

Polymer Science at the NIST Combinatorial Methods Center

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INTRODUCTION

The measurements, standards, and test methods developed by NIST, in partnership with other organizations, often help unlock the potential of new discoveries and budding technologies. Combinatorial methods are a textbook example. These emerging tools can speed innovation in many fields - pharmaceuticals, chemistry, and, most recently, materials. In the diverse realm of materials, combinatorial methods hold promise for all classes, including metals, polymers, ceramics, and biomaterials. NIST has established a combinatorial methods center as a model for collaboration, in order to share expertise, facilities, resources, and information, thereby reducing obstacles to participation in this fast-moving and instrument-intensive area. Although collaborations with multiple partners can be difficult, the goal is to foster cross-fertilization of ideas and research strategies, and to spur progress on many fronts by crossing boundaries of organizations, disciplines, and interests. A few examples of combinatorial project currently underway at NIST are in the areas of block copolymer ordering behavior, crystallization kinetics of polymers, quantitative polymer adhesion measurements, strain induced elastomer buckling instability for mechanical measurements, and informatics as described below.

BLOCK-COPOLYMER ORDERING BEHAVIOR

The morphology of symmetric diblock copolymer thin films has been studied extensively with traditional techniques.^{1,2,3} Controlling the morphology of block co-polymers is important in designing polymeric materials with tailored properties since they can be used to produce nanoscale morphologies. For instance, their unique properties in melts, blends and solutions lead to their use in adhesives, emulsifying agents, thermoplastic elastomers, compatibilizers etc. Mechanisms for controlling block-copolymer morphology through surface induced orientation and preferential interactions are important issues.

The reproduction of known symmetric diblock morphological behavior with gradient libraries provides a powerful demonstration of the utility and efficacy of combinatorial methodologies for polymer physical properties characterization. Optical microscopy in conjunction with laser light scattering (under development), using temperature gradient stage in reflection and transmission geometry, are expected to be the primary analytical tools for these high throughput studies.

Gradient libraries have been employed to revisit the well-studied phenomenon of lamella formation in symmetric diblock copolymers by analyzing the effect of film thickness on the morphology of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) thin films on Si substrates. Figure 1 presents optical micrographs showing morphological changes associated with the addition of two lamellae to the surface of the film as *h* increases. The morphological evolution of the surface lamella with increasing film thickness has been observed within a single library allowing a significant reduction in experimental time. This combinatorial approach is found to be useful in discovering and characterizing new features of pattern formation in block copolymer films. Specifically, a range of film thickness were observed where the surface remained smooth up to a constant fraction of chain length, independent of molecular mass, that can be attributed to an increase in the surface chain density in the outer copolymer layer with increasing film thickness. Novel bicontinuous patterns were also observed whose average size scales as an inverse power of chain length.^{4,5}

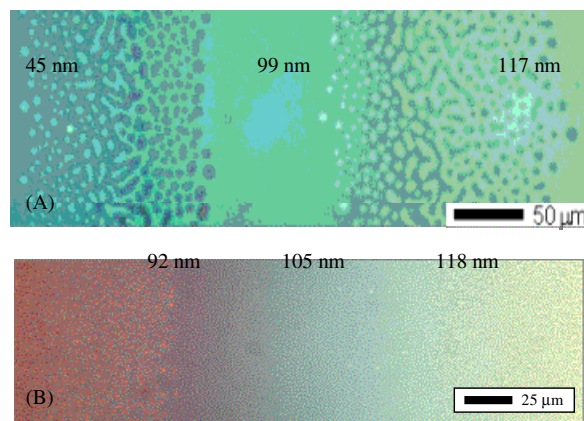


Figure 1. Optical micrographs of (A) $M_w=26,000$ g/mol and (B) $M_w = 104,000$ g/mol PS-*b*-PMMA gradient films showing the addition of lamellae to the surface with increasing thickness. Standard uncertainty in thickness is ± 3 nm.

