Modeling Heat Transfer and Densification during Laser Sintering of Viscoelastic Polymers

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Abstract

Laser sintering (LS) is an additive manufacturing process which uses laser surface heating to induce consolidation of powdered materials. This work investigates some of the process-structure-property relationships for LS of viscoelastic polymers. A one-dimensional closed-form analytical solution for heating of a semi-infinite body, with a convective boundary condition, by a moving surface heat flux was developed. This solution approximates the shape of the Gaussian energy distribution of the laser beam more accurately than previous solutions in the literature. A sintering model that combines the effects of viscoelastic deformation driven by attractive surface forces and viscous flow driven by curvature-based forces was developed. The powder-bed temperature was approximated using the thermal model developed herein. The effect of the enthalpy of melting for semi-crystalline polymers was accounted for using a temperature recovery approach. Time-temperature superposition was used to account for the temperature dependence of the tensile creep compliance. The results of the combined-mechanism sintering model will be compared to the classic Mackenzie-Shuttleworth sintering model. A lab-scale LS unit was constructed to fabricate test specimens for model validation and to test the applicability of materials to LS. In this work, sintering four materials, polycarbonate (PC) and three molecular weights of polyethylene-oxide (PEO) was predicted using the aforementioned thermal and sintering models. Samples were fabricated using the lab-scale LS unit and the sintered microstructures were investigated using scanning electron microscopy. The rheologic, thermal and physical properties of the materials were characterized using standard methods and the relevant properties were used in the models. The choice of an amorphous polymer, PC, and a semi-crystalline polymer, PEO, affords comparison of the effects of the two material forms on contact growth during LS. The three molecular weights of PEO exhibit significantly different tensile creep compliances, however, the thermal and physical properties are essentially the same, and therefore the effect of molecular weight and subsequently the rheologic characteristics on contact growth during LS will be investigated. The effects of particle size, laser power, and bed temperature were also investigated.
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1 INTRODUCTION

New manufacturing technologies offer alternative means of producing prototypes, patterns, models, and low volume parts faster and at reduced costs compared to traditional manufacturing processes. Unlike most traditional manufacturing techniques, these new technologies, termed solid freeform fabrication techniques (or historically rapid prototyping), are additive processes and require no part specific tooling. Only small amounts of waste material are generated during solid freeform fabrication (SFF), unlike subtractive processes such as machining where a significant amount of waste can be generated. The main advantage of SFF processes is the ability to rapidly produce net or near-net shape parts with varying geometries using a single machine with no part specific tooling.

As solid freeform fabrication technologies advance into the realm of low-volume and/or custom manufacturing, the material systems used must afford the same robust mechanical properties which are the norm for parts made by conventional processing techniques. However, most of the materials systems currently available for solid freeform fabrication yield delicate parts that have a short, if any, functional life. Laser sintering (LS), often referred to as SLS® (which stands for Selective Laser Sintering a copyrighted acronym) is one of several different solid freeform fabrication techniques currently in use.

Laser sintering offers several advantages over other solid freeform fabrication techniques, first LS does not involve long-range flow or transport of liquid material, flow distances are typically 50µm or less. Second, LS is based on sintering of powdered material via localized laser heating, therefore, given a laser of high enough power and proper wavelength, LS should be applicable to processing any powdered material. Because of the wide range of potential materials, LS is an ideal candidate for researching and developing new material systems for SFF.

If more material systems were developed, LS could become an increasingly attractive alternative to conventional processes, such as injection molding, when only limited production is required. The growth of 3-dimensional imaging technology has also lowered the barrier to custom manufacturing. For example, Siemens fabricates all of their high-end hearing aids by reverse engineering silicone impressions of a customer’s ear and then manufactures the hearing aid shell using a 3D Systems LS machine. LS can offer both a fixed cost reduction and faster turn around time for limited production parts. LS is particularly attractive for fabricating small complex geometries, which may not be manufacturable as a single object by other technologies. Other applications of LS currently include investment casting patterns, sand casting molds and rapid tool development.

The lack of materials for LS can be attributed to two issues: 1) a large amount of material (approximately 1ft³ of powder) is required for operation of the commercial LS machine and 2) the lack of quantified understanding of the process-structure-property relationships for LS. A path to increasing the number of materials for LS should include the development of analytical and empirical models which include relevant sintering mechanisms and material properties. Such models could then be used to guide material selection and determination of LS process parameters. Additionally, development of a versatile laboratory-scale LS platform which can be used to test small amounts of powdered material could be beneficial in future LS research.

1.1 LS PROCESS

The geometry of a part to be made by LS or any SFF technique is converted to the STL format. In the STL format part geometry is approximated by a triangular surface mesh that bounds the solid volume. Before the geometry is fabricated, the STL file is “sliced” into a series of cross-sections of a given thickness using a slicing algorithm. Each of these cross-sections is then built in succession to form the part. The laser sintering process, schematic shown in Figure 1.1, starts by repeatedly depositing smooth, uniformly dense layers of powder into the part bed until a powder base of a set depth is deposited. The temperature of the part bed is ramped up to its operating temperature as the base layers are added; heaters are positioned above the part bed. The powder is delivered from heated feed cylinders (only one is shown in the figure) on either side of the part bed via a counter-rotating roller. The part bed is then raster scanned by a CO2 laser beam, fusing corresponding areas in the powder bed into a solid image of a given slice. The part bed is then lowered a given distance, (3-6 thousandths of an inch is typical), and additional powder is added to the part bed on top of the layer previously scanned. The next slice of the STL file is then fused onto the previous slice by raster scanning the laser beam. Successive layers are then deposited and fused in the same manner until the desired part geometry is complete. The entire powder bed is then removed from the process station and the part separated from the powder that supported it during fabrication. Unfused powder can then be reused in future builds. The most commonly used material for LS part production is nylon 12 (sold under the trade name DuraForm PA by 3D Systems), an engineering thermoplastic; this powder is available in neat (unfilled) form and glass filled.
DuraForm PA is most commonly used for manufacturing prototypes and functional parts but can also be used for sand casting patterns.

This research will deal with direct processing of polymeric materials via LS; however, there are areas where application to other materials will be appropriate. The key process variables in LS are: laser power ($P$), scan speed ($V$), scan vector length ($L$), scan spacing ($SCSP$), beam diameter ($2\omega$), layer thickness ($LT$), part bed temperature ($PBT$), powder supply temperature ($PST$), the dwell time between scanning and layer addition ($WS$) and the dwell time between layer addition and commencement of scanning the new layer ($WL$). Figure 1.2 illustrates several of these variables; note that the beam is “on” when it moves parallel to the scan vector length and “off” when it moves parallel to the scan spacing direction. The $SCSP$ is typically 3-6 times smaller than the beam diameter so each point on the bed has multiple laser exposures. Polymer powders used for LS processing typically have an average particle size in the range of 20-80µm. To produce geometrically accurate and mechanically robust parts by LS a balance must be struck between maximizing the temperature to increase part density and minimizing the temperature to maintain geometric accuracy. From a materials science point of view laser sintering consist of the following processes: part bed heating, intra-layer densification, layer addition, and inter-layer welding.

1.1.1 Part Bed Heating

Initially, the part bed is heated to a temperature where un-scanned powder does not consolidate over the time scale of a part build. For semi-crystalline polymers the part bed temperature is above the glass transition temperature, $T_g$, and below the melting temperature, $T_m$. For amorphous polymers the part bed temperature is less than or approximately equal to the glass transition temperature. Maximizing the part bed temperature: 1) minimizes the
amount of laser energy needed for consolidation, 2) minimizes the thermal gradient between the consolidated and unconsolidated powder and 3) minimizes the thermal expansion due to heating by the laser. Part bed heating is one aspect of LS where profitability and part quality are at odds; the expense of powder is such that reusing unconsolidated powder is necessary. The powder properties change/degrade with use; for example: nylon 12 undergoes both solid-state polymerization which increases melt viscosity\(^1\) and powder agglomeration which increases part roughness. Using a lower part bed temperature slows degradation. In practice a balance must be struck between making the best possible parts and extending the life of the powder. Better understanding of the mechanisms of material change in the un-sintered powder, could aid in material selection and development for LS.

### 1.1.2 Intra-layer Consolidation

Intra-layer consolidation refers to sintering powder laid down in a single layer; see Figure 1.3. Intra-layer consolidation of polymer powders by LS has historically been attributed to viscous sintering of amorphous liquid\(^2\). This research also investigates the contribution of viscoelastic contact growth to intra-layer sintering. The intra-layer density achieved during LS depends on the properties of the powder, the bed temperature, which is a function of processing parameters, and time - due to the dynamic nature of raster scanning the laser beam over the part bed. The temperature at which intra-layer consolidation occurs depends on laser power, scan speed, scan spacing, vector length, part bed temperature, powder supply temperature, beam diameter, and both dwell times. The temperature dependence on most of these variables will be explored in the thermal modeling section. Previous research has shown, Figure 1.4, that consolidating a single layer of polymer powder by LS can easily be accomplished.

![Figure 1.3: Intra-layer consolidation.](image)

![Figure 1.4: PC-PEEK samples showing intra-layer sintering, individual layer marked by brackets\(^3\).](image)
The optimal layer thickness has been empirically determined to be 2-3 times the average particle size, $\bar{O}_{\text{avg}}$. An explanation for the aforementioned layer thickness observation is: when a layer thickness of 2-3$\bar{O}_{\text{avg}}$ is used, as shown in Figure 1.3, the average random orientation of the powder particles is such that most particles receive direct laser impingement, a much more effective heating mechanism than particle-to-particle conduction. If the layer thickness is greater than 2-3$\bar{O}_{\text{avg}}$, the particles below 2-3$\bar{O}_{\text{avg}}$ will be heated by particle-to-particle conduction. This logic begs the question: why not use a layer thickness of $\sim \bar{O}_{\text{avg}}$ so that only a single layer of powder particles compose each layer? A layer thickness of $\bar{O}_{\text{avg}}$ would result in segregation of the powder by particle size as it is spread by the roller. Typical particle size distributions contain some particles of $\sim 2\bar{O}_{\text{avg}}$, when a layer thickness of 2-3$\bar{O}_{\text{avg}}$ is used then little, if any, size segregation occurs. To average out any size segregation that does occur due to rolling, powder is fed from alternating sides of the part bed for alternating layers.

### 1.1.3 Layer Addition

Layer addition is the first step towards inter-layer consolidation. This step may seem trivial but it is often the limiting step in LS of polymers. As previously stated, consolidating a layer of polymer powder is straightforward; however, density gradients and thermal warping can cause curling of the layer, as shown in Figure 1.5. After the previous layer has been scanned and the dwell time has passed, the part bed drops one layer thickness and a counter-rotating roller spreads powder (at the powder supply temperature) from the powder supply over the previously scanned layer. Curling can make layer addition impossible without moving the curled layer. Assuming a perfectly elastic material that didn’t develop a density gradient, curling would dissipate as the sintered layer returned to equilibrium. However, the viscoelastic deformation of polymers and the density gradients that develop (especially in the first layer) alters the situation.

![Figure 1.5: Layer curling due to density and thermal gradients.](image)

Assuming no curling or a sufficiently small amount such that addition of the next layer is not inhibited, a uniform powder layer is added, via the counter-rotating roller, on top of the previously scanned liquid layer. Minimizing the difference in temperature between the sintered polymer and the new powder layer is of crucial importance. If the powder is too cold curling in the previously scanned layer will be increased or induced. If the powder is too hot it will be too tacky to flow and spread. However, the tacky nature of the sintered surface is advantageous to inter-layer welding because adhesion of powder to the sintered surface increases the area of initial intimate contact between molecules of the two layers. Increased adhesion results in faster healing of the weld, thus the mechanical properties at the inter-layer weld will approach those of the bulk faster.

### 1.1.4 Inter-layer Welding

As is evident in Figure 1.4, some level of intra-layer consolidation can be achieved with out entirely healing the weld between layers; this is logical because the heat to heal the weld must be transferred through the layer to the inter-layer weld. The temperature at which inter-layer welding occurs is dependent on the same properties as intra-layer consolidation with the addition of layer thickness. With one exception known to the author, no distinction is made in the literature between intra-layer consolidation and inter-layer welding.
1.2 POLYMERS PROPERTIES IMPORTANT TO LS

Polymers were the first material to be processed by LS. There are several properties of polymers that make them easier to process by LS than other materials: polymers have a relatively high viscosity in the liquid state, relatively low surface energy, low reactivity with most gases, and low thermal conductivity. The molecular weight (MW) of a polymer to be processed by LS should be above the critical entanglement molecular weight to impart good mechanical properties, but low enough that the melt viscosity, which scales as $MW^{3.4}$ above the critical entanglement length, isn’t so high that the temperature necessary for sintering also causes degradation.

