INTERCONNECTED SELF-PROPAGATING PHOTOPOLYMER WAVEGUIDES: AN ALTERNATIVE TO STEREOLITHOGRAPHY FOR RAPID FORMATION OF LATTICE-BASED OPEN-CELLULAR MATERIALS

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Abstract

Recently, a new technique has been developed to create unique open-cellular materials with micro-scale truss, or lattice features ranging from tens to hundreds of microns. These materials are formed from a three-dimensional, interconnected array of self-propagating photopolymer waveguides. By utilizing this self-propagating effect, three-dimensional open-cellular polymer materials can be formed in seconds. In addition, intrinsic to the process is the ability to control specific micro-lattice parameters which ultimately affect the bulk material properties. Unlike stereolithography, this new fabrication technique is rapid (~ minutes to form an entire part) and relies on a single two-dimensional exposure surface to form three-dimensional structures (thickness > 25 mm possible). This combination of speed and planar scalability opens the possibility for large-scale mass manufacturing. The utility of these new materials range from lightweight energy absorbing structures to thermal management materials to bio-scaffolds.

Introduction

Cellular materials are materials with significant porosity, and thus have considerably lower bulk density than their solid counterparts [1]. Because of their porosity, this class of materials is commonly utilized in lightweight structural applications, or for applications that can directly benefit from the material porosity, such as energy absorption or thermal management [2-4].

Polymer foams are one of the most common types of cellular materials and can be manufactured with a wide range of average unit cell sizes and structures. However, typical foaming processes result in a stochastic structure that limits the mechanical performance and multifunctional application space [1]. Ordered *open-cellular* structures have the potential for improved mechanical performance (higher stiffness and strength per unit mass), as well as accessible open volume for unique multifunctional capabilities [5]. Fabrication techniques for ordered open-cellular polymer materials have relied primarily on rapid prototyping processes, such as stereolithography. Although these techniques enable significant flexibility in the design of the cellular architecture, they also restrict the scalability of the material, and ultimately limit their utility for large-scale or high volume applications.

A new, scalable technique has been developed for fabricating ordered open-cellular polymer materials with micro-lattice features [6, 7]. These materials are formed by exposing a two-dimensional mask with a pattern of circular apertures that is covering a reservoir containing an appropriate photomonomer, as shown in Figure 1. Within the photomonomer, self-propagating photopolymer waveguides originate at each aperture in the direction of the UV collimated beam and polymerize together at points of intersection. By simultaneously forming an interconnected array of these fibers in three-dimensions and removing the uncured monomer, unique three-dimensional lattice-based open-cellular polymer materials can be rapidly fabricated. The following sections include a brief overview of the fabrication capabilities of this new process, as well as highlights from ongoing research. In addition, we have included a detailed comparison

of this fabrication technology with other approaches that can be used to fabricate ordered open-cellular materials, such as stereolithography.
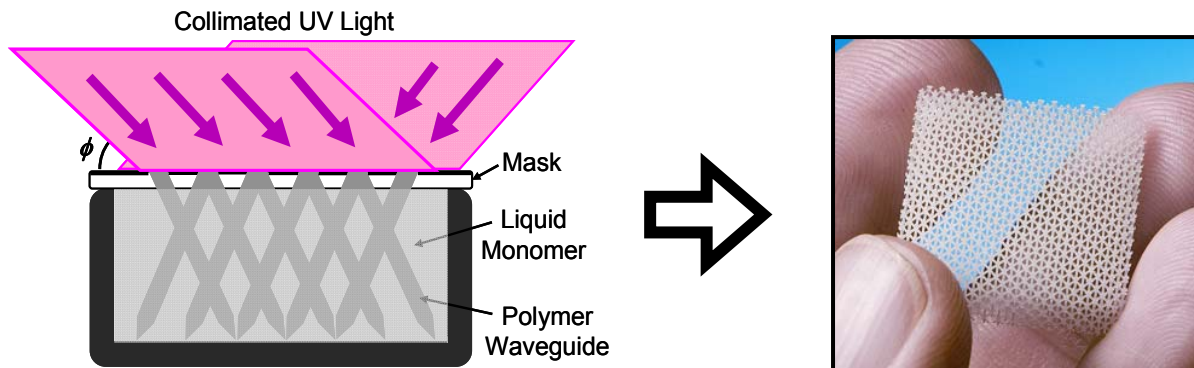

Figure 1. Schematic representation of the process used to form micro-lattice structure from a self-propagating polymer waveguides and an example structure formed by this process.

