Controlled Geometry Fabrication of Polydimethylsiloxane Nanofibers for Biomimetics

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ABSTRACT: The ability to have control of fabricated structures on the nanometer size scale is essential in interfacing inorganic technologies with biological systems in many scientific areas including biomimetics and cell topology studies. Here, we developed a simple and efficient method to produce polydimethylsiloxane (PDMS) nanofibers with controlled aspect ratios that could be used in biological studies. As PDMS is a well studied polymer system, this structure would enable a variety of diverse applications. A template synthesis technique was used to create the fibers by molding a polymer solution into an alumina membrane. The pressure and the template surface chemical characteristics were controlled to enable the easy creation of geometric configurations with up to a 30-fold range of aspects ratios through the use of the same porous alumina template. These fibers can be also used in producing biomimetic synthetic column structures that are found in biological systems such as spider hairs and gecko feet. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2549–2552, 2007

Key words: nanofibers; biomimetic; polydimethylsiloxane; fabrication

INTRODUCTION

The fabrication of nanometer scale structures that maintain high aspect ratios has been investigated for many years leading to technologies such as carbon nanotubes and silicon nanoneedles with many recent applications focusing on the biological world. The ability to create these configurations in controlled schemes though is often limited by the complexity of the fabrication process, which inhibits reproducibility and often requires predefined systems for each geometry in polymeric systems. To develop methods at these size scales, both the ability to form these initial geometries and to have repeatable yet robust control over defining the types and sizes of structures and shapes is essential. The current techniques used to obtain many small scale structured surfaces are based on photolithography and electron beam lithography.[1–5] Unfortunately, these techniques are expensive, require significant training, and are often time consuming. Another method that is able to fabricate islands is based on phase separation of a blend of polymers,[6,7] but the ability to produce nanometer scaled features of controlled size and geometry in this fashion is very challenging.

As the ability to build fiber structures has been developing, their utilization within diverse research areas has shown promise. One area that has garnered attention is within the biological realm. The materials for these fiber structures though are often the limiting factor due to compatibility and mimicking issues. One material that has been utilized in a variety of biological experiments in the past though is PDMS. Cells have been cultured on PDMS to explore how topography of the substrate can influence the general cell responses such as the motility and cytoskeletal structure of individual cells.[8–14] Furthermore, column shaped structures have gained interest for nature-based approaches including biomimetics. The columns can potentially be used to create structures that emulate nature inspired architectures including those found in spiders and geckos. These structures, which are important in biological systems, have received increasing attention due to their unique emergent properties that arise from nanometer scale phenomena.[15–18] To realize the goal of creating complex systems in this realm, developing new and robust techniques to fabricate a range of structures with nanometer scale controlled surfaces that can be interfaced with biologically relevant research is paramount.

To fabricate these nanostructures, template synthesis has provided a potential avenue for success. Template synthesis is a simple and efficient method

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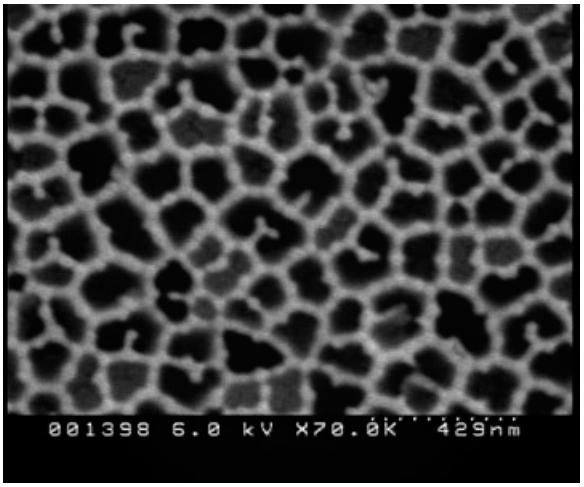

Figure 1 Scanning electron micrograph of the surface of an nodisc alumina membrane that was used as a template.

