ABSTRACT

ZHANG, ZHANRUI. Stress Relaxation Modulus of Polymer Thin Films Measured \textit{via} Buckling-based Metrology. (Under the direction of Dr. Brendan O’Connor).

Polymer thin films are broadly used in areas such as protective coatings, optical components, and electronics. The viscoelastic behavior of these thin films is critical in these applications for it influence the morphology and the performance of organic semiconductor materials. However it is still a challenging task to measure the viscoelastic properties of thin films with thickness below 1 \( \mu \)m. Nevertheless, there have been several methods developed to probe polymer thin film viscoelasticity including nano-indentation, dielectric spectroscopy, and acoustic impedance spectroscopy. However, these methods require sophisticated equipment.

In this work, we introduce a new method to measure stress relaxation in viscoelastic polymers by using a buckling based metrology method. Briefly, this approach consists of placing the polymer thin film on an elastomer substrate and compressing the composite resulting in films buckling. By studying the time dependent behavior of the buckling wavelength and amplitude, the stress relaxation modulus can be determined. A custom experimental station was built with the buckling behavior probed through laser diffraction. The stress relaxation modulus is then interpreted and fitted into Generalized Maxwell Model. We focus on the stress relaxation of polymer semiconductor thin films Poly (3-hexylthiophene-2,5-diyl) (P3HT), and Poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione \(-3,6\text{-diyl})\text{-alt-}(2,2’;5’,2’’;5’’’;2’’’’-quaterthiophen-5,5’’’’-diyl]) (DPP-4T). These represent widely employed polymer semiconductor films with glass transition temperatures below room temperature. The viscoelastic behavior of these films have important implications for flexible and stretchable electronics. In addition to these polymers, polystyrene (PS), which is glass at room temperature is measured to assist in verifying
the setup. The elastomer substrate employed was PDMS. Results indicate that the relaxation time \( \tau \) is 28.90 and 37.96 min, respectively for P3HT and DPP-4T.
Stress Relaxation Modulus of Polymer Thin Films Measured via Buckling-based Metrology

by
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DEDICATION

I dedicate this work to my dear parents, Ronggang Zhang and Hongsong Liu, who love me, trust me and support me in every step of my way. I would also like to dedicate this thesis to my loving girlfriend Weiwei Zhu, from whom I have got unconditional love understanding these three years.
BIOGRAPHY

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INTRODUCTION

Wrinkles can be formed by compressing a relatively rigid thin film on a compliant substrate. The uniaxial or biaxial compression stress can be achieved via many methods such as thermal expansion (Mei, Huang, Chung, Stafford, & Yu, 2007; Yoo, Suh, Kang, & Lee, 2004), mechanical compressing (Efimenko et al., 2005; Stafford et al., 2004), and swelling or shrinkage (Chan & Crosby, 2006; Guvendiren, Yang, & Burdick, 2009), which will lead to different wrinkling pattern, like sinusoidal pattern and herringbone pattern. The underlying physical mechanism of this phenomenon has been systematical studied by researchers, and many theoretical and experimental advances prompt its application and research interest in fields such as stretchable electronics(Khang, Rogers, & Lee, 2009; Lacour, Wagner, Huang, & Suo, 2003), optical devices(P. Kim et al., 2013; Lee et al., 2014), and material properties measurement (A wartani et al., 2013; Balar et al., 2017; Chung, Chastek, Fasolka, Ro, & Stafford, 2009; Chung, Nolte, & Stafford, 2011; Howarter & Stafford, 2010; Stafford et al., 2004; Stafford, Harrison, Karim, & Amis, 2006; Wilder, Guo, Lin-Gibson, Fasolka, & Stafford, 2006). This thesis studies the relaxation procedures of wrinkling patterns in two different bilayer systems, Poly (3-hexylthiophene-2,5-diyl) (P3HT), and Poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione -3,6-diyl)-alt-(2,2’;5’,2’’;5’’’,2’’’’-quaterthiophen-5,5’’’’-diyl)] (DPP-4T) thin films respectively, on Polydimethylsiloxane (PDMS) substrate, by wrinkling-based metrology. It is observed that the wrinkling in the films will relax over time with a custom-built Small Angle Laser Light Scattering system. The relaxation of the wrinkling patterns can be attributed to stress relaxation of viscoelastic polymer thin films. The relaxation modulus of these two polymer thin films are derived at room temperature. Furthermore, a measurement method using buckling-based metrology to investigate the viscoelastic properties of polymer thin films is introduced.
1.1 Analytical formula of wrinkling

