EXPERIMENTAL EVIDENCE OF FRACTURE-INDUCED FORMATION OF ORDERED STRIP STRUCTURES

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Thesis

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ABSTRACT

Periodic nano- or microstructures play an essential role in many fundamental researches and technological applications. This study reports the experimental details in creating periodic parallel silicone strips by simply peel an oxidized silicone sheet from its bonded substrate. This spontaneous formation of strips is initiated by a mixed-mode of separation along the peeling direction and subsequent channeling of initiated cracks. This study also provides experimental evidence on the fracture formation of ordered strips using glassy polymer thin films.

For fracture induced strips formation over a large area following the method developed by Yangjun Cai, both the oxidization extent of the Poly(dimethylsiloxane) (PDMS) sheet using UV/Ozone and the effect of oxidization extent on the strip spacing were examined. The effects of various experimental parameters, including elastic modulus of silica-like layer, pre-crack, and pre-wrinkling of the silicone surface bonded to the substrate, and glassy silica-like layer on the edge were examined. The results showed that these parameters were possible to change the initiation of the cracks during fracture or the spacing between cracks. The effect of other factors including the peeling angle, peeling force, elastic modulus and the thickness of the PDMS sheet were also explored. Those conditions proved to have little to no effect on the spacing or initiation of the cracks.
Fracture-induced structuring (FIS) of glassy polymer thin films developed by Chai et al, was also followed. Similar results on the dependency of strip spacing on film thickness were observed.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II BACKGROUND</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Different patterning methods</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1 Photolithography and soft lithography</td>
<td>6</td>
</tr>
<tr>
<td>2.1.2 Fracture induced method</td>
<td>8</td>
</tr>
<tr>
<td>2.1.3 Peeling test</td>
<td>12</td>
</tr>
<tr>
<td>2.2 PDMS</td>
<td>13</td>
</tr>
<tr>
<td>2.2.1 Characteristics of PDMS</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Characteristics of silica-like layer</td>
<td>14</td>
</tr>
<tr>
<td>2.3 Characterization techniques</td>
<td>15</td>
</tr>
<tr>
<td>2.3.1 Surface wettability-contact angle</td>
<td>16</td>
</tr>
<tr>
<td>2.3.2 Surface composition- FTIR-ATR</td>
<td>17</td>
</tr>
<tr>
<td>2.3.3 Surface morphology and topography-OM and AFM</td>
<td>18</td>
</tr>
<tr>
<td>2.3.4 Modulus measurement</td>
<td>19</td>
</tr>
<tr>
<td>III EXPERIMENTAL APPROACH</td>
<td>28</td>
</tr>
<tr>
<td>3.1 Materials and Equipment</td>
<td>28</td>
</tr>
</tbody>
</table>
3.2 Preparation for the samples

3.2.1 Sample for peeling

3.2.2 Samples for sandwich test

3.3 Experiment design

3.3.1 Basic setup for peel test

3.3.2 Characterization on the extent of oxidization by UV/Ozone

3.3.3 Strip spacing and the Height evaluation

3.3.4 Modulus determination

3.3.5 Thickness determination (PDMS sheet and the surface silica-like layer)

3.3.6 Role of the silica layer at the edges

3.3.7 Effects of pre-crack on the PDMS sheets

3.3.8 Effects of pre-wrinkles on the PDMS sheet

3.3.9 Pre-strain when oxidized

IV RESULT SECTION

4.1 The extent of oxidization of the PDMS sheet using UV/Ozone

4.1.1 Water and methylene iodide contact angles of oxidized PDMS sheets

4.1.2 Surface energy of the oxidized PDMS sheets

4.1.3 FTIR-ATR

4.2 Strips formation by a simple peel test

4.2.1 Spacing and height of strips
4.2.2 Experimental observation on strips formation by peel test ......................49

4.3 The effect of peeling force, peeling angle on formation of strips ..................52

4.4 Modulus determination ..............................................................................53

4.4.1 Stress-strain for PDMS sheet ..................................................................53

4.4.2 JKR method ..............................................................................................55

4.4.3 Buckling method .......................................................................................56

4.5 Thickness determination (PDMS and the silica layer) ..............................58

4.5.1 The effect of PDMS thickness .................................................................59

4.5.2 Gradient .....................................................................................................60

4.5.3 Effect of the UVO exposure time ..............................................................61

4.6 Role of the silica-like layer at the edges of the PDMS sheet .......................61

4.6.1 PDMS was cut for 2 or 3 pieces before peeling ........................................62

4.6.2 Bonding partial of the PDMS sheet ..........................................................63

4.7 Pre-crack effect on strips formation ............................................................64

4.8 Effects of pre-wrinkles on the PDMS sheet ...............................................66

4.8.1 Peeling direction perpendicular to the wrinkle .......................................66

4.8.2 Peeling direction parallel to the wrinkle ..................................................68

4.9 Pre-strained oxidized ..................................................................................71

4.10 Summary ....................................................................................................72

V Conclusion .....................................................................................................73

5.1 Summary ......................................................................................................73
5.2 Future Work

REFERENCES

APPENDIX
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Assignment of IR Spectra of Sylgard-184 Shown in Figure 4.3</td>
<td>44</td>
</tr>
<tr>
<td>4.2</td>
<td>Comparison of the wavelength at edges by different methods</td>
<td>71</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2.12</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>2.14</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>2.15</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2.16</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>2.17</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>
2.18 Schematics of the JKR apparatus and the top view of the contact area under elastic deformation

2.19 Schematic of a conical indenter a polymer sample and leaving a residual impression of depth hf.

3.1 Basic setup for peel test

3.2 The schematic of the different PDMS thickness when oxidized

3.3 The schematic of the gradient test

3.4 The images for PDMS sheet cut in 2 pieces(a), 3 pieces(b)

3.5 The image of the partial bonding

3.6 Two conditions for the pre-wrinkles peeling

3.7 The image of pre-strain test

4.1 Advancing and receding contact angles of DI water (DI) and methylene iodine (MI) on PDMS surfaces oxidized using UV/Ozone

4.2 Contact angles and surface energies for different surfaces

4.3 FTIR spectra of PDMS samples untreated and treated with UVO. (A) range 600-1250 (cm⁻¹) (B) range of 2800-3200 (cm⁻¹)

4.4 An OM image (top) and an AFM topography scan (bottom) of uniform parallel strips (formed by prying open the bonded interface by tweezers.)

4.5 An OM image (top) and an AFM topography scan (bottom) of uniform parallel strips (formed by peel test)

4.6 The mechanism of the Cai’s observation
4.7 Separation front form top to bottom when the PDMS sheet is separated from its bonded glass slide by simply peel test ............................................................. 49

4.8 Different strips spacing for the strips formed at different locations along the separation front .......................................................... 50

4.9 Peeling-to-tunneling angle along the separation front .................. 51

4.10 Peeling-to-tunneling angle along the separation front .................. 52

4.11 The effect of peeling force on formation of strips ......................... 52

4.12 The effect of peeling angle on formation of strips ......................... 54

4.13 Different strips spacing for the strips formed at different locations along the separation front .......................................................... 54

4.14 The elastomer and curing agent of Sylgard® 184 (silicone PDMS) used in this study, the curing process occurs in the presence of a Pt catalyst ........... 55

4.15 AFM image about wrinkles .......................................................... 56

4.16 Modulus with oxidation time ......................................................... 57

4.17 The relationship between wavelength and thickness .................... 59

4.18 The relationship between wavelength and thickness .................... 60

4.19 The effect of the UVO exposure time on spacing ......................... 61

4.20 The pattern formed during peeling when the PDMS sheet was sectioned into two (through the middle in the direction of peeling) ......................... 62

4.21 The pattern after peeling bonding partial of the PDMS sheet .......... 63

4.22 Pattern after peeling pre-crack PDMS sheet ............................... 64

4.23 Some time-sequent snap shots for peeling pre-crack PDMS sheet .... 65

4.24 The strips formed on the glass slide after peeling (peel direction: perpendicular) the bonded pre-wrinkle PDMS sheet form the glass slide .................. 66
4.25 The strips formed on the glass slide after peeling (peel direction: perpendicular) the bonded pre-wrinkle PDMS sheet form the glass slide………………………………68

4.26 The real time image about strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide………69

4.27 The strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide and the red circles were the cracks disappeared …………………………………………………………………………70

4.28 The strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide and the red circles were the cracks reshaped with a little force………………………………………………………………………70

4.29 The comparison of strips formed for pre-strained and no pre-strained ………71
CHAPTER I
INTRODUCTION

Poly(dimethylsiloxane) (PDMS) exhibits many attractive characteristics (low toxicity, high electrical resistance, and biocompatible [1]), and thus has been widely used in various areas, such as anti-fouling coating [2], biomedical applications [3], stamp for soft lithography [4]. Periodic micro- and nanostructures on PDMS stamps play a more attractive role in many fundamental studies and technological applications, such as aligning liquid crystals [5] and particles [6], micro-fluidic system [7] and so on. Conventional methods to generate patterns on the surface with different sizes are photolithography [8], and soft lithography [4, 9-11]. Photolithography is expensive due to the need for the pre-fabricated nontransparent masks and has feature-size limitation to be no smaller than the wavelength of the ultra-violet light. For soft lithography, patterns in the stamp or mold may distort due to the deformation of the elastomer [4], and fabrication of these stamps also requires the masters created by photolithography. As a result, researchers have been seeking alternative, cost-effective and simply methods for generating features for both fundamental researches and technological applications. Recently, some new and simply methods without pre-fabricated mask have been developed, and these methods included wrinkling/buckling [12-17], colloidal assemblies [18], marangoni-flow [19], breath figures [24], and fracture-induced structuring (FIS) [5, 6, 20, 21, 23].
FIS is a low-cost and high-throughput technique to make patterns in a large area. A complementary set of periodic grating patterns leave on two substrates and the fractures contain both cohesive and adhesive failures. One attractive advantage of this method is that no pre-fabricated mask is needed. Another remarkable merit is that the spacing of the strips is possible managed, by other parameters, such as thickness of the thin film, or the oxidation extent. FIS was examined and utilized by several groups, but their results were different, even conversed to each other. This phenomenon was first noticed by Chai in 1986 [23], in which the crack could jump from one interface to the other. As a result, the uniform and symmetrical patterns between the adhesive and substances were obtained by their group. In 2007 and 2009, respectively, Pease and co-workers [21] and S. Kollipoulou et al [6] observed the asymmetrical patterns left between the two rigid plates, and the fracture only contained cohesive failure. Although they observed similar formation of strips, the relationship between spacing ($\lambda$) of the strips and the thickness ($h$) of initial thin film was quite different. Pease et al [21] found that $\lambda$ was 4 times to the initial film thickness, but S. Kollipoulou [6] concluded that was $\lambda\sim 21h$. In addition, Li-Chen Huang et al [5] also observed similar formation of the strips with Pease and the $\lambda\sim 4h$, but the path of crack was around the half of thickness of the thin film or even smaller. Other researchers might found un-easily to utilize this method due to their inconsistent results; so that there is a need to perform a mechanistic study based on FIS before this simple and cost-effective method can be utilized.

