Self-Assembled Axisymmetric Microscale Periodic Wrinkles on Elastomer Fibers

In this work, we demonstrate a novel scalable microscale manufacturing technique that creates self-assembled ring-shaped periodic perturbations in the form of wrinkles on a polymer fiber concentric to the fiber axis. The wrinkles are generated by stretching a soft polymer fiber made of polydimethylsiloxane (PDMS) to strains ranging from 10% to 200%, followed by an ultraviolet (UV)/ozone exposure to create a hard SiO\textsubscript{x} film over the soft fiber before releasing the fiber strain. We identified the key variables controlling the wavelength of the microscale wrinkles. Possible applications of the method in optical and other devices are discussed. [DOI: 10.1115/1.4036112]

Keywords: PDMS, elastomer fiber, periodic wrinkles, self-assembly

Introduction

Surface wrinkles on planar geometries are known for creating a periodic variations in the near-surface properties [1–4] that have been utilized for various applications, such as sensing [3,5], colloidal particle assembly [6], stretchable electronics [7], supercapacitors [8], and lithography masks [9]. The planar wrinkles are created by first stretching a polymer (e.g., a slab of elastomer such as PDMS) to a large strain either by heating or by tensile loading created by first stretching a polymer (e.g., a slab of elastomer such as PDMS) to a large strain either by heating or by tensile loading followed by creating a hard surface skin on the polymer surface [10]. The strain in the bulk of the substrate is then released to cause the skin layer to buckle instead of crushing under the compressive stress [11]. The skin layer is deposited using methods including physical vapor deposition of a relatively rigid material [12–18], a surface chemical reaction that converts surface of the polymer into a hard material [19], or by surface chemical bonding [20]. Note that the mechanics of wrinkle formation on planar surfaces has been investigated by using plasticity theory, finite deformation theory, and finite element modeling [21–24]. In addition to planar substrates, wrinkles have also been studied on curved spherical and cylindrical substrates. Concentric wrinkles of a few micrometers periodicity on polyurethane (PU) fibers coated with a layer of 10 nm gold were formed by prestraining the fibers to \( \sim 2\% \) and using shape memory effect [25]. A biobased system involving random wrinkle patterns on a planar surface that mimicked the polymer assemblies in wood fibers was demonstrated with green materials and processes [26]. Constrained swelling or shrinkage was used to form wrinkles on core–shell cylindrical structures parallel to the axial direction [27]. Spherical Ag core/SiO\textsubscript{x} shell system was used to study the effect of curvature on the surface wrinkle patterns [28]. Sheath–core fibers buckled by stretching a rubber fiber and wrapping it with a multilayer carbon nanotube sheet were demonstrated for use in highly stretchable conductors [29]. The above studies show a high current interest in finding scalable and low-cost manufacturing methods that can create wrinkled structures on curved surfaces for various technological applications.

In this paper, we demonstrate a simple yet scalable micro-manufacturing technique that creates self-assembled ring-shaped concentric surface wrinkles on PDMS fiber surfaces. Fibers of PDMS, 400–1500 \( \mu \)m in diameter, were fabricated and stretched using a custom apparatus to prestrain ranging from 40% to 160% and exposed to UV/ozone treatment in the stretched state for different time spans. This process created a hard surface skin layer, which buckled into concentric wrinkles upon release of the fiber strain. The effect of the input parameters such as prestrain, the time of UV exposure, and fiber diameter on the wrinkle wavelength were experimentally determined.