Semi-crystalline polymers have a first-order melting transition which results in a drastic decrease in viscosity over a relatively small temperature range. Because of the drastic decrease in viscosity, parts fabricated from semi-crystalline polymers have tighter tolerances than parts fabricated from amorphous polymers. Figure 1.6 shows a qualitative schematic of the viscosity as a function of temperature for a semi-crystalline and an amorphous polymer. The drastic drop in the viscosity of a semi-crystalline polymer allows for setting the part bed temperature much closer to the temperature range where rapid coalescence of the particles occurs, while minimizing sintering in the un-scanned regions of the powder bed. Upon cooling from the liquid state, semi-crystalline polymers solidify at a temperature below the melting temperature, known as the re-crystallization temperature. The re-crystallization temperature of a semi-crystalline polymer is important in LS because maintaining the polymer in a liquid state for at least the addition of several layers is speculated to be important for inter-layer welding and maintaining accurate part geometry. Because melting and re-crystallization are first-order phase transitions, there are enthalpies associated with the transitions. Ideally both enthalpies would be equal in magnitude and opposite in sign. The enthalpy of melting is endothermic, thus it acts as an energy barrier to melting. The enthalpy of fusion is exothermic thus it inhibits solidification from the liquid state. A narrow melting peak, as observed by differential scanning calorimetry, is desirable because the part bed temperature can be raised closer to the average melting temperature, thus minimizing the laser power required for melting.

A physical change in an amorphous polymer occurs at the glass transition temperature which is a quasi-second order phase transition. There is no enthalpic change associated with this transformation thus controlling the amount of liquefied powder in the powder bed is more difficult. The relatively weak dependence of viscosity on temperature above the glass transition temperature makes amorphous polymers more difficult to process by LS because more sensible heat (heat associated with increased temperature) is required to decrease the viscosity as compared to semi-crystalline polymers. More heat in the powder bed increases the potential for part growth – an undesirable increase.
in the dimensions of a sintered part resulting from excess heat which sinters powder adjacent to the desired part geometry.

The tensile creep compliance, $D(t)$, describes the rheologic properties of most polymeric liquids. The tensile creep compliance, [1.1], is composed of three terms, each dominating in a specific time range. $D_0$ is the instantaneous elastic compliance which dominates at very short times. $D_v(t)$ is the viscoelastic contribution to the compliance which dominates in the intermediate time range. $t/\eta_0$ is the viscous component of the compliance which dominates at long times. Figure 1.7 is a representative creep compliance curve. The total compliance is represented by the squares, the viscous component is represented by the dashed line and the dotted line represents the sum of the elastic and viscoelastic components some times referred to as the retarded elastic component. Two important features of the compliance curve are: 1) the “plateau” value in the viscoelastic time range of the compliance curve, referred to as $D_n$ and 2) the time when the viscous component exceeds the retarded elastic component, referred to as the characteristic relaxation time $\tau$. Figure 1.8 is a schematic of the mechanical analog for the creep compliance function, which is composed of a Maxwell element in series with an infinite number of Kelvin elements. $D_v(t)$ is calculated using [1.2], where the compliance density (also referred to as the retardation spectrum), $L(\tau)$, is the compliance spectrum of all the individual Kelvin elements as shown in Figure 1.9.

$$D(t) = D_0 + D_v(t) + \frac{t}{\eta_0} \tag{[1.1]}$$
Figure 1.7: Representative creep compliance curve, modeled after\textsuperscript{8}.

\[ D_v(t) = \int_{-\infty}^{0} L(\tau) \left(1 - e^{-\frac{t}{\tau}}\right) d\ln \tau \] \hspace{1cm} [1.2]

Figure 1.8: Mechanical analog of tensile creep compliance function.

Figure 1.9: Compliance density, modeled after\textsuperscript{9}. 
Traditional sintering models for amorphous materials, such as those by Frenkel, Mackenzie-Shuttleworth and Scherer, consider viscous flow as the only mode of deformation by which densification occurs. As is evident from Figure 1.7, the viscoelastic component of the creep compliance is much larger than the viscous component for short times and thus could contribute to densification in this time range. The duration of time a polymer is in the liquid state during LS is short compared to most traditional polymer sintering processes. Therefore, sintering due to viscoelastic deformation may be important. As such, a sintering model for the LS process which considers sintering by viscous and viscoelastic deformation will be developed in this work.

In addition to a sintering model, an analytical thermal model of laser heating will also be developed. The objectives of this research will be detailed later in this chapter. In the following sections, previous research in the three major areas of interest for this work will be reviewed. First, a review of previous efforts to model the LS process will be presented. Second, amorphous sintering models are reviewed, with a focus on contact growth via viscoelastic deformation. Finally, a review of heat transfer models which are applicable to laser heating is presented.

1.3 REVIEW OF LS MODELS

Sun, M.-S. M. Beaman, J. J. Barlow, J.W. 1990

Sun et al present a one-dimensional model of the LS process which considers sintering of a single layer\textsuperscript{10}. The beam energy is modeled as a moving square flux, convective heat loss at the powder surface is not considered and temperature independent material properties are assumed in the solution of this heat transfer problem. However, density dependent thermal properties are considered. The sintering behavior is modeled using Scherer’s viscous sintering model. The heat transfer problem is solved using a finite difference method. The temperature as a function of position for each time step is used to determine the polymer viscosity and the density dependent thermal properties of the powder bed as a function of position. In Reference \textsuperscript{10}, the upper plot in Figure 4 is a plot of the temperature as a function of depth into the bed for several different times for LS of acrylonitrile-butadiene-styrene plastic powder. The authors’ model predicts surface temperatures in excess of 1000°C for short times. In Reference \textsuperscript{10} Figures 6 and 7 are plots presented by Sun et al comparing the sintering depth as a function of laser power and exposure time (which is proportional to the scan speed) as predicted by their model to experimental results for ABS powder. The authors’ model consistently underestimates the sintering depth as a function of laser power by approximately 20%. However, the authors’ model does not predict the sintering depth as a function of laser exposure time to the same level of accuracy.


The authors’ proposed a sintering model based on an energy balance between the total surface energy reduction and the energy dissipated through viscous flow\textsuperscript{11}. The unit cell structure for densification is a shrinking cube, as shown in Figure 1.10, which could also be represented by a simple cubic unit cell. The authors chose a simple cubic geometry for their sintering model because the relative densities of most powders used in LS are similar to that of a simple cubic packing of mono-sized spheres, 0.523. The authors’ model predicts the rate of cube shrinkage for an amorphous powder being laser sintered to be that of equation [1.3], where $\rho$ is the instantaneous density, $\gamma$ is the surface energy, $\eta$ is the viscosity and $\xi$ is a factor representing the probability that a neck will form between adjacent particles.

\begin{equation}
2x
\end{equation}

\textbf{Figure 1.10:} Shrinking cube densification geometry.
\[
\dot{x} = -\frac{3(1 - \rho)\pi a^2}{24\eta x^3} \left[ r - (1 - \tilde{\xi})x + (x - (\tilde{\xi} + \frac{1}{2})R) \frac{9(x^2 - r^2)}{18rx - 12r^2} \right]
\]  

[1.3]

Sun, M.-S. M. Beaman, J. J. 1991

Sun and Beaman extended their previous model\(^\text{10}\) of laser sintering into a three-dimensional model of a single layer\(^\text{12}\). Densification was modeled using the sintering model discussed just above\(^\text{11}\). The model extended the previous work by assuming the incident laser energy is a moving Gaussian internal heat source, considering the optical absorptivity of the packed powder bed, considering heat loss through the powder bed surface by convective and radiative heat transfer and the temperature dependence of material properties. As in their previous work, the authors compared the sintering depth as a function of laser power and inverse scan speed predicted by their model to experimental results, Figures 6 and 7 in Reference \(^\text{12}\). The model predictions for sintering depth as a function of inverse scan speed and laser power are in good agreement with experimental results for LS of polycarbonate powder. The authors stated that the results of the three-dimensional model were similar those of the previously reported one-dimensional model.


Nelson et al proposed a dimensional group\(^\text{13}\), the energy density (sometimes referred to as the Andrew number), based on combining some of the major process variables in LS, laser power \((P)\), beam radius \((\omega)\), scan velocity \((V)\) and scan spacing \((\text{SCSP})\). The authors postulated that this group could be used to simplify the LS process parameter space. The energy density is a measure of the energy input into the powder bed per unit area.

\[\text{Energy Density} = \left(\frac{P}{\pi \omega^2}\right) \left(\frac{2\omega}{V}\right) \left(\frac{2\omega}{\text{SCSP}}\right) = \frac{4P}{\pi V \text{SCSP}}\]  

[1.4]

Nelson et al rationalized the group as follows: the first term in the un-simplified equation is proportional to the laser energy absorbed by the powder under the beam. The second term approximates the time that a circle of radius \(\omega\) is directly impinged upon by the laser beam. The third term approximates the number of laser pulses incident on any point in the powder bed. The third term arises from the fact the scan spacing is smaller than the beam diameter so each scan vector partially overlaps the previous. The authors showed that the energy density can be used to correlate process parameters with physical characteristics such as depth and degree of sintering. The authors showed a qualitative correlation between the energy density and the observed degree of sintering.

Childs, T. H. C. Cardie, S. Brown, J. M. 1994

Childs et al recognized that when the scan spacing is smaller than the beam diameter and the scan speed is relatively fast, the densification front appears to move uniformly in the direction perpendicular to the scan vectors\(^\text{14}\). Thus, Childs et al approximated the rastering beam as a moving rectangular heat flux of constant intensity. This approximation does not account for any effect of raster-scan-related thermal gradients. The authors numerically solved the classical moving rectangular heat flux equation to obtain the temperature distribution as a function of position for a single layer. The temperature distribution for the layer was then used in conjunction with a simple Arrhenius sintering model to predict the density of multi-layer polycarbonate (PC) parts. The thermal properties of the powder bed were assumed to be independent of temperature and density. Figure 6 in Reference \(^\text{14}\) is a plot of part density as a function of energy density. The upper and lower solid lines are the authors’ model results assuming the thermal properties are that of a PC powder bed at 154 C and assuming the thermal properties are that of solid PC at 154 C, respectively. The open and closed circles are experiential density values measured by Childs et al. The black crosses are data previously presented by Nelson et al. When properties of solid PC are assumed the authors’ model is in fair agreement with experimental results.
Weissman, E. M., Hsu, M. B. 1991

Weissman and Hsu developed a multi-layered, one-dimensional finite element model of the LS process using MARC finite element analysis software\textsuperscript{15}. The authors’ model used a moving square flux boundary condition to represent the laser beam energy and convective and radiative heat losses were not considered. The model assumed temperature dependent viscosity based on an Arrhenius relationship. Temperature and density dependent thermal conductivity was assumed. Sintering was modeled using the Scherer model for relative densities less 0.94 and the Mackenzie-Shuttleworth sintering model was used for relative densities above 0.94. Temperature and density were reported as a function of depth into bed for ABS plastic. The model predicted surface temperatures in excess of 4000K.

Lee, B.-L. 1991

Lee proposed that three densification mechanisms are at work in to LS of polymer powders: contact growth by viscous flow which is driven by surface energy reduction, contact growth by viscoelastic deformation which is driven capillary forces and viscous squeeze flow which is driven by the force exerted from mass above the contact area. The author proposed that the first mechanism can be described by Frenkel’s model of viscous sintering. Equation [1.5] is Lee and Radok’s equation for contact growth by viscoelastic deformation which was proposed to describe the second mechanism. In [1.5], $a$ is the contact radius, $c$ is a packing constant, $J_c$ is the time dependent creep compliance, $\gamma$ is the polymer surface energy and $R$ is the particle radius. The author proposed modeling squeeze flow using a classical fluid mechanics model for squeeze film flow. Lee made no reported attempt at developing a model which incorporates these densification mechanisms.

\[ a^3 = c J_c(t) \gamma R^2 \]  

[1.5]

Miller, D. Deckard, C. Williams, J. 1997

Miller et al developed a parametric equation using data from a two-level fixed factorial experiment (design of experiments approach) to predict part strength as a function of processing parameters\textsuperscript{16}. This work was completely empirical, no physically significant process-structure-property relationship were used in the model. However, the authors acknowledged that the energy density approach to modeling LS does not account for: the influence of the scan vector length on the temperature distribution in the bed, the effects of dwell time between layers or heat loss by convection and/or radiation.

