Critical Thickness in Silicone Resin

by

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Abstract

The critical thickness at which a toughness transition occurs in a polymer was determined for the Dow Corning 4-3136 silicone resin. 4-3136 is macroscopically brittle, but becomes up to ten times more ductile when it is processed in the form of a sufficiently thin film. Thickness was controlled for the thin films of amorphous polymer through solution composition variation. The films were spun on highly polished stainless steel at a constant angular velocity. The transition was observed over a range of film thicknesses at several different curing temperatures. Observation of cracking induced by bending and tensile strain was used as the gauge for the transition from brittle to ductile.

The critical thickness was observed to have an unambiguous value at low curing temperatures. At higher curing temperatures, the transition occurred more gradually. The critical thickness also increased up to intermediate curing temperatures, then decreased at the highest cure temperature. Crosslink density is theorized as the cause for this cure temperature induced alteration of the critical thickness.

Advisor: Frederick J. McGarry
Title: Professor of Materials Science and Engineering
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1 Introduction

The scope of this research is the investigation of the critical thickness phenomenon in a silicone resin. The critical thickness phenomenon, a brittle to ductile transition induced by reducing the thickness of a material to below a critical value, has been observed with a number of thermoplastic polymers. However very few thermosetting polymers have been included in previous investigations. Thickness dependence of silicone resin toughness has not been studied despite the industrial importance of these polymers. In this work a condensation cure silicone resin was cured as thin films and tested mechanically to characterize the toughness dependence on film thickness. A convincing brittle to ductile transition across a critical thickness was discovered, which would certainly have far reaching implications in many industrial applications.

1.1 Polymers as Structural and Electronic Materials

The uses of polymer systems has expanded greatly in the past few decades, and their potential seems boundless. Silicone polymers offer thermal stability far exceeding that of traditional carbon chain polymers. However, the inherently brittle nature of these polymers limits their use in many applications. The toughening of such polymers has become a widely researched topic. By toughening inherently brittle polymers, the use of these polymers can be expanded substantially. Many polymers are by themselves too brittle to be used as structural materials but after being toughened have become major successes in these applications. Use of polymers in electronic applications has been
extensive. The electronic properties of certain silicone polymers, such as the dielectric constant, make it an excellent candidate for such applications. The thin film is one of the primary forms in which these electronic polymers are used. A full understanding of the properties of these thin films is necessary. One of the important properties to understand in these films is their toughness and how it changes by varying process parameters.

1.2 Toughening of Polymeric Systems

Toughening of polymeric systems has been conducted by two primary methods. The first method involves the alteration of the molecular structure of the polymer. The second involves the addition of outside particles into the bulk of the material. The purpose of this process is to increase the toughness and crack resistance of the polymer without diminishing the valued inherent properties of the material. In the case of silicone resins, work has been done to increase the toughness of the material while retaining properties such as thermal stability. Great success has been found with the introduction of second phase rubbery particles into the bulk of the material. This success offers the possibility of the use of such toughened resin systems in structural materials. It is important to note that the toughening of polymers spans numerous polymeric families and involves many methods. The concept of critical thickness in polymers and its possible applications provide a new approach by which greatly increased toughness can be obtained from these otherwise brittle polymers, potentially with zero compromise on other properties since the composition and chemical structure of the polymers are not altered.
1.3 Polymer Characterization

A broad line can be drawn to divide polymers into two major categories. Brittle polymers typically will have a high modulus and fracture at a relatively low strain. Ductile polymers, on the contrary, typically fail at a very high strain, with a stress peaking at some point before that. The impact of this observation is the simplicity that allows the use of failure strain for determination of a brittle to ductile to transition.

Typical polymer elongation plots can be found in Figure 1-1.\textsuperscript{6}

![Figure 1-1 Polymer Behavior A.) Brittle B.) Ductile C.) Elastomeric](image)

In addition to this observation of the behavior of brittle and ductile polymers, there are some other straightforward methods to identify brittle vis a vis ductile behavior. The fracture type of a brittle polymer will appear different from that of a ductile polymer. This manifests itself in both the fracture surface and the general appearance of the crack. The fracture surface will not be discussed in the course of this research, while the general nature of the crack will be identified often. From an energy standpoint, brittle polymers dissipate less energy in fracture than ductile polymers.\textsuperscript{7} Unlike thermoplastics,
thermosets are a group of polymers that cannot be reformed after curing. During the curing process, they go through a chemical change in which the long chain molecules react to form a three-dimensional lattice. This cross-linking results in a rigid material that retains its properties through a wide range of temperatures. However, as a result, thermosets are often less ductile than thermoplastics.

1.4 Silicone Polymers
Silicone polymers are the materials of primary interest in this research. They are thermosets and exhibit the properties synonymous with that designation. These polymers are quite brittle. They have a high modulus and will fail at a very low strain. As mentioned previously, they have outstanding thermal stability and do not oxidize at high temperatures. They differ from most other polymeric systems in that the building block of silicone is the silicon-oxygen bond, rather than the carbon-carbon bond. The bond energy of the Si-O-Si bond, the length and angle of that bond, and its resistance to oxidation provide the unique properties of silicone polymers. Many silicone polymers with organic substitutions such as the methyl group have very low moisture absorption, another attractive property. They all of these properties combine to make silicone an ideal polymer for structural applications, especially those that may involve high temperatures and possibly fire.

The primary material of interest in this research is the Dow Corning condensation resin, 4-3136. The issue of the fracture toughness in films of the untoughened 4-3136 has been studied before by Spain. Spain used the modified edge lift off test to determine the properties of the thin film, finding them to be similar to the bulk. However, new
methods of determining the critical thickness transition in 4-3136 thin films have been used in this research. An explanation of the concept of critical thickness, prior methods used for its determination, and the new methods used in this research will follow.
2 Critical Thickness

2.1 The Concept of Critical Thickness

Critical thickness is defined as the absolute thickness at which there is an intrinsic change in the mechanical behavior in a polymer, from brittle to ductile.\textsuperscript{1} The basis for the existence of this transition is the inherently ductile nature of essentially all polymers at the micro level. By lowering the absolute dimension of the polymer to a critical level, this inherent ductility of the material is utilized, despite the bulk properties of the material. Thus far, a few methods have been explored to determine this critical thickness in a few polymers, most notably the thermoplastic, polystyrene.\textsuperscript{1} The ramifications of this property manifest themselves in the area of polymer toughening. The successful application of critical thickness concept opens a new method of achieving this goal, without changing the molecular structure or the introduction of foreign particles into the bulk of the material.

2.2 The Basis of the Critical Thickness

Thus far, the primary material candidate for the study of critical thickness has been polystyrene, and the research with this material has been conducted at the Eindhoven University of Technology by M. C. M. van der Sanden and H. E. H. Meijer.\textsuperscript{1} The idea was explored further through modeling of the same concept by T. N. Krupenkin and G.H. Fredrickson.\textsuperscript{12} Three primary concepts that provide proof of the existence of critical thickness are discussed below.
2.2.1 Extension of Fibrils in Glassy Polymers
Polystyrene fails primary through the mechanism of crazing, which continues as cracks after the application of a higher strain. An illustration of this concept can be found in Figure 2-1. These crazes consist of numerous fibrils, for which it has been proven that the elongation before failure is on the order of 200%. It has been further suggested that the nature of these craze fibrils varies with the thickness of the bulk material. In bulk materials under some critical dimension, the craze fibrils form a two dimensional network, as opposed to the normal three-dimensional network in macroscopic samples. If these fibrils were somehow isolated, or if the bulk material were made to such dimensions that the entire deformation mechanism was the same as the fibrils, the material would not fail in a brittle manner. It is from this concept that the idea of the critical thickness originated.