Experimental Procedure

We chose PDMS as the fiber material because of its stretchability, transparency, and biocompatibility. Further, PDMS surface can turn into a hard skin layer of SiO\textsubscript{x} (\( x \sim 0–2 \)) by UV/ozone or plasma treatment [19,30–32]. To make the PDMS fibers, a sili-con elastomer base and the curing agent (Sylgard 184; Dow Corning, Midland, MI) were mixed at a weight ratio of 10:1 and vacuum degassed to remove the bubbles. The mixture was then injected into cylindrical Teflon tubes with 0.4, 0.7, 1.0, and 1.5 mm inner diameters using a syringe. The PDMS was completely cured in an oven at 93.3°C for 2 h followed by breaking the Teflon shelf to get PDMS solid cylindrical fibers. The fibers were cleaned with ethanol and stretched to a predetermined strain using a custom-built apparatus that could also rotate the fibers under stretch. Two UV lamps, one with a wavelength of 185 nm (Aquafine 3052; Serv-A-Pure, Bay City, MI) and another with a wavelength of 254 nm (EW-09815-02; Cole-Parmer, Vernon Hills, IL), were used to simultaneously expose the stretched fibers to the UV/ozone treatment (see the schematic in Fig. 1 for the wrinkle formation process). The vertical distance between the lamps and samples was kept constant at about 5 cm. Either one side of the fiber (Figs. 1(a)–1(c)) or both the sides of the fiber (by rotating the fiber at 0.9 rpm; Figs. 1(d)–1(e)) were exposed to UV. Since the transmittance of UV light through PDMS is low (about 30% for UV light at 254 nm and <10% for UV light at 185 nm [33]), we did

1Corresponding author.

Contributed by the Manufacturing Engineering Division of ASME for publication in the JOURNAL OF MICRO- AND NANO-MANUFACTURING. Manuscript received September 25, 2016; final manuscript received February 15, 2017; published online March 24, 2017. Assoc. Editor: Nicholas Fang.
not observe wrinkles on the other surface of the fiber samples exposed to UV only from one side.

The experimental conditions, such as fiber diameter, prestrain, and UV exposure time, are summarized in Table 1. Note that for the samples rotated under the UV lamps, the actual exposure time along the circumference was lower than that for the case with no rotation, which required it to have higher strain to generate observable wrinkles. The thickness of the SiO\textsubscript{x} layer on the fibers after UV/ozone treatment was measured using a wet-etch method. We assumed that the thickness of the transformed SiO\textsubscript{x} layer was related only to the UV exposure time and was same for both the planar and the fiber substrates. Accordingly, five flat PDMS substrates were subjected to different UV exposure times (Fig. 2(a)). After the UV exposure, part of the samples was covered with electrical tapes separated with a gap of about 2 mm (Fig. 2(b)). The samples were dipped in NaOH solution (10% w/w) at 80°C for 10 mins to selectively wet-etch the gaps between electric tapes (Fig. 2(c)). The tape and residue were then cleaned by ethanol (Fig. 2(d)). A control PDMS sample with no-UV/ozone exposure was also wet-etched using the same method. A profilometer (DektakXT; Bruker, Kennewick, WA) with a triangular tip (radius of 2.5 μm), a low force (0.1 mg), and a low scanning speed (10 μm/s) was used to measure the surface profile to get the thickness of the SiO\textsubscript{x} layer (four readings per sample). For SiO\textsubscript{x} layer having a thickness under 1 μm (the sample with UV exposure of 5 mins), a ZYGO white light interferometer (Newview 7000; ZYGO, Middlefield, CT) was used to measure the thickness.

Optical microscopy (AxioScope-A1, Carl Zeiss GmbH, Munich, Germany) and scanning electron microscopy (SEM, FEI Quanta 200F; FEI Corporation, Hillsboro, OR) were used to image the fibers and measure the wrinkle wavelength (ten measurements per fiber).

