Fracture Toughness Measurements of Thin Film Silicone Polymers Using the Modified Edge Lift-off Test

by

Darin R. Spain

B.S. Mechanical Engineering
Oklahoma State University (1998)

Submitted to the Department of Mechanical Engineering
in Partial Fulfillment of the Requirements for the
Degree of Master of Science of Mechanical Engineering

at the
Massachusetts Institute of Technology
September 2000

2000 Massachusetts Institute of Technology
©All rights reserved

Signature of Author

__________________________________________

Department of Mechanical Engineering
June 30, 2000

Certified by

__________________________________________

Fredrick J. McGarry
Professor of Polymer Engineering
Thesis Supervisor

Accepted by

__________________________________________

Mary C. Boyce
Professor of Mechanical Engineering
Thesis Reader

Accepted by

__________________________________________

Ain A. Sonin
Chairman, Department Committee on Graduate Students
Fracture Toughness Measurements of Thin Film Silicone Polymers
Using the Modified Edge Lift-off Test

by
Darin R. Spain

Submitted to the Department of Mechanical Engineering
on June 30, 2000 in Partial Fulfillment of the Requirements for the
Degree of Master of Science of Mechanical Engineering

Abstract

This thesis concentrates on the fracture toughness measurements of thin film silicone resins. Previously, no study has been done to measure the fracture toughness of these silicone resins as thin films. The silicone resins tested range in thickness from 0.1x10^{-6} m to 5.0x10^{-6} m and are spin coated on 100 mm silicon wafers. The Modified Edge Lift-off Test (MELT) is used to evaluate the fracture toughness of the silicone resins. The MELT is a simple and very accurate test that measures the fracture toughness, K_{IC}, of thin film polymeric materials. One great advantage of the MELT is the test can be used to evaluate the K_{IC} of materials without any knowledge of any mechanical properties of the test material.

The MELT was used to evaluate the fracture toughness of two silicone resins made by the Dow Corning Corporation. The first resin is 4-3136, a condensation cure diphenyl, methyl, phenyl, phenyl-methyl silicone resin. With 4-3136, rubber toughening was used to improve the fracture toughness of the resin. Rubber toughening can be divided into two categories, phase I and phase II. Phase II rubber is a rubber that forms a second phase particle. Phase I rubber reacts into the polymer and forms a homogeneous matrix. The effects of phase I and phase II toughening of silicone resin 4-3136 improves the fracture toughness of bulk samples and thin films. MELT measurements show that unmodified 4-3136 has a fracture toughness, K_{IC}, of 0.301 MPa*m^{1/2}. Adding 10 parts of phase I PDMS rubber increases K_{IC} to 0.402 MPa*m^{1/2}. Adding 5 parts of phase II PDMS rubber along with 10 parts of phase I rubber further increases the K_{IC} to 0.522 MPa*m^{1/2}. Comparisons of the K_{IC} measurements of bulk material single edge notched samples and thin film MELT samples are similar, which validates the accuracy of the MELT. Single edge notched bulk values for similar rubber toughened systems of 4-3136 are 0.253 MPa*m^{1/2} (unmodified 4-3136), 0.453 MPa*m^{1/2} (phase I modified 4-3136), and 0.540 MPa*m^{1/2} (phase I and phase II modified 4-3136).

The second resin tested with the MELT is MetFlex, a Dow Corning methyl-T silicone resin. Three different variations of MetFlex were studied. This study showed how the K_{IC} decreased with an increase in curing temperature. MetFlex cured at 275°C has a K_{IC} of 0.306 MPa*m^{1/2}, while raising the curing temperature to 400°C decreases the K_{IC} to 0.171 MPa*m^{1/2}. Another Dow Corning silicone resin, X1-2672, an addition cure phenyl, methyl-vinyl silicone resin was intended to be tested. There are no MELT results of X1-2672 because it could not be made into a thin film by conventional spin coating techniques.

Thesis Supervisor: Fredrick J. McGarry
Title: Professor of Polymer Engineering
Department of Material Science and Engineering
# Table of Contents

Abstract ............................................................................................................................................. 2  
Table of Contents .......................................................................................................................... 3  
List of Figures .................................................................................................................................. 5  
List of Tables ................................................................................................................................... 7  
Acknowledgements ......................................................................................................................... 8  
Chapter 1. Background ...................................................................................................................... 10  
1.1 Introduction ................................................................................................................................. 10  
1.2 Thin Film Applications ............................................................................................................... 10  
1.2.1 Microelectronics Industry ..................................................................................................... 10  
1.2.2 Coatings ................................................................................................................................ 11  
1.3 Silicone Resin Chemistry .......................................................................................................... 11  
1.3.1 Synthesis of Silicone Resins ................................................................................................. 12  
1.3.2 Curing Silicone Resins ......................................................................................................... 13  
1.4 Toughening Silicone Resins ...................................................................................................... 13  
1.4.1 Phase I Toughening ............................................................................................................... 14  
1.4.2 Phase II Toughening ............................................................................................................. 15  
1.5 Scope of Thesis ........................................................................................................................... 16  
Chapter 2. Adhesion Test Methods ................................................................................................. 17  
2.1 Introduction ................................................................................................................................. 17  
2.2 Scratch Tests ............................................................................................................................... 17  
2.3 Peel and Peel-Type Tests .......................................................................................................... 18  
2.3.1 Peel Test ............................................................................................................................... 18  
2.3.2 Topple Test .......................................................................................................................... 19  
2.4 Lap Joint Shear Tests ................................................................................................................... 20  
2.5 Blister Tests ............................................................................................................................... 21  
2.6 Stress-Corrosion Crack Test ...................................................................................................... 23  
2.7 Edge Delamination Test ............................................................................................................ 23  
2.8 Edge Lift-off Test ....................................................................................................................... 24  
2.9 Modified Edge Lift-off Test ...................................................................................................... 25  
Chapter 3. Analytical and Theoretical Basis .................................................................................. 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>26</td>
</tr>
<tr>
<td>3.2</td>
<td>Fracture Mechanics Overview</td>
<td>27</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Stress Analysis Near a Crack</td>
<td>27</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Energy Balance</td>
<td>30</td>
</tr>
<tr>
<td>3.3</td>
<td>Fracture Mechanics of Multilayer Thin Coatings</td>
<td>31</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Experimental Procedures</td>
<td>34</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>34</td>
</tr>
<tr>
<td>4.2</td>
<td>Depositing Test Materials</td>
<td>34</td>
</tr>
<tr>
<td>4.3</td>
<td>Test Procedure and Sample Preparation</td>
<td>35</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Experimental Procedure for Modified Edge Lift-off Test</td>
<td>35</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Ultra Violet-Ozone Surface Treatment</td>
<td>35</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Application of Epoxy Backing Layer</td>
<td>36</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Dicing Samples</td>
<td>40</td>
</tr>
<tr>
<td>4.3.5</td>
<td>Polishing Samples</td>
<td>40</td>
</tr>
<tr>
<td>4.4</td>
<td>Cryostage</td>
<td>41</td>
</tr>
<tr>
<td>4.5</td>
<td>Calculating the $K_{IC}$ from MELT</td>
<td>43</td>
</tr>
<tr>
<td>4.6</td>
<td>Failure analysis of MELT samples</td>
<td>44</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Results and Conclusions</td>
<td>47</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>47</td>
</tr>
<tr>
<td>5.2</td>
<td>Materials Tested</td>
<td>47</td>
</tr>
<tr>
<td>5.3</td>
<td>Modified Edge Lift-off Test Results of 4-3136 Resin</td>
<td>48</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Various Thickness of Neat 4-3136</td>
<td>48</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Phase I and Phase II Toughened 4-3136</td>
<td>50</td>
</tr>
<tr>
<td>5.4</td>
<td>Comparing 4-3136 MELT Data with Bulk Sample Data</td>
<td>52</td>
</tr>
<tr>
<td>5.5</td>
<td>MELT Results of MetFlex Resins</td>
<td>55</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Effects of Curing Temperature</td>
<td>55</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Comparison of MF1, MF2 and MF3</td>
<td>57</td>
</tr>
<tr>
<td>5.6</td>
<td>Comparison of 4-3136, MetFlex and MK-Wacker Silicone Resins</td>
<td>58</td>
</tr>
<tr>
<td>5.7</td>
<td>X1-2672 Experimental Silicone Resin</td>
<td>59</td>
</tr>
<tr>
<td>5.8</td>
<td>Index of Refraction Measurements</td>
<td>59</td>
</tr>
<tr>
<td>5.9</td>
<td>Conclusions</td>
<td>61</td>
</tr>
<tr>
<td>Bibliography</td>
<td></td>
<td>63</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1-1. Hydrolysis or Step Polymerization of Diorganodichlorosilane ..................... 12
Figure 1-2. Ring-Opening Polymerization of Octamethylcyclotetrasiloxane .................... 13
Figure 2-1. Illustration of Scratch Test ........................................................................ 18
Figure 2-2. Diagram of Peel Test .................................................................................. 19
Figure 2-3. Topple Test of Thin Films .......................................................................... 20
Figure 2-4. Lap Shear Test ......................................................................................... 20
Figure 2-5. Diagram of the Standard Blister Test .......................................................... 21
Figure 2-6. Diagram of Constrained Blister Test ........................................................... 21
Figure 2-7. Diagram of Island Blister Test .................................................................... 22
Figure 2-8. Diagram of Peninsula Blister Test ............................................................... 22
Figure 2-9. Figure of Edge Delamination Test ............................................................... 22
Figure 2-10. Diagram of the Edge Lift-off Test ............................................................... 23
Figure 2-11. Diagram of the Modified Edge Lift-off Test ............................................. 25
Figure 3-1. Illustration of a Modified Edge Lift-off Test Specimen. The Test Resin
           Thickness is Thin Compared to the Backing Layer Thickness ......................... 27
Figure 3-2. Three Modes of Loading in a Cracked Structure ....................................... 28
Figure 3-3. Stress Distribution Near Crack Tip ............................................................. 29
Figure 3-4. Crack in a Large Plate .............................................................................. 30
Figure 4-1. UV-Ozone Surface Treatment Experimental Setup ................................... 36
Figure 4-2. Application of Epoxy Backing Layer ......................................................... 37
Figure 4-3. Stress-Temperature Profile of Epoxy Backing Layer on a Si Wafer .......... 37
Figure 4-4. Failure Envelope of 4-3136 MELT Specimens ........................................ 38
Figure 4-5. Failure Temperature Predictions for Different Fracture Toughness Films with
           Various Epoxy Layer Thickness ........................................................................... 39
Figure 4-6. Polishing Edges of MELT Specimens ......................................................... 41
Figure 4-7. Diagram of Cryostage for MELT Use ......................................................... 42
Figure 4-8. Example of a Debonded MELT Specimen .................................................. 43
Figure 4-9. Cohesive Failure in Test Resin .................................................................... 44
Figure 4-10. Adhesive Failure at the Test Resin and Substrate Interface ...................... 44
Figure 5-1. MELT Data of 4-3136 of Various Thicknesses ........................................... 49
Figure 5-2. Spin Coating Speeds Used to Deposit Phase I and Phase II Rubber Modified
4-3136..................................................................................................................51
Figure 5-3. Diagram of ASTM Standard D5045, Three Point Bend Test for Fracture
Toughness, KIC........................................................................................................52
Figure 5-4. Comparison of KIC Measurements of MELT and Bulk Samples.............53
Figure 5-5. MELT Data for MetFlex at Various Cure Temperatures .......................57
List of Tables

Table 4-1. Example of $K_{IC}$ Calculation from Modified Edge Lift-off Test .........................43
Table 4-2. Ellipsometer Measurements of Failed MELT Samples ........................................46
Table 5-1. MELT Data of Neat 4-3136 ..............................................................................49
Table 5-2. MELT Data for Unmodified and Modified 4-3136 .............................................51
Table 5-3. MELT and Bulk Fracture Toughness Measurements of 4-3136 .........................53
Table 5-4. Listing of Phase I and Phase II Materials Used ..................................................54
Table 5-5. MELT Measurements of MetFlex Silicone Resins ..............................................56
Table 5-6. MELT Measurements of Similar Cured MF1, MF2, and MF3 .............................58
Table 5-7. MELT Results of 4-3136, MetFlex and Wacker-MK Silicone Resins ...............58
Table 5-8. Ellipsometry Data of Films Tested ......................................................................60
Acknowledgements

I would like to thank many people for their assistance in performing this thesis work and preparing this document. First and foremost, I would like to thank my advisor, Professor Frederick McGarry for his guidance, support, and encouragement. Thru this and other projects, he always worked hard to help me with my work. I would also like to thank three gentlemen at the Dow Corning Corporation: Dr. Bizhong “Rocky” Zhu, Dr. Dimitris E. Katsoulis, and John Keryk. These three helped me tremendously by supplying the materials for this work and also provided valuable incite to many of the questions that came about during the project. I would like to thank Professor Mary Boyce for being my academic advisor and for the help in reading my thesis.