Unit Cell Architectures and Feature Size Range

Inherent to the photopolymer waveguide process is the ability to control the architectural features of the bulk cellular material by controlling the fiber angle, diameter, and three-dimensional spatial location during fabrication. The general unit cell architecture is controlled by the pattern of circular apertures on the mask and the orientation and angle on the collimated incident UV light beams.

The unit cell architecture shown in Figure 2a is formed by exposing a mask with a square pattern of equally spaced, identical circular apertures to four collimated beams. The collimated beams are rotated 90° apart with respect to the mask normal and have equal incident angle (α) on the mask surface. The dimension L represents the node-to-node spacing, while H is the unit cell height [6].

If a hexagonal mask pattern is employed, unit-cell architectures with three-fold and six-fold symmetry are possible. Figure 2b is a unit cell formed from three equally angled exposure beams, where each beam is aligned along the major axis of the hex pattern but rotated 120° apart with respect to the mask normal. Figure 2c is the unit cell that is formed if six angled exposure beams are used. Each of these beams is also aligned with a major axis of the hex pattern but rotated 60° with respect to the mask normal [8].
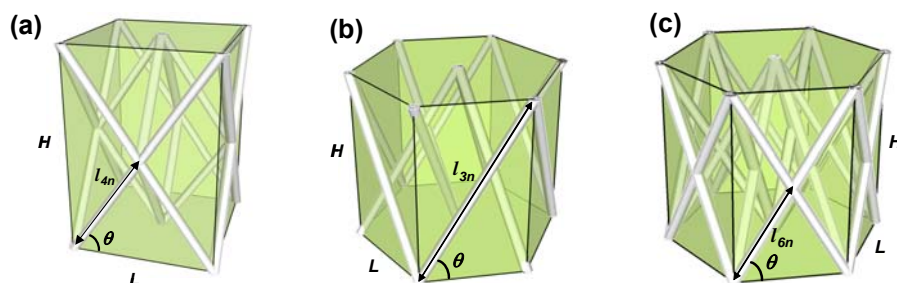

Figure 2. Example unit cell architecture with (a) 4-fold symmetry, (b) 3-fold symmetry, and (c) six-fold symmetry.

In all cases, the angle of the lattice members with respect to the exposure plane (θ) are controlled by the angle of the incident light beam. Small changes in this angle can have a significant effect on the resultant mechanical properties of the material. For example, the compressive modulus (E) of a micro-lattice material comprised of a unit cell shown in Figure 2 is proportional to $\sin^4\theta$. This means a 10° change in the lattice member angle (from $\theta = 50°$ to $\theta = 60°$) can result in a > 50% change in the compressive modulus.

We have investigated the limits of this process and with our current UV exposure capabilities, we can fabricate open-cellular materials with lattice member diameters ranging from ~10 μm to > 1 mm with a relative density (or solid volume fraction) between ~ 5 % up to 30%. The overall material thicknesses can range from 100 μm to over 25 mm. Generally the maximum achievable material thickness, which is dependent on the waveguide propagation distance, is roughly 100X the lattice member diameter. The lattice member angle with respect to the exposure plane can be controlled between ~ 50° - 65° for directly intersecting waveguides. Vertical, or near vertical members are also possible. At lattice member angles between ~ 70° - 80°, intersecting waveguides can couple together to form a single propagating element. Three examples of possible unit cell sizes are shown in Figure 3. These variations in the lattice feature dimensions are possible by changing aperture spacing and diameter on the mask.

In addition to the unit cell architectures shown in Figure 2, non-symmetric architectures, such as functionally graded materials, or hierarchical structures are also possible. An example of a hierarchical structure, with two distinct interpenetrating unit cell sizes is shown in Figure 3c.
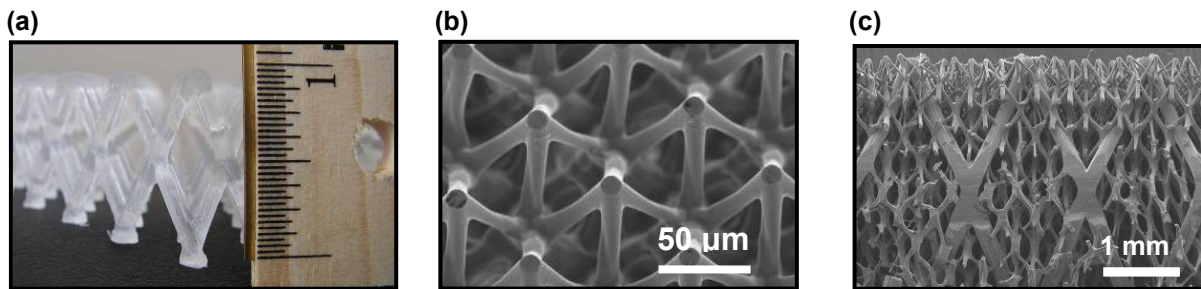
(a)   **(b)**   **(c)**

Figure 3. Images of micro-lattice structures with different unit cell sizes: (a) a single unit cell structure > 25 mm thick, (b) a small unit cell structure with ~ 10μm diameter truss members, (c) a hierarchical structure.

