A TEMPLATE-BASED FABRICATION TECHNIQUE FOR SPATIALLY-DESIGNED POLYMER MICRO/NANOFIBER COMPOSITES

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ABSTRACT

This paper reports a template-based technique for the fabrication of polymer micro/nanofiber composites, exercising control over the fiber dimensions and alignment. Unlike conventional spinning-based methods of fiber production, the presented approach is based on micro-transfer molding. It is a parallel processing technique capable of producing fibers with control over both in-plane and out-of-plane geometries, in addition to packing density and layout of the fibers. Collagen has been used as a test polymer to demonstrate the concept. Hollow and solid collagen fibers with various spatial layouts have been fabricated. Produced fibers have widths ranging from 2 μm to 50 μm, and fiber thicknesses ranging from 300 nm to 3 μm. Also, three-dimensionality of the process has been demonstrated by producing in-plane serpentine fibers with designed arc lengths, out-of-plane wavy fibers, fibers with focalized particle encapsulation, and porous fibers with desired periodicity and pore sizes.

KEYWORDS

Micro/nanofibers, Microtransfer molding, Collagen, Fiber composite

INTRODUCTION

Over the past few decades, substantial research has been directed towards the fabrication of polymer micro/nanofiber reinforced composites for a variety of applications including clothing, aerospace engineering, and biological applications. One of the prime features offered by a fiber composite is its enhanced mechanical characteristics as compared to the constituent matrix material or the fibers. The mechanical properties of fiber composites are governed not only by the fiber properties and dimensions, but also by the fiber distribution and volume fraction in the matrix. Randomly aligned fibers pose a difficulty in packing large proportions of fibers tightly, also making it harder to predict the mechanical behavior of the composite. A controlled and orderly fiber arrangement enables tunability of the mechanical properties of the resultant composite material. In addition to good fiber alignment, certain applications require control over the shape and spatial layout of the fibers. Although considerable advancements have been made in the currently existing methods of polymer micro/nanofiber production, such as electrospinning [1], wet-spinning [2], and drawing [3], it is challenging to obtain precise control over the dimensions, alignment and layout of the fibers produced in these fashions within a composite.

The presented method exploits molding techniques to fabricate parallel fibers with desired placement, sizes and shapes. Conventional MEMS fabrication processes are utilized to sculpt and demold the fibers. Also, this process obviates handling of large numbers of fibers for building composites as it involves a simple transfer of the fabricated fibers to the matrix material without disturbing the arrangement.

FABRICATION METHOD

The reported fabrication method is based on microtransfer molding [4], a process used for building free-standing three-dimensional polymer negative replicas of a template. Figure 1 shows a schematic of the fabrication process sequence. Trenches with the required fiber layout design are etched into a silicon wafer using inductively coupled plasma (ICP) etching. This step is optionally followed by a potassium hydroxide (KOH) etching process to sharpen the tips of the trenches. This helps reduce polymer webbing due to surface tension effects, and facilitates the fiber individualization and demolding of fibers. The template is then coated with a thin layer of parylene to aid in fiber release (Figure 1a). A desired volume and concentration of collagen solution is poured on the template and degassed in vacuum.

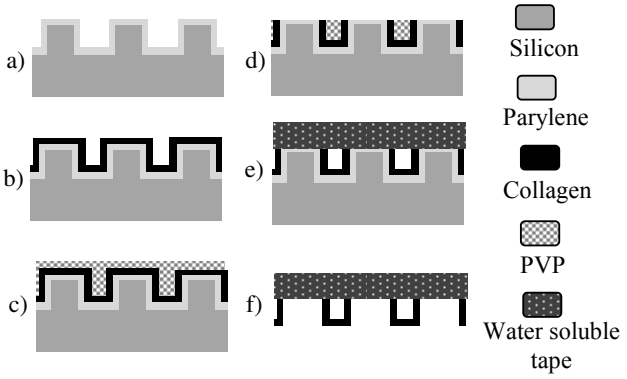

***Figure 1**. Fabrication process sequence, a) Deposit parylene on the silicon template, b) Solvent cast collagen solution, c) Spray coat PVP protectant, d) Individualize fibers by dry mechanical grinding or RIE, e) and f) Extract fibers using a water soluble tape after dissolving away PVP.*

This is followed by solvent casting to form a conformal collagen film on the template (Figures 1b and 2b). Polyvinylpyrrolidone (PVP), a water soluble polymer is spray coated on the template. The polymer fills up the trenches, selectively masking the collagen film in the troughs. It acts as a protectant for the fibers during fiber individualization (Figure 1c). The portion of the film on the upper part of the trenches is removed by dry mechanical polishing or reactive ion etching (RIE), forming individualized collagen micro/nanofibers in the trenches (Figure 1d). The fibers are extricated from the trenches using a water-soluble tape with their alignments retained (Figures 1e, 1f and 2c).