The majority of my research is to provide adequate experimental evidence; to be for developing the theoretical analysis of FIS. I will repeat some experiments based on the above FIS method to generate features and attempt to obtain empirical
correlation between strip spacing and the thickness of initial thin film. The experimental evidence will include real time images and post fracture characterizations.

Besides the above FIS method, one of the former students (Dr. Yangjun Cai) from our group developed a new fracture-induced method (peel test) to obtain the uniform strips between PDMS sheet and one rigid substrate. The thesis will also provide detailed experimental evidence, including real time images and post fracture characterizations by Cai’s peel method. Based on the experimental evidence collected and collaborated with theoreticians, the optimal long term goal of the project is to develop the theory behind FIS. With this understanding the mechanistic behind FIS, both experimentally and theoretically, a fully utilization of such a simple and cost-effective fabrication technique can be realized.

Generally, the objectives of this work have three major parts as follows:

1. To determine the effect of various experimental parameters (peel angle, peeling force, thickness of PDMS sheet, elastic modulus of PDMS sheet) on formation of the fracture induced strips.

   Hypothesis: these experimental parameters are considered as important parameters on the formation of the fracture induced strips.

2. To determine whether or not a glassy silica-like layer at the edge of the PDMS sheet is needed to initiate cracks during fracture.

   Hypothesis: without the glassy silica-like layer at the edge, the cracks could not initiate from the edge.
3. To examine the oxidization extent of the PDMS sheet oxidized using UV/Ozone and relate how the oxidization extent to the formation of strips by fracture.

Hypothesis: The oxidization extent of the PDMS sheet may cause effect on the formation of the fracture induced strips.

An outline of this thesis is as follows:

At the beginning of the Chapter II, there is a brief opening for different patterning methods. Then, the conflict of different conclusions on FIS method is presented. In section 2.2, we will discuss the oxidization extent of the PDMS sheet oxidized using UV/Ozone. Chapter II also explains different characterization techniques, such as atomic force microscopy (AFM), optical microscopy (OM), Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), contact angle goniometer. At the end of Chapter II, a brief introduction about different methods to measure the modulus for PDMS sheet and silica-like layer is presented.

Chapter III will provide the experimental details on the materials, and equipment used in this study. It gives details of measuring the oxidization extent of the PDMS sheet. The information of how to prepare the sample for peel test is also presented. It also explains the different methods to examine the modulus of the PDMS sheet and silica-like layer. Some details about other tests, derived from the basic peel test, are list at the end of this section.

Chapter IV gives the details of the experimental results and they are separated into three sections. Firstly, we study the oxidization extent of the PDMS sheet oxidized using UV/Ozone. Next, I will discuss the results for the basic peel test by
weight and compare these results to the patterns prying open with tweezers. The third section describes the results on other tests, derived from the basic peel test.

Finally, the main findings of this study along with the suggestions for future work will be included in Chapter V.

CHAPTER II
BACKGROUND

Periodic nano- or microstructures on the surface were very essential in many fundamental researches and technological applications, such as drug delivery [8], microelectronics [25] and so on. Though photolithographic technology and soft lithography were wisely utilized in the past, both of those technologies needed a pre-fabricated master. Under above conditions, Chai [23] first created the FIS method to generate patterns without pre-fabricated master in 1986. Several groups followed his idea to generate strips-like patterns on the surface, but their results were different, even conflicted to each other. On the other hand, one of the former students from our group Yangjun Cai, developed another fracture-induced method (peel test) to generate patterns on both rigid support and PDMS sheet. This chapter includes different patterning methods, the conflict among different research groups on FIS method, characteristics of PDMS sheet, silica-like layer, and some characterization techniques.
2.1 Different patterning methods

2.1.1 Photolithography and soft lithography

The ability to transfer the pattern is important to modern science and technology, which has been used in confinement of cells [26], polymer thin film [27], microelectronic devices [25] and architectures that incorporate biological materials or cells [5]. Photolithography (in Figure 2.1) and soft lithography are the most important two techniques to transfer patterns. Soft lithography [4] (in Figure 2.2) includes three major techniques such as replica molding(REM), micro-molding in capillaries(MIMIC), and micro-transfer molding(μTM).

Figure 2.1 The procedure for photolithography
2.1.2 Fracture induced method

Both photolithography and soft lithography needed a pre-fabricated mask, and the non-transparent mask was expensive for photolithography. Though transparent (elastomer) mask could instead of non-transparent mask in soft lithography, this kind of mask was easily to be deformed. Under this condition, Chai [23] first developed a fracture-induced method to generate features without a pre-fabricate mask. In his experiment, there was a thin adhesive film (epoxy) was deposited between two rigid substrates (aluminum). When the force was applied to split the two rigid substrates, the crack formed along an alternative path along the two interfaces. As a result, some symmetrical and uniform strips left on both aluminum surfaces and the wavelength was several times the thickness of initial thin film. The method and result could be viewed in the following Figures 2.3 and 2.4:
In 2007, Leonard F. Pease et al repeated Chai’s method to fabricate micro-and nano-scale stripes by splitting two rigid plates with polystyrene (PS) thin film in between. The wavelength ranging from 120nm to 200μm was possible to be generated by their group. The most exciting discovery was that the wavelength was always four times about the thickness of the glassy film, and the wavelength was only depended on the thickness of initial thin film, regardless of its molecular weight and chemical composition. The difference between their results (in Figure 2.5) and Chai’s was that the strip-like patterns were asymmetrical on their samples. Meanwhile, they found that FIS grating could not happen on rubbery or highly cross-linked polymers.
Li-Chen Huang et al [5] repeated Pease’s method in 2009 for alignment control of liquid crystal molecules. They found that $\lambda \sim 4h$, which was consistent with the conclusions of the previously published report [21]. They also used PS as the adhesive, and their strips formation was similar to Pease’s group, but the path of crack was around the half thickness of initial thin film or even smaller (in Figure 2.6). In the meantime, they found that the separation direction was perpendicular to the direction of the strips.

S. Kollipoulou et al [6] utilized the same method to fabricate a gold nanoparticle line in 2009. He obtained the asymmetrical feature on the surface like Leonard F. Pease, but the adhesive was photoresist. The results between their group and other groups were the grating spacing. In this paper, the grating spacing was about 22 times the thin film thickness, but other papers concluded about 4 times.
When splitting the two rigid substrates, the crack could grow several paths, such as along one interface, within the adhesive, jump from one interface to another [28]. Base on other researchers, they would like to figure out the condition when the crack could grow along the alternate path between two interfaces. Then, they tried to predict the wavelength $l$ of the alternate crack.

Figure 2.7 Image geometry for a crack in an adhesive layer$^{[28]}$

Figure 2.8 A crack kinking out of the interface$^{[28]}$
A.R.Akisanya et al [28] found that the interfacial crack kinked out of the interface, when the stress intensity factors $K_2 \geq 0$ and $K_1 > 0$. When $K_2 < 0$, the crack would kink back to the interface. The stress intensity factors $K_1$, $K_2$ were depended on the orientation $w$, the pre-existing flaw length $s$, elastic mismatch parameters $\alpha$, $\beta$ and phase angle $\psi$, where

$$\psi = \arctan\left[\frac{\text{Im}(Kh^w)}{\text{Re}(Kh^w)}\right]$$

(2.1)

The phase angle was determined by $\alpha$, $\beta$ and $l/h$. He and Hutchinson [29] reported that the critical interfacial phase angle $\psi$ was a function of $\alpha$, $\beta$. At the beginning of separation, $K_2$ was less than 0 and the phase angle was smaller than the critical phase angle so that the separation happened between substrate and adhesive. The length $l$ increased, which led the phase angle $\psi$ to increase. When the phase angle $\psi$ was equal to the critical phase angle, the kink occurred.

Meanwhile, A.R.Akisanya et al [28] found that the wavelength of the alternating crack was depended elastic mismatch parameters, $\alpha$, $\beta$ and on the level of residual stress in the layer, which was related to the adhesive thickness, modulus quantity and the toughness of the interface.

The material parameters $\alpha$, $\beta$ and $\varepsilon$ represented the elastic mismatch between the adhesive material 2 and the substrate material 1 and defined as,

$$\alpha = \frac{(1-\nu_2)/\mu_2 - (1-\nu_1)/\mu_1}{(1-\nu_2)/\mu_2 + (1-\nu_1)/\mu_1}$$

(2.2)

$$\beta = \frac{1}{2} \frac{(1-2\nu_2)/\mu_2 - (1-2\nu_1)/\mu_1}{(1-\nu_2)/\mu_2 + (1-\nu_1)/\mu_2}$$

(2.3)

$$\varepsilon = \frac{1}{2\pi} \ln \frac{1-\beta}{1+\beta}$$

(2.4)
Where $\nu$ and $\mu$ are the Possion’s ratio and the shear modulus, respectively.

2.1.3 Peel test

From the above different tests, there are two important requirements for FIS. One is the glassy polymer, and another is strong bonding between thin film and rigid plates. The former student, Dr. Yangjun Cai developed a new method [20] to fabricate highly regular strips by peel test (in Figure 2.9).

![Figure 2.9 The set up for Yangjun Cai’s experiment][20]

In his experiment, UV/Ozone was applied to achieve silica-like layer on PDMS surface and tweezers were used to separate glass and PDMS sheet. The whole process was recorded by two microscopes which was beneficial for our group to have a better understanding of this interesting phenomenon.

Additionally, he explained more details about his experiment so that it was easy to follow to create the strips with the spacing between 5μm to 80μm. He found that wavelength and bending strain had a linear relationship and the best oxidation time used to generate strip-like patterns. The most significant part of Cai’s paper [20] was that he found some possible mechanisms on how the strips formed though recording the whole peeling process. According to his observation, the interfacial
crack C1 formed first at the interface of the glass and silica-like layer, followed by kinked crack of A1 and B1. As the kinked crack B2 intersected with the kinked crack A1, the triangular shape of the strip formed so that the spacing of the strips could be determined.

