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Material characterisation

Temperature-dependent dynamic moduli of Parylene-C columnar microfibrous thin films

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ABSTRACT

Columnar microfibrous thin films (μFTFs) of the polymer Parylene C with different microfiber inclination angles were fabricated using a physicochemical vapor deposition process whereby a collimated flux of hot monomers is obliquely directed towards a planar substrate. Each μFTF was then subjected to cyclic elastic loading in one of two orthogonal directions lying wholly in the substrate plane: either (i) normal or (ii) parallel to the morphologically significant plane of the μFTF. Dynamic storage and loss moduli were determined in the 1–80 Hz frequency range for temperatures between −40 °C and 125 °C. For all columnar μFTFs, the storage and loss moduli for normal loading did not exceed their counterparts for parallel loading. All columnar μFTFs were found to be softer than a bulk film of Parylene C. In both bulk and columnar forms, Parylene C was found to be rheologically not simple.

1. Introduction

Thin films have been researched as optical, electrical, magnetic, chemical, mechanical, and thermal coatings for over 150 years [1]. These films range in thickness from a few angstroms (even molecular monolayers) to hundreds of micrometers, depending on the specific application. They are made of a wide variety of raw materials including metals, glasses, and polymers [2].

Parylene C is a polymer with long-standing industrial use for electrically insulating coatings [3] and moisture barriers [4]. Bulk films of Parylene C are fabricated on substrates using a physicochemical vapor deposition process devised originally by Gorham [5]. Free of pin holes, these films are used as interconnects [6,7] and in microelectromechanical systems [8]. They are known to withstand temperatures as high as 220 °C and are resistant to most solvents [3,9]. Accordingly, they are used as biomedical substrates [4,10–13].

Microfibrous thin films (μFTFs) of Parylene C can be fabricated on substrates by a modification of the now-standard Gorham process [14,15]. An μFTF is porous, as it is an assembly of parallel microfibers of diameter ~5 μm. The shape of the microfibers can be upright circular-cylindrical, slanted circular-cylindrical, chevronic, helical, etc. The spacing between neighboring microfibers on a smooth substrate is ~3 μm, but almost any larger spacing between the microfibers can be obtained by pre-patterning the substrate [15]. The potential of these μFTFs for tissue growth [16] and protein assays [17] has been experimentally established, and theoretical analysis indicates their promise for ultrasonic filters as well [18].

A μFTF comprising microfibers of circular-cylindrical shape, whether upright or slanted with respect to the substrate plane, is called a columnar μFTF. All microfibers are inclined at an angle $\chi \in (0°, 90°]$ with respect to the substrate plane. We recently characterized the molecular and microstructural differences between columnar μFTFs and bulk films of Parylene C [19]. Whereas bulks films are 83% crystalline and have only one crystal plane, the columnar μFTFs have 55–68% crystallinity and four crystal planes. However, the static contact angles of water droplets on columnar μFTFs were similar to the static contact angles of water droplets on the bulk films [19].

Biological cells growing on a substrate subject the latter to contractile stress [20,21]. Likewise, service as biomedical assays and ultrasonic filters will be stressful. Parylene-C μFTFs also show

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promise as multifunctional materials [22,23]. Although comprehensive knowledge of the mechanical properties of μFTFs of Parylene C would be useful for these applications, only a preliminary report on just one columnar μFTF has been published as yet [24]. Moreover, for day-to-day applications, these properties should be determined as functions of both temperature and frequency.

In this paper, we report our experimental investigation of the frequency- and temperature-dependent storage and loss moduli of columnar μFTFs of Parylene C (grown on planar substrates) subjected to cyclic elastic loading in one of two orthogonal directions lying wholly in the substrate plane: either (i) normal or (ii) parallel to the morphologically significant plane (MSP) of the μFTF. The storage and loss moduli for normal loading are denoted by $E'_{\perp}$ and $E''_{\perp}$, while those for parallel loading are denoted by $E'_{\parallel}$ and $E''_{\parallel}$. We determined the dependences of all the measured moduli on the microfiber inclination angle χ.

The plan of this paper is as follows. In Sec. 2.1 we describe the procedure for fabricating the columnar μFTFs of Parylene C. Next, in Sec. 2.2 we describe cross-sectional imaging and in Sec. 2.3 the mechanical experiments to determine $E'_{\perp,\parallel}$ and $E''_{\perp,\parallel}$. The measured data are presented and discussed in Sec. 3.

2. Materials and methods

2.1. Fabrication of columnar μFTFs

A 2.5×1.3 cm^2 substrate of silicon (Si) was cleaned first for 10 min with acetone, then for 10 min with deionized (DI) water, then for 10 min with isopropyl alcohol, and finally for 10 min with DI water. The substrate was then attached to a platform mounted on a motor assembly placed inside the *large chamber* of the PDS 2010 Labcoater (Specialty Coatings and Systems, Indianapolis, IN, USA), as shown schematically in Fig. 1 (a). The shaft of the *rocking motor* in the assembly was oriented so that, during deposition, a collimated monomer flux of Parylene C would be obliquely incident on the substrate at an angle $\chi_v \in (0°,90°]$ with respect to the substrate plane, as shown in Fig. 1(b). To fabricate the columnar μFTF, 4 g of solid Parylene-C dimer (Specialty Coatings and Systems, Indianapolis, IN, USA) contained in a semi-cylindrical aluminum boat was placed in the *vaporizer* of PDS 2010 Labcoater. The chamber was then pumped down to 28 mTorr. In an automated process, the solid dimer was sublimated to gaseous form in the vaporizer held at 175 °C. This vapor of dimers was passed into a furnace, held at 690 °C, where it was dissociated into monomers [5]. This monomer flux was collimated by passage through a pipe and released through a nozzle towards the Si substrate. The monomers condensed on the substrate to form an assembly of slanted microfibers.