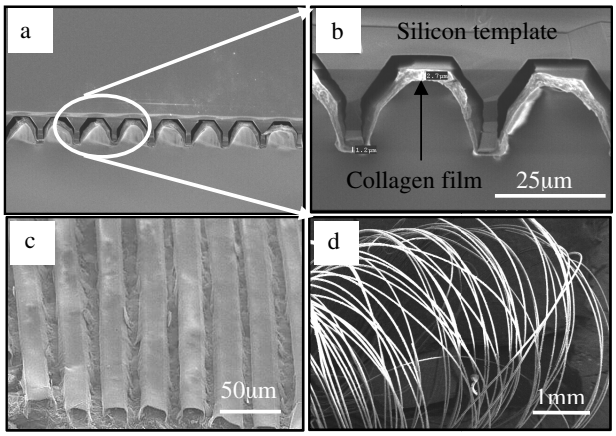

Figure 2. *SEM images of, a) and b) cross section view of solvent cast collagen film on a silicon template with tip sharpened trenches, c) 25 µm wide individualized hollow collagen fibers extracted from the template using tape, alignment of the fibers is retained, d) 25 µm wide collagen fibers separated from the template by direct peeling.*

HOLLOW AND SOLID FIBER DIMENSIONS

The wall thickness of the fibers depends on the concentration, and volume of the collagen solution used for a given surface area. The solvent cast film thickness can be roughly estimated by equation (1).

$$T_d = T_w \times M = \frac{V}{S} \times \frac{C}{\rho} \qquad (1)$$

Where,

T_d = Thickness of dry cast film
T_w = Thickness of wet film
M = % of solid collagen in the solution
V = Volume of collagen solution used
S = Effective surface area of the template used for solvent casting
C = Concentration of collagen solution used
ρ = Density of collagen

Figure 3 illustrates the variation of the fiber wall thickness with the concentration and volume of collagen solution. The measured values follow the same trend as the estimated values. The noted differences in the values may be attributed to losses resulting from seepage of the polymer solution to the bottom of the die, increasing the effective surface area.

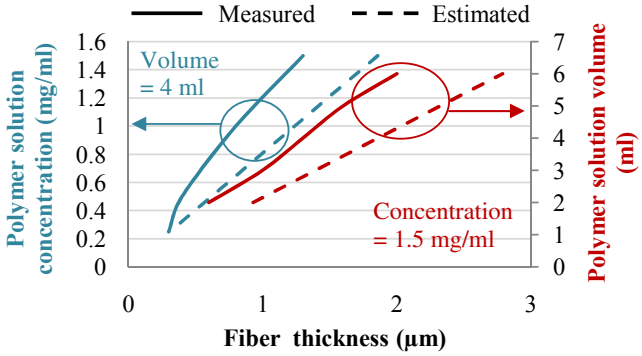

Figure 3. *Variation of fiber wall thickness with collagen solution concentration for a fixed volume of 4 ml, and volume of the collagen solution for a concentration of 1.5 mg/ml.*

By regulating the dimensions and cross sections of the template, and the collagen solution properties used, hollow or solid fibers are obtained. Figures 4a and 4b illustrate a rectangular cross-section hollow fiber fabricated using a 20 µm deep template with 3 ml of 1.5 mg/ml concentration collagen, and a ribbon-like solid fiber fabricated using a 4 µm deep template with 5 ml of 2 mg/ml concentration collagen, respectively.

The width and length of the fiber are determined by the template design. This method has been used to fabricate fibers with widths spanning from 2 µm (length-1cm) (Figure 4c) to 50 µm (length- 4cm) and wall thicknesses varying from 300 nm to 3 µm.