2.2 PDMS

2.2.1 Characteristics of PDMS

Recently, PDMS has been widely used in a large area, which includes soft lithography, micro-fluidics [25, 30], antifouling coating [2], and some biomedical applications [3]. The reason for this widespread use is related to its attractive material properties, such as a hydrophobic surface, constant and high ductility over a wide range of temperatures, low toxicity, high electrical resistance, long-term endurance. Due to its low surface energy, it is easy to spread on the other surfaces. After polymerization and cross-linking, solid PDMS sheet presents external hydrophobic, which makes it difficult for polar solvents (such as water) to wet the PDMS surface.
2.2.2 Characteristics of silica-like layer

Another advantage of PDMS is that the surface properties could be modified easily. Based on published literatures [31-35], UV/Ozone and oxygen plasma are the most common methods, which lead to the modification of the hydrophobic surface to hydrophilic. UV/Ozone treatment is an oxidation process that leads the material properties to change by adsorption of UV radiation. The whole process involves some chain scissions, which include both main backbone and side groups. At the same time, SiOₓ layer will form, which makes the PDMS surface hydrophilic. The thickness of the corresponding SiOₓ layer has been estimated to be between 10 and 160nm [35]. The difference in reported thickness value is attributed to different treatment conditions and to methods measure thickness of this layer.
The process of UV/Ozone has been illustrated in Figure 2.12. The UV lamp emits two kinds of radiation $\lambda_1 = 184.9\text{nm}$ and $\lambda_2 = 253.7\text{nm}$. At the first step, the surface of PDMS sheet is oxidized by atomic oxygen, which comes from molecular oxygen or ozone. Some methyl groups will disappear, and hydroxyl groups will form on the surface, which show the performance of hydrophilic. Simultaneously, some organic PDMS will react with ozone to form carbon dioxide and water molecules, which could easily leave from the PDMS surface. After CO$_2$ and H$_2$O releases, a thin SiO$_x$ layer forms on the PDMS surface. When the oxidization time continues increasing, the atomic oxygen will keep on reacting with the subsurface to increase the thickness of SiO$_x$ layer on the surface.

2.3 Characterization techniques

When PDMS sheet exposes to UV/Ozone, PDMS surface undergoes chain scission and the surface of PDMS sheet contains a large number of hydrophilic (mainly –OH) groups [36]. Some characterization techniques, contact angle
measurement, Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), are applied to study the oxidization extent of the PDMS sheet. Based on Cai’s result, there are some zigzag patterns left on both glass and PDMS surfaces. Optical microscopy (OM) and atomic force microscopy (AFM) are utilized to understand the surface morphology and topography of the patterns.

2.3.1 Surface wettability-contact angle

The wettability of a solid surface is an important physical property and depends on the chemical composition and the micro structure of the surface. The angle, at which a liquid/vapor interface meets a solid surface, is the contact angle, which is commonly used to evaluate wettability [49]. The contact angle (in Figure 2.13) is specific for any given system and is determined by the interactions across the three interfaces. The shape of the droplet is determined by the Young’s relation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

(2.5)

Where, $\gamma_{SV}$= the surface free energy of the solid in contact with vapor; $\gamma_{SL}$= the surface free energy of the solid covered with liquid; $\gamma_{LV}$= the surface free energy of the liquid-vapor interface; $\theta$= the contact angle.
The total surface energy includes dispersion and polar components. The dispersion and polar components of a particular surface are calculated using the two-liquid-method in equations (1) and (2):

\[ 2(\gamma_{SV}^{d} + \gamma_{LW}^{d})^{1/2} + 2(\gamma_{SV}^{p} + \gamma_{LW}^{p})^{1/2} = \gamma_{LW} (1 + \cos \theta_1) \]

(2.6)

\[ 2(\gamma_{SV}^{d} + \gamma_{L2V}^{d})^{1/2} + 2(\gamma_{SV}^{p} + \gamma_{L2V}^{p})^{1/2} = \gamma_{L2V} (1 + \cos \theta_2) \]

(2.7)

\( \gamma_{ij}^{d} \) and \( \gamma_{ij}^{p} \) stand for the dispersive and polar components of the surface (or interfacial) energy between substances of i and j, and S, L and V in the subscript symbolize the solid, liquid and vapor phase, respectively. The two unknown parameters: \( \gamma_{SV}^{d} \), \( \gamma_{SV}^{p} \), can be solved by the above two equations. Then the total surface energy is:

\[ \gamma_{SV} = \gamma_{SV}^{d} + \gamma_{SV}^{p} \]

(2.8)

2.3.2 Surface composition FTIR-ATR

Infrared (IR) spectroscopy is an extremely reliable method to obtain the surface composition. ATR is an IR sampling technique that provides excellent quality data in conjunction with the best reproducibility of any IR sampling technique. It also
has many other advantages, such as faster sampling, minimizing user-to-user spectral variation and so on [51]. ATR uses a property of total internal reflection resulting in an evanescent wave and this reflection forms the evanescent wave which extends into the sample. A beam of infrared light passes through the ATR crystal in such a way that it reflects several times off the internal surface in contact with the sample. Then, the beam is then collected by a detector as it exits the crystal and IR spectrometers can be obtained via ATR [51].

![Sample in contact with evanescent wave](image)

Figure 2.14 The FTIR-ATR technology[51]

2.3.3 Surface morphology and topography-OM and AFM

The surface morphology is obtained by OM, in which reflect light mode is used to take pictures and record videos. OM uses a piece of glass to support the PDMS sample and focus light rays in order to produce enlarged images of small subjects, such as strips or cracks. The most significant part is the high magnification video of how the crack initially formed from the edge, which is beneficial for me to understand the mechanism behind the peeling process.
Surface topography is determined by AFM, which is a very high-resolution type of scanning probe microscope, with demonstrated resolution on the order of fractions of a nanometer. The AFM consists of a cantilever with a sharp tip at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip with radius of curvature around nanometers. When the tip moves forward to the sample surface, forces between tip and sample lead to a deflection of the cantilever. The various topography information of the material could be produced by the deflection.

2.3.4 Modulus measurement

Many researchers found that the thickness of the silica-like layer increased with the increase of oxidation time [35]. From Cai’s result above, it was easy to find that the crack first formed on the interface of the glass and silica-like layer, so that understanding the mechanical properties of this silica-like layer became an important part in my project.

Young’s modulus (E) is one of the important parameters among the mechanical properties and it is defined as the ratio of the uniaxial stress over the uniaxial strain. In the following paragraphs, we will briefly introduce some techniques, such as buckling, JKR, nanoindentation, which are widely used for measuring the Young’s modulus of PDMS sheet and silica-like layer.

2.3.4.1 Stress-strain

During tensile testing of a material sample, the stress-strain curve is a simple method to obtain the modulus of PDMS sheet. The slope of the stress-strain curve is
the Young’s modulus. Stress derives from the load applied on the sample, and the strain comes from the deformation of the sample [54].

![Figure 2.15 The process of strain-stress method](image)

When a constant force applies to the PDMS sheet, the elongation of PDMS sheet is from \( L_0 \) to \( L_1 \). The modulus of the PDMS sheet could be obtained by the following equations:

\[
E = \frac{\text{stress}(\sigma)}{\text{strain}(\varepsilon)} \quad (2.9)
\]

\[
\sigma = \frac{F}{W \times T} \quad (2.10)
\]

\[
\varepsilon = \frac{L_1 - L_0}{L_0} \quad (2.11)
\]

Where \( W \) and \( T \) are the length of two sides of PDMS sheet.

2.3.4.2 Buckling method

Though stress-strain method is convenience to obtain the modulus of the PDMS sheet, it could not apply to calculate the modulus of the silica-like layer. Then,
another simple method called surface buckling/wrinkling method applies to test the modulus of the silica-like layer. Oxygen plasma treatment for generating wrinkle was first reported by Bowden [38]. Bowden et al [38] created such a surface layer by a thermal shrinkage process in Figure 2.16:

![Diagram](image)

**Figure 2.16** The preparation the wrinkle of metal films on PDMS sheet.[38]

After that, researchers began to apply this method to generate wrinkle on the surface of PDMS sheet. The oxidation process was able to convert the topmost layer of PDMS sheet into silica-like layer and a force was applied within the oxidation process. After the oxidation process finished, the uniform wrinkle formed by the mismatch of the equilibrium states of the upper thin film and substrate after releasing the force. The reason for this phenomenon was that the substrate PDMS sheet could easily go back to original state, but the top brittle silica-like layer could not. The procedure of generating wrinkles is shown schematically in Figure 2.17.
After that, researchers found that the wavelength and altitude could be predicted by analytical theories [15]. The spacing of those highly uniformed wrinkles and the film’s elastic modulus could be calculated by applying well-established buckling mechanics. There was a critical wavelength, which minimized the total strain energy in the system, and this wavelength was dependent on the material properties of both the film and the substrate. The critical wavelength (λ) could be expressed by:

$$\lambda = 2\pi h \left[ \frac{(1-\nu^2_f)E_f}{3(1-\nu^2_f)E_s} \right]^{1/3}$$

(2.12)

Where h is the thickness of the upper film, ν is Poisson’s ration, and E is the Young’s modulus (f and s means the film and substrate). So the above equation could be rearranged to solve the modulus of the upper film:

$$E_f = 3E_s \left( \frac{1-\nu^2_f}{1-\nu^2_s} \right) \left( \frac{\lambda}{2\pi h} \right)^3$$

(2.13)

The Poisson’s ratio could obtain from the reference [52, 53] and the wavelength came from the OM images. The most challenging part of this method was the thickness of the silica-like layer. Edwin P. Chan [13] found that the UV/Ozone
oxidation converted the top surface of the PDMS sheet into a silica-like thin film which was about 100nm thick. Kirill Efimenko’s et al [22] found that the uniform silica-like layer was around 10-30nm. Because the silica-like layer was really thin, the researchers still could not gain the accurate value about the thickness of this thin layer. Then researchers start to think about alternative method, which capable to obtain the value of modulus, and avoid the thickness of the thin film.