I also want to thank Dr. Edward Shaffer II of the Dow Chemical Corporation for teaching me the intricacies of the Modified Edge Lift-off Test and taking time out of his busy schedule for numerous helpful discussions we had over the past year. My officemate, Zhongtao “Mike” Li helped me with countless tutoring of silicone polymer chemistry and showed me how things at MIT actually get done. After many hours in the lab and office we developed a great friendship, and he taught me what real Chinese food tastes like. Qingye “Dave” Zhou, a post-doctoral associate with Professor McGarry, introduced me to the world of polymer chemistry when I began here at MIT. I would also like to thank Yuhong Wu, another graduate student studying under Professor McGarry, who also helped me with lab work.

Leslie Regan at the graduate student office in the Mechanical Engineering Department was extremely helpful from the time I started at MIT until the time I finished. She was a tremendous help getting me started in a research group and helping me finish this thesis. Diane Rose and Marj Joss, two secretaries of Professor McGarry, were also supportive during my time at MIT. Tim McClure and Libby Shaw at the Center for Material Science and Engineering at MIT for their assistance and helping me use the testing equipment in their labs. Tim McClure also provided a great wealth of information that helped me get many things done. I also want to thank Ryan Kershner and Professor Cima at the Materials Processing Center and Darrell Irvine and Professor Anne Mayes for use of their spin coating machines. Martin Brinkman and Professor Edward Thomas
also provided the UV-Ozone Machine used in this work. Without the use of these machines and their labs, this research would have never been accomplished.

Not only at MIT but throughout my life, my parents Jan Spain and John Spain have been tremendously supportive and inspiring. My mother taught me the true meaning of hard work and sacrifice, which helped me accomplish everything I have in life. Most of all, I would like to thank my wife AnnMarie. She sacrificed countless evenings and weekends being patient with me as I worked in the lab and spent time away from her. She also sacrificed two years of her own educational interests as she waited for me to finish my master’s degree at MIT before she started law school. Her daily support and encouragement was the biggest factor in my success at MIT.
Chapter 1. Background

1.1 Introduction

Silicone based polymers are used in industries such as automotive and aerospace to electronics to personal care products. Products include greases, sealants, adhesives, protective coatings, electronic encapsulants, interlayer dielectric materials, and structural composites. This thesis will concentrate on thin film applications typically used for electronic interlayer dielectric materials. The films will range in thickness from $0.1 \times 10^{-6}$ m to $5.0 \times 10^{-6}$ m. In this first chapter, an overview of the how materials are used in the microelectronics industry is given. A brief explanation of how silicone resins are produced and how the fracture toughness can be improved with phase I and phase II toughening methods is also given along with the definition of phase I and phase II toughening methods.

1.2 Thin Film Applications

1.2.1 Microelectronics Industry

The microelectronics industry is pushing to increase the speed of processors and the size of memory. In order to accomplish this, manufacturers must increase the density of components on microelectronic devices. Thin film packaging is a technology which promises to meet this need to increase the density of components on multi-chip modules (MCMs). MCMs typically have 3 to 10 dielectric layers each 1 μm to 20 μm thick. Dielectric layers are usually polymeric because of the electrical and processing properties. Thin film packaging is one of the fastest growing technologies in the 21st century.

Technology in the microelectronics industry is advancing at tremendous speeds. Length scale of microprocessors, dynamic memory (DRAM), and system-on-a-chip (SoC) is currently at 200 nm in 1999, and is predicted to approach 100 nm by the year 2005, and 50 nm in the year 2011. The dielectric constant ($\kappa$) of materials used today is...
3.5-4.0, predicted to be 2.5 by the year 2005, and below 1.5 by 2011^2. Silicone resins can be used in microprocessors and memory chips due to their ability to tailor the dielectric constant of these materials to certain needs. Two of the main factors hindering the implementation of these silicone resins are low fracture toughness and difficulties in processing.

One area of concern to MCM producers is the reliability and service life of microelectronic components. Failures in the thin films of MCMs can alter the physical and electrical properties of the materials used in the various MCM layers. The reliability and failure of thin films has been investigated since the 1950s. The failure of thin polymer films in MCMs is mostly due to thermal stresses created during processing. When developing new materials for MCM use, the failure characteristics are one of the most important criteria for accepting new materials into industrial applications for MCMs^3. One of the material properties now being used to characterize the failure of thin films is fracture toughness, $K_{IC}$. $K_{IC}$ is an intrinsic property which is essentially a measure of the resistance to crack growth in a material, this will be explained more in chapter 3.

### 1.2.2 Coatings

Many materials have protective coatings such as aircraft skins, paneling for homes, and electronic components. Silicone resins used as coatings can provide good protection from many environments. Silicone resins can withstand high levels of heat and humidity and numerous temperature cycles from cold to hot and still maintain structural and electrical property integrity. Rigid silicone resins do not combust and are typically 95%-100% intact after being subjected to a flame at temperatures of 2000°F for 20 seconds^4. These factors make silicone resins very attractive for coatings that can withstand corrosion and weathering by nature, and harsh conditions under a flame.

### 1.3 Silicone Resin Chemistry

Technology has been advancing in the past few decades improving the properties of silicone resins for many applications including: coatings, pre-ceramics, insulating
materials, composite matrix materials, adhesives, electronic packaging and resist materials for microelectronics. Currently, researchers at the Dow Corning Corporation are trying to improve silicone resins for structural and microelectronics use. The major advantages of using silicone resins are the temperature and heat resistance, little to no combustion at high temperatures and low dielectric constant. The drawback of silicone polymers is the low resistance to cracking, the low fracture toughness. A brief overview of the synthesis and curing of silicone resins is given in the next section.

1.3.1 Synthesis of Silicone Resins

There are two main ways to produce silicone resins and silicone rubbers. The first method consists of hydrolysis or step polymerization of diorganodichlorosilanes, and the second method is a ring-opening polymerization of hexamethylcyclotrisiloxanes, octamethylcyclotetrasiloxane, and other cyclosiloxanes. Hydrolysis of diorganodichlorosilanes is a step polymerization that produces unbranched and branched silicones and a by-product of HCl. Reactant concentrations, reaction temperature, amount of HCl, coupled with other factors control the degree of polymerization. Ring opening polymerization can be done with cationic polymerization or anionic polymerization with the use of catalysts. Ring opening polymerization allows higher degrees of polymerization. Figure 1-1 illustrates the hydrolysis of diorganodichlorosilane into polydimethylsiloxane (PDMS). Figure 1-2 shows the ring opening polymerization of octamethylcyclotetrasiloxane that produces PDMS. The end product of the reactions shown in Figure 1-1 and Figure 1-2 are both PDMS rubber. To make silicone resins similar to the resins tested in this thesis, the reaction is similar to the process used to make PDMS, but one or both of the CH₃ groups shown in Figure 1-1 and Figure 1-2 are substituted with other structural units or more chains of Si-O backbones.

\[ \text{CH}_3 \text{Si-Cl} + \text{H}_2\text{O} \rightarrow \text{HO-Si-OH} + \text{Cl-Si-Cl} \]

\[ \text{CH}_3 \text{Si-OH} + \text{HO-Si-OH} \rightarrow \text{Si-O-Si} \]

**Figure 1-1. Hydrolysis or Step Polymerization of Diorganodichlorosilane**
1.3.2 Curing Silicone Resins

Polyorganosiloxanes have a Si-O backbone with various side chain units. These can be one of the four following structural units: Mono-unit, $R_3SiO_{1/2}$; Di-units, $R_2SiO_{2/2}$; Tri-units, $RSiO_{3/2}$; and Quadra-units, $SiO_{4/2}$. The type of $R$ groups found in the resin dictates the material properties. To crosslink the resin, reactive groups are brought together to form polymer chains that form highly crosslink rigid silicones. Silicone elastomers can be long chain polymers with no crosslinking or a moderate amount of crosslinks. Unbranched and non-crosslinked polysiloxanes can be a fluid, i.e. silicone oils.

A siloxane that has T and/or Q-functional groups can be crosslinked. Crosslinking T and Q units forms a three-dimensional network, a highly crosslinked rigid silicone. Generally, silicone resins are crosslinked either by condensation between silanol ends (condensation cure) or by hydrosilylation of vinyl with SiH terminations (addition cure)\textsuperscript{6}. Techniques for manipulating the resin network and adding constituents to the network generally apply for both condensation cure and addition cure resins. These techniques can improve the material properties of the resin.

1.4 Toughening Silicone Resins

Polymeric materials, both thermoplastics and thermosets are often brittle. Therefore, polymer toughening is an important topic in polymer engineering. Phase I toughening of a polymer is accomplished by altering the three dimensional molecular network, improving the intrinsic toughness of the material. Phase I toughening modifies
the resin network to improve plastic deformation of the matrix. Decreasing the crosslinking density without sacrificing the rigidity improves plastic deformation of the network. Another form of toughening a polymer is done by adding a second phase material. This second phase material can be rigid or rubbery particles, and improves the fracture toughness of most polymers. This technique is called phase II toughening. Thermoplastics that have been successfully toughened by phase II materials include, high-impact polystyrene (HIPS), rubber toughened polyvinyl chloride (PVC), poly methyl methacrylate (PMMA), polyethylene, polycarbonate and others. Phase II toughening is also successful with thermosets such as epoxies, unsaturated polyesters, vinyl esters and others7.

### 1.4.1 Phase I Toughening

Phase I toughening of thermosetting polymers is accomplished by altering the polymer network and changing the crosslinking density. One way to alter the network is by changing the types of crosslinkers used to form the three-dimensional network. In 1997, Zhu reported a new technique that can toughen condensation type rigid silicone resins8. The commercially available silicone resin used in Zhu’s work is *Dow Corning* 4-3136 Silicone Binder Resin. This is one of the test materials used in this thesis work. First, the silicone resin structure was modified by an incorporation of a short chain polydimethylsiloxane (PDMS) rubber to alter the number of rigid crosslinks, decrease the crosslink density, and incorporate some flexibility into the resin network. The PDMS rubber is reacted into the resin structure to form a homogeneous system before the resin is cured. The materials used for phase I toughened systems do not phase separate from the resin before or after it is cured. With phase I PDMS rubber modification, the fracture toughness, $K_{IC}$, of the resin was improved from 0.25 MPa*m$^{1/2}$ to 0.46 MPa*m$^{1/2}$.

Li found a way to improve the toughness of an addition cure rigid silicone resin by phase I methods. The resin is *Dow Corning* X1-2672 experimental silicone resin. Instead of incorporating flexible rubber segments into the polymer network, Li used different crosslinkers with organic side groups to alter the crosslinking density to improve the mobility of network segments while maintaining the rigidity of the polymer9. This method increases the fracture toughness, $K_{IC}$, from 0.29 MPa*m$^{1/2}$ to 1.08 MPa*m$^{1/2}$.
1.4.2 Phase II Toughening

Phase II toughening of a polymer is done by incorporating second phase materials into the polymer matrix. Rigid or rubbery particles can be used as second phase materials. For each different polymer system, optimal particle size and good dispersion of phase II particles must be achieved in order to improve the toughness. The size of second phase particles in highly crosslinked polymers typically range from $0.1 \times 10^{-6} \text{m}$ to $100 \times 10^{-6} \text{m}$ in size and amounts range from a few wt% to 10 wt% for most polymeric systems\(^7\). Phase II toughening works singly to toughen most polymers, but this is not the case for the rigid silicone resins tested in this thesis\(^8,9\). Phase I toughening must be accomplished first for silicone resins in order for phase II toughening to be effective. The toughenability of a glassy polymer by the phase II route is determined by the intrinsic toughness of the material.