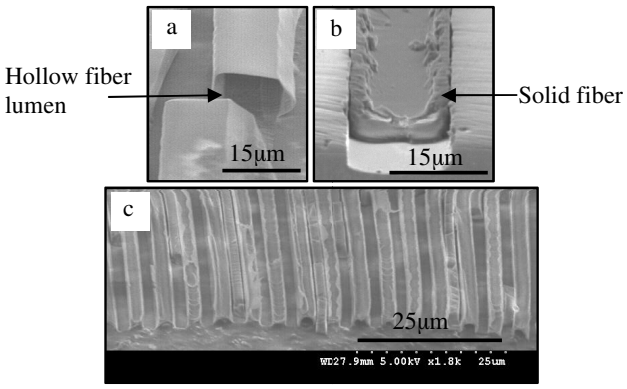

Figure 4. *SEM images of, a) a hollow collagen fiber, b) a ribbon like solid collagen fiber, and c) 2 µm hollow fibers on tape.*

SPATIALLY DESIGNED FIBER COMPOSITE

For applications demanding three-dimensional control over the manipulation of the fibers, appropriate silicon template designs with the desired structure in the horizontal and vertical planes of the mold are used to obtain the required spatial fiber layouts.

In-plane and out-of-plane crimped fibers

A certain amount of slack in the load bearing fibers held in a matrix material can improve the elasticity of the resultant composite material. Many soft tissues in the human body, such as tendons and ligaments, are made up of crimped fiber bundles for this reason [5]. Such in-plane and out-of-plane wavy fibers can be fabricated using the template-based method. For in-plane undulated fibers, templates with serpentine trenches are used (Figure 5). The arc lengths of the serpentine patterns are modified to fabricate in-plane wavy fibers with designed failure strains ranging from 11 % to 57 %. The templates for out-of-plane wavy fibers are fabricated to have a multi-depth structure necessary for delineating the out-of-plane geometries of the resultant fibers (Figure 6a). Sequential plasma and KOH etching steps are used to fabricate these templates. For this process, solvent casting of collagen solution is replaced by spray coating over the template. This forms undulated fibers, preseparated from one another, transferred directly to a water soluble tape (Figure 6b).

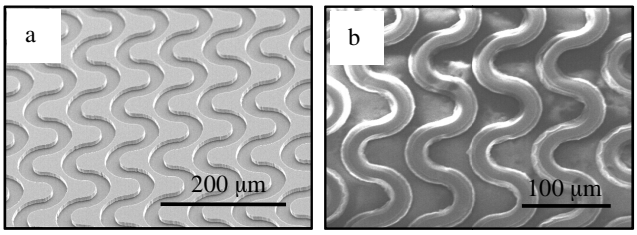

Figure 5. *SEM images of, a) a serpentine silicon template, and b) in-plane serpentine collagen fibers with a designed strain of 57%.*

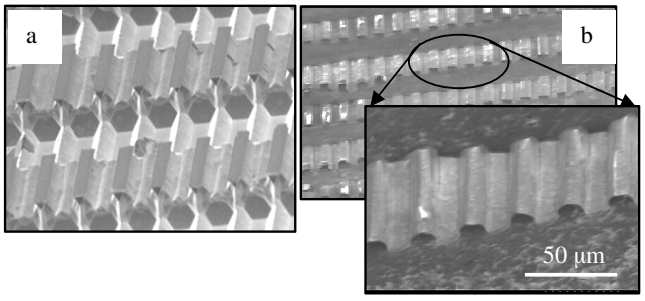

Figure 6. *SEM images of, a) a multi-depth silicon template for the fabrication of out-of-plane wavy fibers, and b) out-of-plane wavy collagen fibers.*

Fibers with localized particle encapsulation

Often applications demand entrapment of material such as drug loaded particles [6] and cells [7] in hollow fibers. Silicon templates used in the template-based method can be tailored to fabricate fibers for focalized particle encapsulation. These templates have wells periodically placed in the trenches to capture the particles (Figure 7a). The well diameter is designed to be larger than the target particle size. This concept is demonstrated using glass beads (diameters: 10-30 μm) as test particles. A collagen film is cast over the template. After fiber individualization, the glass beads are driven into the fiber wells by template pattern guided self-assembly (Figure 7b). A second layer of collagen is cast on the template, forming enclosed hollow fibers with glass beads encapsulated in the periodic wells (Figure 7c).

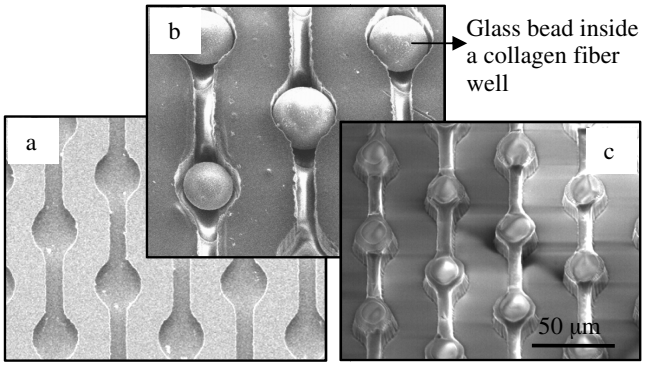

Figure 7. *SEM images of, a) a silicon template for the fabrication of fibers for particle encapsulation, b) glass beads placed in periodic wells along hollow collagen fibers inside the trenches of the template, and c) glass bead encapsulated collagen fibers extricated using tape.*

Porous fibers

Using templates with pillars in the trenches, porous fibers are fabricated (Figure 8). The pore size and placement can be designed as required. Such porous fiber networks can find applicability in the area of filtration and chemical sensing.