to develop nanomaterials with controlled dimensions.[19–21] This technique allows the deposition of materials within the pores of a membrane that can be used to create configurations, which are challenging to build through other methods. Here, we used this general approach to fabricate PDMS nanofibers with a controlled array of aspect ratios, which are varied up to 30-fold. We pursued this challenge through using a simple PDMS molding process in combination with a porous alumina membrane used as a template. Using the same template and varying the deposition parameters and surface characteristics, we created fibers with different lengths, while maintaining the same diameter. We accomplished this through controlling the input in the fabrication step, the pressure, and the hydrophobicity of the template, to create fibers. Hydrophilic porous alumina membranes were used in an unmodified state yet we also created hydrophobic membranes through modifying the silane. This inexpensive, easy, and rapid process to fabricate PDMS nanofibers has many potential applications including the study of cell-substrate interactions and also in creating synthetic gecko foot-hairs.[22,23]

EXPERIMENTAL

Alumina templates and PDMS

Porous alumina Anodics membranes (Whatman, Inc.) were used as templates, which had a thickness of 60 μm and an average pore diameter of 200 nm (Fig. 1). A solution that was 5% (v/v) in octadecyltrimethoxysilane (C_{18}) was prepared in ethanol. Acetate buffer (50 mM, pH = 5.1) was added to this solution to 5% (v/v) in the buffer. Octadecyltrimethoxysilane was obtained from Aldrich. The resulting solution was stirred for 30 min before immersing the alumina membrane. After 2 h, the membrane was removed from the solution and rinsed with ethanol. Next, the membrane was sonicated for 10 min in ethanol to remove unreacted silane and the C_{18}-modified membrane was cured at 150°C in air for 20 min. The modified membranes were very hydrophobic. The C_{18} coating and the hydrophobicity were found to be similar to what was observed previously.[24] These C_{18}-modified membranes, along with the unmodified alumina membranes, were then used as templates for fabrication of PDMS nanofibers. The PDMS liquid was mixed with a crosslinking reagent (Sylgard 184 Silicone Elastomer Kit, Dow Corning) and then degassed for 2 h prior the molding process.

Nanofiber template synthesis

We used two methods that were a combination of manipulating the physical and chemical characteristics of our system. First the PDMS fibers were fabri-

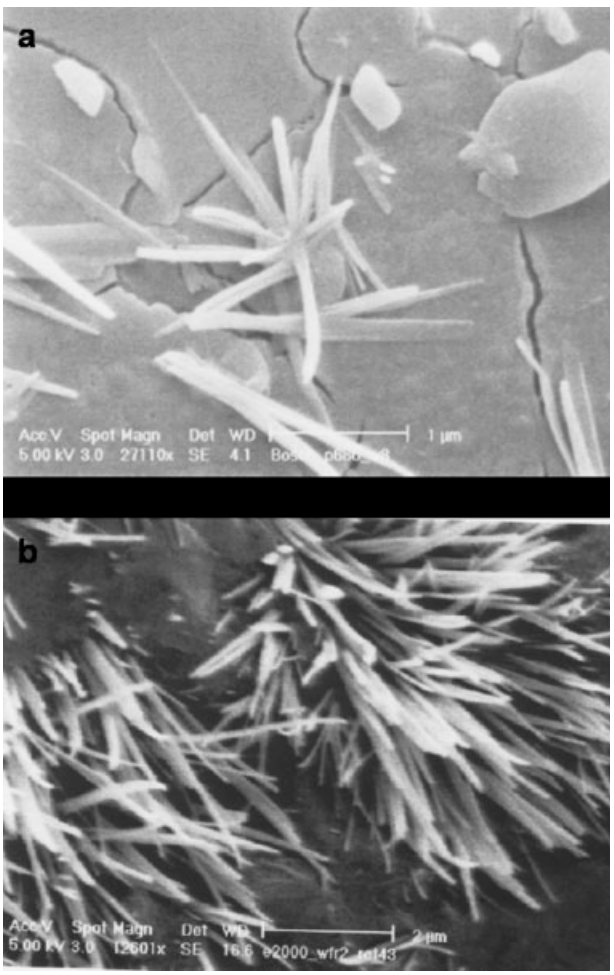

Figure 2 Scanning electron micrographs of the polydimethylsiloxane (PDMS) nanofibers obtained using an unmodified alumina membrane (a) at atmospheric pressure, 760 Torr and (b) under a 10^{-3} Torr vacuum.