A bilayer system consisting of a thin film on a soft elastic substrate, when placed in compression, an interface instability develops that results in the thin film wrinkling on the elastomer substrate. In the bilayer system, the compression deformation of the compliant substrate favors short wavelength, however, the bending of the stiff film favors long wavelength. The balance between these two deformations determine the wavelength of the wrinkling (Chen & Hutchinson, 2004). A uniaxial loading will lead to sinusoidal pattern in the perpendicular direction of compression stress, e.g. Figure 1.1a. A biaxial loading will result in more complex mode of wrinkling, such as herringbone (Figure 1.1b), checkerboard or hexagonal pattern (Bowden, Brittain, Evans, Hutchinson, & Whitesides, 1998; Breid & Crosby, 2011; Cai, Breid, Crosby, Suo, & Hutchinson, 2011; Yin, Yagüe, Eggenspieler, Gleason, & Boyce, 2012).

Figure 1.1 different pattern of wrinkling a) sinusoidal pattern of wrinkling PDMS with UV Ozone treatment skin (Efimenko et al., 2005) b) herringbone pattern of buckled PS films on PDMS substrate (Cai et al., 2011)
Euler first studied the instability phenomena of struts and columns in the 18th century. The mathematical formula proposed by Euler predicted the onset of buckling of column in axial compressive load (Landau & Lifshitz, 1986). Biot used linear perturbation to investigate the instability of a hyper elastic half space (Biot, 1963). This method was also used in solving the critical loading condition and wavelength of wrinkling, for wrinkles possess infinitesimal strain deviating from the flat state and the smooth undulation pattern (Jin, 2014). People further developed several linear and nonlinear mechanics formula to describe the wrinkling surface (Breid & Crosby, 2011; Chen & Hutchinson, 2004; Groenewold, 2001; Huang, 2005; Huang & Suo, 2002; Huck et al., 2000; Lu, 2009; J.-Y. Sun, Xia, Moon, Oh, & Kim, 2012). In these theories, typically both the film and the substrate are modeled as elastic solids. The thin film can be taken as a von Karman plate for the thickness of film is much smaller than the wavelength of the wrinkling pattern. And the substrate is treated as semi-infinite under plain strain condition. Here, a classic theory derived by force balanced approach to predict surface wrinkling is listed in detail.

The bending of a stiff plate on a compliant substrate can be described by following equation:

$$\bar{E}_f I \frac{d^4 z}{dx^4} + F \frac{d^2 z}{dx^2} + kz = 0$$

(1)

Where $\bar{E} = E/(1-\nu^2)$ is the modulus in the plane-strain condition, $E$ and $\nu$ are the Young’s modulus and the Poisson’s ratio, respectively, the moment of inertia is $I = wh^3/12$, where $w$ is the width of the thin films, and $h$ is thickness of the thin films. The f and s, subscripts of $E$ represent film and substrate, respectively. The Winkler’s modulus of elastic half-space, $k$, can be represent by equation, $k = \bar{E}_f w \pi / \lambda$. $F$ is the uniaxial compression loading which its direction is x axis, and $z$ axis is perpendicular to the surface of thin films. Equation (1) includes two part. The first and third terms that denote the bending force in the film belong to the Euler-Bernoulli beam bending
equation. The effect of uniaxial loading $F$ is represented by the second term. The sinusoidal pattern of wrinkling surface can be formulated as:

$$z(x) = A \sin \left( \frac{2\pi x}{\lambda} \right)$$  \hspace{1cm} (2)

Substitute (2) into equation (1),

$$16 \bar{E}_f I \left( \frac{\pi}{\lambda} \right)^4 z - 4 \bar{F} \left( \frac{\pi}{\lambda} \right)^2 z + \bar{E}_w \left( \frac{\pi}{\lambda} \right)^{-1} z = 0$$  \hspace{1cm} (3)

By canceling all the $z$ term, and solving for compression loading $F$ is:

$$F = 4 \bar{E}_f I \left( \frac{\pi}{\lambda} \right)^2 + \frac{\bar{E}_w}{4} \left( \frac{\pi}{\lambda} \right)^{-1}$$  \hspace{1cm} (4)

When $\frac{\partial F}{\partial \lambda} = 0$, system has minimum $F$ to minimizes the total energy and establish wrinkling, which yields the wavelength of wrinkling pattern:

$$\lambda = 2\pi h \left( \frac{\bar{E}_f}{3\bar{E}_s} \right)^{\frac{1}{3}}$$  \hspace{1cm} (5)

This equation establish the relationship between the elastic modulus and the wavelength of wrinkling, and make it possible to measure the elastic modulus of polymer thin films, i.e. the buckling-based metrology.

