Dynamics of Confined Polymer Films Measured via Thermal Wrinkling

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INTRODUCTION

In the past several years there have been a number of advances in the understanding of the physics of polymer thin films. However, there still remains a wide range of opportunities to further this understanding through the development of measurement tools capable of probing the physical behavior of polymer films on the sub-micrometer size scale.

We have developed a measurement method capable of determining the elastic modulus of nanoscale polymer films by utilizing a strain-induced elastic buckling instability that occurs in a composite material consisting of a stiff, thin film coated on a thick, soft substrate.[1,2] It was shown that by measuring the wavelength of the wrinkles that are formed on the surface of the film, the elastic modulus could be calculated for films over a wide range of thicknesses. Recent work has shown that a similar buckling instability arises in a system consisting of a supported polymer film capped with a thin metal layer.[3,4] As the system is heated, stresses build up in the composite film. When the polymer is above its glass transition temperature, an instability is formed which causes regular sinusoidal wrinkling of the surface in order to relieve the stress. The dynamics of this wrinkling process are dictated by a number of parameters, some of which are the temperature and the viscoelastic properties of the underlying polymer film. Theoretical analysis of this phenomenon indicates that the wrinkle amplitude should grow exponentially with time and that by studying the early and late stages of the amplitude growth, one can determine the viscoelastic properties of the polymer thin film.[5]

Here we employ a laser-light, surface scattering technique to probe the early stages of the development of the wrinkle wavelength and amplitude of a polystyrene film capped with a thin layer of aluminum subjected to isothermal annealing. Due to the regular, isotropic sinusoidal surface structures that develop on the surface of the film, an intense scattering ring is observed when a laser is reflected from the surface. The position of the maximum in the scattering intensity is related to the wavelength of the wrinkles through the following relationship:

$$q_{\max} = \frac{4\pi}{\lambda}\sin\theta \approx \frac{2\pi}{d}$$

where q_{max} is the position of the maximum in reciprocal space, 2θ is the scattering angle, λ is the wavelength of the laser light, and d is the wrinkling wavelength. The intensity of the peak at q_{max} is proportional to the square of the buckling amplitude. By analyzing time resolved images of the scattering intensity, it is possible to probe the early stages of amplitude growth as well as any changes in the wavelength that occur during isothermal annealing. The results of our preliminary experiments are presented in this paper.

EXPERIMENTAL

Materials. Polystyrene (PS) was purchased from Scientific Polymer Products, Inc.[6] and had a molecular mass of 600 kg/mol and polydispersity of 1.04. The silicon wafers were cleaned through a series of ethanol, acetone, and toluene rinses, followed by a UV-ozone treatment for 20 min.

Sample Preparation. Polymer films were prepared by spin casting a PS solution in toluene onto silicon. The film thickness was determined to be 270 nm ± 3 nm via interferometry. The films were annealed under vacuum for 24 h at 180 ºC to remove residual solvent and erase any thermal history in the polymer film. An aluminum (Al) layer of approximately 25 nm ± 1 nm was then thermally evaporated onto the polymer film. The maximum temperature at the polymer surface during evaporation was 47 ºC as measured by a Thermax indicator.

Light Scattering. The light scattering was performed using a setup as depicted in Figure 1. The films were placed on a hot stage held at a predetermined annealing temperature and image data were collected every 2 s. The scattering images from the CCD camera were radial averaged and the scattering intensity as function of the scattering vector, q, was determined. The position and intensity of the scattering maximum were determined as a function of time over a range of temperatures.

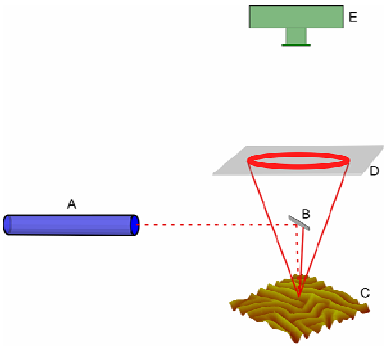

Figure 1. Schematic of the experimental setup: (A) 15 mW He-Ne laser (B) mirror (C) wrinkled polymer-aluminum film (D) diffuser plate to capture scattering image (E) thermo-electrically cooled CCD camera.

RESULTS AND DISCUSSION

A representative plot of time-resolved scattering behavior for a PS-Al film annealed above the glass transition temperature of PS (T_g = 105 ºC) can be seen in Figure 2. Initially, the scattering profiles are featureless and of relatively low scattering intensity. With time, the wrinkles begin to develop and the regular, isotropic sinusoidal surface structures give rise to a maximum in the scattered intensity that increases exponentially in time. This behavior in the growth of the wrinkle amplitude has been predicted by theoretical modeling of the wrinkling of an elastic film on a viscoelastic substrate.[5] The initial stages of amplitude growth reflect the viscous response of the polymer film to the buckling instability, while the long-time amplitude behavior is

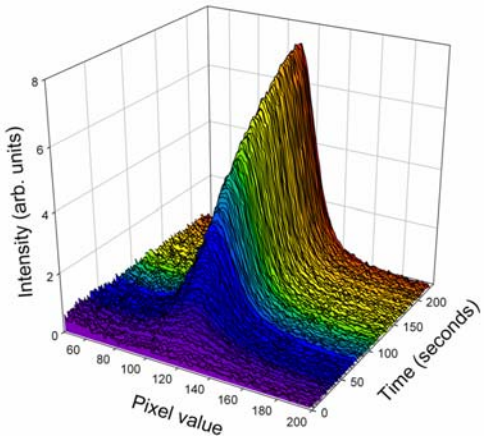

Figure 2. Time-resolved scattering showing the evolution of the scattering intensity as a function of time for a polystyrene-aluminum bilayer during annealing.

related to the rubbery nature of the material and can reveal information about the relaxation behavior of the polymer chains in this confined geometry.

It is expected that this measurement platform will provide the means by which one can measure the temperature-dependent viscoelastic relaxation behavior of a variety of confined polymer systems. Initial qualitative studies have shown that the time-scale of polymer relaxation, during the initial stages of wrinkling, can be determined over a wide range of annealing temperatures. By employing the equations established by theoretical buckling mechanics,[5] it should be possible to quantitatively elucidate the rubbery modulus, or, in the case of high temperature, the viscosity of a thin polymer film. We are currently optimizing the experimental setup to accurately measure the scattering intensity as a function of time and to extract relaxation times and, ultimately, the physical properties of polymer films using surface light scattering.

Aside from measuring the viscoelastic properties of polymer thin films using the surface scattering technique outlined above, this technique has also been used to measure the wrinkling of a polymer brush that has been grown from a silicon surface and capped with an aluminum layer. Initial results indicate that it is possible to measure the dynamics in the early stages of the wrinkling process for these uniquely confined polymer systems.

In conclusion, we have presented here a new measurement platform that employs laser light scattering to probe the kinetic process of thermal wrinkling of a thin polymer film capped with an aluminum layer during the initial stages of wrinkle amplitude growth. It is possible using this technique to characterize the viscoelastic relaxation behavior of polymer thin films over a range of temperatures. With this new, robust metrology it is possible to measure the relaxation behavior of a variety of confined polymer systems including, but not limited to polymer brushes, polymer nanocomposite thin films, and block copolymers.

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6. Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.