CRYSTALLIZATION KINETICS OF POLYMERS

The ability to direct or suppress order in polymeric thin films has many practical implications for industrial applications. In particular, the degree of crystallinity in semi-crystalline polymer films can be dramatically affected by a host of processing conditions such as solvents, thermal history, additives, etc. The challenge is to achieve desired mechanical, optical, or thermal properties in semi-crystalline thin film coatings by control of crystal structure and domain size. Developing a high-throughput method of screening these effects has the potential to quickly optimize the processing of materials, as well as probe many of the outstanding theoretical issues regarding the nature of polymer crystallization.⁶ One example is by creating a gradient in film thickness and/or temperature in polymer films. High speed automated scanning methods such as optical and microscopy techniques can be used for evaluation of growth rate and other properties under orthogonally varying process variables such as temperature or stress gradients. Current research efforts have focused on factors affecting crystallinity in thick film coatings, specifically, the effect of temperature and film thickness on the morphology and kinetics of crystallization. Utilizing flow coating film preparation, spot ellipsometry for thickness characterization and automated optical microscopy for imaging on a temperature gradient stage, complete libraries of the kinetics and morphology of high molecular mass isotactic polystyrene (*i*pS) on Si have been mapped in the course of a few hours. Typical optical micrograph images of *i*pS crystallizing are shown in Figure 2.

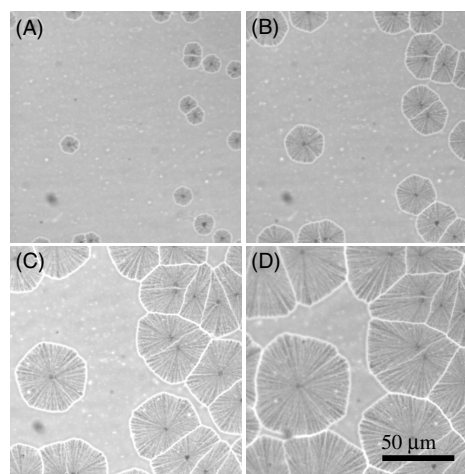


Figure 2. Optical images of *i*PS crystallizing at $T = 170$ °C. $h = 45$ nm, (A) $t = 21$ min, (B) $t = 51$ min, (C) $t = 96$ min and (D) $t = 146$ min

QUANTITATIVE POLYMER ADHESION MEASUREMENTS

Polymer adhesion is important to numerous technologies including electronic packaging, coatings and paints, biomedical implants, and pressure-sensitive adhesives. The challenge is to understand the fundamental driving forces for the development of adhesive strength at polymer/polymer, polymer/metal, polymer/ceramic, and polymer/biomaterial interfaces in multivariable environments. Recent methods for characterizing adhesion are either inefficient or ineffective. The goal is to develop a methodology for quantitatively measuring the adhesive strength of polymer interfaces in a combinatorial manner. The combinatorial libraries consist of two components: 1) an array of microlenses with a well-defined geometry (Figure 3) and 2) a flat substrate. The processing of these libraries will dictate a unique combination of adhesion-controlling variables at each microlens contact point. By monitoring the contact area and relative displacement of each microlens during contact and separation from the flat substrate, the adhesion energy can be mapped across the multivariable library. A combinatorial method has been developed and implemented to qualitatively and quantitatively map polymer interfaces to assess the dependence of polymer adhesion on multivariable parameters. Research efforts in our lab have focused on the design and preparation of the microlens combinatorial libraries, the instrumentation for controlling contact and separation, and the development of software to automate the data collection and analysis.⁷ The microlens array is a powerful tool for measuring adhesion across gradient libraries; however, issues concerning the most efficient means of analyzing these libraries are present. The microlens arrays currently in use at NIST can contain from 100 to 1000 individual lenses over a 1 cm² area, each lens representing its own JKR test. The gradient samples currently under investigation span an area many times larger. Therefore, the ability to efficiently analyze this large parameter space, is of concern. Currently, we are working on a method to incorporate design of experiments into our research to determine the most efficient path to create a representative adhesion map of the entire surface area.