Phase I toughening increased the toughness of condensation curing silicone resin 4-3136 from 0.25 MPa*\(m^{1/2}\) to 0.46 MPa*\(m^{1/2}\), and with the addition of long chain PDMS rubber as phase II tougheners, the fracture toughness increased further to 0.55 MPa*\(m^{1/2}\).\(^8\) As previously stated, the fracture toughness of addition cure silicone resin X1-2672 has also been toughened by phase I and phase II methodology. With the alteration of crosslinkers, phase I toughening, X1-2672 fracture toughness increased from 0.29 MPa*\(m^{1/2}\) to 1.08 MPa*\(m^{1/2}\), and increased further with the rigid phase II particles to 1.70 MPa*\(m^{1/2}\).\(^9\)

The increase in the fracture toughness of rigid silicone resins 4-3136 and X1-2672 is very significant. The K\(I_c\) values of the modified silicone resins are both comparable to the fracture toughness of many structural resins used today, such as epoxy, polyester, and vinyl ester.
1.5 Scope of Thesis

The primary goal of this thesis is to study the fracture of thin film rigid silicone resins. Films tested range in thickness from $0.1 \times 10^{-6}$ m to $5 \times 10^{-6}$ m. Toughened and untoughened versions of silicone resins from the *Dow Corning Corporation* will be tested. The Modified Edge Lift-off Test (MELT) developed by Shaffer$^{10}$ will be used to test the fracture toughness of the test resins.

Chapter 2 is an overview of various test methods that were used in the past to test the adhesion of thin films to various substrates. A brief explanation of the modified edge lift-off test is also given in this chapter. The development of the mathematical model for the edge lift-off test is given in chapter 3 along with a fracture mechanics overview. Chapter 4 describes the testing techniques for the MELT. The *Dow Corning Corporation*, a leader in the development of silicone materials, provided all the silicone resins tested. The materials are explained in chapter 5. Chapter 5 also gives the results and conclusions of the Modified Edge Lift-off Test.
Chapter 2. Adhesion Test Methods

2.1 Introduction

This chapter discusses various adhesion test methods of thin films. An overview and brief description of simple and complex test methods is given. Scientists and engineers evaluate adhesion and fracture of thin films with many of the tests explained in this chapter. Advantages and disadvantages of each test are explained and compared. The focus of the work in this thesis is the Modified Edge Lift-off Test, it is explained briefly at the end of this chapter in section 2.8; a mathematical model and testing procedures of the MELT can be found in chapters 3 and 4.

2.2 Scratch Tests

An adhesion test which has been used a great deal is the scratch test. Figure 2-1 illustrates the scratch test. The scratch test has found wide acceptance due to its simple nature. The test was first used quantitatively by Heavens\textsuperscript{11} and further developed by Weaver and Benjamin\textsuperscript{12}. The scratch test measures the adhesion by drawing a vertically loaded stylus across the film. The critical load required to strip the film from the substrate leaving a clear channel is considered the measure of adhesion. This test is quite simple to perform, but the actual failure process is quite difficult to quantify. Models based on a friction analysis\textsuperscript{13} and an energy balance\textsuperscript{14} have been developed to quantify the scratch test. The reliability of the test has been investigated quite extensively. Investigations with scanning electron microscopes have shown that the fracture process is complex and the mechanisms vary with different film and substrate systems\textsuperscript{15}. The scratch test maybe used comparatively on the same film-substrate system, but factors such as surface conditions, density, and grain size can lead to inaccurate measurements when comparing two different film-substrate systems.
2.3 Peel and Peel-Type Tests

2.3.1 Peel Test

Another common method for testing adhesion is the peel test. The peel test consists of a film that is patterned onto a substrate, typically by photolithography or scribing. One end of the strip is released and a normal force is applied removing the film from the substrate. One advantage of the peel test is the ease of fabrication and testing. The film is pulled at a constant rate and the force is measured during peeling. A diagram of the peel test is shown in Figure 2-2. From the peeling force, the energy required to remove a unit area of the film is obtained. This test can be applied to polymer and metallic films. Recent studies by Kim et al. have shown that the peel test is an accurate measure of the adhesion energy, $\gamma_a$, only when equation (2-1) is satisfied. When equation (2-1) is not satisfied, plasticity occurs in the test film which can skew adhesion energy measurements.

$$\frac{6EP}{(h\sigma_y^2)} < 1$$  \hspace{1cm} (2-1)

where $E$ is the elastic modulus, $P$ is the peel force, $h$ is the film thickness, and $\sigma_y$ is the yield stress of the adhered film. For polyimides on copper coatings, the condition in equation (2-1) requires a film thickness greater than 500 $\mu$m, which is larger than most thin films used in microelectronic applications which typically range from 1 to 50 $\mu$m.
To increase the applicability of the peel test, Kim et al.\textsuperscript{16} developed the "Universal Peel Diagram". The adhesion energy, $\gamma_a$, is calculated from the measured force and a known thickness. Use of the diagram requires a description of the stress-strain behavior of the coating and substrate. For many systems used in the microelectronics industry, the adhesion energy is a small percentage of the total applied energy measured during the test. The Universal Peel Diagram is difficult to use since large errors can arise during testing, due to plastic deformation in the test film. Stress-strain curves of the polymer coating are difficult to obtain, which limits the use of the Universal Peel Diagram.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{peel_test_diagram}
\caption{Diagram of Peel Test}
\end{figure}

### 2.3.2 Topple Test

The topple test used by Butler\textsuperscript{18} is closely related to the peel test. As shown in Figure 2-3, a notched bar is attached to the test film. A horizontal force, $F$, is applied to the bar which applies a moment to the film. One leg is in compression and the other is in tension. The force, $F$, is applied until failure occurs between the film and substrate. The main objective of the topple test is to pull the film off the substrate and relate the applied force to a measure of adhesion. The topple test does not recreate the actual failure process which occurs in thin film/substrate systems typically found in MCM use.
2.4 Lap Joint Shear Tests

Single lap shear test is used to determine the shear strength of adhesives for bonding metals. This test is standardized by ASTM19. This test is primarily used to compare shear strength between different adhesives tested under the same loading conditions. It is also used to test the effects of surface treatments on bonding surfaces, and adhesive behavior under static or fatigue loading which can also include thermal cycling and environmental changes. Strength values determined by this test are not to be design parameters, but only a means of comparing strength.

A diagram of the lap shear test is shown in Figure 2-4. The two metal strips are bonded together and the strips are pulled uniaxially in tension until failure, to measure the apparent shear strength of the adhesive. This is a good test for structural adhesives and thin films, but it lacks the ability to measure any fracture parameters.
2.5 Blister Tests

Blister tests inject a gas beneath a coating at the coating-substrate interface and the hydrostatic pressure is increased until the coating begins to peel away from the substrate. The beginning of the peeling action is usually indicated by a discontinuity of the fluid pressure under the film. Dannenberg first reported the use of the standard blister test in 1961\textsuperscript{20}, since then there have been many improvements and variations of the standard blister test. Variations of the standard blister test (SBT) include the constrained blister test (CBT), the island blister test (IBT), and the peninsula blister test (PBT). Figure 2-5 illustrates the standard blister test.

![Figure 2-5. Diagram of the Standard Blister Test](image)

**Figure 2-5. Diagram of the Standard Blister Test**

The constrained blister test, shown in Figure 2-6, was developed because the maximum stress typically occurs in the center of the blister causing the blister to rupture in the center in the SBT. In the CBT, a plate parallel to the substrate reduces the occurrence of rupturing the film at the center of the blister and thus maximum applied stress is at the film-substrate interface. Chang\textsuperscript{21} et al. tested adhesive tape on polycarbonate substrates using the CBT and Lai and Dillard\textsuperscript{22} performed an analysis using elementary plate theory with a finite element analysis.

![Figure 2-6. Diagram of Constrained Blister Test](image)

**Figure 2-6. Diagram of Constrained Blister Test**
Allen and Senturia developed the Island Blister Test (IBT) shown in Figure 2-7. Unlike the SBT and CBT, the IBT accounts for residual stresses in the film and is less likely to tear the film during testing. The geometry of the film has certain analytical advantages because of the axisymmetric conditions, but the fabrication of the test samples is quite difficult. An extensive discussion and analysis of the IBT is done by Sikorski, which includes a finite element analysis and a large amount of test data.

Further improvements on the IBT led to developing the peninsula blister test (PBT). The PBT has many advantages as compared to the previous blister tests: lower stress at the crack tip, constant strain energy release rate, and samples are easier to fabricate. One disadvantage of the PBT is that modeling is more difficult since the axisymmetric conditions of the IBT are gone with the change of the circular island to the rectangular shaped peninsula. Dillard et al. show that the PBT is the most efficient blister test for the reasons listed above, followed by the IBT and then the CBT or the SBT.

Figure 2-7. Diagram of Island Blister Test

Figure 2-8. Diagram of Peninsula Blister Test
2.6 Stress-Corrosion Crack Test

The stress corrosion crack test\(^{28}\) can evaluate the fracture properties by measuring the crack extension from a starter crack in a thin film exposed to various environments. An indentation typically made from a Vickers indenter generates impressions from which cracks originate. The initial cracks are an order of magnitude greater than the film thickness. Test specimens are exposed to environments of dry N\(_2\) gas, ambient air (moderate relative humidity, \(-50\%\)), moist air (high relative humidity, \(-99\%\)), and water. The different environments affect the advancement of the crack. The crack driving force is the residual stress in the film due to processing conditions. The cracks propagate from the original indentation, and the advancing crack can be measured by optical microscopy in the various environments. The crack length measurements are made at various time intervals from a few seconds up to 100 hours. The stress corrosion crack test can be used to compare the crack speed and fracture behavior for different materials in different environments, but the test lacks a fracture mechanics or applied mechanics basis.

2.7 Edge Delamination Test

The edge delamination test (EDT) takes advantage of the residual stresses that develop during processing in the thin film due to the differences in thermal expansion of the film and substrate\(^{29,10}\). Circular holes are etched in the coating on the substrate. The test geometry parameters, illustrated in Figure 2-9, include the hole radius, \(r\); debond length, \(a\); and film thickness, \(h\).

![Figure 2-9. Figure of Edge Delamination Test](image-url)
Cracks grow as the film-substrate is cooled and the stresses in the film create a debond ring, \( a \), around the etched hole in the film. The EDT has several advantages over previously mentioned tests. First, the radius of the etched hole, \( r \), is very small as compared to the size of the substrate. Hundreds of test measurements can be made with one wafer. Second, various hole sizes and surface treatments can be applied to a single wafer, allowing to test different variables on a single wafer. Last, and most important, the test relies on the residual stress in the film to initiate debonding. No external loads are applied during the test. External loading can produce complications during fabricating, testing, and handling test specimens.

### 2.8 Edge Lift-off Test

The edge lift-off test (ELT) was developed from the edge delamination test (EDT). Where the edge delamination test analyzes the debonding of a film around an etched hole, the edge lift-off test analyzes the fracture toughness of the film without any etched patterns. Not having to etch any patterns in the test samples, the ELT samples do not go through the harsh processing conditions required to make the etched hole patterns. Like the EDT, the ELT relies on the residual stress in the film to provide energy to cause a failure/debonding of the film from the substrate. ELT samples are diced squares of the coated substrate, typically 1 cm by 1 cm square. The tensile stress in the film comes from the differences in the coefficient of thermal expansion of the film and substrate and is described in a simplified form by equation (2-2) below.

\[
\sigma_b = \frac{E \Delta \alpha \Delta T}{1 - \nu} \tag{2-2}
\]

The biaxial tensile stress in the film, \( \sigma_b \), arises due to the difference in the thermal expansion of the wafer and substrate, \( \Delta \alpha \), and the change in the temperature incurred during processing, \( \Delta T \). \( E \) and \( \nu \) are the modulus and the Poisson’s ratio of the film. Knowing the tensile stress in the film and applying basic fracture mechanics (explained in detail in Chapter 3), the fracture toughness, \( K_{IC} \), can be obtained with the ELT by knowing only the stress-temperature profile and the thickness of the film. Shown by
equation (2-3) and illustrated in Figure 2-10 is the calculation of the fracture toughness of the film, \( K_{IC} \), using the ELT.

\[
K_{1C} = \sigma_b \sqrt{h/2} \quad (2-3)
\]

Figure 2-10. Diagram of the Edge Lift-off Test

2.9 Modified Edge Lift-off Test

The ELT can be modified to measure the fracture toughness of thin film brittle materials. The Modified Edge Lift-off Test (MELT) is also good for materials that do not generate high tensile stress from the stored energy in order to cause failure. A backing layer is applied on top of the test resin. The backing layer must have a higher failure stress than the test resin, and must be well adhered to the test resin. One big advantage of the MELT is the properties of the test resin are not required to evaluate its fracture toughness. Only the stress-temperature profile of the backing layer needs to be known. Equation (2-3) is also used to calculate the fracture toughness, \( K_{IC} \) of the test resin. In the MELT, the \( \sigma_b \) is the biaxial stress in the backing layer instead of the test film as in the ELT. The backing layer must be significantly thicker than the test film thickness, \( t \gg h \). Figure 2-11 is a diagram of the MELT. The next chapter shows the development of the mathematical model for the MELT, and the test procedures will also be explained in chapter 4.