Williams, J. D. Deckard, C. R. 1998

Williams and Deckard developed a numerical model similar to Sun’s et al.’s. However, the objective of the modeling exercise was to account for the experimentally observed dependence of part properties on beam diameter, dwell time and scan spacing, independent of scan speed and laser power\textsuperscript{17}. The model was solved using a feed forward finite difference method. The thermal profiles presented show the dependence of the layer temperature on the aforementioned variables regardless of scan speed and laser power. Figures 12 and 13 in Reference\textsuperscript{17} show the temperature as a function of time for raster scan patterns with different scan vector lengths, $L=2.54\text{mm}$ and $L=254\text{mm}$, respectively. The solid line is the surface temperature and the dashed line the temperature at an undefined depth below the surface. For the shorter scan vector length, the effects of the initial and final passes are minor. For the longer scan vector length, the effects of the initial and final passes are additional minor temperature increases. $A_n$, referred to in the plots, is the energy density which is constant for both plots. The differences in the two temperature profiles explicitly show that the energy density does not entirely described the thermal process which occurs during LS. Additionally, the authors showed that the energy density does not correctly account for differences in beam diameter.

Cervera, G. B. M. Lombera, G. 1999

Cervera and Lombera developed a three-dimensional finite element model for LS of a single scan vector\textsuperscript{18}. A coordinate transformation was used to obtain a quasi-steady state solution for the heat transfer equation. Sintering was modeled using the Scherer and Mackenzie-Shuttleworth models in their respective ranges of absolute applicability. Convective and radiative heat losses from the surface were considered. Temperature dependent viscosity was modeled by an Arrhenius relationship. Figures 6 and 7 in Reference\textsuperscript{18} show plots of the temperature and density distributions, respectively, in a PC powder bed resulting from LS at the laser power and scan speed.
indicated. Since the energy delivered to the powder surface is symmetric about the path of the beam center, only half of the distribution needs to be modeled. Both of the aforementioned distributions are symmetric about their left planes. The validity of the model is questionable because the authors presented results of a model which used an unrealistically high laser power, 200W, and very low scan speed, 0.5 m/s which resulted in bed surfaces temperatures in excess of 2500K.

Tontowi, A. E. Childs, T. H. C. 2001

Tontowi and Childs developed a two-dimensional finite element model for LS of nylon 12 which accounts for the latent heat of melting, $L$, of the semi-crystalline polymer. A temperature recovery method was used to account for the phase change; Equation [1.6] and Figure 1.11 describe phase change as approximated by the temperature recovery method. $\alpha$ is the fraction of solid material and varies from 1 for a solid material to 0 for a liquid material. $c_p$ is the specific heat. Finite element solutions step through time in discrete intervals and the temperature change, $\Delta T$, is calculated for each node during a specific time interval. For nodes with temperatures above the melting temperature, $T_m$, and $\alpha$ less than 1, the nodal temperature is reduced to the melting temperature and $\alpha$ is incremented according to [1.6]. No mention was made of the effect phase change had on the temperature distribution; nor were temperature or density distributions in the powder bed reported. Sintering was modeled using an empirical Arrhenius relationship developed by Childs previously and shrinkage was assumed to occur only in the direction normal to the powder surface. Figure 5 in Reference 19 shows predictions of part density as a function of energy density for three bed temperatures and experimental data from parts fabricated at the highest bed temperature. A step change in part density as a function of energy density is observed and noted by the authors to be different from what is observed for amorphous polymers. However, no explanation was given for the observed step change.

\[ \Delta \alpha = \frac{c_p}{L} \Delta T \]  

[1.6]

![Schematic of the temperature recovery method.](image)

Rimell, J. T. Marquis, P. M. 2000

Rimell and Marquis investigated LS of ultra high molecular weight polyethylene for use in fabrication of custom orthopedic prostheses. Unsatisfactory curling and polymer degradation (chain scission, cross-linking and oxidation) were reported. Low-density powder (porous particles) was used and reported to be one possible source of part curling. Environmentally controlled lasing studies were proposed to determine degradation reactions. Rimell and Marquis concluded that LS was limited to commercial equipment and specialized powders.
1.4 REMARKS ABOUT LS RESEARCH

Over the short period that LS has existed, many efforts at modeling the process have been made. Modeling is particularly important to understanding the LS process because there is no practical means of measuring the local bed temperature around the beam or observing the sintering processes. With the exception of the work of Nelson et al, all of the modeling efforts to date have used numerical techniques to determine the temperature and density distributions in the powder bed. Nelson et al’s approach of trying to explain LS in terms of a group of process variables, the energy density, has much merit and has been somewhat successful in predicting the effects of process parameter changes on part properties such as density and layer thickness for specific systems. However, in the limit as the velocity goes to zero the energy density term goes to infinity. Additionally, the energy density term does not consider the rate effects of the scan vector length or the material properties of the powder bed. Attempts at numerical modeling of the LS process have produced a wide spectrum of temperature distributions in the powder bed and a relatively narrow distribution of densities.

Numerical models offer no means of reproducibility to other authors and little means of quantitatively understanding the functional relationships that exist between material properties, boundary conditions, and the underlying transport processes (i.e. heat transfer and sintering). Numerical modeling also tends to be directed at modeling experimentally observed behavior in a specific system. The lack of analytical tools for understanding LS on a global level (non-system specific) should be addressed. Specifically, development of a closed-form analytical solution for predicting the temperature distribution in the powder bed due to laser heating would provide a basis for development of future LS models.

In all of the LS models presented in the literature, sintering is modeled using either the classic viscous sintering models for amorphous liquids, Frenkel, Scherer, and Mackenzie-Shuttleworth, or an empirical-Arrhenius shrinkage model based dilatometry data. In the classical sintering models particle deformation occurs by viscous flow which is driven by curvature-based surface forces. However, as noted by Lee, polymers often exhibit viscoelastic deformation prior to the onset of viscous flow, as shown in Figure 1.7. Advances in understanding and modeling of contact growth between polymeric particles have shown that significant contact growth can occur by viscoelastic deformation for polymeric powders. The amount of contact growth is dependent on the particle radius and the creep compliance. Additionally, attractive surface forces have also been shown to be a significant driving force for contact growth of small particles prior to the onset of viscous flow.

In the following sections, sintering and thermal models relevant to LS of polymers will be reviewed. Following each review, there will be a summary and discussion of the relevance of the models to this research.

1.5 REVIEW OF SINTERING MODELS

Sintering of polymer powders differs from sintering of metal or ceramic powder in that significant contact growth can occur by elastic and/or viscoelastic deformation. Below, two classic viscous sintering models are discussed and then more recent experimental and theoretical work regarding viscoelastic sintering of polymers follows. Much of the work on viscoelastic sintering of polymers has been conducted or funded by Du Pont.

Frenkel 1945

Viscous sintering of amorphous material was modeled by Frenkel in 1945 using a two-sphere geometry. In this model a neck of radius, \( a \), grows between two adjacent spheres of radius, \( R \), as shown in Figure 1.12. Frenkel’s model, which is based on equating the rate of energy dissipation by viscous flow to the rate of energy release from surface area reduction, predicts that neck growth is described by \([1.1.7]\). \( \gamma \) is the particle surface energy, \( \eta_0 \) is the zero-shear viscosity of the amorphous material at the sintering temperature and \( t \) is time. Frenkel’s sintering model predicts that neck growth is proportional to the square root of the surface energy and sintering time and inversely proportional to the square root of the zero-shear viscosity.

\[
\left( \frac{a}{R} \right)^2 = \frac{3}{2} \left( \frac{\gamma t}{R \eta_0} \right)
\]  

[1.1.7]
Mackenzie, J. K. Shuttleworth, R. 1949
The Mackenzie-Shuttleworth sintering model is based on a shell, or closed pore, geometry as shown in Figure 1.13. Because of the closed pore geometry the model is strictly valid for relative densities above 0.94. However, the Mackenzie Shuttleworth model yields results equivalent to those of the Scherer model at relative densities as low as ~0.2. The Scherer model is strictly valid for relative densities less than ~0.94. The rate of pore closing was calculated by equating the energy dissipated by viscous flow of material in the shell to the change in total surface energy of the pore. The driving force for pore closure is the negative pressure resulting from the concavity of the pore. Equation [1.8] is the differential equation for the rate of density change as determined by Mackenzie and Shuttleworth, where \( a_0 \) is the initial pore radius. Using the relationship in [1.9], which relates the number of pores, \( n \), to the density and the initial pore diameter, [1.8] can be simplified to [1.10].

\[
d\rho/dt = \frac{3}{2} \left( \frac{4\pi}{3} \right)^{1/3} n^{1/3} \frac{\gamma}{\eta_0} \left( 1 - \rho \right)^{2/3} \rho^{1/3} \tag{1.8}
\]

\[
n^{1/3} = \left( \frac{1 - \rho}{\rho} \right)^{1/3} \left( \frac{3}{4\pi} \right)^{1/3} \frac{1}{a_0} \tag{1.9}
\]

\[
d\rho/dt = \frac{3\gamma}{2a_0\eta_0} (1 - \rho) \tag{1.10}
\]

Johnson, K.L. Kendall, K. Roberts, A.D. 1971
Johnson, Kendall and Roberts developed a model describing deformation of elastic bodies due to surface attraction. Previous work by Kendall and Roberts showed that the contact area between elastic spheres under zero applied load was finite, not zero as predicted by the Hertz model of elastic contact. The authors attributed the finite contact area under zero applied load to surface attractive forces and developed a qualitative explanation based on
balancing the energy stored by elastic deformation of the particles with the surface energy lost due to particle contact. A more rigorous model was developed by setting the change in total system energy (2 sphere system) with respect to the change in the contact radius, \(dU/da\), equal to zero and solving for the contact radius. The contact radius, \(a\), between two identical spheres of radius, \(R\), under zero applied load was predicted to obey, \[1.11\], where \(\nu\) is the Poisson’s ratio and \(E\) is the elastic modulus. The authors validated their model by showing good correlation with the contact radius between a flat rubber surface and an \(R=2.2\) cm sphere, as measured by low power optical microscopy. The authors also noted time dependence in the contact radius when loads were applied or changed.

\[
a^3 = \frac{18\gamma \pi R^2 (1-\nu^2)}{E} \tag{1.11}
\]

Mazur, S. Plazek, D.J. 1994

Mazur and Plazek studied the contact growth kinetics of linear acrylic spheres on an isolated surface\(^{25}\). Isothermal contact growth was measured in situ over a time range of \(10^5\) to \(10^5\) seconds using an inverted light microscope equipped with a hot stage. The torsional creep compliance of acrylic was measured for three temperatures and a creep compliance master curve was constructed. The shift factors determined in construction of the compliance master curve were used to create a contact growth master curve from contact growth data at temperatures corresponding to those used in construction of the creep compliance master curve. The shape of the contact growth master curve is noted to be very similar to the shape of the torsional creep compliance master curve. The authors proposed a viscoelastic contact growth model based on the elastic contact equation, \[1.11\], developed by Johnson, Kendall and Roberts. The authors substitutes the right had side of equation \[1.12\], which includes \(D_r\), the sum of the elastic and viscoelastic components of the time dependent torsional creep compliance, for the elastic modulus. The resulting viscoelastic neck growth equation is \[1.13\].

\[
E(t) = 2(1+\nu)G(t) \cong \frac{2(1+\nu)}{D_r(t)} \tag{1.12}
\]

\[
a = \left(\frac{9\pi\gamma(1-\nu^2)D_r(t)}{R(1+\nu)}\right)^{1/3} \tag{1.13}
\]

In development of their contact growth model, the authors also considers viscous contact growth by adding a viscous sintering term, such as Frenkel’s equation, to \[1.13\] yielding a contact growth model of the form \[1.14\]. Figure 4 in Mazur and Plazek’s paper is a plot which shows the contact growth master curve (open symbols), contact growth as predicted by equation \[1.14\], contact growth as predicted by Frenkel’s sintering model and contact growth as predicted by a finite element simulation which considers only viscous contact growth. The contact growth predicted by Mazur and Plazek’s viscoelastic sintering model is uniformly too fast by approximately a factor of 100 which the authors tentatively attributed to their model’s neglect of Boltzmann superposition. The key observation made by Mazur and Plazek is: significant contact growth can occur prior to the onset of viscous flow, which occurs at the characteristic relaxation time, \(r\). Additionally, it is noted that if the particle size is small enough, sintering to full density without viscous flow should be possible.