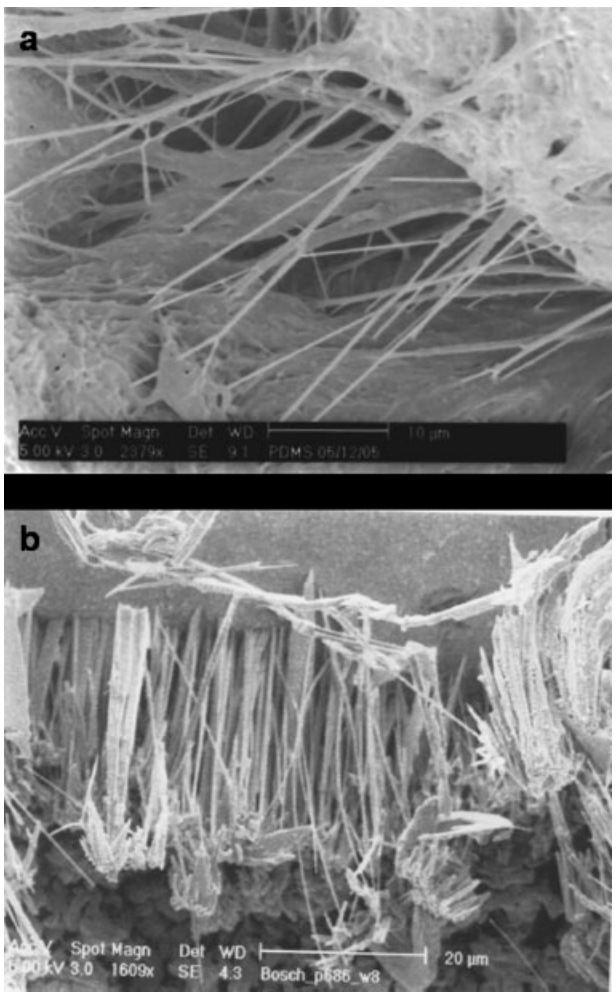

Figure 3 Scanning electron micrographs of the PDMS fibers obtained using C_{18}-modified alumina membranes at (a) atmospheric pressure, 760 Torr and (b) under a 10^{-3} Torr vacuum.

cated through using unmodified alumina templates. A thin layer of PDMS was created with part of the degassed solution placed over the unmodified alumina template under vacuum. Then another portion of the PDMS was added on the top of the templates at atmospheric pressure for 7 h. Our second method was to fabricate the fibers using C_{18}-modified alumina templates with a similar protocol as the mold. In both methods, the PDMS-filled templates were cured for 24 h at room temperature. The length of the fibers was controlled by implementing different temporal activation scenarios. At high temperatures though, the PDMS solution cured too rapidly to allow diffusion into the template pores. After molding and curing, the PDMS nanofibers were released from the templates either by peeling the PDMS layer off the alumina or by dissolving the alumina templates in a 4*M* aqueous sodium hydroxide solution.

The nanofibers were imaged using a Philips XL30 Field Emission Scanning Electron Microscope (FE-SEM). The FE-SEM samples were made conductive by sputtering a thin layer of gold using a Polaron model E6100 sputter coater.

RESULTS AND DISSCUSSION

We demonstrate our ability to create controlled aspect ratio fibers on the nanometer scale. To create nanofibers of defined lengths and aspect ratios, we controlled the applied pressure and surface chemical characteristics of the templates during the molding process. Initially PDMS nanofibers were created through simply using an unmodified alumina template where the PDMS was cured at room temperature under both atmospheric pressure, 760 Torr, [Fig. 2(a)] and under a 10^{-3} Torr vacuum [Fig. 2(b)]. The templates with the PDMS layers have been placed into a Buchner funnel mounted on a filtering flask and the vacuum was applied. The PDMS nanofibers were observed to be longer when fabricated under vacuum than those obtained at atmospheric pressure (2 μm, compared with 1 μm in length). The fibers obtained through vacuum molding were longer because the PDMS was forced through the template by the application of reduced pressure. In addition, the vacuum molding is faster than the atmospheric molding, allowing a great percentage of the pores to be filled in the same period of time. Next, through utilizing a C_{18}-modified alumina template, we were able to create nanofibers that were distinct from using with the unmodified mold [Figs. 3a,b)].