![Figure 2-1 Illustration of craze fibrils within the craze zone of a crack](image)

2.2.2 The Theoretical Draw Ratio
The theoretical draw ratio of a material ($\lambda_{\text{max}}$) is calculated through knowledge of the molecular weight between entanglements ($M_e$). Although it is only a theoretical figure, it gives a basic indication that certain polymers are ductile, such as polystyrene,
which has a $\lambda_{\text{max}}$ of $\sim 4.2$. This can be compared with the macroscopic data for polystyrene, which fails at a strain of approximately 5%. This bulk value falls approximately 315% below the anticipated strain to break. Therefore, there is an indication that the macroscopic failure of polystyrene involves mechanisms that are detrimental to its ductility. There should be a method with which to approach the theoretical properties of the brittle polymer. Processing the material in a manner that takes advantage of the critical thickness of the material accomplishes this goal.

2.2.3 The Behavior of Polymers in Compression

Another possible indication of the inherent ductility of polystyrene can be seen in its compression behavior. The behavior of polystyrene under tension is brittle, compared with polycarbonate, which is quite ductile. However, under compression both of these materials behave similarly. Figure 2-2 presents this phenomenon by comparing the draw ratio and strain versus the applied stress. This property again suggests that polystyrene is inherently ductile.

![Figure 2-2](image)

**Figure 2-2 (left)** Tension behavior and (right) compression behavior of PC, PS, and PMMA
2.3 Identification of the Critical Thickness

2.3.1 Elongation at Failure
As mentioned in Chapter 1, one of the key differentiations between a ductile and a brittle polymer is the elongation at break. This is the primary property described in this thesis for the determination of the toughness of the material. Figure 1-1 plotted the typical load elongation curves for the two types of polymers. The yield stress for most amorphous and glassy polymers is comparable to within a factor of two to three. At around 50 to 100 MPa, the material will yield. As indicated by the figure, the typical strain to fracture is approximately 1 or 2%, which is substantially less than the ductile polymers, which will typically fail at more than 100%. Knowledge of the elongation at break provides an indication of the fracture toughness of the material, which is the material property of interest for this research.

2.3.2 Stress Intensity Factor
Though not directly measured as a criteria for determination of the transition in this research, the stress intensity factor, $K_{lc}$, offers a measure of the toughness of the material. The stress intensity factor and its ability to indicate the critical thickness can be visualized best through consideration of a representative curve as shown in Figure 2-3. $K_{lc}$ is a material property, and can be thought of as the material resistance to fracture. This increase in the $K_{lc}$ can also be considered an indication of an increase in the ductility of the material. A direct measurement of this property could be used in future research as a determination of the critical thickness of 4-3136.
2.4 Prior Methods of Critical Thickness Determination

Previous methods used for the determination of critical thickness were conducted in bulk materials by researchers at the Eindhoven University of Technology. The two methods used to identify the critical thickness were to fabricate alternating layers of the brittle material (polystyrene) and a ductile material (polyethylene), and to introduce non-adhering rubbery particles into the bulk of the material. These methods resulted in the successful determination of the critical thickness of polystyrene. Other tests were run by the same researchers to determine the critical thickness of various crosslinked versions of an epoxide based on the diglycidyl ether of bisphenol A. They attempted to determine the critical thickness of this thermoset by adding rubbery particles into the bulk.\textsuperscript{16}

However, they did not have a great amount of success in doing so. The highly crosslinked epoxies returned poor results from a fracture toughness test, and high-speed impact testing was used instead. As such, the data determined for the thermosets did not
use the same method as the thermoplastic, and even then returned limited results. In the present study, a different testing method was used. The successful methods used to determine the critical thickness of polystyrene will be described in detail below.

2.4.1 Alternating Thin Film Layers

The critical thickness of polystyrene was first determined through the manufacture of a solid through sequential compression and extension of alternating layers of polymer tapes. One of the layers was made of the brittle polymer polystyrene, while the other layers was composed of the ductile polyethylene. Use of the apparatus, the Akzo Multiflux static mixer, allowed very thin sections of the solid to be made up of polystyrene, yet still be large enough on the whole to subject it to traditional testing methods. In order to assure that the samples were amorphous, rather than oriented in some fashion, the samples were annealed at an appropriate temperature.

![Figure 2-4 Illustration of alternation thin film layers](image)

One important aspect of the process was the lack of adhesion between the two differing layers. This allowed the use of the principle of superposition to determine the properties of the less ductile polystyrene. Tests were run with differing thicknesses of alternating
layers so that the critical thickness could be determined. An illustration of the resulting bulk material used for testing can be found in Figure 2-4.

2.4.2 Introduction of Rubbery Particles

The critical thickness of polystyrene was determined through the introduction of rubbery particles into the bulk. This method was mentioned in the introduction as a common method for toughening of polymer systems. The purpose of the particles is to act almost as holes, allowing the amorphous polymer to form a network of thin ligaments. As in the case of the multilayered tapes, it is very important that the particles are nonadhering. For the purpose of illustration, adhering particles were used in a control test by the researchers to show that an alteration of the bulk properties of the material did not occur.$^{1}$ The critical thickness was established in this manner through knowledge of the average distance between the particles. This number could be calculated and controlled through the alteration of a few variables such as the particle diameter, the volume fraction of the particles, and a spatial distribution factor.$^{17}$ A simple illustration of the polymer with particles can be found in Figure 2-5.

![Illustration of polymer with rubbery particles](image)

**Figure 2-5** Illustration of polymer with rubbery particles
2.5 Analytical Models

An analytical model was proposed by van der Sanden in order to better understand and predict the critical thickness behavior that he characterized through his research. While the model presented here is only a minimal analytical description of the mechanics involved in the fracture of polymers, it does provide some insight into the phenomenon of critical thickness.

2.5.1 The Thin Film Energy Approach

This energy approach to the fracture in thin films is based upon the supposition that brittle fracture in polymers occurs due to a higher elastic energy in the fibril than is required for failure.\(^{16}\) The following model is based upon this assumption and was developed by van der Sanden.

The material properties of a polymer pertinent to this model are the following: the Poisson’s ratio \(v\), the applied stress \(\sigma\), the Young’s Modulus \(E_f\), and the length of a crack already in existence, \(a\). The driving force \((G)\) for the growth of a crack is described in equation 1.

\[
G = \frac{B(1-v^2)\sigma^2a}{E_f}
\]

Equation 1

When this force equals the crack resistance \((\Gamma_r)\), the crack will grow. Now consider that the size of the crack is approximately equal to the thickness of the film \((h)\). Changing the variable in equation 1 allows for the driving force to be thought of in terms of film thickness, rather than the original crack length. If the yield stress \((\sigma_f)\) is then used to replace the applied stress \((\sigma)\), \(h\) in equation 1 will now be the variable, indicating the film
thickness at which the yield stress will cause the driving force to exceed the crack resistance. If the crack resistance is then redefined in terms of van der Waal’s surface energy (\(\gamma\)), the polymer backbone energy (\(k_1\)), and the entanglement density (\(n_e\)) as in Equation 2, the critical thickness can be determined only from knowledge of material properties.

\[
\Gamma = \gamma + k_1 n_e^{\frac{1}{2}} \quad \text{Equation 2}
\]

The critical thickness of a polymer can now be described by combination of the above formulas into the expression in equation 3.\(^{17}\)

\[
h_c = \frac{(\gamma + k_1 n_e^{\frac{1}{2}})E_f}{\beta(1 - \nu^2)\sigma_y^2} \quad \text{Equation 3}
\]
3 Experimental Procedure

3.1 Summary of Procedure

The procedure used for fabrication and testing of the samples was conducted in a systematic manner and the basic steps are outlined below. A more thorough description will follow.