Scalability

This process is the only known fabrication approach that enables such flexibility and precision of the material micro-architecture in combination with the potential for scalable, cost-effective manufacturing. The key distinction of this approach is the ability to fabricate a three-dimensional material from a single, two-dimensional exposure plane. We have fabricated polymer micro-truss samples up to 8" x 8" in a single exposure lasting approximately one minute. Although there are limitations on the maximum dimensions possible for a fixed exposure area utilizing feasible collimated UV sources (~ 24" x 24"), we envision this fabrication approach to be compatible with rapid batch or roll-to-roll type processing, as depicted in Figure 4.
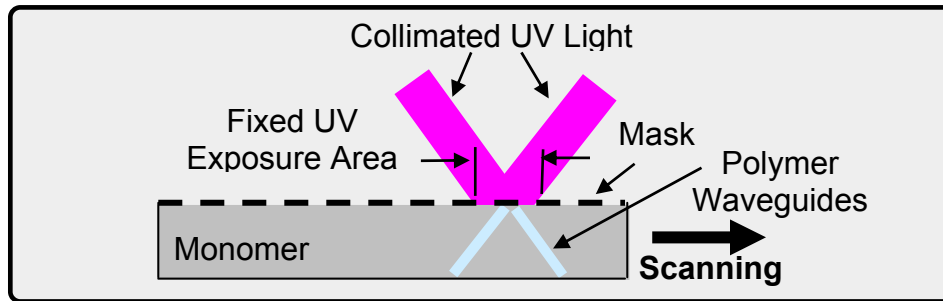
Figure 4. Schematic of scanning approach for roll-to-roll type processing of polymer micro-lattice materials.

Net-Shape Manufacturing of Complex Curvatures

The simplest fabrication set-up for photopolymer waveguide prototyping results in planar micro-lattice structures. After formation of the structure and subsequent clean-out of the uncured monomer, the polymer is not fully cross-linked and can be shaped into complex curvatures. If the thermal post-cure procedure described in [6] is completed with the structure constrained in the desired, non-planar shape, the micro-lattice structure will maintain this shape after the thermal post-cure. Figure 5 is an example of an 8" x 8" micro-lattice structure post-cured to maintain a complex curvature. This anticlastic curvature is not possible with conventional honeycomb cellular materials and difficult to achieve with stochastic foams.

Figure 5. Example of a micro-lattice structure with anticlastic curvature.

Comparison to Other Fabrication Techniques

A comparison of a variety of methods for making ordered, open-cell lattice type structures is given in Table 1. We compared standard stereolithography methods [9], 2-photon stereolithography [10], wire layup [11] and other modular assembly methods [12], and expanded perforated sheet methods [13] to the self-propogating photopolymer waveguide process. Key attributes of each method were assessed, including the ability to fabricate lattice-type materials with precise and independent control of relevant architectural features, the size/shape limitations and other relevant length scales, and other attributes such as throughput and production rate that are important for scale-up manufacturing. Additionally, the range of material options and post-processing techniques were also included for comparison.

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HRL's micro-lattice fabrication technology occupies a unique space in the landscape of available methods for making ordered open-cell lattice type structures. Although the optical waveguide method does not allow for *arbitrary* shapes to be formed within the starting resin bath, it has the potential to form a wide range of free-standing 3D polymer structures based on linear rod-type elements. The pre- and post-processing steps are directly analogous to single and two-photon stereolithography (both start with a bath of uncured resin, and are followed by solvent-based or physical removal of the remaining uncured resin). The major difference arises in the speed with which polymerization can form the resulting 3D structure. For stereolithography, elements within the structure are formed in a serial fashion whereas the optical waveguide process can form all rod-type or linear elements in the structure in parallel with a single exposure step (typically lasting < 1 minute). The optical waveguide method combines aspects of solid free-form manufacturing methods, such as stereolithography, with the scalability of mechanical methods, such as deformed perforated sheet manufacturing, to form lattice-type cellular materials.