The critical loading, $F_c$, is the compression loading at the wavelength equal to equation (5). Then the critical stress and critical strain can be determined by $F_c$, and film’s geometry properties:

$$\sigma_c = \frac{F_c}{h w} \left( \frac{9\bar{E}_f \tilde{E}_s}{64} \right)^{\frac{1}{3}}$$  \hspace{1cm} (6)

$$\varepsilon_c = \frac{\sigma_c}{\bar{E}_f} = \frac{1}{4} \left( \frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}}$$  \hspace{1cm} (7)
From equation (7), the critical strain only depends on the materials properties of thin film and substrate, however the geometry properties, like thickness of thin films do not involve in $\varepsilon_c$. When applying a compression loading, once the compression strain exceeds the critical strain, the wrinkling wavelength is established. The extra strain will lead to the increasing of amplitude of wrinkling, however based on equation (5), wavelength will remain constant, with $\lambda$ is independent of strain. Hence, the amplitude can be represented by:

$$
\varepsilon - \varepsilon_c = \frac{1}{\lambda} \sqrt{1 + \left( \frac{dz}{dx} \right)^2} dx - 1
$$

(8)

The left hand of equation (8) is the overstrain, and the right hand is the release of tensile strain in the bilayer system. With the assumptions that $A \ll \lambda$ and $dz / dx$ is relatively small, there is an approximation. $\sqrt{1 + \left( \frac{dz}{dx} \right)^2} \approx 1 + \frac{1}{2} \left( \frac{dz}{dx} \right)^2$, and equation (8) can be expressed as:

$$
\varepsilon - \varepsilon_c = \frac{\pi^2 A^2}{\lambda^2}
$$

(9)

By substituting equation (5) and (7) into equation (9), the amplitude of wrinkling is:

$$
A = h \sqrt{\frac{\varepsilon - \varepsilon_c}{\varepsilon_c}}
$$

(10)

Equation (5) and (10) fully describe the central properties of wrinkling pattern, wavelength and amplitude, and predict the onset strain of wrinkling. These formulations also provide an elegant and versatile method to measure the materials properties of thin films (Figure 1.2).
Figure 1.2 Validation of amplitude prediction a) AFM graph of flat surface of PS coated silicone b) At a strain of 0.010, the surface start wrinkling c) At a larger strain of 0.073, amplitude increased from 0.08 to 1.37 μm d) The blue line is amplitude predicted by equation (10), red dot denotes to AFM results (Harrison, Stafford, Zhang, & Karim, 2004)

1.2 Applications of wrinkling surface

Instability used to be treated as a kind of failure, however, recently, the instability of bilayer systems with a rigid thin film on a soft substrate has been exploited to investigate materials properties(Stafford et al., 2004), fabricate stretchable electronics(Lacour et al., 2003), microfluidics(Khare, Zhou, & Yang, 2009), controllable optical devices(Lee et al., 2014), wettability(Chung, Youngblood, & Stafford, 2007) and many other applications(Rand & Crosby, 2009). Wrinkling pattern can be achieved easily with many fabrication methods, like thermal expansion and mechanical compression. And its geometry can be rapidly and easily adjust by controlling the compression loading. All these advantages spur research interest in wrinkling behavior.
One example of applications exploiting wrinkling is stretchable interconnection (Khang et al., 2009; Lacour et al., 2003). Stretchable electronics can consist of intrinsically stretchable Materials, or rigid device islands. For rigid devices, to implement stretchable of the electronics, stretchable electrical connections are employed. In this method, a buckled bilayer system with thin metal films on elastomeric substrate is used as the interconnection between the rigid device islands, with a sinusoidal shape like Figure 1.3 shows. When external loading is applied on the sample, the wrinkling metal connections will absorb the strain, hence the whole sample would be stretchable.

Another application of wrinkling surface is optical devices (Lee et al., 2014). Tilted micropillar arrays are fabricated on wrinkling PDMS substrate to achieve a switchable optical window. The transmittance can be controlled by the apply strain of the sample. Before apply the external tensile loading the micro pillars are accommodated in the wrinkling patterns and confined inside of wrinkling undulation. The external loading will flatten the wrinkling surface and array micro pillars, which make the sample become more transmit.