1.) Prepare substrate

2.) Prepare silicone resin solution

3.) Spin coat samples

4.) Cure silicone resin film

5.) Measuring film thickness

6.) Apply strains on film

7.) Observe under microscope for cracking in film

3.2 Substrate Preparation

The primary substrate used for the experiments was a #8 Mirror Polished 304 Stainless Steel. The sheet was purchased as one 120 x 48 inch sheet. This 1 mm thick sheet was subsequently cut into 24 inch squares. All sheets were sheared with a large metal press. The substrate template for the experiments was a much smaller "coupon" substrate that had the dimensions of approximately 0.75 x 3 inches. The exact dimensions of the substrate were not emphasized, due to the lack of any effect on the actual testing results. The spinning and bending procedure did not require substrates of consistent dimensions.
The polished side of the substrate was protected by the manufacturer with a double layer adhesive coating. It was determined through experiment that the adhesive did not contaminate the substrate. All solvents wet the surface readily. Furthermore, washing the substrate surface with both soap and water and solvent prior to the experiment did not produce any appreciable differences in film properties. Any form of washing also appeared to degrade the surface polish. Having attempted to create films on the inferior #8 polish and failed, it was determined that the preservation of the polish was of the utmost importance in creating a quality film.

Several other substrates were considered for the experiments and tested. Polycarbonate was originally considered as the most promising substrate due to its ductility and optical characteristics. Polysulfone was also considered due to its higher glass transition temperature. Both polymer substrates were abandoned due to their poor solvent resistance. Aluminum was also considered as a substrate. It had serious thermal mismatch and surface polish issues and was also abandoned. However, despite the problems with the polycarbonate, some interesting and corroborative results came from tests with polycarbonate substrates. Data from these tests will be included, and as such, the substrate preparation procedure is listed below.

The polycarbonate sheets purchased were 12 inches square. The 1/16 inch thick sheets had a glass transition temperature of approximately 145 °C and a recommended maximum use temperature of 115 °C. The sheets were cut into “coupons” of dimensions similar to those of stainless steel at 0.75 x 3 inches using a band saw. The edges of the substrate were stripped of burrs using a rotary polisher. During this time, the protective coating on both sides of the polycarbonate coupons remained on so as to protect the
surfaces of the strips from scratching and adherence of dust particles. The substrates were annealed to 135 °C prior to spinning or curing. The annealing took place in an air circulating oven for 20 minutes and was then cooled slowly at approximate 2 °C per minute to room temperature.

3.3 Preparation of the silicone resin solution

Dow Corning 3136 condensation cure resin was used for all samples. Several organic solvents were considered and tested for use with the resin. Toluene, Methyl Isobutyl Ketone (MIBK), Methyl Ethyl Ketone, Ethyl Acetate, and Dioxane were each tested with the parallel goals of fully dissolving the 3136 resin and minimally affecting the polymer substrates. The polycarbonate substrates were exposed to each of the solvents for approximately 30 seconds. Optical microscopy was conducted on each of the samples and the results are presented in Appendix 1. MIBK was chosen as the primary solvent due to its minimal impact on the polymer substrate. Stainless steel eventually became the primary substrate, and as such, the effect of the solvent on polycarbonate became irrelevant. However, for the sake of continuity in the experimentation, MIBK remained as the primary solvent throughout the entire project.

The thickness of the films was solely dependent on the composition, and thus the viscosity of the solution. As such, the exact composition of the solution was of the utmost importance. The solutions each required the addition of a small amount (0.05 wt% of resin) of curing catalyst, Y-177. A “stock solution” of 0.05 wt% Y-177 catalyst in MIBK was made. Into each gram of 3136 resin, one gram of the stock solution was added. When the remainder of the solvent was added to the solution, the amount of
solvent in the stock solution was taken into account. For the most part, the solution was prepared such that it would have a final mass of 5 grams. Solutions varied in concentration between 3 wt% and 70 wt.% 3136 resin in MIBK. A magnetic stir bar was used to mix the solution for approximately 15 minutes, or until all visible signs of the 3136 resin solid were gone. After mixing the solution thoroughly, the solution was filtered three times with a Norm-Ject 5mL syringe and through a Whatman Puradisc 0.2 micron PTFE membrane filter. The more viscous solutions were allowed to sit for up to 30 minutes to allow any bubbles in the solution to escape. Degassing of the solutions was also attempted but eventually abandoned due to the minimal effect it had on the solutions and the films.

3.4 Spin coating of the samples

The spin coater used for creation of the films had a control module and a spinning cavity. The control parameters allowed for the variation of the acceleration, the final angular velocity, and the time spent at that velocity. The spinning stage was approximately 3 inches in diameter and was enclosed by an approximately 6 inch diameter capsule. The stage itself had a rubber o-ring at the center through which the vacuum was pulled on the bottom of the sample. The vacuum pulled by the spin coater was not substantially below atmospheric, and as such, retention of the substrate on the spinning stage was a major issue and extreme care was taken to spin coat the films onto stainless steel.

Spin coating was conducted at a constant acceleration and velocity, with the solution composition providing the variation in film thickness. Multiple acceleration and
velocities were attempted in order to determine the optimum combination to use with the solution viscosity and the particular substrate. Through experimentation, it was determined that the maximum final angular velocity possible would provide the most consistent films. However, the stainless steel substrates often had slight curvature, due to the substantial shearing force required to make each of the coupon substrates, which complicated the issue of keeping the substrates on the stage during spinning. As a result, the maximum velocity that could be maintained in the spin coater was 1300 rpm. This value was lower than ideal velocity and resulted in some unwanted aspects of the film. A thicker “lip” formed on the edges of the film. A schematic of a typical profile of the film can be seen in Figure 3-1. This lip was measured to be as much as seven times the thickness of the center of the film. However, the center of the film remained consistent in thickness, as determined through stylus profilometry. After straining of the film only the center region of the film was closely examined for cracks, rather than the edges.

![Diagram showing lip thickness and film thickness](image)

**Figure 3-1** Illustration of thickness inconsistencies in films caused by spinning.

The film spinning procedure consisted of four basic steps. First, the spinner was programmed for the appropriate acceleration (424 revolutions / minute²), spinning velocity (1300 revolutions / minute), and time (1 minute). Then the stainless steel
substrate was placed on the spinning stage after removing the protective coating. Immediately after removing the coating, three to four 0.0220 g drops of the solution were placed at the center of the substrate. Finally, the cover of the spinner was placed over the substrate and the spinning sequence initiated. After completion of the procedure, the substrate was removed and taken immediately to the oven for the cure.

The spinning procedure for the polycarbonate substrates was in most respects the same as the stainless steel. The only major difference in the procedure was the spinning velocity that could be obtained with the polycarbonate substrates. Due to the fact that the polycarbonate was cut with a band saw, rather than sheared, the surface of the substrate was completely flat. In addition, the polycarbonate was much less dense than the steel, minimizing the wobble caused by inexact placement of the substrate on the spinning stage. As a result a faster spinning velocity of 2000 rpm was used for these samples.