Let the MSP of a columnar μFTF, which is the plane defined by the direction of the collimated monomer flux and the direction of inclination of the microfibers, be denoted as the *xz* plane, while the substrate plane be denoted as the *xy* plane. In a predecessor study on columnar μFTFs of Parylene C grown with different χ_v, the dependence of χ on χ_v was classified into four regimes as follows: χ varies very weakly with $\chi_v \in (30°,45°)$, increases linearly with $\chi_v \in (45°,58°)$, varies very weakly with $\chi_v \in (58°,75°)$, and again increases linearly with $\chi_v \in (75°,90°)$ [19, Fig. 4(b)]. The X-ray diffraction (XRD) spectrums of all columnar μFTFs in each regime were found to be identical [19, Fig. 7]. Hence for this study, two columnar μFTFs each were fabricated with χ_v=30°, χ_v=52.5°, χ_v=67.5°, and χ_v=80°, i.e., one in each of the four regimes. For each chosen value of χ_v, the substrate was aligned (i) as shown in Fig. 1(c) for one sample and (ii) as shown in Fig. 1(d) for one sample. In addition, one columnar μFTF was grown with χ_v=90°.

A bulk film was also deposited over a Si substrate but in the *reduced capacity chamber* of the PDS 2010 Labcoater, using 24 g of Parylene-C dimer. For this deposition, the motor assembly was not used and the nozzle was substituted by a baffle.

2.2. Cross-sectional imaging

Cross-sectional images of the MSPs of all columnar μFTFs were taken using a scanning-electron microscope (SEM) [Model LEO 1530, Carl Zeiss, Darmstadt, Germany]. Each sample was first cleaved manually along the *xz* plane and sputtered with iridium in a sputter coater [Model K575X, Emitech, Fall River, MA,USA] on that plane for 28 s with 40 mA current. The SEM imaging software was used to measure χ with an accuracy of ±0.1°.

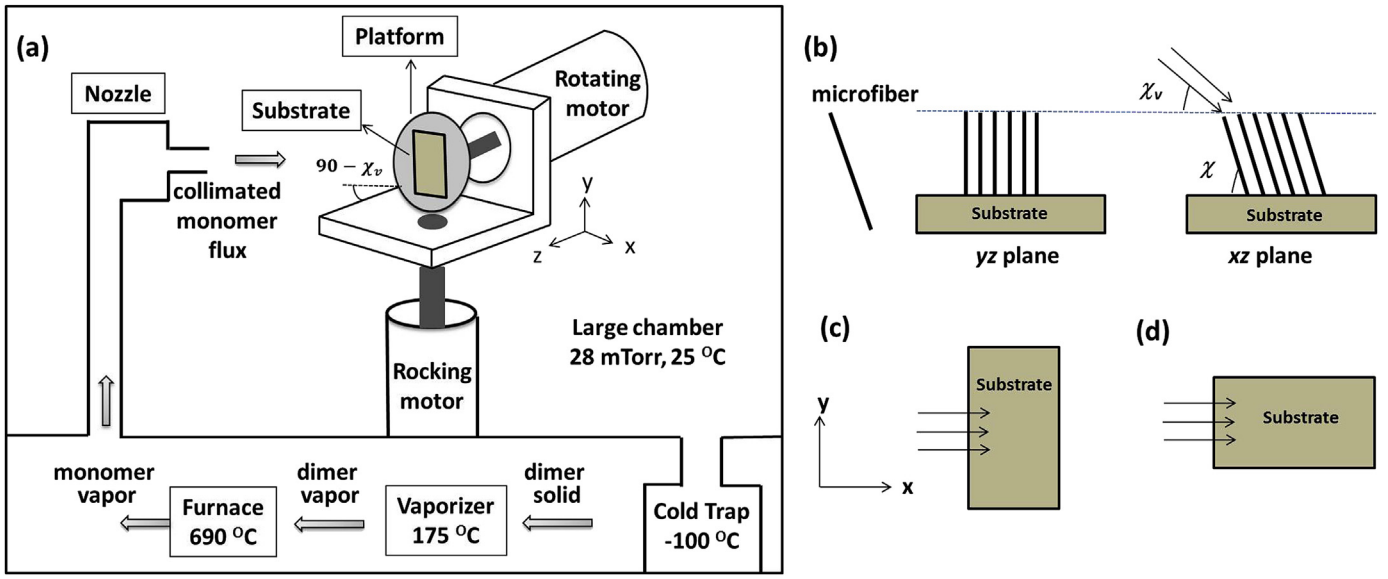

Fig. 1. (a) Schematic of the process to deposit columnar μFTFs of Parylene C. (b) Planar views of a μFTF on an Si substrate in the *xz* and *yz* planes. The angle χ_v of the collimated monomer flux with respect to the plane of the Si substrate and the microfiber inclination angle χ are marked. For each value of χ_v chosen, one substrate was aligned as shown in (c) and the other as shown in (d) during deposition.