Future Research

The study in Chapter 2 can be extended to cover a wider range of photoresist materials either commercially available or custom-made. Apart from the Raman spectroscopy used in this work for quantifying the degree of polymerization of the structures other quantification methods could be implemented in the future. It would be of high interest to understand further the chemical mechanism of the two-photon polymerization by possibly developing an in situ real time quantification of the degree
of cross-linking. Additionally, the neural network model presented in this work can be extended further in order to be trained for predicting the dynamic response of the photoresists materials.

Moreover, the double-wall tube architecture presented in Chapter 3 as well as the idea of the sandwich construction (and combinations of different materials in the sandwich configuration) shown in Chapter 4 can also be implemented onto different base geometries such as plate and shell lattices. By changing the architecture (double wall) and/or the materials (sandwich), design maps can be generated providing the design guidelines for leveraging the desired mechanical property for the requirements of specific applications. As far as the topology selection is concerned, further optimization of the designs for achieving desired properties of the metamaterials is essential and will pave the way to a more targeted design and material selection for each application [144].

Furthermore, the future research focus could also be concentrated on scaling up the two-photon lithography technique. In my opinion, having the capability of fabricating such micro- and nanolattices in a time- and cost-efficient manner as well as in large quantities will pave the way to a new era of actual industrial applications by implementing the research conducted the past two decades on real-life products.
Publications & Presentations

Refereed journal publications

Work described in this thesis:


Related work not covered in this thesis:


Presentations


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