\[
a = \left(\frac{9\pi\gamma(1-\nu^2)D_r(t)}{R(1+\nu)}\right)^{1/3} + \left(\frac{a}{R}\right)_{\text{viscous}} \tag{1.14}
\]

Mazur, S. Beckerbauer, R. Buckholz, J. 1997

This work focused on the effect of particle size on sintering by viscoelastic contact growth\(^{26}\). An equation, based on the JKR theory of elastic contact, \[1.11\], for calculating the maximum particle radius which can be sintered to full density by viscoelastic contact growth was developed, \[1.15\]. \(D_n\) is the plateau value in the creep compliance prior to the onset of viscous flow and \(\rho_0\) is the initial packing density. Figure 1.14 is a schematic of spherical particles before and after deformation by viscoelastic contact growth. As in Mazur’s previous work, acrylic powders were
Scanning electron microscopy (SEM) was used to investigate sintering of acrylic powders with radii smaller, approximately equal to and larger than the $R_{\text{max}}$. Mazur et al show SEM images of particles with radii smaller, approximately equal to and larger than the $R_{\text{max}}$, sintered using the indicated conditions which preclude viscous flow. For particles much smaller than $R_{\text{max}}$, full density is observed over the vast majority of the field of view. For particles approximately equal to $R_{\text{max}}$, full density is observed where the initial packing configuration was close-packing. In areas where the initial packing density was less than close-packing, full density was not reached. The difference in local density due to the initial packing configuration is consistent with the dependence of $R_{\text{max}}$ on the initial packing density as shown in [1.15]. For particles larger than $R_{\text{max}}$, contact growth is observed, however, full density is not observed, even in areas of close-packing.

\[ R_{\text{max}} = 0.47 \frac{\gamma D_n}{(1 - \rho_0^{1/3})^{3/2}} \]  

[1.15]

---

**Figure 1.14**: Close-packed spheres and spheres sintered by viscoelastic contact growth.

---

Jagota, A. Argento, C. Mazur, S. 1998

Jagota et al presented a finite element model (FEM) of contact growth between a viscoelastic sphere and a rigid frictionless plate. The model combined the contributions of attractive van der Waals forces and curvature-based forces into a single surface traction force; this surface traction formulation was previously developed by two of the authors. The curvature-based component of the surface traction was determined using the Young-Laplace equation in which the pressure is proportional to the surface energy and inversely proportional to the surface curvature. The van der Waals interaction potential used to model the attractive forces between the sphere and plate is inversely proportional to the separation distance to the 6th power. Incorporation of the attractive van der Waals forces required that a new length be introduced into the problem. The new length scale defines the size of the region ahead of the contact area where attractive forces are significant. The mechanical properties of the sphere were modeled by a Maxwell material as defined in [1.16]. The FEM simulation showed an initial elastic contact which agrees with JKR theory. The initial elastic growth contact is followed by a period of viscoelastic contact growth which is driven by attractive forces acting ahead of the contact zone. This mode of contact growth was referred to as zipping contact growth by the authors. Zipping contact growth is not predicted by JKR contact growth or viscous contact growth because both models ignore viscoelastic deformation and attractive forces acting outside the contact area. Zipping contact growth is followed by viscous sintering driven by surface curvature. This mode of contact growth was referred to as stretching contact growth by the authors.

\[ J(t) = \frac{1}{G} + \frac{t}{G \tau} \]  

[1.16]

Jagota et al present a plot of the normalized surface traction for a 100nm sphere as a function of normalized radial distance from the contact center for four normalized times. The traction values are normalized by the maximum value of the JKR contact pressure. Positive traction values represent compressive stresses and negative traction values represent tensile stresses. The time values are normalized by $t'$, as defined by [1.17], which is a measure of the time required for viscous sintering to occur. At $t=0$, the instantaneous particle contact is due to JKR-type elastic contact. Initially, the compressive stress is a maximum in the center of the contact area. Moving away from the center, the stress level is reduced and becomes tensile at the edge of the contact area. The radial distance where the
tensile stress reaches a maximum, ~0.055, is the position of the contact edge. Continuing the explanation for \( t=0 \), for values of the normalized radial distance greater than approximately 0.055, the tensile stress begins to decrease to zero as the separation distance between the spheres increases and the surface attractive forces decrease. As the contact time increases the contact radius will increase. Because of the viscoelastic nature of the material, the compressive stresses at the center of the contact area decay and the contact edge advances to maintain equilibrium between the compressive and tensile traction forces. As the contact edge advances, the rate of increase in the separation distance ahead of the contact edge increase due to the spherical geometry and thus the attractive forces ahead of the crack tip diminish.

The authors present a plot of the normalized traction as a function of the normalized radial distance comparing Jagota et al’s theory of contact growth to JKR theory and the theory Lee and Radok. At the time of initial contact, the surface traction follows JKR theory almost exactly until the contact edge is reached. JKR theory erroneously predicts an infinite tensile stress at the contact edge, discussion of this error will follow in further reviews. The authors’ prediction of the surface traction as a function of radial distance matches the predictions of Lee and Radok’s model reasonably well for the contact radius shown. In Lee and Radok’s model, viscoelastic contact growth is driven by an external force not attractive surface forces or curvature-based forces, both of which vary as the contact radius increases. Determination of the change in the total traction force over time would require calculating the rate of contact growth, thus Lee and Radok’s model is not useful for predicting contact growth kinetics when attractive surface forces and curvature-based forces are the primary driving forces for contact growth.

\[
t^* = \left( \frac{4\pi}{3} \right)^{1/3} \left( \frac{R \eta}{\gamma} \right)
\]

[1.17]

Jagota et al also present a plot of the normalized contact radius (a/R) as a function of normalized time as predicted by: 1) Frenkel’s sintering equation, 2) considering only curvature-based forces, 3) considering only attractive van der Waals forces, 4) Jagota et al’s total surface traction formulation which considers surface traction due to van der Waals interactions and curvature-based forces and 5) Lee and Radok’s equation for viscoelastic contact growth under an external force. The external force used in the Lee and Radok model was calculated by equating the work done by the external force to the energy released due to contact growth. As previously stated, contact growth predictions using Lee and Radok’s formulation when no external force is applied are flawed because the force driving contact growth is not now a priori. For normalized times less than \(~5\times10^{-2}\), the contact radii predicted by Frenkel’s equation and by considering only curvature-based forces are significantly smaller than those predicted by Jagota et al’s formulation, considering van der Waals attractive forces only and the model of Lee and Radok. As the normalized time approaches unity the contact radii predicted by considering only van der Waals attractive forces begins to diverge. Comparing the total surface traction force model to its components, it can be stated that: for normalized times less than \(~5\times10^{-2}\) contact growth is driven by attractive van der Waals surface forces and viscoelastic particle deformation dominates, and for times greater than \(~5\times10^{-2}\) contact growth is driven curvature-based forces and viscous particle deformation dominates.

Hui, C.-Y. Baney, J. M. Kramer, E. J. 1998

Hui et al discussed the major problem of JKR theory\(^{29}\) which is the infinite tensile stress at the edge of the contact area. The authors recognized the problem as a characteristic also associated with linear elastic fracture mechanics (LEFM). Specifically, the authors asserted that JKR theory is conceptually equivalent to the small scale yielding problem in LEFM because both assume that the cohesive zone adjacent to the contact area is extremely small compared to the contact radius and thus has no significant effect on contact growth or shrinkage. Further, the authors explained the complications which arise from trying to describe the behavior of viscoelastic materials with elastic theories, such as JKR. Specifically, the instantaneous deformation of an elastic material depends only on the load at that instant. However, the instantaneous deformation of a viscoelastic material depends on the loading history because of the time dependence of the compliance. Therefore, the contact radius between viscoelastic particles at any instant can not be determined from knowledge of the instantaneous surface traction forces alone. Hui et al developed a contact growth model for viscoelastic spheres subjected to an external load. However, the same approach can be applied to contact growth with no external load.
Hui et al presented a solution to viscoelastic contact growth in which the problem is broken into a local adhesive bonding problem and a global contact mechanics problem. Figure 1.15 shows schematics of the global contact mechanics problem (a) and the local adhesion problem (b). The local adhesion problem is solved using the model of viscoelastic crack healing presented by Schapery, where the attractive surface forces are approximated using the Dugdale model. In the Dugdale model, Figure 1.16, the adhesive stress at the surface is constant, $-\sigma_0$, for values of the surface separation, $\Delta$, less than $\Delta_C$; for larger separation distances the adhesive stress is zero. The authors stated the Dugdale model captures the behavior of a realistic force law reasonably well. The problem of global contact mechanics was solved in a Hertzian manner: deformation is exclusively due to an external load. The solutions of the global and local problems were coupled through $K_I$, the mode one stress intensity factor.

![Figure 1.15: Global (a) and local (b) problems of viscoelastic contact growth.](image)

![Figure 1.16: Attractive surface forces: (a) Dugdale approximation and (b) physically realistic; Note: the sign of the stress is negative resulting in crack healing.](image)

**Hooper, R. Macosko, C. W. Derby, J. J. 2000**

The finite element model presented by Hooper et al considers sintering of viscoelastic particles by curvature-based forces only, ignoring surface attraction. An increase in the stress in the neck region was observed for viscoelastic particles as compared to purely viscous particles. However, the flows and particle shapes observed in the viscoelastic particle system were nearly identical to those of the purely viscous particle system. The authors concluded that contact growth due to surface attraction, as considered by JKR theory, Jagota et al and Hui et al should be incorporated into a sintering model for viscoelastic particles. The authors also proposed an approximation, similar to that of Mazur, for the maximum contact radius attributable to viscoelastic deformation which is given by [1.18]. Assuming a Poisson’s ratio of 0.5, further consolidation of the terms in [1.18] leads to
where $De$ is the Debora number, the ratio of the fluid response time to the process duration, defined by \[ 1.20 \]. For a sintering process defined by $De$, Equation \[ 1.19 \] can be used to predict the extent of viscoelastic contact growth.

\[
\frac{a}{R} = \left( \frac{9\pi\gamma(1-n)D_n}{8R} \right)^{1/3} \tag{1.18}
\]

\[
\frac{a}{R} \approx (1.767De)^{1/3} \tag{1.19}
\]

\[
De = \frac{\tau \gamma}{\eta R} = D_n \frac{\gamma}{R} \tag{1.20}
\]


Lin et al extended the work of Hui\[29\], one the co-authors, on viscoelastic contact growth under an applied load, to sintering by setting the external load in the contact growth formulation equal to zero\[31\]. The formulation developed for viscoelastic sintering by adhesive contact is not analytically solvable and as such the authors use a numerical technique to determine the contact radius as a function of time. Additionally, the authors present an analytically solvable solution to the aforementioned problem in the limit of long times (long times being comparable to the characteristic relaxation time). Equation \[1.21\] is the long time viscoelastic limit for contact growth by adhesive surface traction; $m$ and $D_1$ are terms in the power law fluid formulation \[1.22\], $c_m$ is given by \[1.23\], $\delta_C$ is the critical separation distance for the Dugdale attractive surface force, $\gamma_m$ is given by \[1.24\] where $\Gamma$ is the gamma function and $W$ is the work of adhesion, $2\gamma$.

\[
\frac{a}{R} = \left( \frac{9\pi}{2} \right)^{m+1} \left( \frac{4m+3}{m} \right)^2 \left( \frac{\delta_C}{R} \right) \left( \frac{\gamma_m D_1 W}{c_m R} \right)^{\frac{1}{m+1}} \tag{1.21}
\]

\[
D(t) = D_0 + D_1 t^m \tag{1.22}
\]

\[
c_m = \frac{2m+1}{m+1} \tag{1.23}
\]

\[
\gamma_m = \frac{\left( \frac{\pi}{4} \right)^{\frac{1}{4}} \Gamma(m+1)}{\Gamma(m+1.5)} \tag{1.24}
\]

Lin et al also derived a solution for viscoelastic contact growth of spheres by adhesive surface traction where a finite cohesive zone (zone of adhesive attraction ahead of the contact) was considered. In Hui et al’s work, the cohesive zone was assumed to be small compared to the contact radius which is not a valid assumption for the initial stages of contact growth. For comparison Lin et al also presented a FEM of viscoelastic contact growth where the attractive surface forces were modeled using the Dugdale approximation. Lin et al present a plot of the normalized contact radius as a function of reduced time for viscoelastic contact growth by attractive surface forces only for 100nm spheres with $\delta_C = 0.4nm$. Contact growth is predicted using several different models: Hui et al for zero applied load, the long time viscoelastic limit, the finite cohesive zone model developed by Lin et al and the aforementioned FEM. At long times all of the models converge as would be expected because the small cohesive zone assumption is
satisfied for larger contact areas. The viscoelastic contact growth results of the finite cohesive zone model and the FEM are in good agreement. The model of Hui et al for zero external load predicts the largest contact radii for any time prior to convergence of all the models. Excluding the long time viscoelastic approximation all of the solutions show an initial JKR-type elastic contact radius at short times, $C_i/\gamma_0<0.1$. Note, these models consider only attractive surface forces, curvature-based forces are neglected.

