

Synthesis and Characterization of Polymer Brushes from PDMS Surfaces

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INTRODUCTION

In recent years, poly(dimethylsiloxane) (PDMS) has found increased application in the areas of microfluidic devices, chromatographic packing materials and membranes, as well as in medical and drug delivery devices. However, the hydrophobic surface of PDMS is normally modified prior to each use especially in aqueous or biological systems to allow wetting of the surface as well as to decrease bio-fouling. In this work, a novel and facile modification scheme based on hydrochloric acid treatment was found to introduce hydroxyl groups to the surface of PDMS, which serve to covalently attach initiator groups for subsequent atom transfer free radical polymerization. These initiator-functionalized PDMS surfaces can then be used to form a wide variety of biocompatible and bioactive polymer brushes (Figure 1). In contrast to popular approaches such as ultraviolet/ozone or plasma treatment, the interface between the newly formed polymer brushes and the PDMS substrate is well defined so that wrinkling metrology, attenuated total reflectance infrared (ATR-IR) spectroscopy, and spectroscopic ellipsometry can be used to characterize their mechanical properties and chemical composition. Moreover, we showed that our wrinkling metrology and ATR-IR offer new routes to overcome difficulties associated with thickness measurement of polymer brushes on transparent and flexible substrates. The covalent attachment of the polymer chains to the substrate also enables the wrinkled pattern to be completely reversible (wrinkled/flat) by alternating thermal and solvent treatments. The ability to switch between wrinkled and flat states suggests applications in fields such as biosensors and microfluidics, where surface morphology plays a key role in governing device performance.

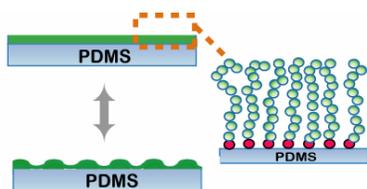


Figure 1. Schematic of wrinkling of a polymer brush grafted from the surface of PDMS.

EXPERIMENTAL[†]

General. All chemicals were obtained from Aldrich and used as received, unless otherwise noted.

Polymer Brush Preparation. First, a 1 cm × 7 cm toluene-extracted PDMS (Sylgard 184, Dow Corning) was exposed to 10 % by volume HCl for 24 h. During the surface initiated ATRP, a monomer mixture (6 mL of 2-hydroxyethyl methacrylate (HEMA) and 6 mL of DI water) was degassed for 2 h and then transferred to a tube containing the degassed catalyst complex. In order to create a discrete thickness gradient of tethered poly(HEMA) (PHEMA) chains, the monomer/catalyst solution was pumped stepwise into a degassed test tube containing both a modified PDMS. Polymerization proceeded at room temperature and was terminated by exposure of the monomer solution to air. The PHEMA-grafted PDMS substrate was cleaned with dimethylformamide (DMF) in an ultrasonic bath for 2 min and rinsed copiously with methanol to remove any unreacted monomer.

Wrinkling Metrology. Prior to wrinkling, the Young's modulus of the PDMS substrates was determined on a Texture Analyzer (model TA.XT2i, Texture Technologies Corp.) in tension mode, and the brush thickness was determined on a spectroscopic ellipsometer (M-2000DI,

J.A. Woollam Co.). Wrinkling of the PDMS-g-PHEMA brush specimens was achieved through both mechanical compression and thermal cycling. For mechanical compression, a small compressive strain was applied via a pair of tweezers, and photographs of the wrinkled pattern were taken using an optical microscope (Nikon Optiphot) at a magnification of 100×. Thermal wrinkling of the polymer brush layer was achieved by heating the sample in a convection oven at 100 °C for 20 min and then cooling to room temperature. Atomic force microscope images (Dimension 3100, Veeco Instruments, operating in tapping mode) and optical microscopy images were taken of the wrinkled surfaces. Fourier image transforms were conducted on each optical micrograph to determine the average wavelength of the wrinkling pattern. In addition, the reversibility of the wrinkling process was tested by solvent swelling (water or DMF) of the brush layer to "erase" the wrinkled pattern, followed by thermal wrinkling as described above. This cycle was repeated several times. An optical image was taken at a single position along the gradient after each solvent and thermal treatment.

RESULTS AND DISCUSSION

We have previously employed our wrinkling metrology^{1,2} on a number of different thin film systems. A wrinkling pattern with a characteristic wavelength (λ) emerges on the surface of a thin, stiff film undergoing planar compression on a thicker, compliant substrate. The modulus of brush layer can be related to the wrinkling wavelength (λ), the thickness of the brush (h_b), as well as the mechanical properties of the film and substrate as:^{3,4}

$$\bar{E}_b = 3\bar{E}_s[\lambda/(2\pi h_b)]^3 \quad (1)$$

where \bar{E} is the plane-strain modulus, defined as $E/(1-\nu^2)$; E is the Young's modulus; and ν is the Poisson's ratio. The subscripts b and s refer to the film and substrate, respectively. Figure 2 shows the linear increase of wrinkling wavelength with the thickness of PHEMA brush layer grafted from the PDMS substrate. Based on Eq. 1, the average Young's modulus of PHEMA brush, E_b , is 2.6 GPa ± 0.5 GPa, comparable to a flow-coated PHEMA film ($E = 1.9$ GPa ± 0.4 GPa) measured also by surface wrinkling. Both of these values for the modulus of PHEMA are in agreement with literature values ($E \approx 2$ GPa) reported for bulk PHEMA at room temperature.⁵ The linear relationship between wavelength and brush thickness was also observed for the thermally-induced wrinkling pattern. In addition, one of the most salient features of polymer brush wrinkling lies in its reversibility in response to alternating solvent and thermal treatments. Because it is covalently bound to the PDMS, exposure of the PHEMA brush layer to a good solvent (water or DMF) does not remove it from the surface, but rather allows the chains to relax and release any strain energy stored in the system, causing the wrinkled surface to return to its original flat state.

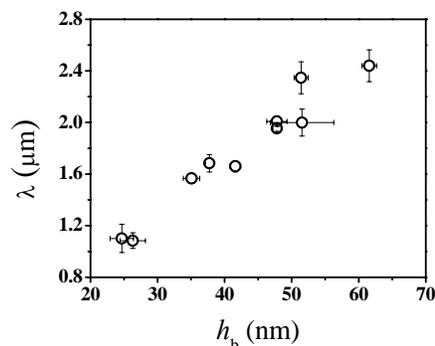


Figure 2. Wavelength (λ) of the wrinkling pattern as a function of brush thickness (h_b) on a PDMS substrate. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

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[†] Equipment and materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply that the materials are necessarily the best available for the purpose

* This work was carried out at the NIST Combinatorial Methods Center. More information on the center and current research projects can be found at <http://www.nist.gov/combi>.

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