Figure 2-11. Diagram of the Modified Edge Lift-off Test.
Chapter 3. Analytical and Theoretical Basis

3.1 Introduction

The Modified Edge Lift-off Test (MELT) measures the plane-strain fracture behavior of multilayer, thin, coatings adhered to a rigid substrate by cooling the assembly until fracture occurs. The test consists of applying an epoxy layer on top of the test assembly. The higher coefficient of thermal expansion of the epoxy backing layer creates a tensile stress in the test resin, which is stored as energy. Failure occurs when the applied energy exceeds the fracture energy of the weakest interface, typically between the test film and substrate. With very good adhesion, the test measures the fracture toughness of the coating or the substrate whichever is less.

In a simple form, adhesive failure is predicted when some applied energy exceeds a critical property of the adhesive or adherend, whichever is less. The challenge in designing and measuring adhesion is to establish the details of both the applied energies and the critical performance properties. Difficulties arise in determining performance properties since they are strong functions of processing and environmental conditions. Thus, any test used to measure these must represent the preparation conditions of real multilevel builds. This is especially true for interconnects, since a good amount of work is being done to develop new dielectric materials and integrate them into existing processing methods.

To overcome these complexities the Modified Edge Lift-off Test (MELT) has been developed by Shaffer and applied to testing thin film coatings on rigid substrates. The MELT is well suited to testing thin film microelectronic structures in that it allows samples to be constructed with standard microelectronics processes such as spin-coating, chemical vapor deposition, physical vapor deposition, etching, etc. The primary advantage of the MELT is the simplicity of sample design and ease of testing. Another advantage of the MELT is that it yields true fracture energies of the least tough portion of the multilayer system. Therefore, reliability can be assessed easily with the MELT.

The MELT consists of applying thick epoxy layers to test films that are on a rigid substrate and dicing into samples with edges that are 90° to the interface. The parts are cooled and the stored energy in the epoxy debonds the test resin from the substrate and
the temperature which this occurs is recorded. The backing layer material is chosen to have good adhesion to the test layer and high toughness. Also, the backing layer is much thicker than the test layer since we assume that the energy released is the energy stored in the backing layer. Samples are made and then cooled until the temperature of debonding is observed. From the stress-temperature profile of the epoxy backing layer, the residual stress, $\sigma_0$, in the backing can be determined. The critical fracture energy of the coating layer is calculated by the equation below.

$$K_{IC} = \sigma_0 \sqrt{h/2} \quad (3-1)$$

where $h$ is the backing layer's thickness, and this is derived in section 3.3.

Figure 3-1. Illustration of a Modified Edge Lift-off Test Specimen. The Test Resin Thickness is Thin Compared to the Backing Layer Thickness

3.2 Fracture Mechanics Overview

3.2.1 Stress Analysis Near a Crack

Two different methods are used to mathematically explain the phenomenon of fracture in a structure. The first is based on a stress intensity factor, $K$, and the second is based on a energy balance analysis. The stress intensity factor method will be explained first.
The stress intensity factor, \( K \), is a parameter that quantifies the stress around a crack tip that occurs when a stress is applied to a cracked structure. There are three modes of loading, and they are shown in Figure 3-2. Mode I loading is the opening mode where the applied force is normal to the crack face. Mode II loading is the in-plane shear mode and the applied force is parallel to the crack interface and parallel to the direction of crack propagation. Mode III is the anti-plane shearing mode and the applied stress is parallel to the crack interface and perpendicular to the direction of crack propagation. Typically Mode I loading is encountered in an overwhelming majority of engineering situations. Mode II and Mode III conditions are much less typical and are often neglected in mathematical analysis.

The magnitude of the stress intensity factor is calculated by a stress analysis based on elastic theory shown in equation 3-2. G. Irwin, M. Williams, and H. Westergaard published solutions for crack-tip stress distributions and analyses of the stress intensity factor, \( K \).\(^{30,31}\)

\[
\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta) \tag{3-2}
\]

where \( \sigma_{ij} \) is the local stress at a point near the crack tip, \( r \) is the radial distance from that point to the crack tip, \( \theta \) is the angle of the point from the center line of the crack, and \( f_{ij}(\theta) \) is a geometrical function which is characteristic of the shape of the analyzed specimen (see Figure 3-3).
The stress intensity factor describes the stress field around a crack tip. Fracture occurs when the stress intensity factor reaches a critical level denoted by $K_C$, which is a material property. Westergaard\(^{32}\) showed that the localized stress $\sigma_{ij}$ in equation 3-2 can be related to the applied stress, $\sigma_o$, in the following relation in equation 3-3.

$$\sigma_{ij} = \sigma_o \sqrt{\frac{a}{2r}} f_{ij}(\theta) \quad (3-3)$$

where $a$ is the crack length and $\sigma_o$ is the applied stress (see Figure 3-4).
When the applied stress, $\sigma_o$, causes a failure becomes the failure stress, $\sigma_f$; and the critical stress intensity factor is reached. Combining equation 3-2 and 3-3 into equation 3-4, expresses the critical stress intensity factor, $K_C$, in a relation with the failure stress, $\sigma_f$, the crack length, $a$, and $Y$, a test specimen geometrical factor.

$$K_C = Y\sigma_f \sqrt{\pi a} \quad (3-4)$$

The linear elastic analysis described above explains the fracture of brittle materials accurately and is appropriate for the materials tested in this thesis.

### 3.2.2 Energy Balance

The second method used to describe fracture phenomenon uses an energy balance consideration. Quantitative relations that engineers use today to determine and predict the fracture of a cracked solid was first stated in 1920 by A.A. Griffith. The energy required to propagate a crack a finite distance, $da$, is equivalent to the energy required to create the additional surface area ($\gamma$). The surface energy term, $\gamma$, is the specific surface energy term multiplied by the surface area ($\gamma_s(2a/2t)$, where $a$ is the crack length and $t$ is the specimen thickness. This energy must be balanced by the external work that is applied to the system ($W_{EX}$) minus the energy elastically stored in the system ($U_{EL}$) and the energy dissipated ($W_{DIS}$) through plasticity or viscoelasticity (equ. 3-5):
Griffith used a stress analysis of an elliptical hole in an infinitely large plate (Figure 3-4) by Inglis to relate the decrease in stored elastic energy and applied energy from loading to the increase in energy needed to create a new surface due to the crack (elastic analysis, \( W_{DIS} = 0 \)).

\[
\gamma = \frac{dW_{EX}}{da} - \frac{dU_{EL}}{da} - \frac{dW_{DIS}}{da} \tag{3-5}
\]

where \( \sigma_o \) is the applied stress, \( t \) is the thickness of the plate, and \( E \) is the elastic modulus. (similar to Figure 3-4) At the point of fracture, equation 3-5 and 3-6 simplifies into the widely used equation 3-7.

\[
\sigma_f = \sqrt{\frac{2E\gamma_s}{\pi a}} \tag{3-7}
\]

Orowan modified Griffith's previous work to include a plastic deformation energy term \( (\gamma_p) \). The resulting equation of Griffith and Orowan's work is shown in equation 3-8.

\[
\sigma_f = \sqrt{\frac{2E(\gamma_s + \gamma_p)}{\pi a}} \tag{3-8}
\]

### 3.3 Fracture Mechanics of Multilayer Thin Coatings

Previous work has shown that one parameter characterizing the durability of an interface is the critical strain-energy release rate, \( G_c \), or debond energy. This is the work required to cause an existing flaw to propagate over a unit area of the interface. The strain energy release rate is defined for an elastic system as:

\[
G = \frac{\partial U}{\partial A} \tag{3-9}
\]

where \( U \) is the stored elastic energy and \( A \) is the area of the interface. For a biaxially stressed coating on a rigid substrate the applied strain energy, \( G_b \), for a long, two-dimensional, plane-strain crack is:
\[ G_b = \frac{\sigma_o^2 h (1 - \nu^2)}{2E} \]  
(3-10)

where \( h \) is the film thickness, \( \sigma_o \) is the residual stress in the coating, and \( E \) and \( \nu \) are the Young’s modulus and Poisson’s ratio of the coating.

For multilayer systems the steady-state energy release rate must account for the energy stored and released in each layer. The applied released energy during peeling of \( n \)-layers is:

\[ G_{app} = \sum_{i=1}^{n} \Delta G_i \]  
(3-11)

where \( \Delta G_i \) is the total energy stored in the \( i \)th layer before peeling, less the amount of energy stored after peeling due to the constraint of the other layers. When multiple layers peel it results in a new equilibrium strain, so the final stress (therefore stored energy) in each layer is not necessarily zero. To solve for the final equilibrium strain, \( \varepsilon_f \), we use the condition that the sum of the forces in the plane of the layers must be zero. Where \( E_i \) is the modulus, \( h \) is the thickness, \( \nu \) is the Poisson’s ratio, and \( \varepsilon_o \) is the initial mechanical strain of the \( i \)th layer.

\[ \sum_{i=1}^{n} \frac{E_i h_i (\varepsilon_o,i - \varepsilon_f)}{(1 - \nu_i)} = 0 \]  
(3-12)

So, the final strain \( \varepsilon_f \) is expressed as:

\[ \varepsilon_f = \frac{\sum_{i=1}^{n} \frac{E_i h_i \varepsilon_o,i}{(1 - \nu_i)}}{\sum_{i=1}^{n} \frac{E_i h_i}{(1 - \nu_i)}} = \frac{\sum_{i=1}^{n} \sigma_o,i h_i}{\sum_{i=1}^{n} \frac{E_i h_i}{(1 - \nu_i)}} \]  
(3-13)

Using Hooke’s Law, the steady-state energy release rate for a \( n \)-layer system is:

\[ G_{app} = \sum_{i=1}^{n} \frac{\sigma_o^2_i h_i (1 - \nu_i^2)}{2E_i} - \sum_{i=1}^{n} \left( \frac{\sigma_o,i - \varepsilon_f E_i h_i}{(1 - \nu_i)} \right)^2 \frac{(1 - \nu_i^2)}{2E_i} \]  
(3-14)
When the backing layer thickness is significantly greater than the thickness of the test material, equation 3-14 simplifies to equation 3-10 for the Modified Edge Lift-off Test geometry.

This engineering approach to fracture does not require knowledge of the plane-strain moduli of the multilayers to predict failure. The applied fracture intensity, \( K_{app} \), can be compared to the critical fracture toughness of the system, \( K_c \), when failure occurs. To relate the applied stress intensity to the applied strain energy we treat the \( n \)-layers of materials as a homogenous material with an effective plane-strain modulus, \( E'_{eff} \), defined as:

\[
\frac{1}{E_{eff}} = \frac{1}{h_{tot}} \sum_{i}^{n} \frac{h_i}{E'_{i}} E'_{i} = \frac{E_i}{(1 - \nu_i^2)} \tag{3-15}
\]

Then the applied stress intensity, \( K_{app} \), is:

\[
K_{app} = \sqrt{G_{app} E'_{eff}} \tag{3-16}
\]

Again, when the backing layer thickness is much greater than the test resin thickness the applied stress intensity in equation 3-16 reduces to:

\[
K_{app} = \sigma_o \sqrt{h/2} \tag{3-17}
\]

where, \( h \) and \( \sigma_o \) are the backing layer thickness and residual stress, respectively.
Chapter 4. Experimental Procedures

4.1 Introduction

The Modified Edge Lift-off Test (MELT) is a simple and very accurate test of how thin films fracture. It accurately measures the fracture toughness, $K_{IC}$, of thin film polymeric materials. One great advantage of the MELT is the test can be used to evaluate the $K_{IC}$ of materials without any knowledge of any mechanical properties of the test material. This chapter will focus on the procedures to perform the MELT showing examples of how to calculate the $K_{IC}$ from the test data. The chapter will explain the test method from depositing test materials, applying the epoxy backing layer, running the test, and analyzing debonded test samples.