Table 1. Comparison of known fabrication methods for open-cellular lattice-type material.

Approach to architected cellular structures	Photopolymer waveguide prototyping (HRL micro-lattice)	Wire or textile layup; modular assembly	Deformed perforated sheet lattice	Stereo-lithography	2-photon stereo-lithography
Unit cell type	3D, Periodic or aperiodic	3D Periodic	3D Periodic	3D Periodic or aperiodic	3D Periodic or aperiodic
Multiple sizes of trusses in unit cell	Yes (Intrinsic to process)	Difficult	No	Yes (maximum flexibility)	Yes
Control of solid member diameter	Independent control	Limited	Limited	Independent control	Independent control
Member angle control*	~50-90°	0-90°	~30°-70°	0-90°	0-90°
Fabrication area	~0.4 m^2	0.1 m^2	~1 m^2	0.25 m^2	0.005 m^2
Thickness range	100 μm - 5 cm	1-20 cm	1mm - 10 cm	1mm – 0.1 m	10 μm – 100 μm
Nominal max. volume	0.02 m^3	0.02 m^3	0.1 m^3	1 m^3	10^{-6} m^3
Max # unit cells through thickness.	~10	~10	1	10's	~10
Min. unit cell size	<50μm	~100 μm	~250 μm	<10μm	<2μm
Min. feature size	<5μm	~10 μm	>100 μm	<1μm	<<0.1μm
Max. # truss elements in a cubic volume	~4000	~4000	3-4	>10000	~1000
Potential to grade properties	Yes	Limited	Limited	Yes (highest flexibility)	Yes
Possible base materials	Polymers	Metals, polymers	Ductile metals, thermoplastics	Polymers	Polymers
Post-processing material options	Template for CVD/CVI, electroplating, investment casting, slurry coating, carbonization	Annealing	Annealing	Template for CVD/CVI, electroplating, casting, slurry coating, carbonization	Limited for very small structures: electroplating or CVD are possible
Rate of manufacture	Minutes	Hours	Minutes	Hours to days	Minutes to hours
Potential for scalable manufacturing	High >1 m^2/ min for continuous process	Medium (single parts only)	High ~1 m^2/ min continuous process	Low (single parts only)	Low (single parts only)

*(relative to horizontal)

Fluid Flow Through Micro-Lattice Structures

Potential micro-lattice applications that span the broad areas of heat and mass transfer require understanding of their fluid flow characteristics. We have combined finite element modeling with physical experiments to create an analytical equation describing the fluid mechanics of flow through the micro-lattice architectures that can be easily fabricated using the photopolymer waveguide prototyping technique. Finite element models of a single unit cell with periodic boundary conditions in 3-dimensions (see Figure 6) were built using Comsol Multiphysics. Experiments were performed on wide range of micro-lattice samples; varying the unit cell size (L), waveguide diameter (D_n), flow velocity and superficial flow angle (ϕ). Non-dimensionalization of the pressure drop versus flow rate data reveals an Ergun-type relationship between friction factor (f_ϕ) and Reynolds number (Re_n), where A_ϕ and B_ϕ are fitting constants and $\varepsilon_{A,\phi}$ is the open area ratio [4]. This equation is useful for design and optimization of multifunctional materials, for instance bio-scaffolds where transport of nutrients is necessary.

$$f_\phi = \frac{A_\phi \left(\dfrac{L}{D_n}\right)^{-8/3}}{Re_n} + B_\phi \left(\frac{1-\varepsilon_{A,\phi}}{\varepsilon_{A,\phi}}\right)^2 \qquad \text{(Eq. 1)}$$
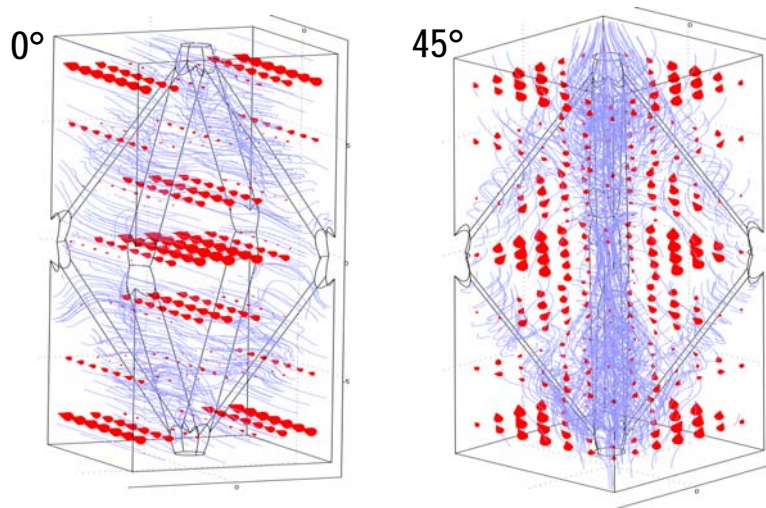

Figure 6. Finite element model of flow through micro-lattice unit cell at two superficial flow orientations.