2.3.4.3 JKR method

In order to avoid measuring the thickness of thin silica-like layer, another rapid and efficient device was developed to measure the modulus of the thin layer, named JKR method [39]. The JKR method, which was developed by Johnson, Kendall and Robert, was applied to measure the adhesion between two spheres or a sphere and a plane surface [40]. In most cases, the hemispherical PDMS lens was brought down into contact with the flat substrate. All the materials were elastomers so that deformation of surfaces happened when load was applied and different applied loads corresponded to different contact areas. According to M.K.Chaudhury’s result [40], chemical modification of PDMS lens surface would not affect its bulk properties. Based on this character, PDMS lens was able to study the contact mechanical behavior [41, 42]. In this case, the radius of the contact zone was related to the work of adhesion (Figure 2.18):
Equation (2.14) states the relationship between the contact area, the load, and the elastic constants of the materials involved. The equation is:

\[ a^3 = \frac{R}{K_1} \left( P + 3\pi KR + (6\pi WR P + (3\pi WR)^2)^{1/2} \right) \]
Where, $P$=the applied load;

\[ K = \text{the elastic constant of the system}; \]

\[ R = \text{the radius of curvature of the hemispherical lens}. \]

By rearranging it was obtained:

\[
\frac{a^{3/2}}{R} = \frac{1}{K_1} \left( \frac{P}{a^{3/2}} + \left( \frac{6\pi W}{K} \right)^{1/2} \right)
\]

(2.15)

\[
K_1 = \frac{2E}{3(1-\nu^2)}
\]

(2.16)

When two different materials applied,

\[
\frac{1}{K_2} = \frac{3}{4} \left( \frac{1-\nu_C^2}{E_C} + \frac{1-\nu_L^2}{E_L} \right)
\]

(2.17)

Where, $E_C, E_L$=the Young modulus for the coating, lens;

\[ \nu_C, \nu_L = \text{Poisson ratio of the coating, lens}. \]

The PDMS lens ($E_L$) was deduced from the known elastic modulus ($K_1$) of the system. The modulus of coating ($E_C$) was obtained from the known value modulus of the elastic lens ($E_L$) and elastic modulus ($K_2$) of the system.

The elastic modulus of PDMS sheet and silica-like layer coating were measured using JKR method, and the lens was made of the Sylgard 184, which would bring into contact with the non-oxidized and oxidized PDMS surface. The force acting between these two surfaces was determined with an analytical balance with a measurement accuracy of 0.1mg.

2.3.4.4 Nanoindentation
From the above discussion, the silica-like layer was thin and played a significant role in research. Nanoindentation [43, 44] was another normally used experimental technique to measure the mechanical properties of the thin film. When a force applied to the surface, the surface would show elastic deformation. Through the atomic force microscopy, the force-distance curve could be achieved to study surface interaction and elasticity. Monclus et al [45] applied nanoindentation to measure the modulus of glass flake-reinforced polypropylene sample at lead-free Cu-solder joint. Compared their results to instrument indentation method [46], which was able to obtain high lateral resolution, the results were close. Charles [47] found some quantification issues in modulus measurement by force-distance curve with sufficient accuracy.

![Figure 2.19 Schematic of a conical indenter a polymer sample and leaving a residual impression of depth $h_f^{[46]}$](image)

The above figure illustrated a conical indenter and a residual impression left after removal of the force. It also showed the maximum total indentation depth, $h_{\text{max}}$, which was viewed as the total of the $h_f$ and $\delta$. $h_f$ was the depth of the residual impression and $\delta$ was the maximum elastic indentation depth. In AFM nanoindentation, the equations to calculate the modulus were developed in the following [48,49]:

```latex
\text{Equations for modulus calculation:}
```

26
\[
\frac{1}{E^*} = \frac{1-v_{\text{sample}}^2}{E_{\text{sample}}} + \frac{1-v_{\text{tip}}^2}{E_{\text{tip}}}
\]  
(2.18)

Where, \( E^* \) was the indentation modulus;

\( E_{\text{sample}} \) and \( E_{\text{tip}} \) were the Young’s modulus for the sample and tips;

\( v_{\text{sample}} \) and \( v_{\text{tip}} \) were the Poisson ratios for sample and tips.

\( v_{\text{tip}} \), \( v_{\text{sample}} \), \( E_{\text{tip}} \) were the known values. As a result, the modulus of the sample could be obtained after solving the indentation modulus, which obtained from the force-distance curve.
CHAPTER III
EXPERIMENTAL APPROACH

In this chapter, the essential details about the materials and equipment used, and the methods of creating strips on the surface will be provided.

3.1 Materials and Equipment

Cured PDMS was achieved by using Dow Corning’s Sylgard® 184 PDMS kit which contained two different components, Sylgard® 184A and Sylgard® 184B.

The glass slides used for bonding PDMS were purchased from VWR Scientific, and they were pre-cleaned with dimensions 25mm*75mm*1mm.

Other chemicals used in the study included concentrated sulfuric acid (H₂SO₄) from Fisher and 30% hydrogen peroxide H₂O₂ from VWR. Toluene (HPLC grade) was purchased from Sigma-Aldrich and used as received. Polystyrene (PS, MW=280,000) was obtained from Sigma-Aldrich. Octadecyltrichlorosilane [CH₃(CH₂)₁₇SiCl₃, OTS] was purchased from Gelest. Deionized (DI) water was purified in house and had a conductivity of 0.1 Siemens or less.

The equipment included a UV/Ozone chamber (model 42, Jelight), a vacuum oven (National Appliance, Model No. 5831), a hot plate (Corning), a pump (Cole Parmer Instrument Company, Masterflex L/S), a spin coater (Speedline Technologies), an optical microscope (Olympus IX70), a contact angle goniometer.
(Model 100-00 from Rame-Hart, Inc.), a FTIR-ATR instrument (NICOLET), an AFM (NT-MDT) and One-Touch Software.

3.2 Preparation for the samples

3.2.1 Sample for peel test

In order to generate a sample for peel test, a piece of cured PDMS sheet and a pre-cleaned glass slide were oxidized for 15 minutes to achieve the suitable degree of oxidation. Then the oxidized side of the PDMS sheet and the glass slide were pressed together, and left on a hot plate at ~ 100 °C for ~ 60 minutes to allow sufficient covalent bonding to occur.

The PDMS sheet was prepared with a 10:1 Sylgard®184A/Sylgard®184B mass ratio, and the solution was mixed with a glass rod in a plastic cup. The solution was poured into a flat Petri-dish to be cured for 120 minutes at 70°C to crosslink the polymer network. Normal, 12 grams of liquid PDMS were poured into the flat Petri-dish with 9cm in diameter, to make cured PDMS sheet with 2mm thickness.

Then, a glass slide (25mm*75mm*1mm) was cut with a diamond pen into 6 individual pieces (25mm*12.5mm*1mm). Only scratches to the surface of the glass were needed, since once the lines were made, the glass could be wrapped in a KimWipe before breaking apart in order to keep any shard contained. Once the pieces were separated, each of them was cleaned by using air to blow off any remaining glass shard. All of the glass sides were placed in the bottom of a glass dish, and a freshly prepared piranha solution (a 30 v.% hydrogen peroxide (H₂O₂) and 70 v.% concentrated sulfuric acid (H₂SO₄) solution) was poured over the glass slides. Then, the glass dish was then placed on a hot plate and heated for 40 minutes at 100 °C.
The heat was turned off, and then the solution cooled down for a few minutes before removal from the hot plate. Then, the piranha solution was poured into a special glass container, which was used to collect waste acid. To further clean the glass samples, DI water was used to rinse over the glass samples five or six times. The final step for cleaning the glass was to dry the glass samples off with a stream of N₂. Place the glass samples in a Petri-dish to protect it from contamination. Since that the glass samples were prepared, the cured PDMS polymer should be cut into samples with the size a little smaller than the glass samples. Both of those glass samples and PDMS sheet should be UV/oxidized for 15 minutes, placing the oxidized surfaces facing up. After oxidation, the PDMS sheet immediately should be adhered to the glass sample by pressing the two oxidized surfaces together, so that hydrophobic recovery [55, 56] would not be considered. Make sure that there was no air bubble between the two oxidized surfaces, which might cause some effects during the peeling process. If some air bubbles appeared, tweezers were used to give slight pressure to push the air out between the materials. Then, placed the samples (PDMS sheet exposed) on a hot plate at ~ 100 °C for an hour.

3.2.2 Samples for sandwich test

Different concentrations of PS solutions were obtained from dissolving PS in toluene (HPLC grade). Then, a glass slide (25mm*75mm*1mm) was cut with a diamond pen into 3 individual pieces (25mm*25mm*1mm). The glass sides were cleaned with the same process in 3.2.1. Then, PS was spun coat on those cleaned glass surfaces to create a thin film layer. The glass slide with the thin film layer was heated at 110 °C for 10 minutes to evaporate toluene. Then another cleaned glass slide was
used to achieve the sandwich sample. Put some weight on the surface of the whole sample and then heated them at 140 °C for 40 minutes to change the glassy PS film into a rubbery film [5].

3.3 Experiment design

3.3.1 Basic setup for peel test

The samples (PDMS sheet bonded to glass slide) were prepared by the procedure described in 3.2.1. First, I repeated Cai’s method to separate PDMS sheet and glass slide with tweezers. The peel test as illustrated in Figure 3.1 was used to separate PDMS sheet from the glass. The purpose of this change was to obtain the accurate value of force, which was not possible by separating the PDMS sheet from the glass slide using tweezers. Also, a constant force was beneficial to generate nicely uniform strips. The tweezers were still needed to initiate the strips by pushing in between the PDMS sheet and glass at one edge of their contact. Once the strips initiated at the edge of the contact, a weight (i.e. a known peel force) was utilized to completely separate the PDMS sheet from the glass slide. The detail comparison on
the results of peel test by tweezers and weight would be reported in the result section. After separating, the glass surface with a set of strips left was subjected for AFM characterization.

Two microscopes were utilized in this experiment. One of them was used to record the peel process from the bottom to observe how the strips were formed. Meanwhile, it provided some useful experimental evidence to develop the FIS theory. Another camera was placed to obtain a side view of the peel test, which offered information about the peel angle, bending strain and radius of curvature of the separating silicone sheet. With those kinds of information, it was possible to analysis the relationship between spacing and other parameters.

Prior to describe the details of different tasks, some standard steps of real time recording and post fracture characterization were described below. Real time recording of the process meant that the pictures were taken to provide strips information after getting rid of weight. Post fracture characterization meant the OM and AFM images, which were able to provide the morphological and topographic information of the strips formed by fracturing. OM was used to record the whole process of how the strips form on the glass surface. The most significant part was the high magnification video of how the crack initially formed from the edge, which was benefit to understand the mechanism about the peel process. The AFM pictures provided the three-dimensional surface profile so that the height, toughness and other properties of crack could be gained.