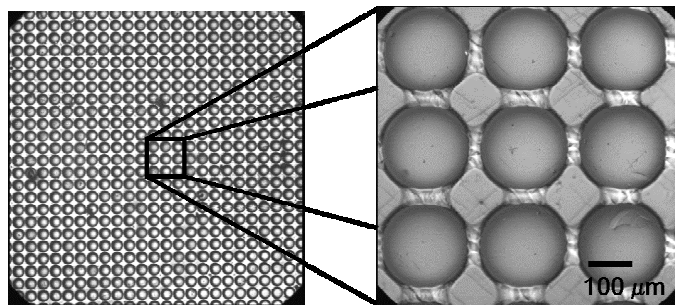


Figure 3. Poly(dimethylsiloxane) PDMS microlens used for combinatorial adhesion tests. (Courtesy of Al Crosby)

STRAIN INDUCED ELASTOMER BUCKLING INSTABILITY FOR MECHANICAL MEASUREMENTS (SIEBIMM)

There is a need for a simple, robust, and flexible measurement technique for the mechanical properties of thin polymer films. A technique like this would benefit the coating industry, semiconductor industry, and optical adhesives industry. Conventional techniques measure properties of coatings in bulk using a dynamic mechanical analysis (DMA), universal testing machine, or a depth sensing indentation instrument to measure Young's modulus, yield stress, viscoelastic recovery, cracking thresholds, and adhesive/interfacial energy. The aim in our lab is to develop a combinatorial method for measurements of the tensile modulus of thin films. The mechanical properties of thin films or coatings are paramount to their utility; materials that are unacceptably soft or rigid may not perform adequately. Modulus measurements of sub-micron films are a challenge to most conventional methods. To remedy this we have developed a robust, inexpensive methodology which measures the modulus of coatings with moduli from Mpa to Gpa and higher. This technique is applicable to films down to tens of nanometers and up to dozens of microns. We developed SIEBIMM (Strain Induced Elastomer

Buckling Instability for Mechanical Measurements), a reliable, high-throughput technique by which the elastic modulus of a thin polymer film can be measured. This technique relies upon a highly periodic strain-induced buckling instability that arises from a mismatch of the moduli of a relatively stiff polymer coating on a soft silicone sheet.⁸ The modulus-dependent buckling wavelength, typically 1 μm to 10 μm for 100 nm thick glassy films, is rapidly measured by static laser light scattering (Figure 4a). This technique is ideally suited for measurements of combinatorial libraries prepared by existing methodologies developed at NIST. As an example, Figure 4b shows the measured modulus of polystyrene films upon addition of dioctyl phthalate (DOP). The modulus decreases in a sigmoidal fashion with increased loading of DOP. We are currently extending this technique to nanocomposite films, UV-curable coatings and adhesives, and multi-component formulations. The method also looks promising for exploring the viscoelastic properties of films.

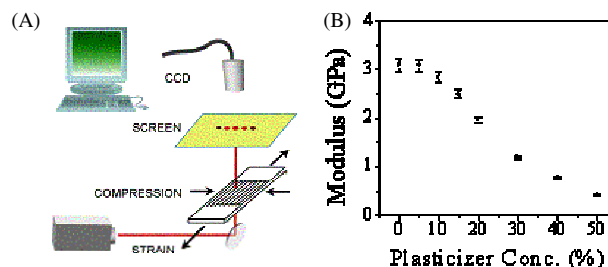


Figure 4. (A) Experimental setup for rapid measurement of buckling wavelength as a function of spatial position on the sample. (B) Modulus of PS films as a function of loading with a common plasticizer, dioctyl phthalate. Standard uncertainty is one standard deviation.

INFORMATICS FOR COMBINATORIAL MEASUREMENTS

The systematic high throughput nature of combinatorial methods, where sample preparation and measurement are automated, generates overwhelming amounts of data. An informatics project has been established at NIST to address this problem. A database system has been designed to follow the procedure of a research cycle. It provides a central and secure environment for data storage that is specifically geared to accept research data from a variety of sources, including numbers, images, videos, and charts. The database is supported by sets of interface software connecting experimental instruments with the database through which automatic data entry and retrieval is achieved. In this process, raw data are automatically processed and presented to the researcher, eliminating such tedious work as data maintaining and processing. Another important topic that will be covered by this project deals with setting protocol to standardize the experiments, data, and procedures, making them easily comparable to one another. As the database increases in content, it will serve as a library of scientific data, referring to itself during an experiment, dramatically reducing trial and error.

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