3.5 Curing the silicone resin
The curing procedure for the films was conducted in accordance with the recommendations of the Dow Corning Corporation. Numerous curing temperatures were used for research purposes, ranging from 177 °C to 300 °C. However, the basic curing sequence remained the same for each curing temperature. The temperature was ramped at 10 °C / min from room temperature to 70 °C for a soft bake. Following 30 minutes at the soft bake, the temperature was ramped at 5 °C / min to the final cure temperature. After remaining at the cure temperature for one hour, the temperature was ramped down to room temperature at 2 °C / min.
The exact parameters for the process were determined through a systematic process of balancing each of the important factors in the film production. These properties included: thermal induced strains in the film, trapped gas evacuation, and film thickness consistency. Of the utmost importance to determining the critical thickness of 3136 resin was a film of consistent thickness. The aforementioned lip that formed on the periphery of the film had a thickness many times that of the film. While this abnormality did not cause a major problem with the thin films, the more viscous solutions used for thicker films created lips of much higher volume (determined both through width and height), causing thickness inconsistencies in the center of the film. During the curing process, the lip would migrate towards the center of the film until it finally was cured. A typical profile of the stages of this phenomenon can be seen in Figure 3-2. In some cases, the lips met at the center, leaving no region of consistent thickness at the center of the film. Due to the fact that this progression of experimentation was not an exercise in process refinement, the simplest approach to minimizing the affect of this phenomenon was used. By reducing the time spent ramping to the curing temperature, the amount of time for the migration of the lips was reduced. In almost all cases, this allowed for a region of consistent thickness in the center of the film for study.

---

Cure Profile

-------- Pre-Cure Profile

Figure 3-2 Illustration of lip migration during curing
Reducing the ramping time reduced the “migration effect” but adversely affected the results with the other two aforementioned process parameters. Bubbles did, in fact, often appear on the surface on the film. The size and dispersal of the bubbles were small and sporadic, respectively. As such, they were accepted as a side product of attaining a consistent thickness film. Regions of the film remained such that even at a low magnification (100x), no bubbles were visible in the region of interest. The thermal strains possibly caused by the quick ramping of the temperature were reduced by very slow return to room temperature. This allowed for a relaxation of strains in the film on the substrate.

The curing steps differed slightly for the polycarbonate substrates. Due to concerns about the glass transition, the cure was conducted at a much lower temperature, 120 °C. As with the stainless steel substrates, the temperature was ramped at 10 °C / min from room temperature to 70 °C for a soft bake. Following 30 minutes at the soft bake, the temperature was ramped at 5 °C / min to the final cure temperature. After remaining at the cure temperature for one hour, the temperature was ramped down to room temperature at 2 °C / min.

3.6 Measuring film thickness

A stylus profilometer was used to determine the thickness of the films. The length of the scans varied among the methods used for determining the thickness of the films. Three methods were attempted, of which two were found to be successful. The first and most straightforward method of determining the thickness involved making the profilometer scan long enough such that it would pass from the clean substrate and over
the lip profile as shown in Figure 3-2. This method was most successful with the thinner films, as the lip region of the film was thin enough where the thickness of the center region of the film could be determined within a reasonable 800-1000 micron scan.

The height of the thicker films could not be determined with the first method. The stylus profilometer would often stray from the original horizontal reference plane with scans exceeding 2000 microns. In addition, the slightest error in horizontal calibration would cause errors of up to a full micron in the thickness measurement. As such, a new method was explored through scratching the film with a standard steel razor blade. However, there was a wide variation in measured thickness depending upon the pressure exerted on the razor blade. As such, this "scratch test" was modified. Rather than making a vertical scratch in the film, the razor blade was used to shear the film from the surface of the substrate. In most cases, the adhesion of the film to the substrate was on a level such that the film could be completely removed from the surface of the substrate. A typical profile of the film/substrate after razor film removal can be seen in Figure 3-3.

![Diagram showing film profile](image)

**Figure 3-3** Illustration of typical film profile after razor film removal
3.7 Testing of Films

3.7.1 Applying strain on the film via bending

The cured films on the substrates were strained in controlled increments via manual bending against a round stainless steel bar of pre-determined diameter. The coupon substrates were made with such dimensions (3 inches in length) that they could be bent over the rod without directly contacting the film. The only region of the film that needed to be strained to the appropriate degree was the very apex of the curved substrate surface. Concern of substrate spring back was not substantial, as only approximately 1/64 of the circumference of the bent surface was visible with microscopy. Hand bending was possible up to rod diameters of 0.5 inches. Any further bending around smaller rods was conducted with mechanical aid. In some cases, strains exceeding the smallest available rod were necessary. In these cases, the substrate was bent further with mechanical aid. The curvature of the substrate was then measured using calipers. The strain on the film was then estimated through these measurements. A representation of the bending process and the data of interest can be seen in Figure 3-4.

![Diagram of Substrate and Film](image)

**Figure 3-4** Illustration of the strain application
The calculation of the strain was conducted through equation 3.1. Due to the fact that the straining was conducted by bending the substrates over a limited number of fixed diameter rods, the strain values to which the films were subjected were limited. Some of the strain values most commonly used can be found in Table 3-1.

\[
\varepsilon = \frac{\Delta l}{l} = \left[ \frac{2 \cdot \left( r_i + r_o \right) \cdot \pi}{2 \cdot \left( r_i + r_o \right) \cdot \pi} - 2 \cdot r_o \cdot \pi \right] = 1 - 2 \cdot \frac{r_o}{(r_i + r_o)} \tag{Equation 4}
\]

<table>
<thead>
<tr>
<th>Rod Diameter (in)</th>
<th>3.25</th>
<th>2</th>
<th>1.5</th>
<th>1.25</th>
<th>1</th>
<th>0.875</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain (in/in)</td>
<td>0.011969</td>
<td>0.019305</td>
<td>0.025575</td>
<td>0.030534</td>
<td>0.037879</td>
<td>0.043057</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rod Diameter (in)</th>
<th>0.75</th>
<th>0.625</th>
<th>0.5</th>
<th>0.375</th>
<th>0.25</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain (in/in)</td>
<td>0.049875</td>
<td>0.059259</td>
<td>0.072993</td>
<td>0.095012</td>
<td>0.136054</td>
<td>0.164474</td>
</tr>
</tbody>
</table>

3.7.2 Applying strain on the film via tension

In order to provide corroborative evidence of the critical thickness phenomenon, the 3136 films were also tested under tensile strain. However, the new method of applying strain to the film required an entirely new process for processing and testing. One of the primary concerns involved in tensile testing was uniform strain throughout the film region. The “coupon” substrates used in the bending tests would not be able to deliver such a condition, as there would certainly exist a large stress concentration near the clamped surfaces. This would result in an uneven distribution of strain across the test specimen. As such, the ASTM E 8 dimensions for sheet type tensile specimens were
followed. Although the material properties of the substrate were not of interest, the consistent strain in the gage region provided by the tensile samples was considered most advantageous. Table 3-2 and Figure 3-5 describe the dimensions of the specimen as dictated by ASTM standards.

Figure 3-5 Profile of tensile specimen

<table>
<thead>
<tr>
<th>Table 3-2 Tensile specimen specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>G, Gage Length</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Sheet Type Specs</td>
</tr>
</tbody>
</table>

Unfortunately, the ASTM standard tensile specimen would not fit inside the spin-coater. The largest substrate that would fit within the dimensions of the spin-coater was 5 inches. As such, some portion of the length of the tensile specimen had to be reduced. It was determined that the gage length should retain the specified dimensions. As the grip section was over 3 inches on each side, it was reduced by 1.5 inches on both sides, leaving over 1.5 inches of grip length on each side. It was determined that this grip length would be reasonable, and that the gage length region of the specimen would behave as normal under a tensile load.
Several factors were of primary importance in the production of the tensile sample substrates. The high polish of the surface of the substrates had to be maintained. The exact specifications also had to be adhered to, while the process needed to create a large number of them within a short time span. After considering the nature of the stock material (large sheets), it was determined that water-jet machining would be the most accurate and expedient method of producing the samples. The major downfall of the water-jet method was the high water pressure and abrasive affecting the surface of the stainless steel. After several attempts, damage to the polished surface was minimized such that films could be reliably spun onto the substrate. However, the process took a substantial amount of time. At two minutes per sample, and an average of one in five being damaged by the high water pressure, only 50 were made after two hours of an excruciatingly tiresome task. This number of substrates was only sufficient for a few runs of tensile tests. However, no better method of producing the substrates was conceived or tested. As such, the tensile substrates were used sparingly.