3.3.2 Characterization on the extent of oxidization by UV/Ozone

3.3.2.1 Water contact angle-wetability
Contact angle measurements were conducted using the contact angle goniometer video system and two probe liquids: DI water, methylene iodide. Three images, each of advancing and receding angles were captured at three different spots on the tested samples. The contact angle value to be used in estimating the surface energy was the average of the advancing and receding angles. The tested samples included a non-oxidized PDMS sheet, and PDMS sheets oxidized for 5, 15, 25, 35, and 45 minutes, respectively. The contact angle measurement was taken immediately after preparation of the sample, so that the hydrophobic recovery effect would not be taken into consideration [55, 56]. Contact angles were estimated using Image J software. The advancing, receding angles and the dispersive, polar, total surface energy were reported.

3.3.2.2 FTIR-ATR

FTIR-ATR measurements were conducted to six different tested samples included the non-oxidized PDMS sheet, and PDMS sheets oxidized for 5, 15, 25, 35, and 45 minutes, respectively. The measurements were received immediately after preparation of the sample, in order to avoid hydrophobic recovery effect. Before scanning the tested samples, a Kimwipe paper was rinsed with ethanol, which was used to clean the black window. Then, waiting for 2 minutes to evaporate the ethanol, the black window was scanned by FTIR-ATR first to make sure it was cleaned in signal. Lastly, FTIR-ATR measurements were carried out with the six tested samples to test the composites of each surface.
3.3.3 Strip spacing and the Height evaluation

After peel test, there were some zigzag patterns left on both glass and PDMS surfaces, and the glass surface with patterns was applied to OM and AFM studies. The glass surface was transparent, so that the transmitted light was able to obtain surface morphology information. The OM pictures and videos were captured by one-touch software. The spacing on the pictures was measured first, and then it was converted to the actual spacing. AFM pictures were utilized to obtain the topography information. HA-NC (from NT-MDT) tips were used with tip radius of 10nm or less. The semi-contacted mode was chosen and the feedback (FB) gain was 0.5 kHz under the threshold of FB noise to get maximum surface scanning accuracy. From the images, both vertical (up-and-down) and horizontal (left to right) scans were done, and the spacing and height of zigzag patterns were confirmed by comparing the patterns’ images in different scanning directions. The OM, AFM images, the spacing, and height evaluation of the strips were reported.

3.3.4 Modulus determination

According to others paper [39, 45-47], there were several methods to measure the modulus of PDMS sheet and silica-like layer. The following paragraphs will provide detail steps about how to measure modulus of PDMS sheet and silica-like layer by different methods.

3.3.4.1 Stress-strain for PDMS sheet

Two different kinds of PDMS sheets were made based on the procedure in 3.2.1. The ratio for the elastomer to curing agent was 10 to 1 and 10 to 2, respectively. The PDMS sheets were cut into following size (25mm*12.5mm*1mm)
and 9 different forces were applied in the test. The modulus of PDMS sheet was examined by the stress-strain method. Then, the two different kinds of PDMS sheets were applied to peel test to examine whether modulus of PDMS sheet has effect on the spacing or initially of crack or not.

3.3.4.2 JKR measurements (the PDMS sheet and the silica-like layer)

The contact mechanics (Johnson-Kendall-Robert, JKR) method was used to attempt a determination of the modulus of the PDMS sheet and silica-like layer of the oxidized PDMS sheet. The JKR measurement was based on an elastomeric lens, which was gradually brought into contact with a flat PDMS surface. Both the lens and un-oxidized PDMS sheet were made according to the procedure 3.2.1. The lens was made by dropping a drop of liquid PDMS on the hydrophobic glass surface, which was achieved by modifying OTS on the clean glass surface. The glass surface was cleaned with the same procedure in 3.2.1. The modulus of PDMS lens was measured by the JKR method. Then, the tested PDMS sheet was oxidized 15 minutes to achieve a silica-like layer and another JKR test was applied to measure the modulus of the silica-like layer. The maximum force applied was the 0.1g and the radius of PDMS lens was obtained by cross section images.

3.3.4.3 Buckling method (the silica-like layer)

Following the Figure 2.14, it was possible to generate uniform strips on the surface of PDMS sheet. The pre-strain for the experiment was 20% and the oxidation time ranged from 5 minutes to 30 minutes. After oxidized, the pre-strain was released to obtain uniform wrinkles on the PDMS surface. Then OM and AFM images were applied to measure the wavelength and aptitude of the strips. Then based on equation
2.13, the modulus of the silica-like layer could be obtained through the wavelength of wrinkle.

3.3.5 Thickness determination (PDMS sheet and the silica-like layer)

3.3.5.1 Relationship between wavelength and the PDMS sheet thickness

![Diagram showing the relationship between wavelength and PDMS sheet thickness](image1)

Figure 3.2 The schematic of the different PDMS thicknesses when oxidized

Three different thicknesses of PDMS sheets were tested, which were 1, 2, and 3 mm. The procedure was based on the common procedure of the peel test in 3.3.1.

The width of the PDMS sheet used was 8mm, and the oxidation time was 15 minutes for this experiment. There was one glass side (1mm thick) placed under the 2mm thick PDMS sheet and two glass slides placed under the 1mm thick PDMS sheet.

3.3.5.2 Gradient

![Diagram showing the effect of UV/O ozone on PDMS](image2)

UV/Ozone

UV/O 30mins

A

B

15
Figure 3.3 The schematic of the gradient test

Two sets of samples were tested, and the oxidation time was 30 minutes. Based on existing paper [22], when the oxidation time increased to 30 minutes, the thickness of silica-like layer on point A and B was basically the same. The distance between point A to top UV/O lamp was 3mm, and it was 2mm for point B. The inclined angle of the PDMS sheet was 15 degree.

3.3.6 Role of the silica-like layer at the edges

3.3.6.1 PDMS sheet was cut for 2 or 3 pieces for peel test

Figure 3.4 The images for PDMS sheet cut in 2 pieces (a), 3 pieces (b)

The sample was made based on procedure 3.2.1; expect using larger size of PDMS sheet (16mm*30mm*2mm). Before glass and PDMS sheet separated by weight, the PDMS sheet was cut into 2 or 3 pieces shown in Figure 3.4. For (a), the peel test was carried on half of the PDMS sheet instead of the whole sheet, in order to test the role of the silica-like layer at the edge. Under this condition, one edge of the PDMS sheet had silica-like layer, but another edge did not have a silica-like layer. For (b), the peel test was down on the middle piece of PDMS sheet. Under this condition, the focus was on the edge of middle piece and neither of edges had silica-like layer.
3.3.6.2 Bonding partial of the PDMS sheet

![Image of partial bonding](image)

Figure 3.5 The image of the partial bonding

The other procedures were the same based on 3.2.1. A plastic paper was set between the oxidized PDMS sheet and glass when they were heated, so that PDMS sheet was partially bonded to the glass surface. The focus part in this experiment was the phenomenon at the weakly bonding edge (the red line in the Figure 3.5).

3.3.7 Effects of pre-cracks on the PDMS sheet

The aim of this experiment was to test the effect of pre-cracks on the PDMS sheet. Force was applied to push the PDMS sheet to form some pre-cracks on the PDMS surface, before bonded it to the glass surface. After pushing PDMS sheet with force, OM images were taken to see whether the pre-cracks were shown on the PDMS sheet surface or not. Then, the pre-cracks PDMS sheet was bonded to the glass surface to heat for an hour.
3.3.8 Effects of pre-wrinkles on the PDMS sheet

The procedure how to form the uniform wrinkle on the PDMS sheet was shown in Figure 2.14, and the process how to generate strips by peel test was in 3.2.1. This experiment combined both of above two experiments. Firstly, some nice wrinkles were generated on PDMS sheet based on Figure 2.14 and then the wrinkled PDMS sheet was utilized to peel test. When the sample was heated, some weight was added to increase the adhesion between glass and PDMS sheet. The peel test was carried out in two directions (in Figure 3.5). One peel direction was parallel to the wrinkle direction, and another peel direction was perpendicular to the wrinkle direction.

![Diagram of peeling directions](image)

Figure 3.6 Two conditions for the pre-wrinkles peeling
3.3.9 Pre-strain when oxidized

![Image of pre-strain test]

Figure 3.7 The image of pre-strain test

After compared the spacing of the strips on glass surface by prying open with tweezers, peel test, and wrinkling, the spacing at the edge had a huge difference. This experiment was designed to examine whether pre-strain had effect on peel test or not. Two sets of samples were tested in this experiment. For each set, one piece of PDMS sheet had 5% pre-strain, while another one had no pre-strain. Both of them were placed about 5mm below the UV/O lamp and the oxidation time was 15 minutes. After bonding the oxidized PDMS sheet with an oxidized glass for heating for 1 hour, then tweezers were used to separate the PDMS sheet from its bonded glass slide.

CHAPTER IV
RESULTS AND DISCUSSION

The results presented in this chapter include the extent UV/Ozone oxidization of the PDMS sheet, the various experimental parameters affecting the strips formed by separating the PDMS sheet from the bonded glass slide, and the various
experimental parameters affecting the strips formed by splitting a glassy polymer layer sandwiched in between two rigid plates (i.e FIS). The detailed experimental evidence associated with each fracture process is also reported and, in some cases, used to explain the resulting strips.

4.1 The extent of oxidization of the PDMS sheet using UV/Ozone

From the previous literatures [31, 34, 35], it is known that the process of UV/Ozone treatment leads to structure/property changes on the PDMS surface. The structures/properties of the oxidized PDMS surface play an important role in the fracture process. Therefore, the oxidization extent of the PDMS sheet was characterized by contact angles of various probe liquids (i.e. wettability and surface energy of the oxidized PDMS surface) and FTIR-ATR scans.
4.1.1 Water and methylene iodide contact angles of oxidized PDMS sheets

![Graph showing contact angles vs. UVO exposure time](image)

Figure 4.1 Advancing and receding contact angles of DI water (DI) and methylene iodine (MI) on PDMS surfaces oxidized using UV/Ozone.