To demonstrate the ability of the long time viscoelastic limit equation, [1.21], to describe experimental behavior, the authors fit the experimental creep compliance and contact growth data for acrylic spheres previously presented by Mazur et al. Lin et al fit the initial portion of the creep compliance curve presented by Mazur et al to a power law fluid model. The viscous portion of the creep compliance was fit as: $D(t)=t/\eta_0$. Using the calculated viscosity, the authors fit the viscous contact growth region of the contact growth data to Frenkel’s model of viscous sintering to determine the work of adhesion for acrylic-acrylic contact. Using the power law fluid description of the initial portion of the creep compliance and the work of adhesion the authors were able determine best fit of the critical separation distance, $\delta_c$, for the viscoelastic contact growth portion of the contact growth data using equation [1.21]. The best fit critical separation distance was determined to be 50 nm. The authors present a plot of the normalized contact radius as a function of time, shown on the graph are: Mazur et al’s contact growth data, the fit to [1.21], the fit to Frenkel’s equation and a FEM model considering only viscous contact growth. The long time viscoelastic portion of the contact growth data are described well by equation [1.21] when the critical separation distance is determined by fitting the model to the data. Frenkel’s sintering model adequately describes the contact growth behavior in the viscous flow regime. The FEM model which considered only viscous deformation produces a poor description of contact growth except at long times where it adequately describes the growth rate.

1.6 SUMMARY OF SINTERING LITERATURE

The validity of the classic sintering models of Frenkel and Mackenzie-Shuttleworth is well established for sintering of amorphous materials. However, the accuracy of these classic sintering models is best for large particles which behave as Newtonian fluids. Johnson, Kendall and Roberts showed that a finite contact area is established between contacting bodies and the normalized contact radius is inversely proportional to cube root of the particle radius. The experimental work of Mazur et al shows the significance of contact growth between viscoelastic spheres by non-viscous deformation. Mazur et al hypothesized that early stage contact growth is driven by JKR-type contact and the time dependence of the contact radius results from the viscoelastic nature of polymers. Additionally, Mazur et al noted the similarity in the shape of the creep compliance and contact growth master curves. Modeling efforts by several groups (Jagota et al, Hui et al, Hooper et al, etc.) have shown that viscoelastic contact growth can not be explained by curvature-based forces alone. Models of polymer contact by Jagota et al, Hui et al and Lin et al suggest that early-stage contact growth between polymer spheres occurs by viscoelastic deformation and is driven by attractive surface forces acting ahead of the contact growth edge. Several numerical solutions and FEMs of viscoelastic contact growth have been presented. However, the long time viscoelastic contact growth equation presented by Lin et al remains the only analytically solvable equation for viscoelastic contact growth under zero applied load which explicitly account for viscoelasticity.

Lin et al’s fit of the long time viscoelastic limit to Mazur et al’s contact growth data is the only application of a model to experimental behavior where no external loading is present. However, fitting the experimental contact growth data to the long time viscoelastic limit yielded a best-fit critical separation distance of 50nm. A 50nm critical separation distance for an attractive surface force is somewhat unrealistic. Lin et al attributed errors in the predictions of Jagota et al’s model to the use of a large critical separation distance, 17nm. However, Lin et al made no reference to the even larger critical separation distance needed to fit the long time viscoelastic limit to Mazur et al’s data. The large critical separation distance needed to fit Mazur et al’s data most likely results from the omission of curvature based forces from Hui et al’s model which was used as the basis for the long time viscoelastic limit.

Lin et al present a schematic of two particles during the early stages of contact growth and qualitative representations of the force vectors acting in the cohesive zone for early stage contact growth assuming the adhesive forces are significantly larger than the curvature-based forces. Resolving the curvature-based forces into components parallel and perpendicular to the contact radius would show that all of the force vectors (with the exception of the vector parallel to the contact radius) have some component that acts to zip the crack closed. The magnitude of the curvature-based forces is inversely proportional to the radius of curvature, which should be half of the critical separation distance or smaller. Returning to Lin et al’s fit of Mazur’s contact growth data for acrylic spheres with $\gamma=0.031 \text{ J/m}^2$, the pressure in the contact area due to curvature-based forces can be approximated by the Young-Laplace equation, [1.25], and is 2.5 MPa assuming a radius of 25nm. The pressure calculated by Lin et
al for the attractive surface forces, $\sigma_0$ in the Dugdale model - Figure 1.16, was 1.24 MPa half of the curvature-based value. Therefore, the assumption that magnitude of the curvature based surface forces is insignificant in the cohesive zone may be erroneous. The large critical separation distance required to fit Mazur et al's data could invalidate the assumption of the insignificance of curvature-based forces. Furthermore, stretching of the contact area could occur by viscoelastic deformation and this mode of contact growth is not accounted for in the long time viscoelastic limit model of contact growth.

$$\Delta p = \frac{2\gamma}{r}$$

The development of the long time viscoelastic contact growth equation is based on contact growth by attractive surface forces and deformation is described by a power law creep compliance function which is assumed to describe the viscoelastic behavior of the polymer. As stated previously, to use the long time viscoelastic limit equation to describe the experimental contact growth data of Mazur et al, a relatively large critical separation distance was required. The requirement of a large critical separation distance could be assumed to account for the effect of curvature-based forces and/or stretching contact growth occurring by viscoelastic deformation. Therefore, when a large critical separation distance is used, ~50nm, the long time viscoelastic contact growth equation can be assumed to approximate the contact growth kinetics for times less than the characteristic relaxation time of the polymeric liquid. Because a large critical separation distance is used to account for contact growth by means other than attractive surface forces, the model should be viewed as quasi-analytical solution for viscoelastic contact growth driven by attractive surface forces and curvature-based forces.

1.7 APPLICATION OF SINTERING MODELS TO LS

The experimental and theoretical work presented in the literature shows that the predictions of classic sintering models for amorphous materials underestimate the contact growth observed in polymeric powders for times less than the characteristic relaxation time because these models only consider curvature-based forces and assume deformation occurs by viscous flow. When a large critical separation distance is assumed, the long time viscoelastic contact growth equation presented by Lin et al has been shown to describe the contact behavior of viscoelastic spheres prior to the characteristic relaxation time. The author of this work hypothesizes that viscoelastic contact growth can be a significant densification mechanism during LS of polymers. The magnitude of contact growth which occurs by viscoelastic deformation will depend on the particle size and the characteristics of the creep compliance.

The long time viscoelastic contact growth equation, [1.21], will be used in this work to predict contact growth during LS prior to the characteristic relaxation time. A critical separation distance of 50nm will be used to account for all forces and modes of deformation by which viscoelastic contact growth occurs. The choice of equation [1.21] was based on its analytical solvability and the fact that it has been shown to describe experimentally observed viscoelastic contact growth. For times greater than the characteristic relaxation time the Mackenzie-Shuttleworth model will be used to predict sintering during LS. The choice of the Mackenzie-Shuttleworth model was based on the facts that it approximates sintering kinetics over a wide range of relative densities and its asymptotic approach to full density which ensures that the relative density predictions never exceed unity. Density predictions made based on these models assume that the sintering kinetics of the powder bed can be described by those of a simple unit, contacting spheres in the case of the long time viscoelastic contact growth equation and a spherical shell in the case of the Mackenzie-Shuttleworth model. Deviations from spherical particles of a single radius and local packing deviations in the powder bed provide sources of inaccuracy. However, using the average of particle size as the particle radius, $R$, in the models should average out the majority of the error due to particle size differences.

1.8 REVIEW OF THERMAL MODELS

As mentioned previously, numerical solutions strategies have been employed to predict the temperature distribution in the powder bed during LS. While the results of numerical solutions provide general qualitative insight into the LS process and quantitative information for specific systems, they do not provide a general solution which can be easily employed by other researchers. Numerical heat transfer solutions are often tedious to develop and computationally intensive. Development of an analytical solution or application of an existing analytical solution for predicting the temperature distribution in the powder bed would provide a new tool for modeling LS. For example, the Rosenthal solution for heating of a surface by a moving point heat source is used for predicting the temperature distributions in the heat effected zone during welding and is often a baseline for comparison of new
thermal models of the welding process. In the following section analytical and numerical heat transfer solutions which have applicability to LS will be reviewed. The numerical solutions reviewed will employ solution strategies other than finite element. The numerical solutions do not meet the requirement for an analytical tool but do provide insight into the significance of different aspect of the problem, such as the number of significant dimensions.

In this work and the work reviewed in this section, several simplifying assumptions are made about the material properties and geometry of the system being heated by the moving heat source. The material properties of a given phase are assumed to be temperature independent as to not introduce a non-linearity associated with temperature dependent material properties. However, in models which consider phase change, the properties of the constituent phases are different. Unless otherwise noted, a semi-infinite geometry is assumed for the substrate. The semi-infinite dimension is the direction normal to the powder bed surface. For models which consider two or three dimensional heat transfer, the orthogonal dimensions parallel to the powder bed surface are assumed infinite.

In modeling of laser surface heating, there are two commonly used methods of accounting for the energy input by the laser beam. The simplest means of accounting for the laser energy is to assume that the beam acts as a flux boundary condition. Thus, the maximum temperature will always occur at the surface. A more rigorous treatment of laser heating is to model the laser energy as a volumetric heat generation term, where the heat generated decays exponentially with depth into the surface. This model of laser heating is known as Lambert’s Law. The volumetric heat generation method is representative of the actual laser heating process in which photon-electron interactions result in heating of the substrate. Yilbas and co-workers33 have presented several analytical solutions using Lambert’s Law to model laser heating of a medium by a stationary beam. However, Lambert’s Law requires more material properties and introduces a non-linearity associated with the exponentially decaying volumetric heat generation term. These additions increase the difficulty in developing a closed-form analytical solution. Due to the increased complexity of considering volumetric heating, this research will focus on solutions which consider heating via a flux boundary condition.

The heat transfer models reviewed below fit into two general categories: solutions which consider a moving heat source and solutions which consider phase change. One of the solutions which considers phase change also considers a moving heat source. In both categories, classic analytical solutions are discussed along with more contemporary solutions. Many of the moving heat source and phase change heat transfer solutions were developed to model welding and/or surface hardening.