4.2 Depositing Test Materials

All the materials tested with the Modified Edge Lift-off Test (MELT) used in this thesis were deposited by spin coating techniques. This was done with a Headway Research spin coater. Most were low viscosity mixtures of silicone resins dissolved in organic solvents such as toluene, methyl iso-butyl ketone (MIBK), or dioxane. The resin solution was poured onto a cleaned 100 mm Si (100) wafer and spread at 2000 RPM for 60 seconds, thus leaving behind a thin film of the resin solution. The solid content of the solution controls the film thickness. Adjusting the speed of the spin coating can also vary the film thickness, but in this work, the speed was kept constant and the solid content was changed to vary the film thickness. Typical film thickness of test samples range from $0.1 \times 10^{-6}$ m to $6 \times 10^{-6}$ m.
4.3 Test Procedure and Sample Preparation

4.3.1 Experimental Procedure for Modified Edge Lift-off Test

1. Receive wafers with test film and measure thickness of test resin and wafer.
2. UV-Ozone treat the test film for 20 minutes to promote adhesion with epoxy backing layer.
3. Place UV-Ozone treated wafer onto a vacuum plate to hold the wafer in place when applying the epoxy backing layer.
4. Drawcoat the epoxy layer onto wafer with a BYK Gardner film casting knife.
5. Cure epoxy for one hour at 177°C.
6. If necessary, apply another coating of epoxy if the desired thickness was not obtained.
7. Dice wafers into 1 cm by 1 cm test samples.
8. Label specimens and measure thickness of epoxy backing layer.
10. Load test samples into Cryostage and heat to 125°C to eliminate any stress relaxation that has occurred in the epoxy backing layer (an oven can also be used).
11. Cool at -3°C/min. in Cryostage until debonding is observed.
12. Record temperature at which debonding occurs and calculate fracture toughness, $K_{IC}$.

4.3.2 Ultra Violet-Ozone Surface Treatment

The UV-Ozone machine is used to promote the adhesion between the test resin surface and the epoxy backing layer. The coated wafer should be diced into strips about 1 cm wide. The size of the UV-Ozone machine used here can only accommodate 1 cm wide strips of the wafer. Many UV-Ozone machines can fit whole wafers, and these machines are recommended since it speeds up the time to produce test samples. Dicing is done by taking advantage of the crystal planes of the silicone wafers. Use a diamond scribe to scratch a line in the wafer parallel to the crystal orientation of the wafer. The crystal orientation of the wafer is perpendicular to one of the two flat edges of the wafer, and parallel to the other flat edge. This scratch is used to snap cleave the wafer into strips. Simply put the scratched side of the wafer in tension, and the wafer will break easily.
The UV light bulb is about the same size of a writing pen. In order for the UV-Ozone treatment to be the same over the entire surface of the sample, the width of the sample should not be much greater than the diameter of the UV-light source, since the intensity of the UV-light is indirectly proportional to the square of the distance away from the light bulb. A Pacific Technology Ozone Generator L21 is used to generate 2wt% ozone in the treatment chamber. Ozone is generated by a voltage discharge between ceramic and metal electrodes of the ozone generator. Dry O₂ is flowed into the corona discharge gap between the electrodes. A voltage is applied across the electrode gap at a high frequency which breaks down the O₂ molecule and forms ozone. The voltage across the electrode in the ozone generator is 3.0 V. Pure O₂ is flowed into the Ozone Generator at 5.0 scfm and 6.5 psig. The UV light source is 254 nm wavelength light from a Pen-Ray UV bulb, part number 90-0049-03. The UV light source is rated at 8 mW/cm² at a distance of 1.9 cm from the light source. The treatment chamber is made of standard laboratory glassware with ground glass connections. The experimental setup is shown below in Figure 4-1. Typically samples are treated for 20 minutes.

![Figure 4-1. UV-Ozone Surface Treatment Experimental Setup](image)

### 4.3.3 Application of Epoxy Backing Layer

Measure the thickness of the wafer and test resin with a micrometer. The backing layer material is draw-coated onto the UV-Ozone treated test resin. Figure 4-2 shows how the epoxy backing layer is applied to the test resin. The drawknife blade is set at a certain height above the test resin surface; the distance is the intended thickness of the backing layer. The epoxy backing layer material is specially formulated to provide good adhesion and wetting to a variety of test resins, and to input sufficient energy to cause a failure. The stress-temperature profile for the epoxy is determined for each batch of epoxy backing material made. The stress-temperature curve is determined by a Tencor
Flexus machine, which measures the change in the curvature of a coated wafer as a function of temperature. Stress vs. temperature profiles are used to calculate the stress in the epoxy, $\sigma$, at various temperatures. Figure 4-3 shows a stress temperature profile for the epoxy backing material used in this thesis. This epoxy is provided by Dow Chemical Co$^{37}$ and is called Beta 21 Epoxy.

Figure 4-2. Application of Epoxy Backing Layer

![Epoxy Backing Layer Diagram](image)

![Stress-Temperature Profile Graph](image)

\[ \sigma = 21.5 - 0.255T - 0.0003T^2 \]

Figure 4-3. Stress-Temperature Profile of Epoxy Backing Layer on a Si Wafer
The thickness of the backing layer is chosen such that sufficient stress intensity is applied to cause failure at a reasonable temperature. The residual stress for the epoxy backing material on a silicon wafer as a function of temperature is shown in Figure 4-3. For example, the fracture toughness of 4-3136 is 0.301 MPa*m$^{1/2}$, a 200 μm backing layer of should induce failure by -50°C because of the applied stress of 33.5 MPa, see Figure 4-4. If the epoxy is used for an unknown test resin, test procedures are explained further on page 39 and in Figure 4-5.

![Figure 4-4. Failure Envelope of 4-3136 MELT Specimens.](image)

The epoxy backing material is applied to the wafer by draw coating. It is recommended that a vacuum plate be used to hold in place the sample that is to be coated with epoxy. The epoxy is applied with a BYK Gardner film casting knife. The film casting knife has an adjustable blade that looks similar to a guillotine. Coating thickness typically ranges from 50 μm to 300 μm. The epoxy backing material is cured for one hour at 177°C in air. If necessary, multiple layers of epoxy can be applied to obtain the desired thickness if the first layer is too thick.
If the $K_{ic}$ of the test resin is unknown, it is recommended that the wafer be diced into four pieces, to avoid coating the entire wafer before testing. Coat the first sample with 100 µm of epoxy. If a test sample is immersed in LN$_2$ and no failure is observed, then the epoxy backing layer is not thick enough. A thicker layer should be applied to the next sample. If the sample breaks during the dicing procedure, the next sample may need a thinner backing layer. Finding the appropriate thickness for the backing layer is an iterative process. The best way to start is to estimate the fracture toughness, and estimate an appropriate backing layer thickness that will cause a failure between -25°C and -50°C. See Figure 4-5 to estimate the thickness of epoxy backing layer material according to an estimate of the test resin fracture toughness and desired failure temperature.
4.3.4 Dicing Samples

MELT samples should be 1 cm by 1 cm. Taking advantage of the crystal planes, use a diamond scribe to scratch the Si wafer and snap cleave the samples. Simply put the scratched side of the wafer in tension, and the wafer will break very easily. If the epoxy backing layer is too thick, usually above 250 μm, when attempting to snap cleave the coated wafer, the epoxy may debond the test resin from the wafer or crack the wafer. Special care must be taken not to ruin the sample.

The disadvantage of silicon wafers is that they are brittle, $K_{IC} \approx 0.7 \text{ MPa} \cdot \text{m}^{1/2}$. Coatings with a fracture toughness higher then 0.7 MPa·m$^{1/2}$ should not be tested on a silicon substrate. In this case, it is recommended that alumina substrates be used. The fracture toughness of alumina is 4 MPa·m$^{1/2}$. However, alumina test samples must be cut with a diamond saw. Note that a diamond saw uses cooling fluids (water with glycol) which may affect the interfacial adhesion or toughness of the coating.

4.3.5 Polishing Samples

After applying the epoxy backing layer and dicing the MELT samples, the epoxy at the edge is often uneven or not perpendicular to the edge. This is mostly caused by the epoxy flowing over the edge during curing before it hardens. These edges must be polished off on a grinding wheel using silicon nitride grinding paper without any lubricant such as water. Figure 4-6 shows a side view of a sample before and after polishing. Special care must be taken to make sure that the edges are 90° vertical to the bottom and top surfaces as not to affect the geometry of the test. This polishing process greatly improves the yield of the number of specimens that provide valid and useful test results. Samples that develop a small amount of delamination at the wafer edge as they are diced can also be polished in order to make more samples. The small area of delamination that occasionally occurs as the samples are made can be removed by polishing the sample past the zone of delamination in order to get a testable sample.
4.4 Cryostage

The Cryostage is designed to cool samples with nitrogen gas from a liquid nitrogen tank via convection. Convection cooling is chosen because of the even cooling of the samples as compared to other heat-transfer methods. Liquid nitrogen gas and dry nitrogen gas are mixed using a cryogenic valve, and then passed through a heat exchanger with heating elements to control the temperature. The chilled N₂ gas is then purged into the sample chamber, see Figure 4-7. Specimens rest in the sample chamber with a glass cover to view the samples as they are cooled. An Omega Engineering controller is used to control both the cryogenic valve and to power the heating elements.
The specimens are placed into the sample chamber for testing. They are first heated to 125°C to avoid any stress-relaxation discrepancies in the backing layer. The samples can also be heated in an oven to 125°C and cooled slowly since the heating element feedback loop of the cryostage controller is often difficult to control. The samples are then cooled at 3°C/min which is the same rate as the stress-temperature profile of the epoxy backing material is calibrated at and is shown in Figure 4-3. The specimens are monitored until delamination is observed visually. The temperature at the time of failure is noted. This is continued until all samples have failed or until the minimum temperature of the cryostage is reached. A good debonding from a MELT run should look like the samples in Figure 4-8.
4.5 Calculating the $K_{IC}$ from MELT

The test has been run and the temperature at which debonding occurred is recorded. The stress in the epoxy backing layer, $\sigma_o$, is calculated using the equation in Figure 4-3, and the fracture toughness, $K_{IC}$, is calculated using equation 4-1. Table 4-1 shows how to calculate the $K_{IC}$ from the test data.

$$K_{IC} = \sigma_o \sqrt{h/2} \quad (4-1)$$

**Table 4-1. Example of $K_{IC}$ Calculation from Modified Edge Lift-off Test**

<table>
<thead>
<tr>
<th>Test Resin Thickness $(10^{-6} \text{ m})$</th>
<th>Epoxy Backing Layer Thickness $(10^{-6} \text{ m})$</th>
<th>Failure Temperature $(^\circ \text{C})$</th>
<th>Stress in Epoxy Backing Layer (MPa)</th>
<th>$K_{IC}$ (MPa$\times$m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>158</td>
<td>-51</td>
<td>34.53</td>
<td>0.307</td>
</tr>
<tr>
<td>2.4</td>
<td>200</td>
<td>-75</td>
<td>40.65</td>
<td>0.407</td>
</tr>
<tr>
<td>2.4</td>
<td>244</td>
<td>-35</td>
<td>30.44</td>
<td>0.336</td>
</tr>
<tr>
<td>2.4</td>
<td>255</td>
<td>-33</td>
<td>29.93</td>
<td>0.338</td>
</tr>
<tr>
<td>2.4</td>
<td>280</td>
<td>-36</td>
<td>30.70</td>
<td>0.350</td>
</tr>
<tr>
<td>2.4</td>
<td>265</td>
<td>-5</td>
<td>22.79</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td></td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S.D.</td>
<td></td>
<td>0.048</td>
</tr>
</tbody>
</table>
4.6 Failure analysis of MELT samples

Three main types of failure can occur during the MELT. The first is a cohesive failure of the test resin, as shown in Figure 4-9; the second is an adhesive failure between the test resin and the substrate, as shown in Figure 4-10. The last is an adhesive failure between the test resin and the epoxy backing layer. The last is unlikely if the test resin surface treatment with the UV-Ozone machine is done properly. An adhesion failure between the test resin and the epoxy backing layer can be easily identified with a steel razor blade which can scratch the test resin atop the substrate if any of the test resin is left after the epoxy backing layer is removed.