Preparation of the tensile films was done painstakingly, due to the small number of available substrates. Despite the protective covering over the polished side of the substrate, water and the abrasive material reached approximately 2 mm under the covering during the water-jet process. As such, the tensile substrates were washed thoroughly with soap and water and air-dried prior to spinning. Due to the thinner center region of the substrate, spinning also became substantially more difficult. Any imbalance in weight immediately caused the substrate to be thrown off the spinner. The light vacuum provided by the spin-coater proved to be inadequate to hold the tensile substrate in place. As such, excessive quantities of silicone vacuum grease were used in order to
create a better seal between the vacuum and the substrate. The large amount of grease also acted as an adhesive itself, helping to stabilize the substrate as it was accelerated. The films were then cured in the standard method after spinning. The shape of the tensile specimens did not cause any problems with curing, as compared with the coupon substrates.

An Instron Model 4505 testing instrument was used for the testing procedure. All tests were conducted above the moving crosshead. The load was tracked by an overhead Instron 100kN static load cell and the strain was logged by a 12.7 mm range Instron 2620-831 extensometer. The extension rate was set at 5 mm/min. Due to the small number of available substrates, all films were strained in succession over a number of “pulls.” The first major impact of this method of testing was the recovery of the steel substrates after being released from the vises. This cyclic method of testing created a major issue in tracking the strain on the film. This problem was first tackled by recording the extension of the gage portion of the sample for each pull, releasing the sample from the vise, and finally recording the recovery of the substrate. Averaging the recovery of the samples over a standard extension was initially considered to be adequate, due to the precise dimensions of each test piece. However, after logging the recovery for several samples, over several subsequent pulls, it became clear that each of the samples behaved differently. This was perhaps due to the thin nature of the substrate. As such, all extension and recovery figures were logged individually for each film/substrate. This resulted in a far more accurate tally of the final strain of the film region of the substrate. One of the other major issues with this method of testing was the inherent cyclic nature of the tests. Unwanted effects from the extension/recovery cycle could have affected
observation of the desired pure strain phenomenon. However, due to the lack of a large number of substrates and the low number of cycles actually experienced by the films, it was determined that this method of testing would be sufficient to gauge the strain to cracking of the films.

3.8 Microscopy Observations

3.8.1 Observation under optical microscope

After the films had been strained, they were observed under reflective light with an optical microscope. Magnifications of 100x, 200x, 500x, and 1000x were available on the microscope. All magnifications were used, but only two were usually captured digitally. The purpose of the microscopy was to visually identify cracks in the film. Microscopy took place between each progression in strain. Brittle, low strain, cracks were easily seen with 100x magnification, and often with the naked eye. More ductile cracks often required 500x to 1000x magnification.

Unstrained and low strain samples were easily viewed using the stage of the optical microscope. This allowed for a full scan of the film in order to thoroughly search for any cracking. However, as the strain increased, and the curvature of the substrate became more pronounced, focus on the apex of the substrate could no longer be maintained, as the stage could not be positioned low enough. The stage had to be removed, and any positioning of the sample had to be done manually. This often made scanning the surface of the strained film more difficult. However, every effort was made to determine if cracking was widespread and dispersed consistently.
One of the primary reasons for wide scans was the aforementioned problem of “lips” on the edges of the films that had a thickness greater than the majority of the film. These thicker regions would develop cracks at lower strain values than the majority of the film, due to the critical thickness effect. The cracks would arrest as soon as they reached the thinner, central portion of the film. A typical profile of a film at lower strain can be found in Figure 3-6. Note the reasonable portion of film that was not cracked at low strain and remains as an observable region with increased strain.

![Diagram of film and cracked region](image)

**Figure 3-6** Illustration of the cracked region of the film

3.8.2 Observation under SEM

Scanning electron microscopy was used in order to obtain a better understanding of the surface of the film. Optical microscopy often did not allow for a clear focus on the surface of the transparent film unless cracking was prevalent in the area of interest. SEM, on the other hand, offered a clear view of the surface even if only minor cracks were present. Due to the fact that the film was nonconducting, the backscatter detector was originally used in order to view the film. However, the primarily flat surface of the
film disallowed a high resolution. Somewhat by accident, it was discovered that the thin nature of the film reduced the charging effect, and the film could be viewed in high resolution with the primary detector. Magnifications of up to 20,000x were possible with the SEM.
4 Results and Discussion

4.1 Determination of the Critical Thickness

The primary objective in observing strained films was to determine whether the film had failed by cracking. However, much of the optical microscopy conducted on the strained samples required a level of subjectivity. The nature of these cracks varied with thickness, cure temperature, and strain. In addition, the surface of the substrate itself varied dynamically with strain. Stress bands on the stainless steel dominated optical microscopy at any magnification due to the transparent nature of the film. Cracks provided a focal point with which to view the surface of the film optically. Conversely, disturbances that left the remainder of the substrate out of focus were determined to be on the film. However, discerning cracks from the substrate was often a difficult task that required substantial experience in the process of identification. Furthermore, cracks were often isolated in specific regions of the film, which might contain some inconsistency. In order to determine the dispersal of the cracks, a large portion of the strained film had to be scanned. Fortunately, scanning electron microscopy provided clear evidence of surface cracks. However, it could only be used sparingly due to the vast number of samples and strain values (up to nine strain values for each film), and the time consuming application and venting of vacuum that would have been required. Many of the optical microscopy pictures will be included in the appendices in order to offer firm proof of the cracking progression in the films and reduce some of the subjectivity.

Determination of the range of critical thickness was conducted primarily through trial and error. A large range of solution compositions, often in increments of 5 wt% to 10 wt% resin, was prepared and tested first. Analysis of the films yielded important
information as to which segment of solution wt%, and subsequently film thickness, contained the largest transition in strain to cracking. This segment was then more closely analyzed through the preparation and testing of solution compositions in an increment of 2 wt% resin. Depending upon the thickness range to which the critical thickness was isolated, this would yield a transition thickness resolution of somewhere between 1000 angstroms and 0.5 microns.

4.2 The Critical Thickness of films cured at 177° C

The starkest transition from brittle to ductile occurred in the films cured at the lowest temperature, 177° C. This was the first temperature to be tested, so the most was known about the transition at this cure temperature. Clear evidence of the transition was discovered long before the processing parameters had been fully defined.

Once the streamlined process had been honed, and consistent thickness films could be produced, the testing procedure identified the transition thickness clearly. Films were spun from solutions of composition 29 wt% through 37 wt% 3136 in MIBK and were tested twice. Table 4-1 contains the data from these tests and Figure 4-1 contains the plot of these data. In order to illustrate the manner in which this data was determined, optical microscopy pictures of the samples immediately above and below the transition thickness can be found in Figures 4-2 through 4-5. As the table and plot indicates, the transition occurred between 2.2 and 2.3 microns. The transition is extremely sharp, and the slight inconsistencies in film thickness caused the transition to occur at the same solution composition. This causes an unreasonable presentation of the data that grossly exaggerates error. In order to facilitate a better understanding of the transition, the
individual data for the 33 wt% solutions are included in the table, and all data for the tests are included in the plot.