Figure 4.1 above summarizes the contact angles of de-ionized water (DI) and methylene iodine (MI). Both advancing and receding angles of DI and MI decreased as the UV/Ozone time increased. The contact angle hysteresis, which was defined as the difference between the advancing and receding contact angles [22], was also analyzed for the oxidized PDMS surface. It depended on the roughness, chemical heterogeneity and molecular mobility in the probed surface region [56]. Normally, when the hysteresis was less than 5°, the surface could be considered as chemically uniform. From Figure 4.1, for the sample oxidized for 5 minutes, the water contact angle hysteresis (39.44°) was found to be larger than that (32.07°) of the untreated surface. With a longer oxidization time (≥ 10 minutes), the hysteresis decreased and it dropped to very small values (3.694°) at the oxidization time of 45 minutes. The small hysteresis indicated a reduced surface heterogeneity and molecular mobility on the
surface region [56]. The contact angle hysteresis of MI continued to decrease as the oxidization time increased.

4.1.2 Surface energy of the oxidized PDMS sheets

Surface energy of a solid surface can be estimated by the contact angles of various probes. In general, the contact angle used for estimating the surface energy is the average of advancing and receding angle. Using equations (2.5), (2.6), (2.7), (2.8) with contact angles of DI water and MI on the PDMS sheet and the oxidized PDMS surface, the solid surface energy of each of these surfaces was estimated. In Figure 4.2, lower contact angles of DI water and MI for the oxidized surface were noticed as compared to those of the non-oxidized PDMS sheet, indicating the oxidized surfaces had a greater wettability. The longer the UVO treatment time was, the more –OH groups should be formed and more –CH₃ groups should be disappeared (being converted to H₂O and CO₂). When the UVO treatment time increased to 45 minutes, the highest wettability for the oxidation modified surface resulted in the largest solid

Figure 4.2 Contact angles and surface energies for different surfaces

[Diagram showing contact angles and surface energies for different surfaces as a function of UVO exposure time]
surface energy of 69.1 mJ/m$^2$, while it was 25.1 mJ/m$^2$ for the non-oxidized PDMS surface. The oxidation rate during the first 25 minutes was faster than that of the latter oxidizing time. A possible explanation was that the oxidation process went thought in the normal fashion without much resistance for the beginning 25 minutes. When the oxidation time increased, the build-up of more dense silica-like layer might block ozone from transferring into the lower sub-surface. After 35 minutes, both contact angles and surface energy only changed slightly, which indicated that the surface of the PDMS sheet had become more saturated with silica-like substances. When the surface became more saturated, it was more difficult for the ozone to diffuse thought the silica-like layer, so the oxidizing process slowed down.

4.1.3 FTIR-ATR
Figure 4.3 FTIR spectra of PDMS samples untreated and treated with UVO. (A) range 600-1250 (cm\(^{-1}\)) (B) range of 2800-3200 (cm\(^{-1}\))

Table 4.1 Assignment of IR Spectra of Sylgard-184 Shown in Figure 4.3
The extent of oxidization was also confirmed with FTIR-ATR scans. FTIR-ATR measurement was able to verify the various functional groups present in the un-oxidized PDMS sheet and oxidized PDMS sheet with different UVO treatment times.

<table>
<thead>
<tr>
<th>Peak</th>
<th>IR region</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>785-815</td>
<td>-CH(_3) rocking and ≡Si-C≡ stretching in ≡Si-CH(_3)</td>
</tr>
<tr>
<td>2</td>
<td>1055-1090</td>
<td>Asymmetric ≡Si-O-Si≡ stretching in(-CH(_2))(_2)Si-O-)(_x)</td>
</tr>
<tr>
<td>3</td>
<td>1100-1170</td>
<td>Vibrations of -(CH(_2))- in ≡Si-(CH(_2))(_2)-Si≡</td>
</tr>
<tr>
<td>4</td>
<td>2950-2970</td>
<td>Asymmetric –CH(_3) stretching in ≡Si-CH(_3)</td>
</tr>
<tr>
<td>5</td>
<td>3100-3500</td>
<td>-OH stretching in ≡Si-OH</td>
</tr>
</tbody>
</table>

Five significant peaks were marked in the spectra shown in Figure 4.3, which elucidated the information about the chemical composition changes on the surface though a series of characteristic IR peaks listed in Table 4.1. With the increase of \(t_{UVO}\), the peaks 1 and 4 (corresponding to -CH\(_3\)) decreased and peak 5 (corresponding
to -OH) increased slightly (see the above spectra). It could be viewed as the evidence that methyl group conversed into hydroxyl group during the oxidization process. Peak 2 also decreased, which indicated that Si-O-Si chain scission occurred in the PDMS network. Figure 4.3(B) also suggested that the chain scission was accompanied by the decrease of peak 4. The spectra of 35 minutes and 45 minutes were basically the same, which indicated that the surface of PDMS sheet became saturated with silica-like substances after 35 minutes oxidization time. To summarize the FTIR-ATR scans, with the increase of $t_{UVO}$, the surface had more –OH groups and less –CH$_3$ groups, leading to a more hydrophilic surface, which agreed with the results drawn from the contact angle and surface energy.

4.2 Strip formation by a simple peel test

After examining the oxidization extent of the oxidized PDMS sheet surface, a basic peel test was carried out to separate the oxidized PDMS sheet that had been bonded to an oxidized a glass slide, in which both the PDMS sheet and the glass slide were oxidized for 15 minutes. The results of separation will be presented first, and the comparison of the results from the peel test and those pried open by tweezers will be described. The spacing and height of the strips, the angle variation along the separation front, and the detailed initiation of the strips at the edge were examined.
4.2.1 Spacing and height of strips

Figure 4.4 An OM image (top) and an AFM topography scan (bottom) of uniform parallel strips (formed by prying open the bonded interface by tweezers.)
(Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes)

Figure 4.5 An OM image (top) and an AFM topography scan (bottom) of uniform parallel strips (formed by peel test)

(Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes, peel force was 246.225 N/m and the peel angle was 45 degree)
Both OM and AFM images indicated that two sets of strips-like patterns over a large area (more than 1 cm²) were resulted, one set on the PDMS sheet and the other set on the glass surface, when the PDMS sheet was separated from the glass surface by tweezers or peel test. The height of the strips was about 1.6μm and 3.5μm, and the spacing was about 10μm and 20μm, respectively, for prying open with tweezers and separation by peel test. The spacing over the entire PDMS sheet was homogeneous, when tweezers were used to force open the bonded interface, but the spacing was heterogeneous for the strips formed using the peel test. From Cai’s observation [20], the kinked crack C2 formed first at the interface of the glass and silica-like layer, followed by the kinks of A2 and B2. The kinked crack B2 opposed the separation direction, and then intersected with the kinked crack A1. Finally, a triangular shape of the strip formed on the glass surface and the spacing of the strips could be determined. More about the strip formation mechanism when separating the bonded silicone/glass-slide interface by the peel test will be discussed in more details in latter section 4.2.2.

Figure 4.6 The mechanism of the Cai’s observation
4.2.2 Experimental observations on strips formation by peel test

Figure 4.7 Separation front from top to bottom when the PDMS sheet is separated from its bonded glass slide by simply peel test (Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes, peel force was 246.2225 N/m and the peel angle was 45 degree, fifteen different measurements for each point)
Figure 4.8 Different strips spacing for the strips formed at different locations along the separation front

From the previous study, the characteristic of formed strips (by peel test) was different from those of strips obtained by prying open with tweezers. With tweezers, the strips tunneled from one edge to the other side and the spacing was uniform over the entire PDMS sheet. Using the peel test, two sets of strips, after initiated at both edges of the PDMS sheet, tunneled from the edge towards the center, spontaneously, and the fracture ceased as the strips merged at the middle of the sheet. In Figure 4.7, five real time snap-shots were taken at five different locations along the tunneling direction. From the images, two sets of strips met each other in the middle and resulting strips were symmetric, along the center line of the sheet, but the strips spacing, and the angle between the peeling direction and the tunneling direction was different at different locations. The spacing of strips was the smallest (9μm) at the edge and reached the maximum in the middle (28μm) as shown in Figure 4.8.
In Figure 4.9, the x axis represented the different positions along the separation front, and angle meant the angle between the peeling direction and the tunneling direction. At the middle of the sample, the peeling direction was basically perpendicular to the tunneling direction, or with the largest angle (90°) compared to other positions. The smallest angle was found to be at the edge, which was the initial point of the separating. The angle was almost symmetrical along the middle line of the PDMS sheet in the direction of peeling.
4.3 The effect of peeling force, peeling angle on formation of fracture induced strips

Figure 4.10 The effect of peeling force on formation of strips (Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes, the peel angle was 45 degree, three samples were tested for each peel force)

Figure 4.11 The effect of peeling angle on formation of strips (Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes, the peel force was 246.2225 N/m, three samples were tested for each peel angle)
The results in the above Figure 4.10 and 4.11 indicated that the independent of the wavelength of the strips on the peeling force and peeling angle acting on the PDMS sheet.

4.4 Modulus determination

To gain a better understanding on the strip formation phenomenon using peel test, some of the physical parameters need to be obtained. From the previous references [34, 35], modulus is a significant parameter for a thin film, which might affect the fracture process. This section discusses the different modulus measurements of thin films/sheets and the effect of modulus on the resulting strips formed by fracture. Strain-stress and JKR methods were used to measure the modulus of PDMS sheet, and JKR and buckling method were applied to determine the modulus of silica-like layer. The experiments were repeated several times for conclusive results.

4.4.1 Stress-strain for PDMS sheet

The stress-strain results indicated that the modulus of PDMS sheet (10:1) was 1.08MPa and the modulus of PDMS sheet (10:2) was 1.81MPa. The PDMS sheet (10:2) was also used for forming strips using the basic peel test and some of the results were summarized in Figures 4.12 and 4.13, with the results from the PDMS sheet (10:1) as the comparison. From Figure 4.12 and 4.13, the modulus of PDMS sheet was found to have no obvious effect on the resulting strips formed by fracture using peel test. Fifteen different measurements were taken for each point as following.
Figure 4.12 Peeling-to-tunneling angle along the separation front

Figure 4.13 Different strips spacing for the strips formed at different locations along the separation front

(Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidization time was 15 minutes, peel force was 246.225 N/m and the peel angle was 45 degree, five different measurements for each point)
To explain whether or not the curing of PDMS to form the PDMS sheet might have an effect on the fracture process, we first need to look at how the PDMS is formed. Cured PDMS was formed by mixing its elastomer and its curing agent in the presence of a Pt catalyst, and the reaction was illustrated in Figure 4.14. The Sylgard® 184 elastomer was composed of dimethylsiloxane with vinyl-terminated end groups and the curing agent included dimethyldimethylsiloxane. The cross-linking process occurred when vinyl and silicon hydride groups underwent a hydrosilylation reaction to form –CH₂-CH₂ linkages between PDMS chains \([57]\). The ratio of elastomer and curing agent was related to only the quantity of \((-\text{CH}_2-\text{CH}_2)\) cross-linking, which mainly tuned the bulk properties of the cured PDMS and seemed to have no effect on forming the strips as the interface separated by the peel test.