![Figure 4-9. Cohesive Failure in Test Resin](image)

![Figure 4-10. Adhesive Failure at the Test Resin and Substrate Interface](image)
A *Gaertner Scientific* three wavelength variable angle ellipsometer was used to analyze the failure of MELT samples. After a sample has been tested, and a failure has been recorded, the backing layer is then removed. The quickest way to see if there is any test resin adhered to the substrate surface is to scratch the substrate with a steel razor blade, or something that will scratch the test resin, but not the substrate. If you see a scratch, then there is definitely some test resin left on the substrate surface. If no scratch is seen, then there is either no test resin left on the substrate surface or there is such a thin amount that a visible scratch is not created. After the epoxy backing layer is pulled off from the used MELT specimen and a scratch is not visible there is still a question whether the failure is cohesive in the test resin or adhesive between the test resin and the substrate. An ellipsometer is used to check if any of the test resin remains on the substrate after the epoxy backing layer is peeled off.

The *Gaertner Scientific* ellipsometer is not able to accurately measure films less than 100 Å thick. The ellipsometer often does not accurately measure the fracture surfaces if the surface is rough. Fracture surfaces are often not smooth, which can disrupt the reflection of the incident light beam of the ellipsometer. Films thinner than 100 Å or films with a rough non-reflecting or non-transmitting surface can be difficult to measure. Occasionally the ellipsometer may return "No Answer" for a measurement of the thickness and index of refraction. Another possibility is the ellipsometer will ask the user to input a value for the index of refraction ($N_f$) because the algorithm cannot make a calculation for the thickness and index of refraction based on the obtained data.

The data in Table 4-2 shows the results of using the ellipsometer to identify the failure type of two 4-3136 MELT specimens. Eight measurements were taken of the first sample. Three times (data labeled 1-1 to 1-3 in Table 4-2) the returned answer from the ellipsometer was "No Answer". One measurement (1-4) required an input of the index of refraction to calculate a thickness of 81 Å. Four other measurements (1-5 to 1-8) returned a measured index of refraction and thicknesses of approximately 150 Å. The second sample was measured five times and returned a measured value of the index of refraction and thickness values of 1900 Å. One measurement (2-1) did require a fixed value of the index of refraction.
To summarize the data in Table 4-2, the ellipsometer data did show that a certain thickness of the test resin was left after the epoxy backing layer was removed. These measured thickness values are about one-tenth of the original test resin thickness. The index of refraction values may be a little inaccurate due to the rough surface of the samples. The average index of refraction (N_f) for 4-3136 is 1.53. This test data verifies that some of the test resin is adhered to the substrate and the failure measured in the MELT is a cohesive failure (Figure 4-9) in the test resin and not an adhesion failure (Figure 4-10) between the test resin and the substrate.

<table>
<thead>
<tr>
<th>Test Resin - Sample # - Measurement #</th>
<th>Measured Index of Refraction</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-3136-1-1</td>
<td>No Answer</td>
<td>No Answer</td>
</tr>
<tr>
<td>4-3136-1-2</td>
<td>No Answer</td>
<td>No Answer</td>
</tr>
<tr>
<td>4-3136-1-3</td>
<td>No Answer</td>
<td>No Answer</td>
</tr>
<tr>
<td>4-3136-1-4</td>
<td>1.53 (fixed)</td>
<td>81</td>
</tr>
<tr>
<td>4-3136-1-5</td>
<td>1.273</td>
<td>131</td>
</tr>
<tr>
<td>4-3136-1-6</td>
<td>1.311</td>
<td>141</td>
</tr>
<tr>
<td>4-3136-1-7</td>
<td>1.145</td>
<td>182</td>
</tr>
<tr>
<td>4-3136-1-8</td>
<td>1.177</td>
<td>163</td>
</tr>
<tr>
<td>4-3136-2-1</td>
<td>1.53 (fixed)</td>
<td>398</td>
</tr>
<tr>
<td>4-3136-2-2</td>
<td>1.363</td>
<td>2011</td>
</tr>
<tr>
<td>4-3136-2-3</td>
<td>1.298</td>
<td>1293</td>
</tr>
<tr>
<td>4-3136-2-4</td>
<td>1.375</td>
<td>1969</td>
</tr>
<tr>
<td>4-3136-2-5</td>
<td>1.358</td>
<td>2053</td>
</tr>
</tbody>
</table>
Chapter 5. Results and Conclusions

5.1 Introduction

This chapter shows the fracture toughness values obtained from the Modified Edge Lift-off Test (MELT) of the silicone resins tested in this thesis. The experimental procedure for the MELT is explained in Chapter 4. The compositions of the silicone resins tested are shown below. Index of refraction measurements of the films are also summarized in section 5.8 of this chapter.

5.2 Materials Tested

Here is a listing of the silicone resins tested in this thesis. Nuclear Magnetic Resonance and Infrared Analysis performed at the Dow Corning Corporation in Midland, Michigan was used determined the compositions of the silicone resins listed below.

*Dow Corning 4-3136:*
(\(\text{MeSiO}_{3/2}\))_{0.45}(\(\text{PhSiO}_{3/2}\))_{0.40}(\(\text{Ph}_2\text{SiO}_{2/2}\))_{0.10}(\(\text{PhMeSiO}_{2/2}\))_{0.05}

*Dow Corning 4-3136 with Phase I Rubber:*
100 parts (\(\text{MeSiO}_{3/2}\))_{0.45}(\(\text{PhSiO}_{3/2}\))_{0.40}(\(\text{Ph}_2\text{SiO}_{2/2}\))_{0.10}(\(\text{PhMeSiO}_{2/2}\))_{0.05} and 10 parts KPE PDMS (Polydimethylsiloxane) Phase I Rubber (DP=55)

*Dow Corning 4-3136 with Phase I and II Rubber:*
100 parts (\(\text{MeSiO}_{3/2}\))_{0.45}(\(\text{PhSiO}_{3/2}\))_{0.40}(\(\text{Ph}_2\text{SiO}_{2/2}\))_{0.10}(\(\text{PhMeSiO}_{2/2}\))_{0.05} and 10 parts KPE PDMS Phase I Rubber and 5 parts Silanol Terminated PDMS Phase II Rubber (DP=245)

*Dow Corning* MetFlex Methyl-T Silicone Resin: referred to as MF1.
(\(\text{MeSiO}_{3/2}\))_{86}(\(\text{Me}_2\text{SiO}_{2/2}\))_1[\(\text{MeSiO}_{2/2}(\text{OH})\])_{13}

*Dow Corning* MetFlex Methyl-T Silicone Resin, Lot#15846-28: referred to as MF2.
(\(\text{MeSiO}_{3/2}\))_{86}(\(\text{Me}_2\text{SiO}_{2/2}\))_1[\(\text{MeSiO}_{2/2}(\text{OH})\])_{13}(\text{O}_{2/2}\text{MeSiC}_6\text{H}_4\text{SiMeO}_{2/2})_5

*Dow Corning* MetFlex Methyl-T Silicone Resin, Lot#15846-7: referred to as MF3.
(\(\text{MeSiO}_{3/2}\))_{86}(\(\text{Me}_2\text{SiO}_{2/2}\))_1[\(\text{MeSiO}_{2/2}(\text{OH})\])_{13}(\text{O}_{1/2}\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{O}_{1/2})_5

*Dow Corning* Experimental X1-2672 Silicone Resin:
(\(\text{PhSiO}_{3/2}\))_{0.75}(\(\text{MeViSiO}_{1/2}\))_{0.25}

*Wacker Silicones* MK Powdered Silicone Resin:
A methyl-T silicone resin.
5.3 Modified Edge Lift-off Test Results of 4-3136 Resin

5.3.1 Various Thickness of Neat 4-3136

*Dow Corning*'s 4-3136 silicone resin was deposited onto Si wafers using a *Headway Research* spin coater. The resin was dissolved in a solution of MIBK (Methyl Isobutyl Ketone). Varying the solid content of the resin solution prior to spin coating controls the thickness of 4-3136 coatings. The spin coating and curing conditions are the same for all 4-3136 MELT samples listed in Table 5-1. All 4-3136 samples were spin coated at 2000 RPM for 60 seconds. All were cured by soft baking at 75°C to remove the majority of the solvent then cured at 275°C for one hour in an air-circulating oven. Heating the samples up to 275°C and cooling down to room temperature was done at slow rates, typically less than 5°C/min.

High quality films; films without cracks, thickness variations, or particles; can be obtained using MIBK as the solvent with neat 4-3136 (without phase I or phase II rubber). The thickest films that have been made with neat 4-3136 are just over 5 μm, using a solid content of 55wt% of 4-3136 in MIBK. Thin films were made with neat 4-3136 with a range in thickness from 0.2 to 5.0 μm by varying the solid content of the resin solution and spin coating the resin at 2000 RPM for 60 seconds.

The thickness of the epoxy backing layer for the MELT specimens tested ranges from 100 to 300 μm. As expected, the thicker the epoxy backing layer, the higher the temperature at which debonding occurred during testing. The average K<sub>IC</sub> of 4-3136 is 0.301 MPa·m<sup>1/2</sup>. Table 5-1 shows the MELT results of 4-3136 with thickness ranges from 0.22 to 2.40 μm. The data in Table 5-1 is also shown in Figure 5-1.
Table 5-1. MELT Data of Neat 4-3136

<table>
<thead>
<tr>
<th>Thickness (10^-6 m)</th>
<th>Solid Content (wt%)</th>
<th>Number of Data Points</th>
<th>Fracture Toughness, Kic (MPa*m^1/2)</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>11</td>
<td>5</td>
<td>0.282</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>0.67</td>
<td>20</td>
<td>21</td>
<td>0.288</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>1.26</td>
<td>30</td>
<td>12</td>
<td>0.324</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>2.40</td>
<td>40</td>
<td>14</td>
<td>0.309</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>52</td>
<td>0.301</td>
<td>0.027</td>
<td></td>
</tr>
</tbody>
</table>

Note: Spin coating speed was kept constant at 2000 RPM for 60 seconds. Resins were all cured for one hour in air at 275°C.

Figure 5-1. MELT Data of 4-3136 of Various Thicknesses

Average $K_c$ of 4-3136 from MELT is 0.301 MPa*m^{1/2}

Error Bars Represent One Standard Deviation
5.3.2 Phase I and Phase II Toughened 4-3136

As discussed in Chapter 1, 4-3136 can be modified with phase I and phase II PDMS rubber to increase the fracture toughness. Triethoxy silyl terminated PDMS (KPE) with a degree of polymerization of 55 is pre-reacted into the 4-3136 resin to form phase I rubber segments. The phase I rubber does not form a second phase particle, but the PDMS rubber is incorporated into the three dimensional network of the silicone resin. This enhances the flexibility of the polymer network. Second phase particles, called phase II rubber, are created by longer chain PDMS with a degree of polymerization of 245. The second phase particles form when the resin is cured. Phase II rubber particles are used to increase the fracture toughness and flexibility of a polymer.

Phase I toughened 4-3136 is also similar to neat 4-3136 in the manner of depositing the films. Both dioxane and MIBK were used as solvents with the phase I toughened 4-3136. Using a solid content of 40wt% in MIBK, a crack free film 6.1 μm thick film can be made. Thin films were made with phase I modified 4-3136 with a range in thickness from 2.0 to 5.0 μm by varying the solid content of the resin solution and spin coating the resin at 2000 RPM for 60 seconds.

Depositing phase I and phase II rubber toughened 4-3136 films is somewhat challenging and difficult. Due to the phase II rubber forming second phase particles as the resin cures, the film is opaque and difficult to inspect under a microscope. As uncured resin, the phase II rubber will separate from the rest of the mixture while in solution if the mixture is not kept mixed together. The toughened resin is dissolved in toluene with a solid content of 37.5wt%. To obtain a good and testable film, first mix up the resin solution and get an even dispersion of the phase II rubber in the solution, and pour onto a cleaned wafer in the spin coater. Slowly turn up the spin coater from 0 to 300 RPM and hold at 300 RPM for 10 seconds to spread the resin. Over the next five seconds, turn the speed up to 2000 RPM, and hold there for 40 seconds. Figure 5-2 shows the spin coating cycle used to deposit the phase I and phase II toughened 4-3136.
Figure 5-2. Spin Coating Speeds Used to Deposit Phase I and Phase II Rubber Modified 4-3136.