Figure 1.3 Stretchable single crystal Si p-n diode with wrinkling Al connection at different applied loading (Lacour et al., 2003).
Among all these above-mentioned applications, materials properties measurement has been broadly studied and used for research purposes. Polymer thin films have attracted dramatic attention of researchers for its unique and prominent materials properties and potential applications involving organic photovoltaics (Yang, Sen, O’connor, & Kudenov, 2017), coating, and optical windows, however, the mechanical properties of thin films which are critical for its pragmatic applications and industry manufacture. Conventional standard mechanical test methods have limitations due to the lack of sensitivity to measure the stress of a polymer thin film. Scanning probe microscopy has been employed by researchers to investigate the moduli of functional polymer films, however there are limitations like the uncertainty of contact area between the tip and samples which challenges its reliability (Du, Tsui, Zhang, & He, 2001; Du et al., 2000). Nanoindentation has demonstrated its power when involving engineering materials like alloys, but when dealing with soft materials like polymer thin films, the viscoelastic behavior of samples effects the result (VanLandingham, Villarrubia, Guthrie, & Meyers, 2001). In addition, artifacts associated with the substrate can complicate data analysis, particularly for soft thin films. To meet the rapidly increasing need for measurement of mechanical properties, Stafford and his group introduced a platform called SIEBIMM (strain-induced elastic buckling instability for mechanical measurements) or buckling-based metrology that possesses the abilities of measuring the modulus of thin films instantaneously and precisely (Chung et al., 2011; Stafford et al., 2004). Here, this method will be described in some detail.

Then underlying governing equations of buckling-based metrology have been briefly discussed at chapter 1.1. With known elastic modulus of substrate determined by conventional mechanical test, the elastic modulus of thin films can derived from the wavelength of wrinkling by equation (5). In buckling-based metrology platform, a small-angle light scattering (SALS) has
been used to determine the wavelength of wrinkling pattern with a low-power HeNe laser ($\lambda = 632.8$ nm), as shown at Figure 1.4 a. Laser beam would generate diffraction pattern after passed through the periodic sinusoidal wrinkling surface (Figure 1.4 b). From Bragg’s Law, the wavelength of the wrinkling pattern, $d$, is expressed by equation: 

$$q_0 = \frac{4\pi}{\lambda} \sin \theta \approx \frac{2\pi}{d}.$$ 

Where $\lambda$ is the wavelength of the laser and $2\theta$ is the angle of diffraction at the first order peak. The features of diffraction pattern can be captured by camera and processed by computer rapidly, which means many different locations of samples can be tested in few seconds. These advantage allows researchers to obtain a more statistically precise result. The same measurement also can achieved by Atomic Force Microscopy or Optic Microscope using the equation (5).

**Figure 1.4** a) Schematic of the buckling metrology b) Diffraction pattern of wrinkling surface (Stafford et al., 2004)

Beyond the elastic modulus measurement, buckling-based metrology also possesses the ability to capture the amplitude of wrinkling surface(Harrison et al., 2004). Another mechanical properties, residual stress of thin films after manufacture processing can be interpreted from amplitude measurement results(Chung et al., 2009). Previously, it was shown that on phase
gratings created by a buckled surface, the local phase shift of coherent light is proportional to the amplitude of the wrinkling surface. This relationship can be expressed by following equation with in the Fraunhofer limit:

\[ I[q] \approx \sum_{p=-\infty}^{\infty} J_p^2 \left( \frac{m}{2} \right) \sin e^{-2} \left[ W \left( q - \frac{2p\pi}{d} \right) \right] \]  

(11)

where \( J_p \) is the Bessel function of the first kind, \( W \) denote the half width in the \( x \) direction of the aperture, \( d \), \( m/2 \), and \( p \) are wrinkling wavelength, the maximum phase shift, and index of diffraction, respectively. This equation could be simplified to a proportional to the Bessel function, \( J_p^2 \left( \frac{m}{2} \right) \) with the feature of sinc function that the distribution in \( q \) about each order \( p \) is relatively narrow. For the first order diffraction intensity \( I \), can be determined by:

\[ I = J_p^2 \left( \frac{m}{2} \right) \]  

(12)

Where the maximum phase shift is

\[ \frac{m(\varepsilon)}{2} = 2\pi \frac{A(\varepsilon)}{\lambda} (n-1) \]  

(13)

In equation (13), \( \varepsilon \) is the compression strain, \( n \) is the index of refraction of the substrate, \( A \) is amplitude of wrinkling pattern, and \( \lambda \) is the wavelength of laser. Hence, with equation (13) and equation (12), the amplitude of wrinkling pattern can be derived from intensity measurement (Figure 1.4).