### 4.4.2 JKR method

The modulus of regular PDMS sheet (the ratio~10:1) measured by JKR method was 1.8MPa according to four different measurements on one sample, which was consistent with result reported by other paper \([43]\). After oxidized PDMS sheet
for 15 minutes to achieve the silica-like layer, another JKR test was applied immediately and the result showed that the modulus of the PDMS with a silica-like layer was 1.9MPa, which was close to the modulus of PDMS sheet without oxidization. Therefore, the JKR test was not able to determine the modulus of only the top silica-like layer, since the modulus value, if was that of the silica-like layer, it was far away from the reported value for pure silica, which was about 70GPa [43]. One explanation for this discrepancy was that the compression of PDMS lens might still went further to the PDMS sheet, which was located under the silica-like layer, because the silica-like layer was really thin. In conclusion, the JKR method was able to measure the modulus of PDMS sheet, but it could not measure the modulus of silica-like layer alone. Some analysis might be derived from the values obtained to deduce the modulus of the thin top silica-like layer, but this is beyond the scope of this study.

4.4.3 Buckling method

![AFM image about wrinkles](image)

Figure 4.15 AFM image about wrinkles
(Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 5mm and the oxidization time was 20 minutes, the pre-strain was 10%, three different samples for each UVO exposure time)

Figure 4.16 Modulus with oxidation time

From previous results, both strain-stress and JKR methods were unable to measure the modulus of silica-like layer on top of the PDMS sheet, a third method, the bucking method was attempted to determine this parameter. When pre-straining and UV/Ozone were applied simultaneously to the PDMS sheet, uniform wrinkles would form on the PDMS surface after oxidization and releasing of the pre-strain, and the spacing of the wrinkles could be related to the corresponding oxidation time, hence the extent of oxidization of the top layer of the PDMS sheet. From Figure 4.15, it indicated that the buckling method was possible to generate uniform wrinkles on the PDMS surface. The spacing and amplitude were found to be 30μm and 3μm, respectively, when the oxidation time was 20 minutes, and pre-strain was 10%. If we assume the thickness of the silica-like layer was 100nm [35], and then the modulus could be calculated by equation 2.14. Figure 4.16 indicated that the modulus
increased with the increase of oxidation time. The literature value for the silica-like layer was about 70GPa, which was close to the data with 5 minutes oxidization (96nm) if the thickness of silica-like layer was 100nm. Therefore, from this data, it would be possible that the silica-like layer was actually much thinner. As indicated in the contact angle and FTIR-ATR results, an oxidization time of ~35 minutes was needed to achieve a saturated oxidation extent on the PDMS surface using UV/Ozone oxidation. Even with such a long time of oxidization, the surface layer only contained ~50% silica [22]. The results of bulking (or wrinkling) method showed that the modulus increased with the increase of oxidation time, so that other data points, if we still used the thickness of the silica-like layer to be 100nm, were larger than the literature value. From the background section, the thickness of the silica–like layer was different with different oxidation time, so that it still needed another method to obtain the thickness of the silica-like layer, because the precise value of the modulus could not be obtained using the bulking method.

4.5 Thickness determination (PDMS sheet and the silica layer)

The following parts discussed about the effects of thickness of PDMS sheet and silica-like layer on resulting strips formed by fracture. The following results were all obtained by using tweezers to force open the bonded interface to achieve fracture.
4.5.1 The effect of PDMS thickness

Figure 4.17 The relationship between wavelength and thickness

(Experimental parameters: the thickness and width of PDMS sheet was 1, 2, 3 mm and 8 mm, respectively, the distance to the top UV/O lamp during oxidization was 2 mm and the oxidization time was 15 minutes, fifteen different measurements for each sample)

Based on the data reported in the above figure, the wavelength was no obvious difference between PDMS sheets with different thickness. Since all these PDMS sheets were oxidized for 15 minutes, the thickness and modulus of the silica-like layer was basically the same for PDMS sheets with different thickness. As a result, if the silica-like layer played the most important role for the strip formation by fracture, the wavelength of the resulting strips was expected to be similar with PDMS sheets with different thicknesses, when they were oxidized under the same condition.
4.5.2 Gradient

Figure 4.18 The relationship between thickness and wavelength

For a sheet with a gradient thickness, the result reported in Figure 4.18, showed that the wavelength increased with the increase of the PDMS sheet. One possible explanation for this observation was that the modulus of the silica-like layer at point B was larger than point A (refer to Figure 3.3), because point B was closer to the UVO lamp. In conclusion, the spacing increased with the increase of the modulus and/or thickness of the silica-like layer.
4.5.3 Effect of the UVO exposure time

Figure 4.19 The effect of the UVO exposure time on spacing

(Experimental parameters: the thickness and width of PDMS sheet was 2 mm and 8 mm, respectively, the distance to the top UV/O lamp during oxidization was 2 mm and the oxidization time was 5, 15, 25, 35 minutes, respectively, fifteen different measurements for each sample)

Results in Figure 4.19 indicated that the spacing (i.e. wavelength) of the strips increased with the increase of the UVO exposure time. When the UVO exposure time increased, the modulus and/or thickness of the silica-like layer increased, as a result, the spacing of the strips increased. The result of this experiment was consistent with the gradient test described in 4.5.2.

4.6 Role of the silica-like layer at the edges of the PDMS sheet

When the PDMS sheet was oxidized in the UV chamber, a thin silica-like layer was formed on the top layer of the PDMS sheet. Meanwhile, there was a thin silica-like layer formed on all four side surfaces of the PDMS sheet, except the bottom one, which was in contact with a glass slide during the oxidation process. The
following parts discussed about the role of the silica-like layer on the sides of the PDMS sheet on the formation of the strips by fracture.

4.6.1 PDMS was cut for 2 or 3 pieces before peeling

![Image of peeling with silica-like layer](image.png)

Figure 4.20 The pattern formed during peeling when the PDMS sheet was sectioned into two (through the middle in the direction of peeling) (see sketch 3.4)

(Experimental parameters: the thickness and width of PDMS sheet was 2 mm and 4mm, respectively, the distance from PDMS surface to the UV/O lamp was 2mm and the oxidization time was 15 minutes, peel force was 492.45 N/m and the peel angle was 45 degree, five samples were tested)

Figure 4.20 was the real time image taken at the edge without silica-like layer. It was obviously that all the strips initiated from the other edge, which had the silica-like layer. There were no strips originated from the sectioned edge, which did not have a silica-like layer along the side surface of the PDMS sheet.

Another piece of PDMS sheet was cut into three sections (see Figure 3.4(b)) and the focus was on the middle one with neither side of the sheet, in the peeling
direction, containing a silica-like layer. When 507.15N/m peeling force, this was much higher force used as compared to other cases, applied to peel test, the peeling could not start. When the force was increased to 727.65N/m, the peeling still could not occur. When the peeling force increased to 731.175N/m, the PDMS sheet broke into two pieces instead of separating from the interface. Therefore, without the silica-like layer on the sides of the PDMS sheet, the fracture could not from the interface, hence initiation of the cracks (or formation of strips), was basically impossible.

4.6.2 Bonding partial of the PDMS sheet

Figure 4.21 The pattern after peeling bonding partial of the PDMS sheet

(Experimental parameters: the thickness and width of PDMS sheet was 2mm and 8mm, respectively, the distance to the top UV/O lamp during oxidization was 2mm and the oxidation time was 15 minutes, peel force was 246.225 N/m and the peel angle was 45 degree, five different samples were tested)

Figure 4.21 was the real time image taken at the sectioned edge that had weak bonding between PDMS sheet and glass slide. A transparent paper was inserted
partially into the interface between the oxidized PDMS sheet and the glass slide during bonding process to prevent a portion of the interface from bonding (see Figure 3.5). From the above Figure 4.21, the strips could initiate from the edge with a weak bonding. From the above observation, it is concluded that the weak bonding at the edge could initiate cracks during fracture.

4.7 Pre-crack effect on strips formation

Figure 4.22 Pattern after peeling pre-crack PDMS sheet

(Experimental parameters: the thickness and width of PDMS sheet was 2 mm and 8mm, respectively, the distance from PDMS surface to the UV/O lamp was 2mm and the oxidization time was 15 minutes, peel force was 246.255 N/m and the peeling angle was 45 degree, three different samples were tested.)
Figure 4.23 Some time-sequent snap shots for peeling pre-crack PDMS sheet

(Experimental parameters: same as the Figure 4.20)

After oxidized using UV/Ozone, the PDMS sheet was stretched with tweezers several times to generate pre-cracks on the oxidized PDMS sheet, before bonding it to the oxidized glass surface. Under the OM, the pre-cracks could not be noticed, and then the pre-cracked PDMS sheet was bonded to the glass slide and the interface was fractured by peel test. From the video, two sets of strips came from two edges of the PDMS sheet and met each other in the middle. The strips were symmetric, along the center line of the sheet, which was similar to the fracture of PDMS sheet/glass slide interface peel test. The obvious difference between this test and the other with fracture by peel was that some irregular strip initiations (shown as A and B in Figure 4.22) appeared at the edge, and once the strips initiated, they also tunneled to form strips having similar shape as those of others. The details of the phenomenon could be viewed from a video clip and some time-sequent snap shots from the clip are shown.
in Figure 4.23. Firstly, a large crack, crack 1 formed, following that strips initiated from crack 1 and tunneled perpendicular to the middle. Then crack 2 and crack 3 formed and grew at the same time. Crack 2 stopped the tunneling of some strips originated from crack 1, leaving the regimes of A in these “blade” shapes. Other strips initiated from crack 1 continued tunneling to the middle. At the same time, some strips initiated from the crack 3, tunneled perpendicular to the middle, and the fracture process repeated.

4.8 Effects of pre-wrinkles on the PDMS sheet

The following parts showed the results of the peel tests with the pre-wrinkles on PDMS sheet. Two peeling directions were examined, one of which was parallel to the wrinkle direction, and another was perpendicular to the wrinkle direction.