Table 5-2 shows the results of rubber toughened 4-3136 fracture toughness values from the Modified Edge Lift-off Test. Unmodified 4-3136 has a measured fracture toughness, $K_{IC}$, of 0.301 MPa*m$^{1/2}$. Adding 10 parts of phase I PDMS rubber, degree polymerization (DP) of 55, increases $K_{IC}$ to 0.402 MPa*m$^{1/2}$. Adding 5 parts of phase II PDMS rubber with DP of 245 in addition to 10 parts of phase I PDMS rubber further increases the $K_{IC}$ to 0.522 MPa*m$^{1/2}$.

Table 5-2. MELT Data for Unmodified and Modified 4-3136.

<table>
<thead>
<tr>
<th></th>
<th>Thickness (10^{-6}m)</th>
<th>Solvent Used</th>
<th>PDMS Rubber Content (DP=55)*</th>
<th>PDMS Rubber Content (DP=245)*</th>
<th>Averages Fracture Toughness $K_{IC}$ (MPa*m$^{1/2}$)</th>
<th>Standard Deviation (MPa*m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>0.2-2.4</td>
<td>MIBK</td>
<td>0</td>
<td>0</td>
<td>0.301</td>
<td>0.027</td>
</tr>
<tr>
<td>Phase I Modified</td>
<td>5.0-6.1</td>
<td>MIBK, Dioxane</td>
<td>10</td>
<td>0</td>
<td>0.402</td>
<td>0.029</td>
</tr>
<tr>
<td>Phase I and Phase II Modified</td>
<td>2.32</td>
<td>Toluene</td>
<td>10</td>
<td>5</td>
<td>0.522</td>
<td>0.025</td>
</tr>
</tbody>
</table>

DP is the degree of polymerization of PDMS (polydimethylsiloxane) silicone rubber additive.
5.4 Comparing 4-3136 MELT Data with Bulk Sample Data

To show the applicability of the MELT, a comparison is shown with the fracture toughness values obtained from the MELT and bulk material property testing. The MELT accurately tests the fracture of thin films, whereas one can reason that bulk material testing may not accurately measure the fracture toughness of thin films due to the differences in thickness (~1 μm thickness for the MELT, and ~5 mm for a bulk sample).

The bulk material properties where obtained using ASTM Standard D 5045, Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials. These test results were obtained from Zhu’s Ph.D. work. This test is a three point bending test of a single edge notch rectangular beam with an existing sharp crack about half way through the beam thickness. The fracture toughness, $K_{IC}$, is calculated by equation 5-1. The geometry used to test the bulk fracture toughness is shown in Figure 5-3.

$$K_{IC} = \left(\frac{P_{MAX} S}{B W^{1.5}}\right) f(Y)$$  \hspace{1cm} (5-1)

where:
- $P_{MAX} = \text{max force applied to advance a crack}$
- $S = \text{support span length}$
- $B = \text{specimen thickness}$
- $W = \text{specimen width}$
- $f(Y) = \text{geometrical factor based on the initial crack length and beam width}$

![Diagram of ASTM Standard D5045, Three Point Bend Test for Fracture Toughness, $K_{IC}$](image)

Figure 5-3. Diagram of ASTM Standard D5045, Three Point Bend Test for Fracture Toughness, $K_{IC}$. 

52
The $K_{IC}$ values measured with the MELT are similar to the values obtained from bulk samples. Figure 5-4 and Table 5-3 show the $K_{IC}$ of unmodified 4-3136, 4-3136 with phase I PDMS rubber and 4-3136 with phase I and phase II PDMS rubber.

### Table 5-3. MELT and Bulk Fracture Toughness Measurements of 4-3136

<table>
<thead>
<tr>
<th>4-3136 Modified Resin</th>
<th>MELT Samples</th>
<th>Bulk Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Rubber Content (phr)</td>
<td>Average $K_{IC}$ (MPa$\cdot$m$^{1/2}$)</td>
</tr>
<tr>
<td>Unmodified</td>
<td>0</td>
<td>0.309</td>
</tr>
<tr>
<td>Phase I only</td>
<td>10</td>
<td>0.402</td>
</tr>
<tr>
<td>Phase I and Phase II</td>
<td>15</td>
<td>0.522</td>
</tr>
</tbody>
</table>

Figure 5-4. Comparison of $K_{IC}$ Measurements of MELT and Bulk Samples
Other than the geometry of the samples, another difference in the MELT samples and the bulk material samples is how the materials are cured. The thin films used for the MELT are cured in a matter of hours, normally heated from room temperature to 275°C at a rate of 4-5°C/min., and held there for one hour, then cooled to room temperature at a rate of 4-5°C/min. The bulk samples are cured with a 13-day cure cycle. Heating slowly over a course of 12 days to 260°C and held there for 8 hours, then cooled slowly. When thick samples (> 5 mm) of these silicone resins are made, heating must be done slowly to evaporate the solvent. If the heating cycle is done too quickly, the resin will harden before the solvent is completely evaporated, trapping the solvent in the casting and creating small voids. These small voids greatly decrease the strength and fracture toughness of the bulk material. Evaporating the solvent of thin films is easier than bulk samples because most of the solvent evaporates during spin coating and the thickness difference is two to three orders of magnitude smaller. The differences in the MELT values and the bulk material values are small and the experimental errors of the tests can account for some of the differences in the average $K_{IC}$ obtained from testing. The differences in the curing of the two different test geometries can also account for some of the differences.

The phase I and phase II materials used in the bulk materials are somewhat different than the materials used in the thin films. The phase I and phase II rubbers used in the bulk samples and the thin films are both PDMS. The results of the MELT and bulk fracture toughness tests show that the difference in the fracture toughness is not significant and the different phase I and phase II materials may be used interchangeably. See Table 5-4 for explanations of the materials used for phase I and phase II rubbers with 4-3136.

**Table 5-4. Listing of Phase I and Phase II Materials Used**

<table>
<thead>
<tr>
<th></th>
<th>MELT Samples</th>
<th>Bulk Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase I Rubber</td>
<td>Phase II Rubber</td>
</tr>
<tr>
<td>Rubber Type</td>
<td>KPE PDMS</td>
<td>PDMS</td>
</tr>
<tr>
<td>DP</td>
<td>55</td>
<td>245</td>
</tr>
<tr>
<td>Termination</td>
<td>Tri-Ethoxy</td>
<td>Silonal</td>
</tr>
</tbody>
</table>
5.5 MELT Results of MetFlex Resins

MetFlex resins are methyl-T silicone resins. The three resins tested are MF1, MF2, and MF3. Their compositions are explained in Section 5.2. The MetFlex resins were all dissolved in MIBK. The thickest film without cracks can be obtained by depositing a solid content solution of 50 wt% leaving a film 3 μm thick by spin coating at 2000 RPM for 60 seconds.

5.5.1 Effects of Curing Temperature

MetFlex, a potential interlayer dielectric material, was subjected to different curing conditions to simulate many of the different temperatures that occur during processing of typical multi-layer chip modules. Curing temperatures for MF1 and MF2 range from 275°C to 450°C. Curing at 275°C was done in an air-circulating oven. Curing for MF1 and MF2 at temperatures above 275°C was done in a high temperature furnace with a controlled atmosphere of argon. This high temperature furnace is typically used to process ceramics. The large furnace that was used has a bulky metal structure that does not heat or cool quickly. The ramp rates available with this furnace are quite slow, approximately 4°C/min. for heating and 2°C/min. for cooling. This does not mimic many of the processing conditions used in multi-layer builds were ramp rates occur as high as a 100°C/min. Although the ramp rates are not fast as typically seen in processing conditions for multi-layer builds, the maximum curing temperature does have a significant effect on the fracture toughness of the silicone resins. MetFlex resin MF1 and MF2 cured at 275°C have a $K_{IC}$ of 0.306 MPa*m$^{1/2}$, while raising the curing temperature to 400°C decreases the $K_{IC}$ to 0.171 MPa*m$^{1/2}$.

MetFlex MF3 was cured in a nitrogen atmosphere furnace at Dow Corning Corporation in Midland, Michigan. Heating and cooling rates for these films was kept at ±5°C/min to match the rates used to cure the MF1 and MF2 films. The films made of MF3 were deposited by spin coating at 2000 RPM for 60 seconds, the same as MF1 and MF2. MF3 has a much lower fracture toughness value as compared to MF1 and MF2.
when cured at similar temperatures. As shown in Table 5-5 and Figure 5-5, MF3 cured at 400°C has a $K_{IC}$ value of 0.112 MPa*m$^{1/2}$, where the $K_{IC}$ of MF1 and MF2 is 0.171 MPa*m$^{1/2}$.

Three versions of the MetFlex resin were tested and the compositions are shown in section 5.2. The MELT test procedures are explained in chapter 4. MELT results are shown in Table 5-5 and Figure 5-5. These tests show that increasing the curing temperature decreases the fracture toughness, $K_{IC}$.

### Table 5-5. MELT Measurements of MetFlex Silicone Resins

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing Temperature</th>
<th>Curing Environment</th>
<th>Thickness</th>
<th>Fracture Toughness, $K_{IC}$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(10$^{-3}$ m)</td>
<td>(MPa* m$^{1/2}$)</td>
<td>(MPa* m$^{1/2}$)</td>
<td></td>
</tr>
<tr>
<td>MetFlex–MF1</td>
<td>275</td>
<td>Air</td>
<td>0.86</td>
<td>0.306</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex–MF1</td>
<td>325</td>
<td>Argon</td>
<td>2.24</td>
<td>0.301</td>
<td>0.021</td>
</tr>
<tr>
<td>MetFlex–MF1</td>
<td>385</td>
<td>Argon</td>
<td>0.49-2.33</td>
<td>0.159</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex–MF1</td>
<td>400</td>
<td>Argon</td>
<td>0.51</td>
<td>0.171</td>
<td>0.020</td>
</tr>
<tr>
<td>MetFlex–MF1</td>
<td>450</td>
<td>Argon</td>
<td>0.49</td>
<td>0.143</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex–MF2</td>
<td>275</td>
<td>Air</td>
<td>0.21</td>
<td>0.289</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex–MF2</td>
<td>400</td>
<td>Argon</td>
<td>0.23</td>
<td>0.172</td>
<td>0.008</td>
</tr>
<tr>
<td>MetFlex–MF3</td>
<td>300</td>
<td>Nitrogen</td>
<td>0.58-1.07</td>
<td>0.141</td>
<td>0.011</td>
</tr>
<tr>
<td>MetFlex–MF3</td>
<td>400</td>
<td>Nitrogen</td>
<td>0.55-1.09</td>
<td>0.112</td>
<td>0.006</td>
</tr>
</tbody>
</table>
5.5.2 Comparison of MF1, MF2 and MF3

The composition of MF1 is \((\text{MeSiO}_{2/2})_{86}(\text{Me}_2\text{SiO}_{2/2})_1[\text{MeSiO}_{2/2}(\text{OH})]_{13}\) and MF2 is the same as MF1 with the addition of 5 parts of a \(\text{(O}_{2/2}\text{MeSiC}_6\text{H}_4\text{SiMeO}_{2/2})\) crosslinker. The crosslinker was added to improve the mechanical properties of the cured resin. The addition of the crosslinker does not improve the fracture toughness, \(K_{IC}\), but it does not decrease the \(K_{IC}\) either, see Table 5-6 and Figure 5-5.