### Table 4-1 177 °C cured film bending test results

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Average Film Thickness (Microns)</th>
<th>Average Strain to Cracking (%)</th>
<th>Standard Deviation of Film Thickness</th>
<th>Standard Deviation of Strain to Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>37%</td>
<td>2.65</td>
<td>2.23</td>
<td>0.070711</td>
<td>0.46669</td>
</tr>
<tr>
<td>35%</td>
<td>2.375</td>
<td>2.45</td>
<td>0.035355</td>
<td>0.777817</td>
</tr>
<tr>
<td>33%</td>
<td>2.25</td>
<td>10.45</td>
<td>0.070711</td>
<td>10.53589</td>
</tr>
<tr>
<td>33% (Brittle)</td>
<td>(2.3)</td>
<td>(3)</td>
<td>(n/a)</td>
<td>(n/a)</td>
</tr>
<tr>
<td>33% (Ductile)</td>
<td>(2.2)</td>
<td>(17.9)</td>
<td>(n/a)</td>
<td>(n/a)</td>
</tr>
<tr>
<td>31%</td>
<td>2.1</td>
<td>13.6</td>
<td>0.141421</td>
<td>0</td>
</tr>
<tr>
<td>29%</td>
<td>1.9</td>
<td>16.65</td>
<td>0</td>
<td>4.313351</td>
</tr>
</tbody>
</table>

**Critical Thickness of 3136 (177 C Cure)**

![Diagram](image)

**Figure 4-1** Plot of 177 °C cured film bending test results
Figure 4-2 33 Percent 3136 in MIBK (Optical Magnification to 1000x)
2.2 Micron Thickness (Below Critical Thickness)
Bent over 0.25” rod (13.6% Strain)

Figure 4-3 33 Percent 3136 in MIBK (Optical Magnification to 1000x)
2.2 Micron Thickness (Below Critical Thickness)
Bent to 0.18” diameter (17.9% Strain)
Figure 4-4 35 Percent 3136 in MIBK (Optical Magnification to 1000x)

2.35 Micron Thickness (Above Critical Thickness)
Bent over 2" rod (1.9% Strain)

Figure 4-5 35 Percent 3136 in MIBK (Optical Magnification to 500x)

2.35 Micron Thickness (Above Critical Thickness)
Bent over 1.25" rod (3% Strain)
The transition, occurring between 2.2 and 2.3 microns, can be seen clearly in the optical microscopy pictures. The widespread brittle cracking, which occurred between 1.9 and 3%, can be seen clearly in Figure 4-5. This contrasts sharply with the smaller, more isolated ductile cracks found in Figure 4-3. None of the more brittle cracks were ever found in the film, even at lower strains. In order to further confirm this, additional microscopy pictures of the thinner film at lower strains are included in Appendix 2. In both pictures, the cracking was found to extend perpendicular to the direction of applied strain, as would be anticipated. However, due to the physical limitations of the microscope stage, the sample had to be turned in a different direction at higher strains.

4.3 The Critical Thickness of films cured at 200° C

The critical thickness transition for the films cured at 200 °C was less stark than in the films cured at 177 °C. The transition was clearly defined, nonetheless. The transition was initially isolated for a film of thickness around 4.9 microns, or the 45 wt% 3136 resin solution. As such, films were spun from solutions of composition 41 wt% through 51 wt% 3136 in MIBK and were tested twice.

As the existence of a critical thickness had already been proven at a lower cure temperature, the most interesting aspect of these experiments was the shift in critical thickness and reduction in the starkness of that transition. The data from the experiments can be found in Table 4-2 and plotted in Figure 4-6. The table contains the data from the first test, which was the most useful test due to the fact that a number of the samples in the second test were damaged and the data could not be used. In spite of the damaged samples, the second test revealed the transition lay at the same thickness range. The data
obtained from the second test is plotted in the figure, along with error bars indicating the standard deviation of the average. The same problem encountered with the 177 °C cure test data occurred again in the 200 °C cure tests. The critical thickness transition occurred at the same solution wt%, causing a large perceived standard deviation in the strain to cracking for one of the data points. This deviation should be ignored due to the fact that it exaggerates the error actually encountered in testing.

The strain withstood by the films in the first test with a thickness above the critical thickness was noticeably greater than that of the films cured at 177 °C. The average strain above the critical thickness for the 177 °C cure was 2.47%, whereas the average strain for the 200 °C cure was 5.13%. Below the critical thickness, the values were more similar, 15.3% for 177 °C and 17.2% for 200 °C. The critical thickness transition range for the 200 °C cure was 4.4 to 4.75 microns compared with the 2.2 to 2.3 micron transition of the lower cure temperature. So, two of these values more than doubled with only an increase of 23 °C in cure temperature. This stark transition in a thermoset indicates a probable increase in the crosslink density of the network.  

### Table 4-2 200 °C cured film bending test 1 results

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Film Thickness (Microns)</th>
<th>Strain to Cracking (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51%</td>
<td>5.55</td>
<td>3.8</td>
</tr>
<tr>
<td>49%</td>
<td>4.9</td>
<td>7.3</td>
</tr>
<tr>
<td>47%</td>
<td>4.75</td>
<td>4.3</td>
</tr>
<tr>
<td>45%</td>
<td>4.4</td>
<td>16.4</td>
</tr>
<tr>
<td>43%</td>
<td>3.75</td>
<td>17.2</td>
</tr>
<tr>
<td>41%</td>
<td>3.6</td>
<td>17.9</td>
</tr>
</tbody>
</table>
Figure 4-6 Plot of 200 °C cured film bending test results

Figure 4-7 45 Percent 3136 in MIBK (Optical Magnification to 1000x)
4.4 Micron Thickness (Below Critical Thickness)
Bent over 2" rod (1.9% Strain)
Figure 4-8 45 Percent 3136 in MIBK (Optical Magnification to 1000x)
4.4 Micron Thickness (Below Critical Thickness)
Bent to 0.20” diameter (16.4% Strain)

Figure 4-9 47 Percent 3136 in MIBK (Optical Magnification to 1000x)
4.75 Micron Thickness (Above Critical Thickness)
Bent over 2” rod (1.9% Strain)
Figure 4-10 47 Percent 3136 in MIBK (Optical Magnification to 500x)
4.75 Micron Thickness (Above Critical Thickness)
Bent over 0.875"" rod (4.3% Strain)

Pictures of the optical microscopy conducted on the film samples cured at 200 °C can be found in Figures 4-7 through 4-10. The same transition that was seen in the films cured at 177 °C can be seen in these films as well. Below the critical thickness, an extremely high strain value was necessary to cause small ductile cracks. Arrows in Figure 4-8 indicate the cracks, which were at times difficult to isolate. Above the critical thickness, the cracks were much more brittle in nature as can be seen in Figure 4-10. However, the cracks did not extend all of the way through the film as they did in the films cured at 177 °C. This fact is somewhat indicative of the change in strain that could be withstood by the films cured at 200 °C below the critical thickness.
4.4 The Critical Thickness of films cured at 225° C

The results from the series of experiments conducted on films cured at 225 °C resulted in the same effect as was seen in the 200 °C cured films. The critical thickness value increased, as was the case with the 200 °C cured films. It was determined that the transition lay somewhere around 6 microns, or a 55 wt% 3136 solution. Films were originally spun out of 51 wt% to 59 wt% solutions, only to discover that the transition lay at the lower end of that series of films. Preexisting data from a 45 wt% and 50 wt% film were used to supplement the collected data for the first series of experiments. The second series of experiments took this into account and revealed the same transition range. The data from the two tests cured at 225 °C compared very closely to one another. In fact, the standard deviation for both the thickness and the strain to induce cracking was the lowest of any of the different cure temperatures.

The increase in critical thickness with an increase of 25 °C in cure temperature was again theorized to be related to crosslink density. The data collected through this series of experiments can be found in Table 4-3. The data is plotted in Figure 4-11.