Moreover, from equation (10), amplitude of wrinkling pattern is dependent on the critical strain and applied compression strain. Stafford and his research group exploits this relationship to measure the critical strain of wrinkling and residual strain during the manufacture of thin films, with a custom-built SALS system (Chung et al., 2009). As Figure 1.5 shows, after onset of
wrinkling, intensity increases with applied strain. In Stafford paper, the critical strain is defined as the intersection of two different fitted lines. Compared with the critical strain from equation (7), which is based on pure elastic formulations without residual strain effect, residual strain, $\varepsilon_R$ resulted from processing procedure can be expressed as:

$$\varepsilon_c = \frac{1}{4}\left(\frac{3E_s}{E_f}\right)^\frac{2}{3} + \varepsilon_R$$  \hspace{1cm} (14)

Due to the nano/micro scale of thin films, measuring the mechanical properties of thin film using conventional testing methods was a challenge. However, compared with conventional test methods, buckling based metrology provides researchers an efficient and versatile method to investigate many properties of thin film. This method indeed meet the growing demand on research interest of functional polymer thin films.

Figure 1.5 Intensity changing versus loading strain, the inset graphs show the diffraction pattern of SALS (Chung et al., 2009)
1.3 Viscoelastic properties of polymer thin films

When polymer materials undergoing deformation, the property of polymers would exhibit both like elastic and viscous, i.e. the viscoelastic properties of polymers. After pioneers such as Maxwell, Boltzmann, and Kelvin first conducting experiments of the creep and recovery of metals and rubbers, viscoelasticity then was continually investigated (C. Kim, Facchetti, & Marks, 2007; McCrum, Buckley, & Bucknall, 1997). Recently, polymer films has exhibited many ubiquitous properties and applications in stretchable electronics, photonics, and optics (Khang et al., 2009; Khare et al., 2009; Lacour et al., 2003; Lee et al., 2014). The viscoelastic properties of polymer thin films are critical to the performance of the devices in these applications. For instance, the morphology of materials plays an important role in the performance of organic transistors, which could be changed by the viscoelastic behaviors of polymer gate dielectric layer underlying in the organic transistors (Chan, Kundu, Lin, & Stafford, 2010). However, the measurement of viscoelastic properties in polymer thin films could be very challenging. For bulk polymer samples, these measurement can be achieved easily by conventional methods like Resonant Ultrasound Spectroscopy (RUS) and Broadband Viscoelastic Spectroscopy (BVS), but these prediction or behaviors are not necessarily related to its analogs in thin films samples. Previous research has suggested the viscoelastic properties are quite dependent on the interfacial properties like film thickness and interfacial energies (Choo et al., 2008). However, due to the lack of sensitivity in conventional test methods, it is quite challenging to directly measure the viscoelastic properties of polymer thin film.

Several approaches were developed to meet the stringent demands of measuring the viscoelastic properties of polymer thin film, such as indentation, dielectric spectroscopy, and acoustic impedance (Cho, Watanabe, & Granick, 1999; Hillman, Efimov, & Ryder, 2005; Tsui,
One example of the earliest attempts was polymer film dewetting (Barbero & Steiner, 2009; Reiter, 1994). A liquid-like polymer thin film deweted and formed holes freely from a nonwetting substrate. The viscoelastic properties of the polymer thin film can be derived from the growth rate of the dewetting holes. In 1997, a modified Surface Forces Apparatus (SFA) was introduced by Israelachvili for rheological and tribological measurement of thin films. By attaching a new SFA attachments for moving samples and measuring the friction forces more precisely (Figure 1.6), viscoelastic properties of polybutadiene thin film was studied in two different approaches: the rheological and tribological (Luengo, Schmitt, Hill, & Israelachvili, 1997). In addition, ellipsometry and fluorescence are also used to characterize residual stress relaxation of thin films. The intensity of specific peak of sample’s fluorescence spectrum was tracked and the relaxation time of residual stress can be inferred from intensity ratio changing like figure 1.7 shows (Askar, Evans, & Torkelson, 2015).