1.8.1 Moving Heat Source Solutions

In a one-dimensional system with an internal point heat source, of strength $q$, located at $x'$, [1.26] describes the energy distribution in the medium. $\delta(n)$ is the Dirac delta function which is exactly zero for all $n$ not equal to zero. To transform [1.26] into the equation of a moving heat source, the location $x'$ is set equal to $x_0 + vt$, where $x_0$ is the initial position of the point source, $v$ is the velocity of the source and $t$ is time. For moving heat source problems there are two solution types. The first type is an exact solution which is valid for all times. The second is referred to as a quasi-stationary or quasi-steady state solution. The later solutions are developed by assuming: the coordinate system moves with the heat source, the length of medium is exceedingly large compared to the heat-affected zone and that after an initial transient period the temperature distribution around the heat source, as observed from the heat source, does not change. Thus, the time dependence of the temperature can be set to zero, eliminating the time variable from the differential equation which describes the temperature distribution in the medium. Eliminating the time dependence affords simpler solutions to the differential equation.

$$q \delta(x - x')$$  

[1.26]

Carslaw, H.S and Jaeger, J. C. 1959

In this classic text, the authors presented solutions for numerous problems of stationary and moving heat sources by integrating the solution for an instantaneous point source in an infinite medium over the appropriate time and space variables. This solution strategy is referred to as the heat source method. The differential equation for heat transfer in an isotropic material with a temperature independent thermal diffusivity ($\alpha$) is [1.27]. Given an instantaneous point heat source in an infinite medium, [1.27] is satisfied by [1.28]. $Q$ is the strength of the point source which is located at the point $(x', y', z')$. By integrating [1.28] with respect to all the spatial variables the total heat in the solid, generated by the point source, is calculated to be: $Q \rho c$, where $\rho$ is the density and $c$ is the specific heat. As $t \rightarrow 0$ the temperature at all points is zero except at $(x', y', z')$ where the temperature approaches infinity.
\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \tag{1.27}
\]

\[
T(x, y, z, t) = \frac{Q}{8(\pi \alpha t)^{3/2}} e^{-\left((x-x')^2 + (y-y')^2 + (z-z')^2\right)/4\alpha t} \tag{1.28}
\]

The authors presented a solution for heating of an infinite medium moving at a constant velocity in the x-direction by a point heat source, which releases heat at a rate \(q\), located at the origin. The solution to this moving heat source problem follows from [1.28] by equating the strength of the instantaneous source, \(Q\), to the amount of heat released by the moving heat source over a time interval \(dt'\), thus \(Q = q \, dt'\). Since the point heat source is located at the origin \(x_0 = y' = z' = 0\). To account for the motion of the medium, \(x'\) is equated to \(-v(t-t')\). The solution for the temperature distribution in the moving medium is given by [1.29], which can not be evaluated analytically. However, for the quasi-steady state condition the temperature distribution can be calculated analytically using [1.30].

\[
T(x, y, z, t) = \frac{q}{8\rho c(\pi \alpha)^{3/2}} \int_0^t e^{-\left((x-v(t-t')x')^2 + y^2 + z'^2\right)/4\alpha(t-t')} dt' \tag{1.29}
\]

\[
T(x, y, z, t) = \frac{q}{4\pi k(x^2 + y^2 + z^2)} e^{-v((x^2 + y^2 + z^2) - x)/2\alpha} \tag{1.30}
\]

Following similar logic, the authors presented a solution for heating of a semi-infinite solid by a strip heat source, with dimensions \(-b < x < b, -\infty < y < \infty\), moving at constant velocity in the negative x-direction in the \(z = 0\) plane. The solution to the aforementioned problem is given in [1.31]. The function \(K_0(x)\) is the modified Bessel function of the second kind of order zero. The authors present plots of the dimensionless surface temperature as a function of normalized distance as predicted by [1.31] for several different values of the Peclet Number. The Peclet Number, [1.32], is a dimensionless group which relates the rate of energy delivery per unit area to the rate of heat diffusion into a medium per unit area. Large values of \(Pe\) represent a rapid rate of energy delivery as compared to the rate of heat diffusion, thus the maximum temperature occurs at the trailing edge of the strip heat source. As the value of \(Pe\) increases, the length of the heat-affected zone ahead of the strip decreases.

\[
T(x, z, t) = \frac{Q}{\pi k} \int_{-b}^b e^{v(x-x')/2\alpha} K_0(v((x-x')^2 + z^2)^{1/2} / 2\alpha) dx' \tag{1.31}
\]

\[
Pe = \frac{vb}{2\alpha} \tag{1.32}
\]

Festa, R. Manca, O. Naso, V. 1990

Festa et al compared one- and two-dimensional heating of a semi-infinite body by constant intensity thermal fluxes. In the one-dimensional problem, the entire upper surface is subjected to a constant flux for times greater than \(\tau\) (not the characteristic relaxation time). The solution to the one-dimensional problem is given by equation [1.33]. In the case of one-dimensional heating the quasi-steady state condition is always satisfied since there no conduction in x- and y-directions. In the two-dimensional case, the surface is heated by a moving heat source, of width 2b, moving in the positive x-direction. The solution for the two-dimensional problem is given by [1.34], which contains an integral that must be evaluated numerically. The goal of Festa et al was to develop a simple model which could be used to determine the depth to which solid state phase transformations occur in laser and electron beam surface hardening.
\[ T_{1-d}(z,t) = \frac{2q_0 \alpha^{1/2}}{k} \left( t^{1/2} \operatorname{erfc} \left( \frac{z}{(4\alpha t)^{1/2}} \right) - U(t-\tau)(t-\tau)^{1/2} \operatorname{erfc} \left( \frac{z}{(4\alpha (t-\tau)^{1/2}} \right) \right) \]  

\[ T_{2-d}(x,z,t) = \frac{q_0 \alpha^{1/2}}{2k\pi^{1/2}} \int_0^\infty e^{-\frac{v^2}{2\mu}} \left( \frac{v}{(2\alpha)^{1/2}} \left( \frac{(x+b)/v}{2\mu^{1/2}} - t + \mu \right) \right) \left( \frac{v}{(2\alpha)^{1/2}} \left( \frac{(x-b)/v}{2\mu^{1/2}} - t - \mu \right) \right) d\mu \]  

The authors compared the solutions of the one- and two-dimensional problems by comparing the maximum dimensionless hardening depth, \( Z_h \), as a function of Peclet number for various dimensionless transformation temperatures. The dimensionless transformation temperature is determined by \([1.35]\), where \( T_{x-D} \) is \([1.33]\) or \([1.34]\). Agreement between the one- and two-dimensional solutions is good for dimensionless transformation temperatures less than 0.15. For dimensionless transformation temperatures greater than 0.15, the prediction of one-dimensional solution exceeds that of the two-dimensional solution. For \( Pe \) greater than \(~0.8\) the dimensionless hardening depth predictions by both models are in agreement for all transformation temperatures. Specifically, the one-dimensional model over predicts the hardening depth for small Peclet numbers (\( Pe < 0.8\)) when the dimensionless transformation temperature is greater than 0.15. The analysis presented by the authors is strictly applicable to second order phase transitions, which by definition have no enthalpy change associated specifically with the transformation.

\[ T_{c*}^* = T_{x-D} - \frac{k}{2bq_0} \]  

\( Hou, Z.B. Komanduri, R. 2000 \)

Hou and Komanduri developed general solutions for moving and stationary plane heat sources based on the heat source method of Jager. Surface heating of a semi-infinite medium by elliptical and rectangular plane heat sources with uniform (square-wave), parabolic and normal (Gaussian) intensity distributions were considered. The solutions presented are exact not quasi-steady state. However, the solutions involve integrals which must be evaluated numerically. The authors present plots of dimensionless temperature as a function of normalized distance for several normalized depths into the medium for elliptical heat sources with uniform and normal distributions. 

\[ T_{c*} = \frac{20\alpha}{v^2} \]  

1.8.2 Solutions Considering Phase Change

Because of the nonlinearity introduced into the heat transfer equation by the addition of a moving boundary, very few closed-form analytical heat transfer solutions are available for problems which consider phase change. Closed-form analytical solutions consider very simple boundary conditions. Typically, numerical techniques are employed to solve heat transfer problems involving phase change. Two closed-form heat transfer solutions are reviewed below, the first a classic solution and the second a more recent solution which is presented as means of approximating melting induced by laser surface heating. A numerical solution in which phase change is considered along a moving heat source and convective and radiative surface boundary conditions is also reviewed.

First-order phase transitions have an associated enthalpy which detracts from or contributes to the sensible heat upon melting or solidifying, in the case of a solid-liquid transition. The Stefan number, defined as \([1.37]\), is the ratio of the latent heat, \( L \), associated with phase transition to the sensible heat associated with reaching the phase transition temperature, \( T_{\text{trans}} \), \( T_0 \) is the temperature of the medium prior to heating or cooling to a phase transition temperature.
A Stefan number much smaller than unity signifies that the heat associated with the phase change has a significant effect on the temperature of the medium around the phase boundary. A Stefan number much larger than unity signifies that the heat associated with the phase change has little effect on the temperature of the medium. Second-order phase transitions, such as the glass transition (a quasi-second order transition), exhibit only a change in specific heat at the phase boundary. Thus, the effect of second-order phase change on the temperature distribution around the phase boundary is typically significantly smaller than for first-order transitions.

\[ Ste = \frac{c(T_{\text{trans}} - T_0)}{L} \]  

**Neumann's Problem**

Stefan first considered heat transfer during solidification of polar ice. However, the exact solution for the temperature distribution in a solidifying semi-infinite region initially at a uniform temperature and where a constant boundary temperature is applied for time greater than zero was presented by Neumann. An exact solution to this problem is afforded by the similarity variable \( x/t^{1/2} \) which groups the independent variables into a single variable and thus allows for solving for the position of the phase boundary as a function of time. The boundary condition at the phase boundary, \( s(t) \) is equivalent to the heat flux difference at the phase boundary between the surface phase and the subsurface phase is equal to the rate of heat liberated or expended by the phase change.

\[ k_i \frac{\partial T_i}{\partial x} - k_j \frac{\partial T_j}{\partial x} = \rho L \frac{ds(t)}{dt} \]

**Zhang, Y. Faghri, A. 1998**

Zhang and Faghri considered laser heating, melting, and resolidification of a powder bed comprised of a two-component mixed metal powder. The difference in melting temperature between the two metal powders is significantly large, such that the lower-melting metal powder will melt and result in liquid phase sintering of the areas heated by the laser. As the laser beam scans over the surface the lower-melting temperature powder melts and liquid phase sintering results. The authors’ model tracks the melting and solidification fronts in the powder bed. Areas where the temperature reaches the melting point of the lower melting temperature metal are assumed to instantly densify, thus, resulting in local shrinkage of the powder. Latent heat of melting is not considered. The model assumes a quasi-steady state condition was reached and a finite difference solution is employed.

The authors’ model considered heat loss at the powder surface by convective and radiative heat transfer. The authors present a plot of the dimensionless surface temperature of the bed as a function of a moving horizontal coordinate. Results are shown with and without convective and radiative heat loss from the surface. The figure shows that a maximum difference of 20% is observed in the temperature distribution following the trailing edge of the heat flux. \( N_r \) is the radiation number and \( Bi \) is the Biot number, which are dimensionless groups which signify the effects of radiative and convective heat loss respectively. Zhang and Faghri present a cross-sectional plot of the powder bed showing the phase boundaries resulting from LS of a mixed metal powder with and without convective and radiative heat loss from the surface. Shrinkage of the powder resulting from liquid phase sintering is not considered. A 20% decrease in sintering depth is observed for the system in which surface heat losses are present. The wedge shapes extending from the surface are the liquid regions and the trapezoidal regions to the left of the liquid wedges are the liquid phase sintered regions. The authors show that the surface boundary conditions have a significant (~20% difference) effect on the melting depth.


Shen et al presented a one-dimensional analytical model for heating a semi-infinite slab by a flux boundary condition which considers phase change. The flux boundary condition makes the solution applicable to any constant-intensity flux heating process. However, the authors were specifically interested in applying their model to laser melting. The initial temperature of the substrate is assumed to be below the melting temperature, \( T_m \). Heat input at the flux boundary raises the temperature in the substrate. A solution of the form \( [1.39] \) was assumed to allow for analytically solving for the time when the surface temperature, \( T_w \), reaches the melting temperature. For times greater than that required for the surface to reach the melting temperature, the problem is reformulated to
incorporate a moving boundary, \( S(t) \). Phase change is incorporated via the boundary conditions [1.41] and [1.42]. The authors assumed solutions for the temperature distributions in the solid and liquid regions of the form [1.43] and [1.44]. The particular solutions for the solid and liquid regions decay from surface temperature and the melting temperature respectively. \( \delta_s(t) \) and \( \delta_l(t) \) are temporal functions representing the temperature penetration depth into the respective region. The authors compared their model to experimentally determined melt depths for laser melting of fused quartz. The authors present a graph of the measured and experimentally calculated melt depths for fused quartz as a function of irradiation time. For irradiation times of 2 seconds or less, the melt depth predictions are in agreement with experimental results. However, for times greater than 2 seconds, the model overestimates the melt depth. The authors attributed the overestimation of their model to its neglect of absorption of laser energy by vapor and plasma generated during long irradiation times.

\[
T_s(x,t) = T_w(t)e^{-x/\sqrt{2\pi t}}
\]  

[1.39]

\[
T_w(t) = T_0 + \frac{AI}{\sqrt{c_s \rho_s k_s}}(2t)^{1/2}
\]  

[1.40]

\[
T_s(x,t) = T_i(x,t) = T_m, \quad x = S(t)
\]  

[1.41]

\[
\rho_s L \frac{dS(t)}{dt} = k_s \frac{\partial T_s(x,t)}{\partial x} - k_i \frac{\partial T_i(x,t)}{\partial x}, \quad x = S(t)
\]  

[1.42]

\[
T_i(x,t) = T_w(t)e^{-x/\delta_i(t)}
\]  

[1.43]

\[
T_s(x,t) = T_m e^{-((x+S(t))/\delta_s(t))}
\]  

[1.44]

1.9 SUMMARY OF HEAT TRANSFER MODELS

Phase change and a moving heat source introduce nonlinearities into the formulation of the heat transfer problem which complicate modeling the thermal distribution in the powder bed during LS. Previous modeling of systems with the same or similar complications provides a basis for modeling the LS process. The heat source method originally developed by Jaeger and reviewed by Carslaw and Jaeger\(^{34}\) provides a means of solving moving heat source problems which do not involve phase change. Carslaw and Jaeger presented solutions for a moving point source and a moving strip heat source (constant intensity) in infinite and semi-infinite geometries respectively. The quasi-steady state solution for the moving point heat source is a closed-form solution. However, the temperature at the heat source is infinity due to singular nature of the heat source. The solution for the moving strip heat source presented by Carslaw and Jaeger requires numerical integration for evaluation.