4.8.1 Peeling direction perpendicular to the wrinkle

Figure 4.24 The strips formed on the glass slide after peeling (peel direction: perpendicular) the bonded pre-wrinkle PDMS sheet from the glass slide
Experimental parameters: the pre-wrinkles were formed with 10% pre-strain and 20 minutes oxidation time, the thickness and width of PDMS sheet was 2 mm and 8 mm, respectively, the distance from PDMS surface to the UV/O lamp was 2 mm and the oxidization time was 15 minutes, peel force was 246.255 N/m and the peel angle was 45 degree, three samples were tested.

Figure 4.24 showed the strips formed after peeling a pre-wrinkled PDMS sheet from its bonded glass surface with the peeling direction perpendicular to that of the wrinkles. Under this condition, the bonding between pre-wrinkled PDMS sheet and the glass slide was not as strong as that of a PDMS sheet without pre-wrinkles, because the folds, away from the contacted interface, of the pre-wrinkled PDMS sheet could not contact with glass surface perfectly, during the thermal bonding process. During the peeling process, two sets of cracks initiated from the edges and tunneled to the middle to form the strips. The tunneling direction was along the wrinkle direction, so that it was perpendicular to the peeling direction. Because the cohesive failure happened during the peeling process, the wavelength of the strips on the glass almost equaled to the wavelength of wrinkles prior to bonding, the distribution of the strips left on the glass was also the same as that of the wrinkles. Some strips formed on the glass surface were not continuously, because the different aptitudes of the wrinkles lead to un-even contacts of the wrinkles with the glass surface, and only those regions that made contact with glass were cohesively reputed to leave behind the bumpy and un-evened strips on glass.
4.8.2 Peeling direction parallel to the wrinkle

Figure 4.25 The strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide

(Experimental parameters: the pre-wrinkles were formed with 10% pre-strain and 20 minutes oxidation time, the thickness and width of PDMS sheet was 2 mm and 8 mm, respectively, the distance from PDMS surface to the UV/O lamp was 2 mm and the oxidation time was 15 minutes, peel force was 246.255 N/m and the peel angle was 45 degree, three samples were tested)

The results of peeling the pre-wrinkled PDMS sheet from its bonded glass surface with the peeling direction parallel to those of the wrinkles are illustrated in Figure 4.25. Under this condition, two sets of strips formed spontaneously and they would cross to each other. One set of strips formed along the x-axis due to the pre-formed wrinkles, and the structures and wavelength of the strips were almost the same as those of the wrinkles. Another set of strips formed along the y-axis, which were caused by fracture using the peel test. The spacing between cracks on the horizontal direction (i.e. x-direction) was about 25-30 μm, which was consistent with the
wavelength of strips formed for the PDMS sheet without pre-wrinkles separated from its bonded glass surface using peel.

Figure 4.26 The real time image about strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide (Experimental parameters: same with Figure 4.23)

The above picture is a snap shot from the peel video and the red line stands for the direction of the wrinkles. The x-axis stands for the peeling and wrinkle direction, and the y-axis represents the tunneling direction. From Figure 4.25, there is one set of strips on the glass surface formed due to the pre-formed wrinkles. From this snap shot, it is clear that one strip (e.g. M in Figure 4.24) from this set of strips combined two parts: cracks 2 and 3. Crack 2 was formed first, and it stopped to tunnel forward when it came cross crack 1. Then, crack 3 tunneled with the same direction as crack 2, and then it changed direction to tunnel in the y-axis, due to peel effect, before it met the intersection of cracks 2 and 1. After crack 3 came across crack 4, crack 2 would continue to tunnel forward along the x-axis.
Figure 4.7 The strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide and the red circles were the cracks disappeared

(Experimental parameters: same with Figure 4.25)

Figure 4.8 The strips formed on the silicone sheet after peeling (peel direction: parallel) the bonded pre-wrinkle PDMS sheet from the glass slide and the red circles were the cracks reshaped with a little force

(Experimental parameters: same with Figure 4.25)
Another interesting phenomenon for the strips formed using pre-wrinkled PDMS sheet was observed in above two images. After 5 days, some OM images for the patterns on the above surfaces were retaken; and they showed that some of the cracks formed in a short time after the fracture disappeared, but they would re-appear when the sample was pulled with a little force (some of these were indicated by red circles in Figures 4.27 and 4.28). 3 different regions were chosen before and after pulling, and the increasing ratio for the crack reappearing was about 30%, 30%, 20%, respectively.

4.9 Pre-strained oxidization

Table 4.2 Comparison of the wavelength at edges by different methods

<table>
<thead>
<tr>
<th>separate</th>
<th>Tweezers</th>
<th>Peel test</th>
<th>Wrinkling method</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength</td>
<td>9.6 ± 0.9(μm)</td>
<td>8.4 ± 1.1(μm)</td>
<td>26 ± 0.5(μm)</td>
</tr>
</tbody>
</table>

Table 4.2 indicates that the wrinkling method resulted in a larger wavelength than using peel test or prying open with tweezers.
Figure 4.29 The comparison of strips formed for pre-strained and no pre-strained

(Experimental parameters: the thickness and width of PDMS sheet was 2 mm and 8 mm, respectively, the distance from PDMS surface to the UV/O lamp was 5 mm and the oxidization time was 15 minutes, fifteen different measurements for each sample)

The above Figure 4.29 showed that the pre-straining was able to increase the wavelength after forcing open the interface by tweezers. One possible reason for this phenomenon was that the modulus and/or thickness of the top silica-like layer on the PDMS sheet were greater for the pre-strained PDMS sheet. The greater modulus was the result of stretching the PDMS sheet during the oxidized process, which might allow more/deeper of the PDMS sheet to be covered into the silica-like layer. After prying open the interface between glass and PDMS, the wavelength of the strips formed with the pre-strained PDMS sheet was larger than the one without pre-strained.

4.10 Summary

Both contact angle and FTIR-ATR results showed that the hydrophobic PDMS sheet surface would lead to a hydrophilic surface during the UV/Ozone process. The peel test was a useful method to generate uniform strips, but the wavelength was not homogeneous on the whole PDMS sheet. The greater the modulus/thickness of the silica-like layer was, the larger the wavelength of the strips was. Pre-strained oxidation was a method to increase modulus/thickness of the silica-like layer. The silica-like layer at the edge of the PDMS sheet was necessary to initiate crack during fracture.
CHAPTER V

CONCLUSIONS

5.1 Summary

The main purpose of our study was to detailed experimental evidence that is essential for developing the theory behind FIS, and to collaborate with theoreticians for developing such fundamental understanding. With this understanding, a full utilization of such a simple and cost-effective fabrication technique can be realized.

The specific objectives of this project were fully satisfied. When a constant force was applied to instead of tweezers in peel test, it was beneficial and easily to obtain more uniform and parallel strips. On the other hand, the force could be managed with high precision by the constant weight (i.e. a known peel force) applied in the experiment.

From both contact angle and FTIR-ATR outcomes, the hydrophobic PDMS sheet surface would lead to a more hydrophilic surface during the UV/Ozone process. With the increasing of $t_{UVO}$, more –OH groups were formed and more –CH$_3$ were disappeared. When the $t_{UVO}$ increased to 35 minutes, the surface of PDMS sheet had become more saturated with silica-like substances, which indicated that it was more difficult for the ozone to diffuse thought the silica-like layer and the oxidization process almost stopped. The spacing of the strips by fracture increased, with increase of the oxidization time.
The effect of factors including the peel angle, peel force, elastic modulus and the thickness of the PDMS sheet had little to no effect on the spacing or initiation of the crack. But the effect of other factors containing elastic modulus of silica-like layer, pre-crack, and pre-wrinkling were possible to change the initiation of the cracks during the fracture or the spacing between cracks.

The modulus of PDMS could be obtained by strain-stress and JKR method. But the modulus of the silica-like layer was still not achieved by JKR, or buckling method. The reason for this was the silica-like layer was really thin, which thickness was less than 200nm [20].

The glassy silica-like layer at the edge of the PDMS sheet was very important to initiate cracks during fracture. Without this thin layer, the crack could not initiate from the edge.

The results for the FIS of a glassy polymer film sandwiched in between two rigid plates showed that the wavelength was about 3 times the initial thickness of the thin film.

5.2 Future Work

The oxidized extent of UV/Ozone can be further looked into more accurate surface chemistry. The detailed change on quantity of –OH groups and –CH₃ group also need to be investigated for a more comprehensive understanding.

To determine the effect of various experimental parameters (peel angle, peel speed) on the aptitude of the fracture induced strips.
Though the effect of modulus and/or thickness of the silica-like layer have been investigated, a deeper investigation into calculating the value of modulus and thickness of the silica-like layer is warranted.

Provide detail experimental evidence of FIS of the glassy polymer films, which include narrowly dispersed homopolymer (e.g. polystyrene) and photo-resist (e.g AZ5214E).

Several studies can be carried out using AFM and SEM to obtain more detailed information on the samples from the FIS of a glassy polymer film sandwiched in between two rigid plates.

After obtaining enough detailed experimental evidence on peel test and FIS, I would like develop the theatrical understanding with the collaboration of a theoretician (or theoreticians). After that, it is better to verify the theory by creating the nano-scale features.
REFERENCES


Another objective in the thesis:

To provide detailed experimental evidence of FIS of a glassy polymer film sandwiched in between two rigid plates that have been carried out by Pease et.al and other researchers.

Hypothesis: the strip spacing is several times of the thickness of the thin film.

Figure A1 showed the procedure to make sandwich samples. The detail procedure of making sandwich samples is in 3.3.2.2. Three different concentrations of PS (10%, 15%, and 20%) were used to create the different thicknesses of the thin film between two rigid glass slides. Then, the force was applied to split the two rigid substrates. The aim for this experiment was to examine the relationship between spacing and the thickness of initial thin film.
Figure A2 The relationship between strip wavelength and thickness of glassy polystyrene thin film

(Experimental detail: Three different concentrations of PS (10%, 15%, 20% by mass in toluene) were used to create the different thicknesses of the thin film between two rigid glass slides. The time for spin coat was 50 seconds.)

Figure A3 The strip-like pattern on the glass surface after splitting two rigid glasses (PS concentration: 15%)
After splitting the two rigid glasses, there were some uniform strips-like patterns on the both glass surfaces (in Figure A3). The wavelength was similar on the whole glass surface. From Figure A2, it indicated that the wavelength increased with the increase of the thin film, and it was about 3 times the initial thickness of the thin film, which is close to the results obtained by Pease and Li-Chen Huang’s group.