Stafford and his co-workers demonstrated that the stress relaxation modulus of polymer thin films via thermal wrinkling. In this work, different thickness polystyrene thin films and Al up-layer were annealed at different temperature to induce different wrinkling pattern (Figure 1.8). A bilayer system of a thin metal layer coated on a layer of polymer thin films was located and heated on a hot stage to induce the wrinkling. The wavelength of wrinkling were measured by custom built SALS system. The viscoelastic properties of polymer thin film was expressed by a function of geometric confinement and annealing times. Time-temperature superposition was
Figure 1.6 Shear element of the dynamic surface forces apparatus. The strain gauges detect the bending of the springs, and the viscoelastic properties are derived from vibration amplitudes and phase delay (Luengo et al., 1997).

Figure 1.7 The intensity ratio from fluorescence spectrum for 680nm MPy-PS films over 12 hours at different temperature are plot versus time. The relaxation time can be determined by intersection between two straight lines. (Askar et al., 2015)

employed to shift the stress relaxation curves and generate a relaxation modulus master curve of PS thin films that above its glass transition temperature (Figure 1.9). However, the annealing temperature must be sufficiently high to induce the thermal wrinkling pattern of system. The
experiments requires special hot-stage and other instruments like thermal evaporation device to deposit the top metal layer. Polymer thin films are located between the superstrate and the substrate of the system which leading to a relatively complicated formulation, especially, when dealing with ultra-thin films (under 100nm), it will require quite high annealing temperature.

**Figure 1.8** Schematic of PS thin film with Al superstrate and substrate (Chan et al., 2010)

**Figure 1.9** relaxation modulus master curve of PS thin films that above its glass transition temperature in different thickness (Chan et al., 2010)
1.4 Outline of the thesis

As mentioned above, polymer thin films are used in many technological applications, and the measurement of viscoelastic properties in polymer thin films still is a challenging task. Several previous reported probing methods require costly and intricate equipment. In addition, the interface energies also involved in the viscoelastic properties of thin films. Recently, many applications like organic transistors, stretchable electronics are built on the PDMS substrates (T. Sun et al., 2017), hence the viscoelastic properties of functional polymer thin films with PDMS interface is vital for the performance of these applications.

To achieve a versatile measurement method with simplicity and less cost, a customize SALS system is set up. The stress relaxation behaviors of polymer thin films, PS, P3HT and DPP-4T are investigated via buckling based metrology. To derive the relaxation modulus of polymer thin films, the evolution of wavelength and amplitude in wrinkling pattern are monitored over time. Besides, several experiments in different conditions are conducted to validate our results.
STRESS RELAXATION OF P3HT AND DPP-4T THIN FILMS

2.1 Experimental section

In this work, we choose P3HT and DPP-4T thin films as our model polymer thin films. These polymer are widely used in organic electronics devices and are know to have a glass transition close to, but below room temperature.

P3HT thin films are prepared by spin casting 20 mg/ml dichlorobenzene solution on octyltrichlorosilane (OTS) treated silicon. DPP-4T thin films are spun cast 15 mg/ml chloroform solution onto octyltrichlorosilane (OTS) treated silicon. The thicknesses of these thin films are 130nm and 140nm, for P3HT and DPP-4T respectively. PDMS substrates are prepared at a ratio of 20:1 of base to curing agent. Thin films are transferred print on the 15% pre-strain PDMS substrate. In addition, polystyrene (PS) thin film prepared by spin casting a 2.5% ratio(by mass) Toluene solution with a 160 nm thickness is also used in this work.

The wrinkling patterns are generated by applied compression strain onto thin films/PDMS substrate bilayers on a custom-built strain stage like figure 2.1 shows. The buckling based metrology experiments are conducted by a SALS system, illustrated in Figure 2.1(Chung et al., 2011; Stafford et al., 2004). A diode laser with a 635 nm wavelength is used as the light source, and result in a diffraction pattern on a screen behing the film, which are captured by a camera. An optic power meter (Newport Corporation) is used to measure the intensity of diffraction pattern. As mentioned at Chapter 1, the wavelength of wrinkling pattern, \(d\), is determined by Bragg’s Law, by equation: 

\[ q_0 = \frac{2\pi}{\lambda} \sin \theta \approx \frac{2\pi}{d}, \]

where \(\lambda\) is the wavelength of the laser and \(2\theta\) is the angle of diffraction at the first order peak. \(q_0\) is calculated by computer with the camera data and Matlab software. The amplitude measurement is based on equation (12) and equation (13). By substituting (13) into (12), the relationship of normalized intensity of fist order peak and amplitude is:
\[ I = \left( \frac{\pi (n-1)}{\lambda} \right)^2 A^2 \] (15)

where \( n \) is the index of refraction of the substrate (1.404 ± 0.004) (Chung et al., 2009), and \( \lambda \) is the wavelength of laser.