Hou and Komanduri\(^{36}\) used the heat source method to solve a series of moving heat source problem with various source intensity distributions, including square and Gaussian, for a semi-infinite geometry. All the solutions presented require numerical integration to determine the temperature distribution. The work of Hou and Komanduri also showed the dependence of the temperature distribution on the geometric representation of the heat source intensity distribution. However, the authors make no direct comparison of the temperature distributions for the different source geometries. Hou and Komanduri and Carslaw and Jaeger both showed that for \( Pe > 5 \) the effect of heat conduction ahead of the source is minimal. Festa et al\(^{35}\) showed that for \( Pe > 1 \) one- and two-dimensional heat transfer solutions predict approximately equal penetration depths for a second-order phase transition. Hou and Komanduri also presented an equation for predicting the time required to reach a quasi-steady state condition for problems with moving heat sources.

Closed-form analytical solutions to heat transfer problems which consider phase change are currently limited to semi-infinite geometries with either a fixed temperature or a constant-intensity flux boundary condition. These solutions are attributable to Neumann\(^{37}\) and Shen et al\(^{39}\). Thus, solutions for problems with moving heat sources which consider phase change are relegated to employing numerical techniques. Zhang and Faghri\(^{38}\) investigated melting in a two-component metal powder system by a moving heat source where only the lower melting temperature metal was liquefied by the laser energy; a numerical solution strategy was employed. Zhang and Faghri
showed that convective and radiative heat losses resulted in a decrease in the melting depth of approximately 20% for the system they modeled. The magnitude of the Stefan number provides a measure of assessing the effects of a first-order phase transformation on temperature distribution near the phase boundary.

1.10 APPLICATION OF THERMAL MODELS TO LS

The Peclet number provides a measure of the effect of motion on the temperature distribution in a medium in contact with a moving heat source. For most polymers the thermal conductivity is approximately 0.25 W/m-K, the density is \( \sim 1000 \text{kg/m}^3 \) and the heat capacity is \( \sim 1200 \text{J/kg-K} \). Thus, the thermal diffusivity of a polymer is typically of the order \( 10^{-7} \text{m}^2/\text{s} \). The radius of the laser beam in the lab-scale LS unit, which will be used in this research, is 1.5mm and scan speed is typically 25.4mm/s. Per [1.32], the Peclet number for sintering polymer in the lab-scale LS unit is approximately 90. For a Pe of this magnitude, the results of Hou and Komanduri and Carslaw and Jaeger suggest that a one-dimensional heat transfer solution should provide an accurate approximation of the thermal distribution in powder bed during LS. The results of Festa et al suggest that a one-dimensional solution should provide an accurate prediction of the penetration depth of the liquid phase boundary into a medium for a Pe of 90. Thus, a one-dimensional solution for heating of the powder bed during LS is justified and allows for a closed-form analytical solution. Considering heat conduction in only one dimension does not limit the geometry of the problem to one-dimension. The one-dimensional heat conduction solution can be used to approximate the temperature distribution in the powder bed for three dimensions given the dimensional dependence of the beam intensity. Per [1.36], the time required to establish a quasi-steady state heat flow, for the material properties and processing conditions given above, would be 0.006 s or the time for the beam to travel 0.15mm.

Comparing the solutions of Carslaw and Jaegar and Hou and Komanduri, who used various approximations of the intensity distribution in the heat source, shows that the shape of the heat source intensity distribution has is a significant effect on the shape of the thermal profiles near the surface and the maximum temperatures near the surface. A comparison of the thermal profiles resulting from several approximations of a Gaussian distribution in which the total energy delivered to the medium is constant would provide a basis for accurately approximating the beam intensity and thus the surface and near surface temperatures. As was observed in the review of LS models, the surface temperature in the LS process is often predicted to be questionably high. Excessive surface temperatures could be attributed to poorly approximating the beam intensity distribution. Over estimating of the surface temperature also results in over estimating the densification rate.

In the LS process densification occurs only in regions of the powder bed where the heat is sufficient to induce a solid-to-liquid phase transition. As previously discussed, semi-crystalline polymers typically are better suited for LS because of the rapid decrease in viscosity associated with the melting transition. Because the semi-crystalline polymers exhibit a first-order melting transition, heat is expended in the latent heat of melting which decreases the temperature in the liquid volume. Calculating the Stefan number for the heating/melting in a typical LS process provides a means of determining the significance of the latent heat on the temperature distribution. For a typical semi-crystalline polymer the latent heat of melting is approximately \( 10^5 \text{J/kg} \) and the \( \Delta T \) between the bed temperature and the melting temperature is typically of the order \( 10^1 \text{K} \). Per [1.37], the Stefan number for LS a semi-crystalline polymer is of the order \( 10^4 \) which signifies that the heat required to increase the temperature of the medium to its melting temperature is significantly less than the latent heat of melting. Thus, ignoring the effects of the phase transition for LS of semi-crystalline polymers will lead to overestimating the liquefied volume and overestimating the temperature in the liquid. However, the analytical heat transfer solutions available for problems with phase change are limited and none of the available solutions are directly applicable to moving heat sources or variable intensity heat sources. Therefore, an approximate means of accounting for the effects of melting on the temperature distribution is the only tack. A method similar to the temperature recovery method used by Tontowi and Childs, Figure 1.11, in their model of LS could be used to reduce the temperatures in the liquid and determine the phase boundary from predictions made by a solution which did not account for phase change.

The results of Zhang and Faghri suggest that the effects of convective and radiative heat loss from the surface have a significant effect on the sintering depth during LS. The authors do not present any results which separate the contributions of the two heat loss mechanisms. Equation [1.45] is that of a thermal boundary with convective and radiative heat loss in addition to a heat flux, \( q_{sup} \). Equations [1.46] and [1.47] are the formulations for convective and radiative heat loss respectively, where \( h \) is the convective heat transfer coefficient, \( T_e \) is the convective boundary temperature, \( e \) is the emissivity of the surface, \( \sigma \) is the Stefan-Boltzmann constant, \( T_s \) is the surface temperature, which can change with time, and \( T \) is the temperature of the radiative boundary. Note: When dealing with radiative heat transfer absolute temperatures must be used. Closed-form analytical solutions to Fourier’s law
of heat transfer for a one-dimensional semi-infinite region initially at a constant temperature with a convective boundary condition can be obtained using the Laplace transform technique. However, closed-form analytical solutions for systems with radiative heat transfer are not available because of the nonlinearity introduced by the forth power surface temperature dependence of the radiative heat loss.

Linearization of equation [1.47] yields [1.48]. \( h_r \) is the radiative heat transfer coefficient described by [1.49] which shows the surface temperature dependence of the radiative heat transfer coefficient. The linearization does not remove the nonlinearity presented by the radiative boundary condition but it does allow for comparison of approximate values of \( h \) and \( h_r \). In the LS process convective heat transfer occurs via free convection. The range of values of the convective heat transfer coefficient for free convection is 2-25 W/m\(^2\)-K\(^4\) and the value of \( h \) is only weakly dependent on temperature\(^{41}\). In a typical LS process the average temperature in build chamber surrounding the powder bed is approximately 10K below the solid/liquid transition temperature. For example, the glass transition temperature for polycarbonate is 423K thus the temperature of the process chamber would be approximately 413K. Figure 1.17 shows a plot of the radiative heat transfer coefficient as a function surface temperature for heat being radiated into bodies at 413K and 298K. The surface emissivity for organic materials is approximately unity, therefore \( \varepsilon = 1 \) was used in generation of Figure 1.17. The entire range of radiative heat transfer coefficients for heat being radiated into bodies of either temperature falls within the upper half of the range of convective heat transfer coefficients for free convection. Therefore, assuming \( T_r \approx T_\infty \), the effects of convective and radiative heat losses are of the same order.

Because one of the goals of this research is to develop a closed-form analytical solution, the effect of radiative heat transfer must be neglected because of the nonlinearity it introduces into the boundary condition formulation. However, if the effects of convective heat loss are significant then it can be assumed that the effects of radiative heat loss are also significant, since \( h \approx h_r \) and \( T_r \approx T_\infty \). Doubling the value of \( h \) could be an approximate means of accounting for convective and radiative heat transfer while maintaining a closed-form analytical solution.

\[
-k \frac{\partial T}{\partial n} = -q_{\text{sup}} + q_{\text{conv}} + q_{\text{rad}}
\]

\[
q_{\text{conv}} = h(T_S - T_\infty)
\]

\[
q_{\text{rad}} = \varepsilon\sigma(T_S^4 - T_r^4)
\]

\[
q_{\text{rad}} = h_r(T_S - T_r)
\]

\[
h_r = \varepsilon\sigma(T_S^2 + T_r^2)(T_S + T_R)
\]

Figure 1.17: Radiative heat transfer coefficient as a function of surface temperature.
1.11 RESEARCH SCOPE

In the review of relevant literature previously presented, laser sintering of polymer powders is exclusively modeled using one or more of the classic sintering models, Frenkel, Scherer and Mackenzie-Shuttleworth. In Lee’s discussion of the forces and deformation mechanisms which could cause coalescence of polymer powder during LS, the author suggested that viscoelastic contact growth could play a role in densification. During the same period LS technology was being developed, researchers such as Jagota and Lin were developing models of viscoelastic contact growth and Mazur and co-workers were experimentally demonstrating that viscoelastic contact growth was a significant sintering mechanism for polymeric powders.

To date, quantitative modeling of LS has been done using numerical modeling techniques such as the finite element method. Such models provide little basis for quantitative understanding of the interplay between the material properties, the material geometry and the processing conditions which define the structural evolution during LS. Therefore, the modeling efforts in this work will focus on closed-form analytical solutions when possible.

The purpose of this research is to investigate viscoelastic contact growth during laser sintering of polymer powders. To this end, the primary objectives of this research are:

1. Develop a closed-form analytical thermal model which can be used to determine the temperature in the powder bed as a function of time and position during LS.
2. Present a sintering model for amorphous liquids which considers both viscoelastic and viscous contact growth.
3. Combine the thermal and sintering models to predict densification resulting from LS of polymers.
4. Construct a lab-scale LS unit which is suited for experimental investigations.
5. Characterize the thermal, geometric, and rheologic properties of demonstration materials.
6. Fabricate samples on the lab-scale LS unit which exhibit a range of densification, then investigate the sintered microstructures using scanning electron microscopy.
7. Use the combined thermal/sintering model to predict the density and dimensions of the samples fabricated using the lab-scale LS unit and compare the model results with experimental observations.

Objectives 1, 2, 4 and 5 are stand alone; they are not dependent on the success of other aspects of the work. The broad nature of the first two objectives should afford application to areas outside LS. Development of a closed-form analytical solution which approximates the temperature distribution resulting from laser heating could also be applicable to modeling welding processes and/or laser surface hardening. Presentation of a contact growth model which considers viscoelastic and elastic contact growth could be applicable to other polymer powder processing techniques such as powder coating and latex film formation. The concept of using laser-based heating methods to investigate contact growth kinetics could prove to be a valuable tool for investigating sintering phenomena in polymeric materials because of the ability of laser-based processes to deliver specific amounts of energy in a predetermined time interval.