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Average Film Thickness (Microns)</th>
<th>Average Strain to Cracking (%)</th>
<th>Standard Deviation of Film Thickness</th>
<th>Standard Deviation of Strain to Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>59%</td>
<td>9.25</td>
<td>2.23</td>
<td>0.565685</td>
<td>0.46669</td>
</tr>
<tr>
<td>57%</td>
<td>8.125</td>
<td>2.23</td>
<td>0.106066</td>
<td>0.46669</td>
</tr>
<tr>
<td>55%</td>
<td>7.125</td>
<td>2.45</td>
<td>0.176777</td>
<td>0.777817</td>
</tr>
<tr>
<td>53%</td>
<td>6.15</td>
<td>3.4</td>
<td>0.070711</td>
<td>0.565685</td>
</tr>
<tr>
<td>51%</td>
<td>5.5</td>
<td>13.6</td>
<td>0.353553</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>5.3</td>
<td>13.6</td>
<td>0.282843</td>
<td>0</td>
</tr>
<tr>
<td>45%</td>
<td>4.625</td>
<td>13.6</td>
<td>0.106066</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4-3 225 °C cured film bending test results

50
Figure 4-11 Plot of 225 °C cured film bending test results

Figure 4-12 51 Percent 3136 in MIBK (Optical Magnification to 1000x)
5.75 Micron Thickness (Below Critical Thickness)
Bent over 0.375” rod (9.5% Strain)
Figure 4-13 51 Percent 3136 in MIBK (Optical Magnification to 1000x)
5.75 Micron Thickness (Below Critical Thickness)
Bent over 0.25” rod (13.6% Strain)

Figure 4-14 55 Percent 3136 in MIBK (Optical Magnification to 1000x)
7.25 Micron Thickness (Above Critical Thickness)
Bent over 3.25” rod (1.2% Strain)
Figure 4-15 55 Percent 3136 in MIBK (Optical Magnification to 500x)

7.25 Micron Thickness (Above Critical Thickness)
Bent over 2” rod (1.9% Strain)

Pictures of the optical microscopy conducted on the film samples cured at 225 °C can be found in Figures 4-12 through 4-15. The pictures illustrate the same transition seen at the other cure temperatures. The post transition film in figures 4-12 and 4-13 show the development of the small ductile cracks at high strains, while the pre-transition films in figures 4-14 and 4-15 show the very brittle ductile cracking at very low strains. The transition was similar to the previous sample cure temperatures with one exception. The strain to cracking of films with a thickness greater than the transition remained low and consistent with the strains found with the 177 °C cure. This counteracts the trend found in 200 °C cured films, in which the strain withstood by films exceeding the critical thickness was twice as high than the films cured at 177 °C. The critical thickness
transition continued to increase, indicating an increase in the crosslinking density, but the strain withstood by the films before and after the transition remained similar to 177 °C.

In order to further investigate the issue, additional high curing temperatures were used.

4.5 The Critical Thickness of films cured at 250° C

The critical thickness transition of the films cured at 250 °C was the most interesting in that there really was no "critical thickness" of which to speak. The strain that could be withstood by the films before cracking did, in fact, increase with reduced thickness. However, the transition was a gentle slope over a dozen microns of film thickness, rather than the sharp transition seen at other cure temperatures. In addition, all of the 250 °C cured films could withstand substantially higher strains at a much greater thickness than any of the other films. Even at a thickness approaching 20 microns, the film had to be strained to 3.8% in order to cause cracking. This value exceeded the base strain for both the 177 °C and 225 °C cured samples. A "film" thickness of 20 microns certainly approaches the bulk properties of the material, indicating that the 250 °C cure temperature creates the toughest film possible. The data collected for these films can be found in Table 4 and plotted in Figure 4-16. The lack of a clear transition in the films is immediately apparent. This phenomenon begs the question as to why the nature of the stark transition alters with a small increase in cure temperature. The primary theory is that the increase in crosslinking density is the cause. While the crosslink density increases with cure temperature, at some curing temperature an ideal density is reached at which the toughness of the material reaches its maximum value. In the same manner, as
that cure temperature is exceeded the crosslinking density begins to have adverse affects on the toughness of the material, and it behaves in a more brittle manner.

The toughness of the 250 °C cured films at greater thicknesses and the lack of a clear transition creates a few adverse effects. In fact, at lower thicknesses, the strain to cracking achieved by the 250 °C cured films is lower than that of both the 225 °C and 200 °C cured films. A direct comparison of this can be found in Figure 4-17.

**Table 4-4 250 °C cured film bending test results**

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Average Film Thickness (Microns)</th>
<th>Average Strain to Cracking (%)</th>
<th>Standard Deviation of Film Thickness</th>
<th>Standard Deviation of Strain to Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%</td>
<td>20.375</td>
<td>3.8</td>
<td>1.237437</td>
<td>0</td>
</tr>
<tr>
<td>65%</td>
<td>13.9</td>
<td>5.8</td>
<td>0.919239</td>
<td>2.12132</td>
</tr>
<tr>
<td>63%</td>
<td>11.9</td>
<td>7.3</td>
<td>0.848528</td>
<td>0</td>
</tr>
<tr>
<td>61%</td>
<td>9.95</td>
<td>8.4</td>
<td>0.494975</td>
<td>1.555635</td>
</tr>
<tr>
<td>50%</td>
<td>5.4</td>
<td>9.5</td>
<td>0.141421</td>
<td>0</td>
</tr>
<tr>
<td>45%</td>
<td>4.725</td>
<td>11.55</td>
<td>0.035355</td>
<td>2.899138</td>
</tr>
<tr>
<td>40%</td>
<td>3.3</td>
<td>13.6</td>
<td>0.070711</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 4-16** Plot of 250 °C cured film bending test results
Maximum Strain To Cracking Comparison

![Graph showing strain to cracking comparison with different cure temperatures.]

- ◆ 250 C Cure
- ■ 225 C Cure
- □ 200 C Cure

**Figure 4-17** Comparison of maximum strains

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**Figure 4-18** 70 Percent 3136 in MIBK (Optical Magnification to 500x)

- 19.5 Micron Thickness
- Bent over 1” rod (3.8% Strain)
Figure 4-19 50 Percent 3136 in MIBK (Optical Magnification to 500x)

5.5 Micron Thickness
Bent over 0.375" rod (9.6% Strain)

Due to the fact that there was no clear transition in the samples cured at 250 °C, optical microscopy pictures of the thickest and thinnest film are presented, and can be seen in Figures 18 and 19. The transition in the type of cracking can be seen clearly in these pictures. The brittle cracking seen in the thickest film gave way to the more ductile cracks seen in the thinner film.

4.6 The Critical Thickness of films cured at 300° C
The transition of the films cured at 300 °C was the least clear of all of the tests. The problem was confounded further by the inconsistency encountered in the experimentation. The first run of tests indicated a slow transition, somewhere between the clear transition of the films cured at low temperatures and the gentle slope
encountered for the 250 °C cure. The strain that could be withstood by these films was also markedly lower than that of the other cure temperatures. This corroborates with the theory that the crosslinking density exceeded the “ideal crosslink density” encountered at the 250 °C cure. As a result, the strain that the films could withstand reduced.

Unfortunately, the second set of tests resulted in strains that did not match well with the first. While the film thickness consistency remained at an acceptable level, a 2 % standard deviation was observed, an error of over 30 %. Despite these problems, the transition was observed to occur in the same range, which was the primary goal of the experimentation. Future research could be conducted to better characterize the exact nature of the transition at 300 °C. The results of the testing can be found in Table 4-5 and plotted in Figure 4-20. Due to the lack of a single transition thickness, optical microscopy pictures of the thickest and thinnest films are included. One of the particularly interesting aspects of the 300 °C cure was the observation that the nature of the cracks did not change considerably with the reduction of thickness. While the cracks did reduce somewhat in length, they were brittle in appearance even in the thinnest films.

The optical microscopy pictures can be found in Figures 4-21 and 4-22.