Figure 2.1 a) Schematic of custom-built SALS apparatus. b) The strain stage with thin films on PDMS substrate. Wrinkling pattern is obtained by compressing the substrate.
2.2 Validation of the stress relaxation measurement

Wavelength and amplitude of wrinkling pattern on P3HT/PDMS bilayer are monitored via buckling based metrology over time at room temperature. As Figure 2.2 shows, both the wavelength and amplitude decreased with the time, and it could be for well to an exponential function, which are similar to the stress relaxation curve of polymers. The wavelength of wrinkles is determined by a balance between the deformation of the substrate and the bending of the film. And from equation (5), (7) and (10), wavelength and critical strain is only dependent on elastic modulus of thin film and substrate, and amplitude is dependent on the critical strain. It is reasonable to relate the decrease of wavelength and amplitude with the changing of relaxation modulus over time. To verify our suggestion, a PS thin film on PDMS substrate is buckled at room temperature and its evolution of wrinkling amplitude are plotted as figure 2.3. The amplitude stay around 183.27 nm during the 2h test, which may suggest there is no viscoelastic behavior in PS thin film at temperature. The glass transition temperature is 95 °C, hence at room temperature, PS will be relatively brittle ‘glassy’ state and does not possess viscoelastic properties. This is in alignment with our experimental result. It is noticeable that at the early stage of the experiments, there is a slight dropping of amplitude. This could be attributed to the viscoelastic properties of PDMS substrate, for its Tg is about -125 °C. We assume PDMS is elastomer in this work, for its effect on result is negligible.

Another possible explanation of the relaxation behavior observed in the P3HT and DPP-4T films is interfacial slip across the film-elastomer interface.
Figure 2.2  a) the wavelength evolution with time of P3HT thin film on PDMS substrate b) amplitude changing curve with time of P3HT thin film on PDMS substrate

Figure 2.3  Amplitude evolution of PS thin film on PDMS substrate with time
To determine if interfacial slip is occurring, another group of experiments were conducted. Two P3HT thin films with the same thickness (130 nm) are transferred onto PDMS and 20min UVO treated PDMS, respectively. Wrinkling is induced by the same compression strain. The amplitude of both wrinkling pattern are plotted versus time in figure 2.4. UVO treatment can increase the adhesion energy at the interface of P3HT thin film and PDMS substrate, which will reduce the probability of interfacial slip (Choo et al., 2008). Results indicate that wrinkling pattern of P3HT thin film on UVO treated PDMS shows similar relaxation behavior with P3HT film on neat PDMS substrate. Hence, the relaxation of wrinkling amplitude and wavelength is not result from possible sliding between films and substrates. However, wrinkling pattern of UVO treated system relax more slowly than its analog on neat PDMS substrate. It can be attributed to the extra rigid thin oxide layer add by UVO treatment. This layer will be is an incomplete silicate layer that will, should be primarily elastic in its response. Thus, it should be time independent resulting in a

Figure 2.4 the amplitude versus time of wrinkled PS thin film on UVO treatment PDMS and neat PDMS
lower relaxation of the composite surface layers with time. Based on the above experiments, the viscoelastic behavior of thin film will lead to the relaxation of wrinkling pattern. And by exploiting this feature, the relaxation modulus of thin film can be determined.

2.3 Stress relaxation of P3HT and DPP-4T thin film

The experimental results can be treated as a stress relaxation problem, the wrinkling pattern is induced by a constant compression strain on the stage. Wrinkles have infinitesimal displacement deviating from each state, and for simplicity, the formulations introduced at Chapter 1 which based on elastic assumption are used to approximate and derive the relaxation modulus of thin films. From equation (5), wavelength is only dependent on the elastic modulus of films and substrates. Hence, the relaxation curve can be derived from the wavelength changing curve. Note that amplitude also changing dramatically. From the equation (10), amplitude is determined by applied strain and critical strain. In stress relaxation, the applied strain should be constant, hence, the amplitude is decreasing with critical strain increasing. And from equation (7), critical strain also dependent on modulus changing of films and substrates. In contract with modulus, critical strain increasing with the decreasing of wavelength. Based on equation (7), and (10), the relaxation modulus also leads to the relaxation of amplitude.