### Results and Discussion

Representative optical and SEM micrographs of wrinkled PDMS fibers fabricated using the above method are shown in Figs. 3(a)–3(d). The wrinkles can be clearly observed around the entire fiber circumference in Figs. 3(a) and 3(b), where the fiber was rotated during the UV exposure. The wrinkle dimensions are indicated on the inset of Fig. 3(a). The boundary between the part of the fiber exposed to UV and that shielded from the UV by the clamps is shown in Fig. 3(b). It is clearly observed that the wrinkle formation was confined only to the area exposed to the UV/ozone treatment. The SEM micrographs in Figs. 3(c) and 3(d) show wrinkles when the fiber was with and without rotation during the UV exposure, respectively. The concentric wrinkles along the fiber surface are observed in the higher magnification images in Fig. 3(c) along with surface cracks. In Fig. 3(d), the wrinkles were observed only on the side where the fiber was exposed to the UV light. It is also seen in the SEM images that the wrinkles have irregularities in terms of pitch and the wavelength, a feature that is similar to that observed when such wrinkles are formed on the planar surfaces [34,35]. The cracks observed in Fig. 3(c) are likely generated because of the Poisson effect during the release of the prestrain of the fibers. For example, the stiff thin SiO\textsubscript{x} layer was compressed in the axial direction when the prestrain was released and put under tensile loading in the circumferential direction so that buckling occurred in the axial direction along with the cracks.

### Table 1 Experimental variables used for the fiber experiments

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Prestrain (%)</th>
<th>UV exposure time\textsuperscript{a} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant fiber diameter (0.4 mm)</td>
<td>40, 50, 60, 100</td>
<td>20, 40, 60, 80, 100, 120</td>
</tr>
<tr>
<td>Fiber was not rotated during exposure (Figs. 1(a)–1(c))</td>
<td>120, 140, 160</td>
<td>20, 30, 40, 50, 60</td>
</tr>
<tr>
<td>Fiber rotated during exposure (Figs. 1(d)–1(f))</td>
<td>80</td>
<td>40, 60, 90, 120</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For the fibers rotated during UV exposure, the time of exposure for a given location was taken to be about half of the total time during the experiment.
perpendicular to the buckles. Figure 3 clearly demonstrates that the self-assembled concentric wrinkles created using the micromanufacturing method proposed in the paper can create microfabrication. Figures 4(a)–4(d) show the dependence of the wavelength ($\lambda$) on the UV exposure time (Fig. 4(a)) and strain (Figs. 4(b) and 4(c)) and the fiber thickness (Fig. 4(d)). The results in Fig. 4(a) show that the wavelength of waviness increases with the UV exposure time for a given percentage of prestrain and tends to flatten out with increasing UV exposure. In addition, for a given UV exposure, the wavelength of the wrinkles reduces as the prestrain level is increased. Note that for wrinkles on a planar surface, the wavelength ($\lambda$) and amplitude ($A$) changes with the thickness of the SiO$_x$ thin film ($h_f$) as [7,21]

$$\lambda = \frac{2\pi h_f}{(1 + \varepsilon_{pre})(1 + \xi)^{1/3}} \left( \frac{E_s(1 - \nu_s^2)}{3E_s(1 - \nu_f^2)} \right)^{1/3}$$  \hspace{1cm} (1)

$$A = \frac{h_f}{(1 + \varepsilon_{pre})(1 + \xi)^{1/3}} \sqrt{\varepsilon_{pre} - 1}$$ \hspace{1cm} (2)

where $E$ is the elastic modulus, $\nu$ is the Poisson’s ratio, and the subscripts $s$ and $f$ refer to the substrate and SiO$_x$ film, respectively. Further, $h_f$ is the thickness of the thin film, $\xi = (5/32)\varepsilon_{pre}$ $\left(1 + \varepsilon_{pre}\right)$ is used to represent the large deformation and also the nonlinearity of the geometry of the substrate [7,21], and $\varepsilon_c = (1/4)(3E_s(1 - \nu_s^2))/(E_f(1 - \nu_f^2))^{2/3}$ stands for the critical strain, which is the minimum strain to achieve buckling on the thin film. The trends observed in Fig. 4(a) are in qualitative agreement with the predictions from Eq. (1) given the fact that the skin layer thickness is expected to increase with the UV exposure time as is confirmed in Fig. 4(e). The wrinkle wavelength is shown as a function of the prestrain when fibers were not rotated during UV exposure (Fig. 4(b)) and when fibers were rotated during the UV exposure (Fig. 4(c)). The wavelength decreases with increasing...
prestrain in both the cases. This trend is also consistent with the predictions of Eq. (1), since $\xi$ increases with $\varepsilon_{\text{pre}}$ and $h_f$ is not expected to change for the same UV exposure time. Figure 4(d) shows the relationship between wrinkle wavelength ($\lambda$) and the UV exposure time ($t$) for fibers with different diameters. It can be seen that as the fiber diameter increases, the wavelength of the wrinkles increases as well. It is expected that the limiting wavelength will be that for wrinkles on a half-plane (i.e., a planar surface).