### Table 4-5 300 °C cured film bending test results

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Average Film Thickness (Microns)</th>
<th>Average Strain to Cracking (%)</th>
<th>Standard Deviation of Film Thickness</th>
<th>Standard Deviation of Strain to Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>61%</td>
<td>10.25</td>
<td>3.18</td>
<td>0.212132</td>
<td>0.876812</td>
</tr>
<tr>
<td>59%</td>
<td>8.675</td>
<td>4.45</td>
<td>0.247487</td>
<td>2.05061</td>
</tr>
<tr>
<td>57%</td>
<td>7.875</td>
<td>5.8</td>
<td>0.247487</td>
<td>2.12132</td>
</tr>
<tr>
<td>55%</td>
<td>7.4</td>
<td>5.8</td>
<td>0.247487</td>
<td>2.12132</td>
</tr>
<tr>
<td>53%</td>
<td>6.2</td>
<td>6.15</td>
<td>0</td>
<td>1.626346</td>
</tr>
<tr>
<td>51%</td>
<td>5.85</td>
<td>6.65</td>
<td>0.141421</td>
<td>0.919239</td>
</tr>
</tbody>
</table>
Figure 4-20 Plot of 300 °C cured film bending test results

Figure 4-21 51 Percent 3136 in MIBK (Optical Magnification to 500x)
5.75 Micron Thickness
Bent over 0.5" rod (7.3% Strain)
4.7 Tensile testing of films cured at 177° C

In order to obtain corroborative evidence of the critical thickness transition in 4-3136, tensile testing of films cured at 177 °C was conducted. These results compared favorably with the bending tests. The same series of solutions was used as in the bending tests. The transition was observed to occur at the same thickness as the bending tests. The main difference in the results was in the strain to induce cracking. The strain values were higher than were seen in the bending test. We believe that the reason for this change was the strain rate. The carefully controlled strain rate of 5 mm/min used on the Instron was substantially lower than could be achieved with the bending tests. This reduction in strain rate translated to higher strains without inducing cracks. The appearance of the cracks seen with the tensile tests differed from the bending tests as
well. This was most likely caused by the inherent differences between tensile and bending testing. The data collected through these tests are listed in Table 4-6 and plotted in Figure 4-23. The strain to induce cracking for 27% is listed as a “greater than” value because a thumbprint induced early cracking.

<table>
<thead>
<tr>
<th>Solution wt% 3136</th>
<th>Film Thickness (Microns)</th>
<th>Strain to Cracking (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37%</td>
<td>2.6</td>
<td>7.7</td>
</tr>
<tr>
<td>35%</td>
<td>2.4</td>
<td>10.5</td>
</tr>
<tr>
<td>33%</td>
<td>2.3</td>
<td>10.5</td>
</tr>
<tr>
<td>31%</td>
<td>2.2</td>
<td>17</td>
</tr>
<tr>
<td>29%</td>
<td>1.9</td>
<td>16.6</td>
</tr>
<tr>
<td>27%</td>
<td>1.5</td>
<td>&gt;13.7</td>
</tr>
</tbody>
</table>

**Table 4-6 177 ° C cured film tensile test results**

**Critical Thickness of 3136 (177 C Cure Tensile Test)**

**Figure 4-23** Plot of 177 ° C cured film tensile test results
Figure 4-24 37 Percent 3136 in MIBK (Optical Magnification to 1000x)

2.6 Micron Thickness (Above Critical Thickness)
10.5% Strain

Figure 4-25 29 Percent 3136 in MIBK (Optical Magnification to 1000x)

1.9 Micron Thickness (Below Critical Thickness)
16.6% Strain
Optical microscopy pictures of a film with a thickness above the transition can be seen in Figure 4-24. The cracks do not extend in the manner that they did in the bending tests, but their brittle nature is readily apparent. Figure 4-25 shows a small ductile crack in a film below the transition thickness. These small cracks were spaced evenly throughout the film.

4.8 Scanning Electron Microscopy of Cracked Films

Scanning Electron Microscopy on a cracked film was conducted in order to provide corroborative evidence for the optical microscopy conducted on all samples. Lower magnifications were used to provide a view similar to that obtained with optical microscopy. Higher magnifications were also used to determine the nature of the crack arrest mechanism. The primary detector was used for all microscopy, as the backscatter detector did not provide ample resolution at higher magnifications. Unfortunately, due to the nonconducting nature of the film and the conducting substrate below, higher magnification microscopy with the primary detector still did not have the resolution necessary to glean a substantial amount of information about the crack arrest mechanism. Figure 4-26 presents the film at 100X magnification, centered at the edge of the thicker lip of the film. The brittle cracks in the lip of the film can be compared to the small ductile cracks in the thinner center portion of the film. Figures 4-27 through 4-30 show increasing magnification of a crack arrest region. There is no clear crack arrest mechanism that can be seen from these pictures, even at 20,000X.
Figure 4-26 29 Percent 3136 in MIBK (SEM Magnification to 100x)
1.9 Micron Thickness (Below Critical Thickness)
13.6% Strain

Figure 4-27 29 Percent 3136 in MIBK (SEM Magnification to 500x)
1.9 Micron Thickness (Below Critical Thickness)
13.6% Strain
Figure 4-28 29 Percent 3136 in MIBK (SEM Magnification to 2000x)
1.9 Micron Thickness (Below Critical Thickness)
13.6% Strain

Figure 4-29 29 Percent 3136 in MIBK (SEM Magnification to 10,000x)
1.9 Micron Thickness (Below Critical Thickness)
13.6% Strain
Figure 4-30 29 Percent 3136 in MIBK (SEM Magnification to 20,000x)

1.9 Micron Thickness (Below Critical Thickness)
13.6% Strain
5 Conclusion and Future Work

The critical thickness transition of the Dow Corning 4-3136 resin and the variation of that property with cure temperature were determined through this research. A substantial increase in toughness with the reduction of film thickness was demonstrated. A plot of all data obtained throughout the tests can be found in Figure 5-1.

![Critical Thickness for 3136](image)

**Figure 5-1** The critical thickness of 4-3136 cured at five temperatures

The intrinsic ductility of the silicone polymer was successfully accessed through a thickness reduction in a thin film. Increased crosslinking density with cure temperature caused a reduction in the transition intensity. Higher cure temperature also caused the
critical thickness to increase, but reduced the maximum attainable strain without cracking. The films cured at 250 °C was the toughest over a wide range, while the films cured at 177 °C had the maximum possible strain without cracking.

Future research should include determining the precise change in crosslink density with increasing cure temperature. Fourier Transform Infra-Red analysis should also be conducted to determine whether there is any change in polymer orientation or composition with cure temperature. A method for the production of freestanding films could be devised, so that substrate interactions can be avoided. Multilayer films that take advantage of the critical thickness, while possessing the size of bulk materials, would also be advantageous for practical applications.
Appendix 1

Polycarbonate after short exposure to toluene.
Magnified 500x
Polycarbonate after longer exposure to toluene.
Magnified 500x
Appendix 2

29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent over 0.375” rod (9.5% Strain)
Optical Magnification to 100x
29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent over 0.375" rod (9.5% Strain)
Optical Magnification to 1000x
29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent over 0.25” rod (13.6% Strain)
Optical Magnification to 100x
29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent over 0.25” rod (13.6% Strain)
Optical Magnification to 1000x
29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent to 0.16" diameter (19.7% Strain)
Optical Magnification to 100x
29 Percent 3136 in MIBK
Stainless Steel Substrate with #8 Mirror Polish
Spun at 1300 RPM for 1 Minute
177 °C Cure Temperature
1.9 Micron Thickness

Bent to 0.16" diameter (19.7% Strain)
Optical Magnification to 1000x
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