Hereby, two polymer thin films, P3HT and DPP-4T are investigate by our SALS setup. DPP-4T also shows the same relaxation procedure of wavelength and amplitude with P3HT thin film system (Figure 2.5). The relaxation modulus curves of these two thin films are derived and plotted in Figure 2.6. To further validate our result, the critical strain curves and the applied strain are also calculated and plotted(Figure 2.6). In this work, the elastic modulus of substrate, PDMS
is 0.6MPa, the Poisson ratio of PDMS is 0.5, the Poisson ratio of P3HT and DPP-4T are approximated as 0.35. General Maxwell Model is employed to fit the relaxation modulus curve:

\[ E_r = E_r \exp \left( -\frac{t}{\tau_1} \right) + E_0 \]  

(16)

*Figure 2.5* a) the wavelength evolution with time of DPP-4T thin film on PDMS substrate b) amplitude changing curve with time of DPP-4T thin film on PDMS substrate

From figure 2.6(a),(b) and fitting result, for P3HT the relaxation time \( \tau_i \) is 28.90 min, and for DPP-4T the relaxation time \( \tau_i \) is 37.96 min. P3HT is relaxing more fast than DPP-4T in constant applied strain. Critical strain increases with wavelength decreasing i.e. the relaxation modulus of thin films decreasing(figure 2.6 (c) and (d)), Applied strain calculated from experiments result is nearly constant which is in alignment with the assumption of stress relaxation. The critical strain and applied strain result confirm that this setup could measure the stress relaxation modulus of polymer thin films.
Figure 2.6 a), c) and e) is the relaxation modulus, critical strain, and applied strain calculate over time of P3HT, respectively b), d) and f) is the relaxation modulus, critical strain, and applied strain calculate over time of DPP-4T, respectively.
SUMMARY

3.1 Future work

With the versatile and costless measurement method of viscoelastic that we developed in this thesis, the viscoelastic properties of many polymer thin films which have potential applications in stretchable electronics, optics, organics solar cells can be investigated. Here we only consider 2 kind of polymer, P3HT and DPP-4T. There are still many interesting polymer thin films to study. More importantly, the viscoelastic properties of polymer thin films also depend on temperature except its geometry confinement. In future, a SALS test platform with temperature control function would be powerful to deliver a more comprehensive understanding of viscoelastic properties of polymer thin films, especially for polymer with higher $T_g$ like PS. The temperature control function could also help us to derive the time-temperature superposition master curve of polymer thin films. And when at the near $T_g$ region, the relaxation of wrinkling wavelength and amplitude should be start or stop, it will be interesting to observe this phenomenon which may lead to a new method to determine the $T_g$ of polymers. In addition, to further validate the results and get a more comprehensive study, other test methods like DMA test or bulk rheology test can be conducted and compared with our results.

To demonstrate the possibility of temperature control on SALS test platform, a low cost heating module was designed and added on our previous experiment setup, as figure 3.1 shows. A heat gun with temperature control function (from 200 to 900 °F) was employed to generate hot air flow. The hot air flow passed through the connection tube made by double layer aluminum foil into the container with 2 small rectangular hole on the front and back side to allow laser light and hot air pass through. The wrinkling samples on the strain stage was allocated inside of container. The hot air flow was cooling down little bit to a desirable temperature when passed through the
connection tube. The sample was heated up gradually by steady hot air flow inside the container until reach a local equilibrium state to keep a certain temperature. Temperature of sample was monitored by IR camera continually. Results indicate that this setup can heat up and keep a temperature of samples from 40 to 160 °C.

Figure 3.1 Schematic of SALS with temperature control function

3.2 Conclusion

In this work, a SALS platform is set up to monitor the geometry changing of wrinkling pattern of polymer thin films over time. With the well-developed mechanics model, the stress relaxation modulus is interpreted and fitted into Generalized Maxwell Model. A non-viscoelastic thin film at room temperature, PS is test on the platform which shows a constant modulus, and UVO treated PDMS substrate is also introduced to eliminate the possibility of sliding between the thin films and substrates. Critical strain and applied strain are calculated and plotted to validate
our results. Results indicate that for P3HT the relaxation time $\tau_1$ is 28.90 min, and for DPP-4T the relaxation time $\tau_1$ is 37.96 min. P3HT is relaxing faster than DPP-4T in constant applied strain.
REFERENCES


