Techniques for Combinatorial and High-Throughput Microscopy

Part 1: Gradient Specimen Fabrication for Polymer Thin Film Research

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Combinatorial and high-throughput (C&HT) approaches accelerate research by addressing multiple experimental parameters in a parallel or otherwise highly efficient fashion[1, 2]. First used by the pharmaceutical industry for product discovery, the C&HT paradigm is being extended to the study of complex materials systems that require measurements of properties and phenomena over a huge number of conditions. As with traditional materials science, microscopy and imaging of morphology are essential for C&HT materials research[3-5]. However, strategies for fabricating specimen arrays amenable to automated microscopic analysis are not always available or affordable. In response to such needs, the NIST Combinatorial Methods Center (NCMC) provides education, information and measurement solutions to help industries and individuals acquire C&HT materials research capabilities. This article, *Part 1* of *2* describes NCMC-developed *gradient specimens* suited for C&HT polymer research. Gradient samples continuously vary in materials or processing parameters with position, and thus present a huge array of experimental conditions *within a single specimen*. Such specimens enable systematic screening of materials behavior over a prescribed range, while permitting researchers to "zoom-in" to regions of interest for detailed investigation. In addition, the fabrication of gradient specimens typically does not involve high-cost robotic platforms, making these methods attractive to researchers from industry to academia. Due to their planar geometry and high-information density, such specimens are also particularly geared towards C&HT microanalysis. Indeed, in *Part 2* we present a custom-built automated optical microscopy platform that is specifically designed for image acquisition and analysis from gradient specimens.

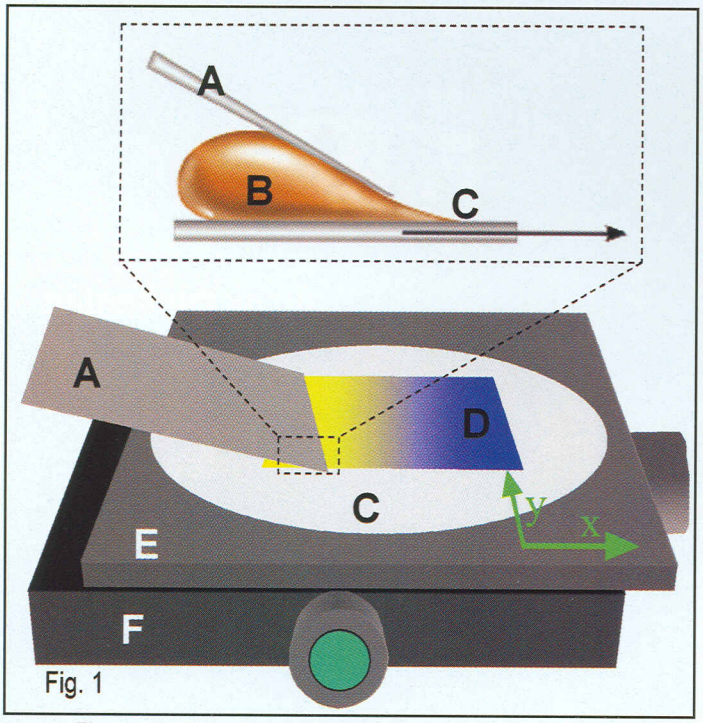

Figure 1: Flow Coater for thickness gradients. **A:** *Doctor Blade,* **B:** *Dilute Polymer Solution,* **C:** *Substrate,* **D:** *Cast Gradient Film,* **E:** *x-translation stage,* **F:** *y-translation stage (for characterization).*