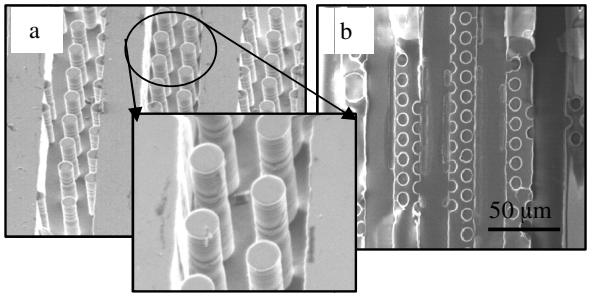

Figure 8. *SEM images of, a) a silicon template with pillars in the trenches, and b) porous collagen fibers on tape.*

Fabrication of composite material

For the fabrication of fiber reinforced composites, the matrix material is cast on the water soluble tape holding the produced fibers. The tape is dissolved away leaving behind fibers embedded in the matrix. A microfiber composite with collagen fibers in biological tissue matrix (elastin) has been demonstrated. Such a scaffold can find use in tissue engineering applications. Figure 9 shows a unidirectional aligned collagen microfiber composite lamina.

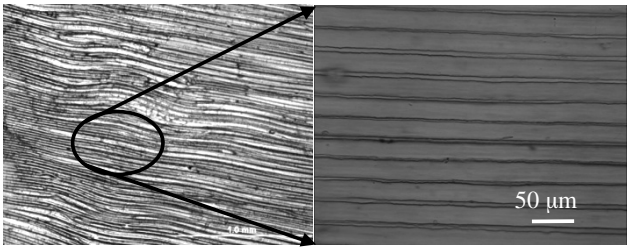

Figure 9. *Microscope image of an aligned collagen microfiber composite in elastin matrix.*

MECHANICAL CHARACTERIZATION

Stress-strain relationship of the fiber composites is derived by applying a constant strain rate to the material until failure. Preliminary mechanical tests suggest that the material exhibits the expected trend of stiffening along the fiber direction as compared to the direction perpendicular to it (Figure 10). Young's modulus of these composite materials along the fiber direction is observed to be 2.2-3 times the modulus in the perpendicular direction, demonstrating their orthotropic nature (Table 1). These tests have been conducted on fiber composites with approximately 1% fiber volume fraction. Non-uniformities of the elastin film have not been taken into account while making these measurements.

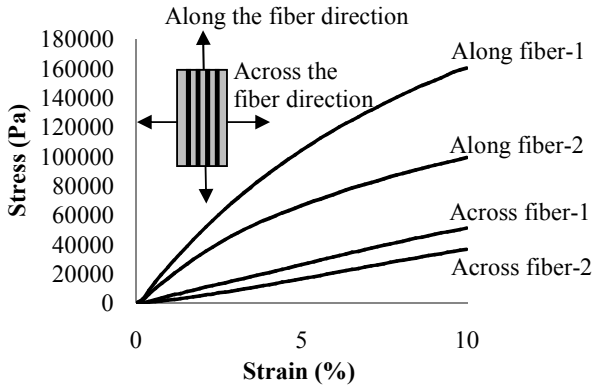

Figure 10. *Stress-strain relationship of collagen-elastin composite illustrating material stiffening along the fiber direction as compared to across the fiber direction.*

Table 1*. Young's moduli of collagen-elastin composite materials along the fiber direction and across the fiber direction, calculated between 4-6 % strains.*

Direction of the applied load	Young's modulus (kPa)	
	Sample-1	Sample-2
Along the fiber orientation	1500	900
Perpendicular to the fiber orientation	500	400

CONCLUSION

Fabrication of polymer micro/nanofiber composites using a microtransfer-molding-based methodology has been established. The fabrication method is shown to offer a well defined spatial layout of the fibers along with a control over their dimensions. A collagen-elastin composite material has been demonstrated for potential application as a tissue scaffold. This technique can be extended to other polymers and also can be potentially scaled down to form nano-width fibers.

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