These nanofibers were an order of magnitude greater in length but maintain similar widths. Furthermore, the fibers that were created with curing under a vacuum were longer than those obtained under atmospheric pressure (30 μm, compared with 20 μm in length). The nanofibers that were inside the C_{18}-modified templates had up to 30-fold greater

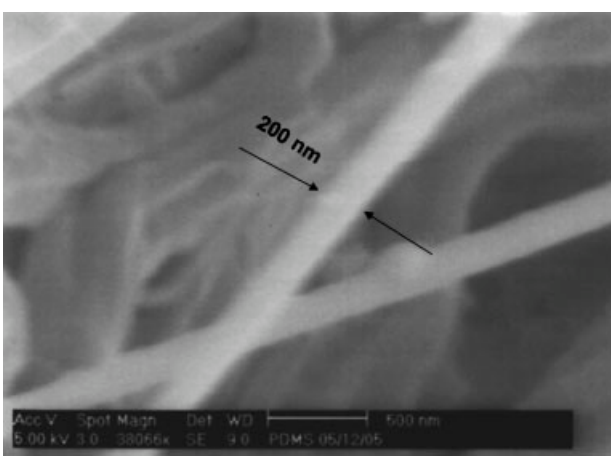

Figure 4 Scanning electron micrograph depicting the width of the PDMS fibers.

TABLE I
Aspect Ratio of the PDMS Nanofibers Obtained Through Controlling Pressure Conditions and Surface Modification

Alumina template	Pressure conditions	Length (μm)	Diameter (nm)	Aspect ratio (diameter : length)
Unmodified	atm. pressure	1	200	1 : 5
Unmodified	vacuum, 10^{-3} Torr	2	200	1 : 10
C_{18}-modified	atm. pressure	20	200	1 : 100
C_{18}-modified	vacuum, 10^{-3} Torr	30	200	1 : 150

aspect ratios than those produced through using unmodified membranes, yet they both maintained similar fiber widths. The diameter of the PDMS nanofibers produced by both methods is $\sim$ 200 nm, which is the same as the diameter of template's pores (Fig. 4). C_{18}-modified membranes are very hydrophobic, having a contact angle of 130°.[24] Also PDMS is a hydrophobic polymer, and we believe that due to the hydrophobic affinity of these two materials, the diffusion of PDMS through the C18-modified membranes is greatly facilitated. This enabled us to have the ability to increase the length of these fibers. The pressure effect on fiber length was slightly different for unmodified templates (factor 2) versus C_{18}-modified templates (factor 1.5). As we did not expect any difference in pressure effect for treated and treated membranes, we believe this can be attributed to the nonhomogeneous pore size distribution of the template; the template has the average diameter of 200 nm, but it varies from 100 to 300 nm, and the amount of molded PDMS varies, leadings to different fiber lengths.

The results of many experiments (Table I) reveals that we can use our simple methods to create fibers with aspect ratios from 1 : 5 up to 1 : 150, while maintaining diameters on the nanometer size scale. These characteristics are solely determined by controlling the pressure during the curing process and the surface characteristics of the template. Creating these fibers with flexibility in their size and aspect ratio is essential for building devices that mimic biological systems. For example, gecko feet and spider hairs are found to be in this range of sizes and thus the ability to synthetically create these systems could be enabled.

CONCLUSIONS

The ability to create high aspect ratio fibers is important in numerous biological applications. While developing these fibers has been accomplished in the past, the ability to have simple and efficient techniques for creating controllable geometries of polymer fibers will open new avenues for a diversity of researchers. Here we have shown the development of a fabrication process for creating PDMS nanofibers within the pores of alumina template membranes to have up to a 30-fold range in their aspect ratio. The characteristics of these nanofibers were controlled by applying different pressures in the molding process and by modifying the surface of the template with a hydrophobic silane. This simple technique has great potential in the fabrication of nanostructures for use in many areas including the study of cell-structure behavior due to nanotopography and also in producing biomimetic synthetic gecko and spider based systems.

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