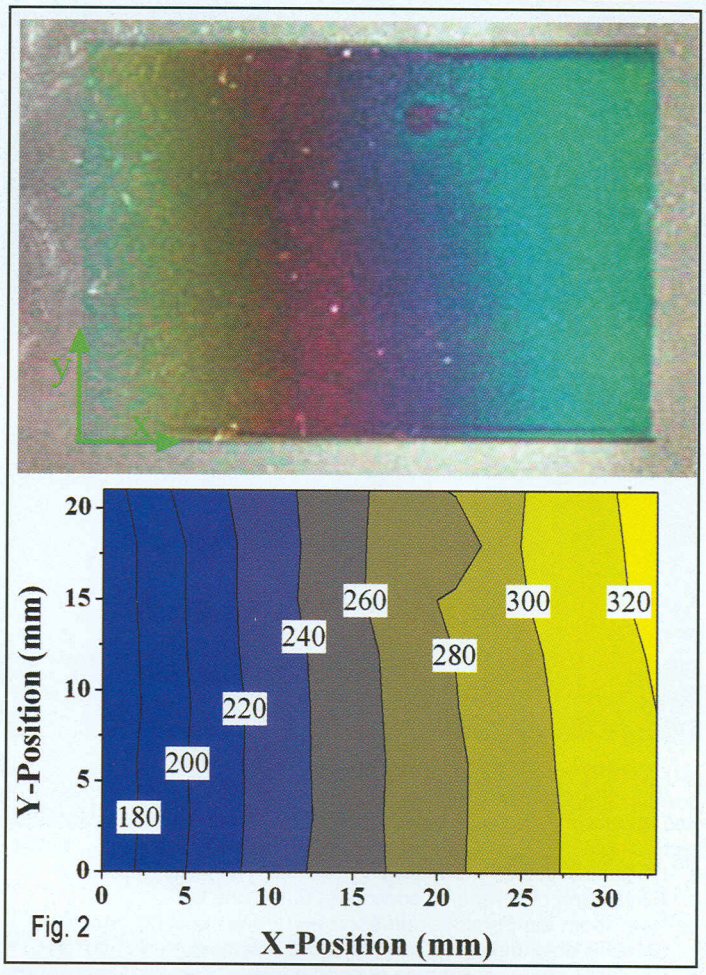

Figure 2: Polymer film thickness gradient cast with flow coating. Top: Optical micrograph of gradient specimen. Bottom: Thickness gradient as measured via spot intereferometry.

This article focuses on three gradient methods useful to the study of substrate-supported polymer film systems. In particular, we describe the preparation of *controlled* gradients in polymer film thickness, substrate surface energy, and temperature. Though developed for polymer research in principle, similar techniques can be applied to a wide range of materials systems.

Polymer film thickness (*h*) gradients. Film thickness can govern the morphology, stability, and surface-chemical expression of polymeric thin films. To gauge the effect of *h* on film behavior[2, 4-8], the NCMC has developed an easy method for producing controlled thickness gradients. This process, *flow coating*[4], is a modified blade casting technique (Fig. 1). First, a dilute solution of polymer in solvent (*e.g.* toluene) is injected {≈ 25 μl total volume}† into the gap between a doctor blade (*e.g.* metal putty knife) positioned over a flat substrate (*e.g.* silicon wafer) mounted on a computer-controlled translation stage. Next, the stage/substrate is accelerated beneath the stationary blade in the x-direction as shown in Fig. 1. As the stage accelerates, increasing amounts of solution are deposited along the substrate. Subsequent solvent evaporation results in a polymer film thickness gradient. The range and slope of the *h*-gradient are tuned through the stage velocity profile {10 mm/s^2 to 100 mm/s^2}, solution concentration {1 % to 5 % wt/vol} and gap height {50 μm to 250 μm}. Thickness gradients produced via flow coating typically encompass 20 nm to 400 nm over 50 nm to 100 nm increments, and exhibit slopes of 1 nm/mm to 10 nm/mm, depending upon processing parameters. In NCMC facilities, *h*-gradients are characterized via spot interferometry. Here, stacked translation stages (including the stage used to produce the specimen) raster the sample beneath the interferometer footprint, resulting in a 2D thickness map (Fig. 2). As seen in Fig. 2, *h*-gradients

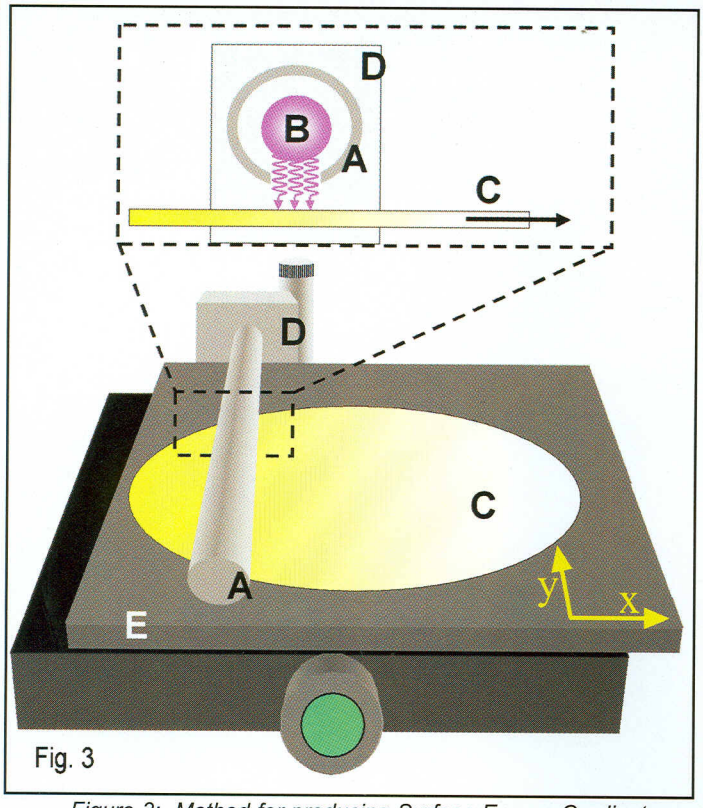

Figure 3: Method for producing Surface Energy Gradients. **A:** *Lamp housing with slit aperture.* **B:** *190nm UV wand source.* **C:** *SiO_2 substrate treated with SAM.* **D:** *Lamp housing mount with height micrometer.* **E:** *Translation stage*

created through flow coating are almost always non-linear (along x), and non-level (along y), so 2D characterization may be necessary for quantitative studies.

