Harnessing Wrinkling Instabilities for Advanced Measurements of Polymeric Thin Films

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INTRODUCTION

Nanotechnology promises to revolutionize a growing set of materials applications ranging from electronics to drug delivery to ballistic protection. However, the quest to engineer materials on the nanoscale is met with the daunting task of measuring the physical and mechanical properties of these systems at these same length scales. For polymers, the challenge is even greater since conventional materials testing platforms lack the resolution for such soft systems. In this presentation, we will briefly review and discuss our current progress and advances in wrinkling metrology for characterizing physical, thermal, and mechanical properties of nanoscale polymeric materials.

First, we will demonstrate a new method to determine the residual stresses in polymeric thin films that arise as a natural consequence of film formation, such as spin casting. We quantify the residual stresses within thin films by measuring the threshold strain at the onset of wrinkling as a stress probe. This unique method utilizes compression-induced wrinkling of a thin film attached to a soft substrate, where the periodic wrinkling wavelength and the onset of wrinkling, assessed simultaneously by small-angle light scattering, yield the theoretical critical strain and actual threshold strain for wrinkling (Fig. 1). By comparing theses values with well-established theory for wrinkling, we reliably quantify the residual stress. In particular, we demonstrate this method with spin-cast, thin (sub-1 μm), glassy polystyrene films and obtain new information on the effect of molecular weight, film thickness, and plasticizer concentration on the residual stress. Furthermore, we gain additional information on the relaxation of residual stress in films upon thermal annealing and succeed to decouple the stress contribution arising due to thermal expansion mismatch during cooling from the coupled residual stress ("thermal mismatch stress" and "internal shrinkage stress").

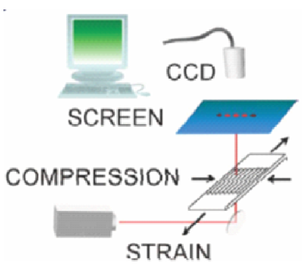

Figure 1. Schematic of the custom-built small-angle light scattering apparatus used to determine the critical compressive strain for wrinkling formation. The diffraction pattern from the wrinkled film is projected onto a screen, and this pattern is acquired by CCD camera.

Secondly, we will present measurements of the temperature-dependent properties of polymeric thin films. This measurement platform will be demonstrated with a glassy polymer film supported by a pre-stretched soft elastic substrate that is placed into a temperature-controlled chamber with a strain stage (Fig. 2). Compression of the sample at a given temperature (ranging from room temperature up to near the glass transition temperature of the polymer) results in spontaneous formation of a periodic, wavy wrinkling over the entire film surface. The periodicity or wavelength of the wrinkling pattern depends, among other factors, on the film modulus at a given temperature, and thus it provides an efficient means of mapping the temperature dependence of Young's modulus. We also explore the wrinkling behavior under thermal loading. The thin film wrinkles upon cooling of a pre-heated sample since it experiences a different level of contraction due to thermal expansion mismatch. The critical temperature for wrinkle formation and the dominant wavelength of wrinkling are associated with both the thermal expansion coefficients and moduli of the film and substrate. The feasibility of accurate critical temperature measurement will be demonstrated by using an optical microscope, light scattering, and AFM. Furthermore, the thermal wrinkling and post-wrinkling behaviors are studied in detail both experimentally and theoretically.

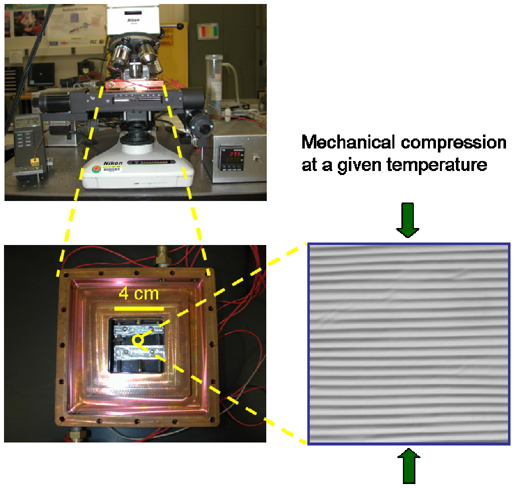

Figure 2. Experimental set-up with a miniaturized strain stage in a temperature-controlled chamber, and an optical microscope image of a wrinkling pattern generated by compressing the film at a given temperature.

Finally, we will demonstrate a novel design that employs observations of a thin film suspended over a small circular hole cut into an elastic substrate (Fig. 3). Upon compression, two distinct regions – film/substrate (outside the hole) and free-standing film (above the hole) – wrinkle independently with different characteristic wavelengths. This geometry further yields a distribution in strain (or stress) around the perimeter of the hole, which can be used to directly determine the critical strain of wrinkling initiation. We demonstrate that, based on the well-established wrinkling mechanics, these measured wavelengths and critical strain can simultaneously render the Young's modulus, Poisson's ratio of the film, and residual stress in the film. In particular, we will show that this measurement platform is highly conducive to combinatorial and high-throughput approaches.

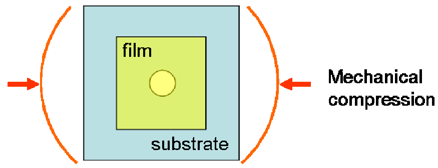

Figure 3. Schematic of a thin film supported by a soft substrate with a small circular hole. Upon compressing a film/substrate bilayer system, both the bilayer and the free-standing film wrinkle independently.

* 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.