The composition of MF3 is very similar to MF2, both with the same base structure of MF1 but the crosslinker is a little different. The crosslinker in MF3 is \((\text{O}_{1/2}\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_{2/2}\text{O}_{1/2})\), where the crosslinker in MF2 is \((\text{O}_{2/2}\text{MeSiC}_6\text{H}_4\text{SiMeO}_{2/2})\). The only difference is in the number of oxygen and methyl groups. By adding the crosslinker in MF3, the \(K_{IC}\) decreases by 35% from 0.172 MPa*m^{1/2} to 0.112 MPa*m^{1/2}, when comparing with MF1 and MF2 samples cured at 400°C. (See Table 5-6)
### Table 5-6. MELT Measurements of Similar Cured MF1, MF2, and MF3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing Temperature</th>
<th>Curing Environment</th>
<th>Fracture Toughness, $K_{IC}$ (MPa* m$^{1/2}$)</th>
<th>Standard Deviation (MPa* m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetFlex-MF1</td>
<td>275</td>
<td>Air</td>
<td>0.306</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex-MF2</td>
<td>275</td>
<td>Air</td>
<td>0.289</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex-MF3</td>
<td>300</td>
<td>Nitrogen</td>
<td>0.141</td>
<td>0.011</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>400</td>
<td>Argon</td>
<td>0.171</td>
<td>0.020</td>
</tr>
<tr>
<td>MetFlex-MF2</td>
<td>400</td>
<td>Argon</td>
<td>0.172</td>
<td>0.008</td>
</tr>
<tr>
<td>MetFlex-MF3</td>
<td>400</td>
<td>Nitrogen</td>
<td>0.112</td>
<td>0.006</td>
</tr>
</tbody>
</table>

### 5.6 Comparison of 4-3136, MetFlex and MK-Wacker Silicone Resins

*Wacker Silicones Corporation* makes a silicone resin somewhat similar to *Dow Corning* 4-3136 and MetFlex silicone resins. This resin is MK-powdered silicone resin that is commercially available from *Wacker Silicones* in Adrian, Michigan. This resin was dissolved in MIBK and deposited onto silicone wafers just as 4-3136 and MetFlex were done. Wacker-MK silicone resin MELT results are shown in Table 5-7 along with MELT results of 4-3136 and MetFlex for comparative purposes. The $K_{IC}$ of Wacker-MK is 0.345 MPa*m$^{1/2}$, which is 12% higher than the $K_{IC}$ of neat 4-3136 and MetFlex cured at the same temperature.

### Table 5-7. MELT Results of 4-3136, MetFlex and Wacker-MK Silicone Resins

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (10$^{-6}$m)</th>
<th>Fracture Toughness $K_{IC}$ (MPa* m$^{1/2}$)</th>
<th>Standard Deviation (MPa* m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat 4-3136</td>
<td>0.2-2.4</td>
<td>0.301</td>
<td>0.027</td>
</tr>
<tr>
<td>4-3136 with Phase I PDMS</td>
<td>5.1-6.1</td>
<td>0.402</td>
<td>0.029</td>
</tr>
<tr>
<td>4-3136 with Phase I &amp; II PDMS</td>
<td>2.32</td>
<td>0.522</td>
<td>0.025</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>0.86</td>
<td>0.306</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex-MF2</td>
<td>0.21</td>
<td>0.289</td>
<td>0.019</td>
</tr>
<tr>
<td>MetFlex-MF3*</td>
<td>0.58-1.07</td>
<td>0.141</td>
<td>0.011</td>
</tr>
<tr>
<td>Wacker-MK</td>
<td>0.54-1.31</td>
<td>0.345</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Note: Spin coating speed was kept constant at 2000 RPM for 60 seconds. Resins were all cured for one hour in air at 275°C, except for MF3. *MF3 was cured at 300°C for one hour in Nitrogen.*
5.7 X1-2672 Experimental Silicone Resin

There are no MELT results for X1-2672 silicone resin. X1-2672 is an addition cure resin. Thin films of this resin could not be made with conventional spin coating techniques. One problem is the reactivity and the vapor pressure of the crosslinkers that were used to cure this resin. The vapor pressure of the crosslinkers is so low that while spin coating the crosslinkers may evaporate along with the solvent. The amount and types of crosslinkers used drastically affect the material properties of the cured resin. Two crosslinkers have been used. The first is the D crosslinker, 1,1,3,3,5,5-Hexamethyltrisiloxane (referred to as D for di-functional in the following discussion) and the second is the T crosslinker, tetrakis(dimethyldimethyldisiloxane)silane (T for tetra-functional). Li has shown that varying the crosslinker content changes the fracture toughness, $K_{IC}$, stiffness and strength. Using 100% T crosslinker, the $K_{IC}$ is 0.29 MPa*m$^{1/2}$. Using a D crosslinker (50%) along with the T crosslinker (50%) raises the $K_{IC}$ to 0.34 MPa*m$^{1/2}$. Using all of the D-crosslinker (100%), the $K_{IC}$ increases to 0.58 MPa*m$^{1/2}$.

In an attempt to make thin films of X1-2672, an equal combination of two crosslinkers were used: the D and T crosslinkers (50% D and 50% T). When a mixture of the crosslinkers and the resin is made the viscosity is very low. The reactivity of the D and T crosslinkers is high enough that the resin will start to cure at room temperature. Since the viscosity of the resin was too low to spin coat a film approximately 1 μm thick. The resin was left to begin to cure in order to increase the viscosity so a film of good thickness could be made. Once the viscosity of the resin got to acceptable level to spin coat it was deposited on an Si wafer at 2000 RPM for 60 seconds and cured at 275°C for one hour. After the resin was cured the film was rough and uneven. The deposited resin did not form a good quality film and was not tested.

5.8 Index of Refraction Measurements

A Gaertner Scientific three-wavelength variable angle ellipsometer was used to measure the index of refraction, $N_f$, of the deposited films. The ellipsometer is located in the Center for Material Science and Engineering Analytical Shared Experimental Facility in Building 13 at MIT. Typically, 10 to 15 measurements were taken of each film to
determine the index of refraction and the thickness of the film. The value reported as the index of refraction is the average of all valid measurements taken.

A change in the index of refraction indicates a compositional change in the polymer film. The change can be from resin additives, different curing conditions, or other factors can alter the composition of a polymer. Table 5-8 lists all the resins tested along with the curing conditions, fracture toughness values, and the measured index of refraction. Although the index of fraction does indicate compositional changes in the polymer, there is not a direct correlation between the index of refraction and the fracture toughness values. The index of refraction of MF1 cured at 275°C in air is 1.384 and MF2 is 1.408. This shows how the addition of five parts of \( (\text{O}_2\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{O}_2\text{Me}) \) crosslinker to the resin changes the index of refraction, although there is no change in the fracture toughness of 0.306 MPa*m\(^{1/2}\) as compared to 0.289 MPa*m\(^{1/2}\), which are both within the measured standard deviation of 0.019 MPa*m\(^{1/2}\) (see Figure 5-5).

Table 5-8. Ellipsometry Data of Films Tested

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing Temperature</th>
<th>Curing Environment</th>
<th>Thickness</th>
<th>Index of Refraction</th>
<th>Fracture Toughness, ( K_{IC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(10^{-6}m)</td>
<td>(Nf)</td>
<td>(MPa*m(^{1/2}))</td>
<td></td>
</tr>
<tr>
<td>4-3136</td>
<td>275</td>
<td>Air</td>
<td>0.2-2.4</td>
<td>1.536</td>
<td>0.301</td>
</tr>
<tr>
<td>4-3136 with 10% Phase I</td>
<td>275</td>
<td>Air</td>
<td>5.1-6.1</td>
<td>1.546</td>
<td>0.402</td>
</tr>
<tr>
<td>4-3136 with 10% Phase I &amp; 5% Phase II</td>
<td>275</td>
<td>Air</td>
<td>2.32</td>
<td>N/A</td>
<td>0.522</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>275</td>
<td>Air</td>
<td>0.86</td>
<td>1.384</td>
<td>0.306</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>325</td>
<td>Argon</td>
<td>2.24</td>
<td>1.383</td>
<td>0.301</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>385</td>
<td>Argon</td>
<td>0.49-2.33</td>
<td>1.355</td>
<td>0.159</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>400</td>
<td>Argon</td>
<td>0.51</td>
<td>1.378</td>
<td>0.171</td>
</tr>
<tr>
<td>MetFlex-MF1</td>
<td>450</td>
<td>Argon</td>
<td>0.49</td>
<td>1.391</td>
<td>0.143</td>
</tr>
<tr>
<td>MetFlex-MF2</td>
<td>275</td>
<td>Air</td>
<td>0.21</td>
<td>1.408</td>
<td>0.289</td>
</tr>
<tr>
<td>MetFlex-MF2</td>
<td>400</td>
<td>Argon</td>
<td>0.23</td>
<td>1.392</td>
<td>0.172</td>
</tr>
<tr>
<td>MetFlex-MF3</td>
<td>300</td>
<td>Nitrogen</td>
<td>0.58-1.07</td>
<td>1.350</td>
<td>0.141</td>
</tr>
<tr>
<td>MetFlex-MF3</td>
<td>400</td>
<td>Nitrogen</td>
<td>0.55-1.09</td>
<td>1.329</td>
<td>0.112</td>
</tr>
<tr>
<td>Wacker-MK</td>
<td>275</td>
<td>Air</td>
<td>0.54-1.31</td>
<td>1.420</td>
<td>0.345</td>
</tr>
</tbody>
</table>

*4-3136 with Phase II rubber is an opaque film, and index of refraction measurement is not valid.
5.9 Conclusions

The Modified Edge Lift-off Test (MELT) is a simple and very accurate test of how thin films fracture. It accurately measures the fracture toughness, $K_{IC}$, of thin film polymeric materials. One great advantage of the MELT is the test can be used to evaluate the $K_{IC}$ of materials without any knowledge of any mechanical properties of the test material. For instance, one can obtain a substrate with an unknown polymer thin film and measure the $K_{IC}$ without any prior knowledge of any mechanical properties of the material. Comparisons of the $K_{IC}$ measurements of bulk material single edge notched samples and thin film MELT measurements are similar which validates the accuracy of the MELT (see Figure 5-4).

Phase I and phase II toughening of the silicone resin 4-3136 improves the fracture toughness of bulk samples and thin films. MELT measurements show that unmodified 4-3136 has a fracture toughness, $K_{IC}$, of 0.301 MPa*m$^{1/2}$. Adding 10 parts of phase I PDMS rubber increases $K_{IC}$ to 0.402 MPa*m$^{1/2}$. Adding 5 parts of phase II PDMS rubber with 10 parts of phase I PDMS rubber further increases the $K_{IC}$ to 0.522 MPa*m$^{1/2}$. Bulk material samples of rubber toughened 4-3136 are also compared to the MELT $K_{IC}$ measurements. Bulk sample $K_{IC}$ values of unmodified 4-3136 are 0.25 MPa*m$^{1/2}$ as compared to 0.30 MPa*m$^{1/2}$ from the MELT. Phase I toughened 4-3136 bulk samples have a $K_{IC}$ of 0.45 MPa*m$^{1/2}$ where the $K_{IC}$ from MELT measurements are 0.40 MPa*m$^{1/2}$. Phase I and Phase II toughened 4-3136 bulk samples have a $K_{IC}$ of 0.54 MPa*m$^{1/2}$ where the $K_{IC}$ from MELT measurements are 0.52 MPa*m$^{1/2}$. This validates the accuracy and usefulness of the MELT to measure the fracture toughness of these materials as thin films and bulk samples.

The MELT was also used to evaluate the fracture toughness of MetFlex resins. This study showed how the $K_{IC}$ decreased with an increase in curing temperature. MetFlex MF1 and MF2 cured at 275°C have a $K_{IC}$ of 0.30 MPa*m$^{1/2}$, while raising the curing temperature to 400°C decreases the $K_{IC}$ to 0.17 MPa*m$^{1/2}$. MF1 and MF2 differ only in that MF2 has an additional crosslinker added with does not improve the $K_{IC}$ of the resin. MetFlex MF3 uses a variant of the crosslinker used in MF2. The crosslinker in MF3 has one less oxygen and one more methyl in the group than the crosslinker used in
MF2. This crosslinker used in MF3 drops the $K_{\text{IC}}$ 35% (relative to MF1 and MF2) to 0.112 MPa*m$^{1/2}$ when cured at 400°C.

The MELT can also be used to evaluate the fracture toughness of many materials, intended for use as thin films or structural resins. Making thin films of some materials is quicker than making thick castings. Instead of waiting long periods for a casting to cure, one could deposit the material as a thin film and use the MELT to test the fracture toughness. Another advantage of the MELT is that depositing thin films does not use very much of the test material. Less than a gram of dry material is needed to coat a 100 mm wafer. About 100 grams of dry material is needed to make a thick casting of the material. The MELT is a very reliable test that measures the fracture toughness of thin film polymer materials. The MELT is easy to perform, uses only a small amount of test material, and requires no knowledge of the material properties of the test material. These are three strong arguments to encourage scientists and engineers to use the MELT to evaluate the fracture toughness of materials, from structural resins to thin films.
Bibliography


37. Dr. Ed Shaffer II, Dow Chemical Company, Midland, Michigan.