Substrate Surface Energy Gradients. Substrate surface chemistry is another controlling factor in the behavior/structure of supported films. For example, coating stability (wetting)[4], and the orientation of nano-domain assembly in block copolymer films[6] are surface energy dependent. The NCMC has developed an elegant technique for producing a surface energy gradient (SEG) on silicon oxide substrates. This method harnesses the graded UV-ozonolysis of a self-assembled monolayer (SAM) deposited on SiO_2[9]. In a typical procedure, a silicon wafer (oxide terminated) or clean polished glass is treated with n-octyldimethylchlorosilane by immersion in a toluene solution {2.5% by wt} or in a saturated vapor. Toluene rinsing followed by drying {nitrogen then 2 h under vacuum at 120 °C} leaves a covalently bound SAM. Graded UV-ozonolysis is achieved through a computer-driven translation stage, which accelerates the silanized substrate beneath a 190 nm UV wand-source projected through a slit aperture {2mm wide} cut into the cylindrical lamp housing (Fig. 3). The gap between the aperture and the substrate {100mm to 300mm} is controlled through a micro-positioner incorporated into the stationary lamp mount. The ascending UV-ozone exposure increasingly oxidizes

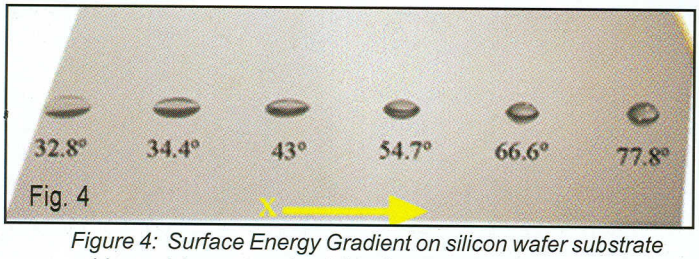

Figure 4: Surface Energy Gradient on silicon wafer substrate as evidenced by water droplets along the gradient. Surface energy decreases from left to right as the water contact angle increases.

the SAM, gradually converting the hydrophobic (CH3 terminated) layer to hydrophilic (OH and COOH terminated) species [9]. Contact angle measurements using two fluids (*e.g.* water and diidomethane) can be used to characterize the resulting SEG (see Fig. 4). NCMC SEGs typically span 20 mJ/m^2 to 75 mJ/m^2, over a tunable length of 1 cm to 5 cm. The range and slope of SEGs are controlled through the stage-acceleration/exposure profile and the aperture gap height. NCMC-generated SEGs generally have a sigmoidal profile along the *x* direction, and are level along *y*.

Temperature Gradients. Polymer thin film behavior can be temperature dependent, with most phenomena (phase transitions *etc.*) occurring below ≈ 300 °C. Accordingly, a temperature (*T*) gradient with modest range can be very useful for mapping the effect of *T* on a polymer film specimen. Controlled temperature (*T*) gradients can be achieved through a *gradient hot-stage*. The NCMC gradient hot-stage (See Fig. 5) consists of an Al sample platen {10 cm x 15 cm x 0.5 cm} perforated with two slots (along *x*). Two Al blocks, with machined heating/cooling channels, are attached to the bottom of the platen through slots; this enables control of the inter-block distance. The block channels hold cylindrical heating cartridges or accommodate plumbing (see Fig. 6) for fluid-mediated cooling. PID *T*-controllers maintain the block temperatures, measured through integrated thermocouples. Different heating (or cooling) of each block results in a *T*-gradient across the platform. Ceramic supports insulate the device, so it can be mounted on a microscope translation stage. The range and slope of the *T*-gradient are tailored through the block tem-