Controllable Degradation for Bio-Scaffolding Applications

This process to fabricate polymer micro-lattice structures is ideally suited for fabrication of bio-scaffolding because of the flexibility in the design of different ordered unit-cell architectures and the range of possible unit cell feature sizes. In addition to controlling the shape, size, and distribution of the open pores, a key characteristic of an ideal bio-scaffold material is the ability to control its degradation rate in the desired environment (for example, the human body) [14].

The degradation time of thiol-ene polymer micro-lattice structures (described in [6]) in a buffer solution at 37°C is estimated to take years. An oxidation chemical pre-treatment can be

performed on the polymer micro-lattice samples to reduce this degradation time to weeks or months, time scales ideally suited for tissue scaffold applications. The exact degradation rate of the polymer micro-lattice structures can be controlled by controlling the parameters of the oxidation treatment, such as the concentration of the hydrogen peroxide solution, or the temperature and time of the treatment.

To demonstrate control of the degradation time, three identical polymer micro-lattice samples were exposed hydrogen peroxide under different conditions. One sample was held in 5% H_2O_2 solution for 10 min. The remaining two samples where placed in 30% H_2O_2 solution, one for 30 minutes and one for 60 minutes. After the H_2O_2 treatment in an ultrasonic bath, each sample was washed with copious amounts of DI water and dried in air. The samples were subsequently placed into a 0.01 M phosphate buffered saline solution (NaCl 0.138 M; KCl 0.0027M; pH=7.4) at 80 ^{o}C, which accelerates the degradation time compared to 37 ^{o}C. After 12 hours in the buffer solution, the sample exposed to 30% H_2O_2 for 60 minutes was completely dissolved whereas the sample exposed to 30% H_2O_2 for 30 minutes was only partially dissolved. The sample exposed to 5% H_2O_2 appeared unaltered. Images of these three samples in the buffer solution are shown in Figure 7.
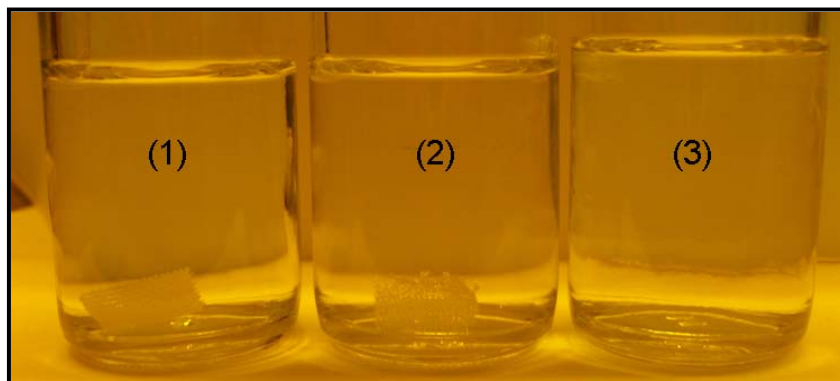

Figure 7. Polymer micro-lattice samples after different hydrogen peroxide pre-treatments and exposure to buffer solution at 80°C for 12 hours. Sample (1) was treated with 5% H_2O_2 for 10 min; Sample (2) was treated with 30% H_2O_2 for 30 min; and Sample (3) was treated with 30% H_2O_2 for 60 minutes.

Summary

A new fabrication technique has been presented for fabricating polymer micro-lattice structures from an interconnected three-dimensional array of self-propagating photopolymer waveguides. This technique enables the potential for large-scale, mass manufacturing of polymer micro-lattice materials without sacrificing the ability to independently control the unit-cell architectural features, such as unit-cell symmetry or lattice member diameter. In addition, the planar polymer micro-lattice structures can be thermally post-cured to form complex curvatures without additional machining steps. The utility of these new materials spans a wide range of different applications, including lightweight energy absorbing structures, thermal management materials, bio-scaffolds.

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