Note that in the past studies for planar wrinkles, the thickness of the SiO$_x$ film was inferred indirectly by fitting the wrinkle wavelength and amplitude data to Eqs. (1) and (2). This estimation was of the order of hundreds of nanometers for UV exposures of tens of minutes [19,30–32]. Figure 4(e) shows the measured
thickness of the SiO$_2$ film as a function of the UV exposure time in the current study. The thickness increase is nonlinear and tends to saturate after a certain UV exposure time as a thicker skin layer will impede the penetration of the UV light and is expected to progressively slow the formation of the SiO$_2$ film. We observed that the measured thickness of the hard layer in this study is much larger than the values estimated in literature [19-30-32]. The reasons behind this discrepancy could be multifold. First, the SiO$_2$ film is not continuous and its composition changes from 100% PDMS at some depth to some mixture of PDMS and SiO$_2$ at the surface. Further, the etching method may be the removing material in excess of an equivalent skin layer and thus increases the apparent thickness. Another reason could be that Eqs. (1) and (2) for a planar surface do not take into account the thickness of the planar slab that may influence the buckling formation in real samples. This is because although the thickness of the film was small compared to the PDMS thickness in the prior studies, the modulus of the SiO$_2$ is 75 GPa which is about 4 orders of magnitude higher than that for cured PDMS (~1 to 3 MPa) [36].

The results presented in this paper clearly demonstrate that axisymmetric surface wrinkles can be fabricated over a PDMS fiber through the simple method described in this paper. We have demonstrated regular and controlled wrinkles on PDMS fibers with wavelengths ranging from 5 to 50 $\mu$m and amplitude of a few micrometers. The manufacturing parameters controlling the wrinkle dimensions are the fiber prestrain, the UV exposure time, and the fiber diameter. The UV exposure time is shown to correlate with the thickness of the surface skin layer which was measured using a wet-etch method. We have also found the effect of the various input parameters on the wrinkled wavelength through systematic experiments. The fabrication technique presented in this brief is fully scalable and can easily be manipulated to produce fibers of different wrinkle dimensions. We note that the wrinkles observed in Fig. 3 show irregularities and kinks. Such features have also been seen on wrinkles on planar surfaces [34]. Methods to reduce the defect density will be the key to adaptation of such structures in devices. Further work is needed to explore the application of the wrinkled fibers for optical devices such as optical sensors and light illuminators.

**Conclusions**

In this work, we have demonstrated a simple micromanufacturing method that uses the buckling phenomenon of a hard skin layer under compression over a PDMS fiber to create controlled concentric wrinkles along the fiber surface. A UV/ozone treatment was applied to oxidize PDMS fibers in stretched state, followed by the release of the fiber strain to create the wrinkles. The proposed method uses energy driven self-assembly principles and is low-cost and scalable. The thickness of the surface skin layer was measured using a chemical method. Important parameters that affect the wrinkle wavelength, namely, the UV exposure time, the fiber prestrain, and the fiber diameter were identified.

**Acknowledgment**

The work was supported by the start-up grant for Dr. Lei Li and Dr. Rahul Panat at WSU. We also acknowledge the support and help from WSU workshop in the School of Mechanical and Material Engineering, Washington State University, Pullman, WA. Help from Mr. Roorbeke Daniaei for Dektak profilometer is also acknowledged.

**References**