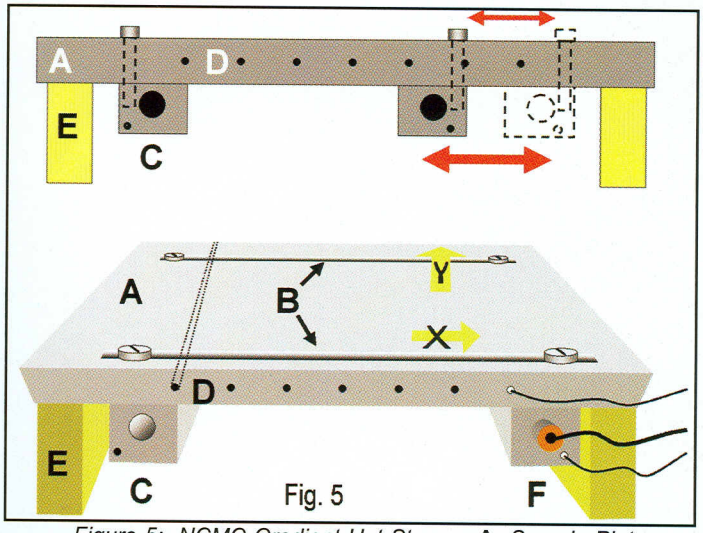

Figure 5: NCMC Gradient Hot Stage. **A:** *Sample Platen.* **B:** *Slots for mounting/positioning of block (***C***).* **C:** *Block with channel for heating/cooling element and port for thermocouple.* **D:** *Thermocouple ports for gradient characterization.* **E:** *Ceramic blocks for mounting hot stage.* **F:** *Block with cylindrical heating element and thermocouple installed.*

peratures and the inter-block distance. Thermocouple ports drilled into the platen edge enable *T*-gradient characterization. Alternately, a moveable surface probe can be used to map the *T*-profile[7]. Typical *T*-gradients span intervals of ≈100 °C over a total range of RT to ≈300 °C. Generally, our *T*-gradients are linear along *x* (Fig. 5). However, if fluid flow maintains the temperature of one end, 2D non-linearity can occur near the corner from which the coolant flows.

Management of Gradient Specimens. Gradient specimens involve complexities not shared by single-condition samples, especially when quantitative analysis is required. However, NCMC conventions and practices make the use of gradient libraries easier:

- *Spatial Reference Grid (SRG).* For gradient specimen, the SRG defines the 2D mesh of points over which measurements (characterization, image capture, etc.) will be made. The SRG enables HT analysis, as it represent a list of sites for automated instrumentation (*e.g.* a motorized microscopy stage) to visit. A SRG is built on a

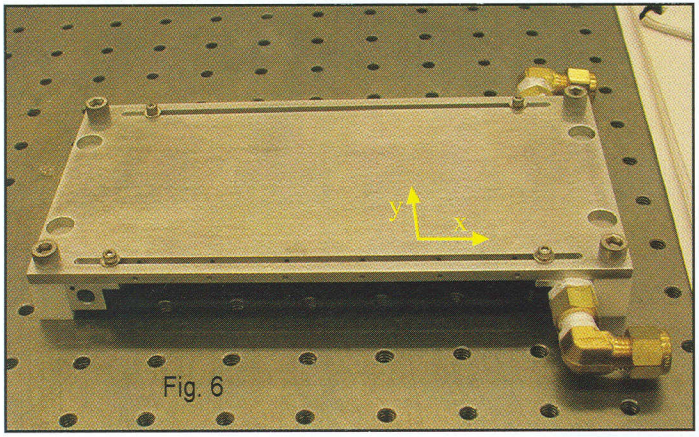

Figure 6: NCMC Gradient Hot Stage equipped with coolant plumbing (right channel).

three-point system of permanent fiduciary marks (on the substrate, specimen corners, etc.). These marks define a vector system that delineates the SRG.

- *2D Gradient Characterization*. As seen in Fig. 2, in-plane non-linearity is a common (often indelible) feature of gradient fabrication. Accordingly, 2D characterization of gradient specimens is often necessary. Automated measurements over a dense SRG exemplify a sound and efficient method for gradient characterization. As described in *Part 2,* 2D gradient characterization enable automated microcopy platforms to track iso-parameter contours.
- *Gradient Slope* is an important aspect of specimen design. High-slope gradients result in high-information density samples. However if too steep, gradients can drive diffusion and other processes that change the specimen over long experiments. In addition, steep gradients can mean that specimen properties appreciably vary over the measurement footprint (*e.g.* micrograph dimension). Accordingly, when designing a gradient specimen such factors should be balanced with respect to the acceptable level of uncertainty for the measurements[2].

With correct practice, gradient specimens accelerate materials research by increasing the number and thoroughness of measurements over a wide range of parameters, while minimizing repetitive, tedious tasks by researchers. These methods are particularly powerful when paired with automated optical microscopy, as will be seen in *Part 2* of this series. ■

For more information on these techniques and the NIST Combinatorial Methods Center, visit the NCMC website at http://www.nist.gov/combi, or contact us via email: combi@nist.gov.

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Footnote

† Values in {} are given to indicate a nominally useful range of parameters for NCMC processes/device operation. These values may not be the best possible for all applications.