In the following sections, a more detailed description of each of the research objectives is presented. The demonstration materials used in the research will be polycarbonate (PC) and three molecular weights of poly(ethylene oxide) PEO. The PC and PEO powders to be used are non-reactive; no artifacts of cross-linking or other reactions are observed in the rheologic data collected in the course of this work. PC is an amorphous thermoplastic and was one of the first materials studied for use in LS. Because PC is an amorphous material, it exhibits a quasi-second order phase transition from the solid to liquid states. Second-order phase transitions do not have a latent heat or enthalpy specifically associated with the phase change; therefore, the effect of the phase change on the temperature distribution around the phase boundary is minimized. Additionally, polycarbonate typically exhibits rheologic properties which can be accurately modeled using classic time-temperature-superposition models, such as the WLF equation.

Poly(ethylene oxide) is semi-crystalline thermoplastic, and was chosen as demonstration material for this research because of its availability in powder form in a wide range of molecular weights. The molecular weights of PEO used in this work are: $M_v = 1 \times 10^5$, $1 \times 10^6$ and $8 \times 10^6$ g/mol. This range of molecular weights should provide a wide range of rheologic properties with essentially no change in thermal properties. Because PEO is semi-crystalline, there is an enthalpy or latent heat associated with the melting/solidification transition. The Stefan number of heating PEO from room temperature to the liquid state is ~0.4 which indicates that the energy absorbed by the phase transition is more than twice the energy required to raise the temperature of PEO from room temperature to its
melting temperature. Therefore, in order to accurately predict the temperature distribution in a PEO powder bed during LS, phase change must be accounted for.

1.11.1 Thermal Model
The objective of the thermal modeling effort is to develop a closed-form analytical solution which can be used to model the thermal distribution in the powder bed during LS. The literature suggests that a closed-form solution for multi-dimensional heat conduction with a moving heat source is not possible. However, previous work showed that for high Pe processes, such as LS, the thermal distributions for one- and two-dimensional heat conduction are approximately equivalent. It is assumed that for Pe numbers much larger than the value where the one- and two-dimensional solutions converge, \( \sim 0.8 \), that a one-dimensional model also approximates the results of a three-dimensional model. This assumption is supported by the one- and three-dimensional modeling efforts of Sun and co-workers. Therefore, a model which considers only heat conduction normal to the powder bed surface will be developed. The model will approximate the thermal distribution resulting from a single scan vector; a single scan vector in the raster pattern is shown in Figure 1.2. There are two sub-objectives in the thermal modeling effort: investigating the effect of the approximation used to model the beam intensity distribution and investigating the effects of convective heat transfer on the temperature distribution in the powder bed during LS; radiative heat loss will not be addressed in this work.

The first of two sub-objectives of the thermal modeling component of this research is to investigate the effects of the approximations used to model the laser beam intensity distribution on the temperature distribution in the powder bed. The ideal shape of the beam is a normal or Gaussian distribution. However, using a Gaussian distribution for the flux boundary conditions excludes a closed-form analytical solution. Therefore, an approximation of the intensity distribution must be made. In previous analytical and most numerical work, the laser beam intensity distribution has been modeled using an instantaneous impulse function, such as the Dirac Delta function, or a square wave distribution. This work will consider both of these approximations and present a triangular approximation for the beam intensity distribution. A comparison of the temperature distributions resulting from the three intensity distributions approximations will be presented.

The second sub-objective is to investigate the effects of convective heat loss on LS of polymeric materials. Zhang and Faghri stated that convective and radiative heat losses were not negligible in LS processing. Closed-form analytical solutions are not available for radiative boundary conditions, so the effects can only be approximated by doubling the effects convective heat transfer as previously discussed. Because convective heat transfer from the surface is being considered, a Laplace transform solution strategy will be used to solve Fourier’s law. To determine the effect of convective heat transfer on the temperature distribution during LS of polymers, multiple convective heat transfer coefficients in the range of free convection will be presented, as well as a solution which does not consider convective losses from the surface.

1.11.2 Sintering Model
The objective of the sintering model is to develop a closed-form analytical formulation which accounts for viscoelastic and viscous contact growth, a combined-mechanism sintering model. The closed-form analytical model of viscoelastic contact growth most applicable to modeling LS is the long time viscoelastic limit presented by Lin et al. As previously discussed, a large critical separation distance should be assumed to account for the contributions of curvature-based forces to zipping contact growth and stretching mode contact growth by viscoelastic deformation. Thus, for times less than the characteristic relaxation time, the long time viscoelastic limit equation for contact growth presented by Lin et al will be used to model contact growth. For times greater than the characteristic relaxation time, contact growth will be modeled using the Mackenzie-Shuttleworth model. At the characteristic relaxation time, the relative density achieved during viscoelastic sintering will be used as the initial density for the Mackenzie-Shuttleworth model. The packing geometry is assumed to be simple cubic and the pore radius for the Mackenzie-Shuttleworth model is assumed to be that of a sphere equal in volume to the void volume in each simple cubic unit cell. For comparison, sintering predictions using only the Mackenzie-Shuttleworth model will also be presented.

1.11.3 Combined Thermal/Sintering Model
The thermal model will be used to calculate the temperature distribution in the powder bed. A temperature recovery approach will be employed to approximate the effects of phase change on the temperature as a function of time for a
semi-crystalline polymer. The temperature as a function of time will be calculated for locations in the powder bed where the thermal energy is sufficient for liquefaction to occur. The temperature as a function of time in the liquid state will be used in conjunction with a time-temperature superposition model to determine the compliance of the liquid at specific locations in the bed. From knowledge of the compliance function and the temperature as a function of time in the liquid state, the fraction of the characteristic relaxation time can also be determined. When the fraction of the characteristic relaxation time reaches unity the contact growth model will be switched from the long time viscoelastic limit to the Mackenzie-Shuttleworth model. Having calculated the aforementioned data using the thermal model in conjunction with temperature recovery method, the relative density as a function of position can then be determined using the combined-mechanism sintering model. Other relevant data such as the time in the liquid state and the average temperature while in the liquid state will also be calculated for locations in the powder bed which reach the liquid state.

1.11.4 Machine Construction
The lab-scale LS unit should incorporate all the major features (laser, heaters, thermal controls, motion control system, powder delivery, etc) required for LS while maintaining the maximum level of process flexibility. The design strategy for the unit is not to duplicate the commercial machine but to develop a platform that is conducive to materials testing. Thus, a small build volume is desired so small amounts of powder can be tested and long heat up and cool down cycles are not required, but still possible. User interaction should be minimized where possible but the user should have complete control over all process parameters during the build cycle. As reported in the literature good thermal control (+/- 2°C) is required for acceptable parts. Atmospheric control is a feature that could prove useful, especially if metals are to be tested in the unit. Software to make geometry from STL files is not required. However, the ability to run programmed scan configurations is desirable.

Properties of parts made in the lab-scale LS unit should be compared to those of parts made in the commercial unit to ensure that differences in the design and operation of the lab-scale LS unit do not result in part properties vastly different from those of parts made using a commercial machine. Thus, the mechanical properties of tensile specimens made using the lab-scale unit will be compared to those of tensile specimens made using the commercial unit.

1.11.5 Materials Characterization
Relevant material properties for polycarbonate and poly(ethylene oxide) powders will be determined using the characterization techniques listed in Error! Reference source not found. The particle size distributions of the as-received powders will be cut into narrower distributions using standard sieving methods. From the small amplitude oscillatory shear data, master curves of the creep compliances will be constructed and the WLF parameters for the creep compliance shift factors will be calculated.

Table 1.1: Powder characterization techniques.

<table>
<thead>
<tr>
<th>Characterization technique for powders</th>
<th>Properties determined (when applicable to material type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential scanning calorimetry (DSC)</td>
<td>glass transition temperature, melting temperature, enthalpy of melting, re-crystallization temperature</td>
</tr>
<tr>
<td>Thermogravimetric analysis (TGA)</td>
<td>degradation temperature</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>qualitative characterization of powder size and shape</td>
</tr>
<tr>
<td>Small amplitude oscillatory shear rheology</td>
<td>storage and loss moduli as a function of frequency and temperature</td>
</tr>
<tr>
<td>Powder packing analysis</td>
<td>tap density, pour density</td>
</tr>
</tbody>
</table>

1.11.6 Sample Fabrication and Characterization
PC and PEO samples will be fabricated at various processing conditions and from various particle size distributions using the lab-scale LS unit. Emphasis will be placed on the process-microstructure relationships for PC and the low molecular weight PEO. The microstructure of the samples fabricated using the lab-scale LS unit will be investigated using scanning electron microscopy. The neck geometry will be of specific interest since evidence of viscoelastic contact growth similar to Mazur’s will support the theory that viscoelastic contact growth occurs in LS.
1.11.7 Comparison of Model and Experimental Results

For each set of conditions at which PEO and PC samples are fabricated, the thermal and combined-mechanism sintering model will be used to predict the density distribution, the average density, the width and thickness of the laser sintered sample. Comparison of the calculated and actual physical characteristics will provide a measure of the models validity and effect of viscoelastic contact growth on sintering kinetics in LS of PC and PEO.

1.12 CHAPTER 1 REFERENCES

1 Conversation with Kevin McAlea and Rick Booth of DTM Corp. August, 1999; Austin, Texas.
4 Conversation with J. C. Nelson of DTM Corp, formally of the Univ. of Texas. August, 1999; Austin, Texas.
2 MATERIALS AND METHODS

As mentioned in the last chapter polycarbonate (PC) and three molecular weights of poly(ethylene oxide) (PEO) were used as demonstration systems in this work. These materials were thermally characterized using thermogravimetric analysis and differential scanning calorimetry. The initial particle size distributions were separated into narrower distributions using standard sieving methods. The particle size and shape of the sieved powders were investigated using scanning electron microscopy. The pour and tap densities of the powders were measured to quantify the packing characteristics of the powders. The rheologic characteristics of the liquid polymers were measured using small amplitude oscillatory shear rheology; the data from these measurements were used to generate creep compliance master curves for each of the materials. Additional material properties were compiled from the literature as needed. At the conclusion of the raw materials characterization section all of the relevant material properties for the four materials used herein are summarized.

PC and PEO samples were fabricated, from various particle size distributions, using various processing parameters. The specific particle size distributions and process parameters will be presented later in the chapter. Microstructural characterization of the laser sintered samples was done using scanning electron microscopy. Scanning electron microscopy was used to investigate the contact growth between the particles and make quantitative estimates of the most probable contact growth mechanism. The observed microstructural characteristics were compared to the prediction of the combined thermal/sintering model to qualitatively determine the accuracy of the model which tested the hypothesis that viscoelastic contact growth can be a significant mode of densification in LS. Initially, the sample dimensions and density were also going to be determined and compared to model predictions. Archimedes density testing was excluded due to two factors. First, the sample size is so small that the error associated with measuring the saturated mass yields the calculated densities quantitatively meaningless. Secondly, the PEO is soluble in water, thus a nonpolar solvent must be used and most have high vapor pressures which makes measuring the saturated mass very subjective. Dimensional characterization of the samples was also planned, however the fragility of the samples and the propensity of the samples to curl during sintering makes measuring the sample dimensions impractical.

2.1 RAW MATERIALS CHARACTERIZATION

The PEO powders used in this research were obtained from Sigma-Aldrich and the viscosity average molecular weights used herein are $M_v = 1 \times 10^5$, $1 \times 10^6$ and $8 \times 10^6$ g/mol (Product numbers: 37,283-8; 37,278-1; 18,198-6). Zero-shear viscosity increases as the molecular weight to the 3.4 power above the critical entanglement molecular weight. Therefore, the aforementioned range of molecular weights yields significant differences in rheologic characteristics. PEO is a water-soluble semi-crystalline aliphatic polyoxide with a glass temperature of approximately -65°C, a melting temperature of approximately 65°C and a critical entanglement molecular weight of $2 \times 10^3$ g/mol. The chemical structure of the repeat unit of PEO is shown in Figure 2.1. The PC used is DTM polycarbonate compound. PC is a linear polyester of carbonic acid with a critical entanglement molecular weight of $4-6 \times 10^3$ g/mol and a glass transition temperature of approximately 150°C. The molecular weight of the PC used was not measured. The chemical structure of the PC repeat unit is shown in Figure 2.2.

\[
\left( -\text{CH}_2\text{CH}_2\text{O} - \right)_n
\]

Figure 2.1: PEO repeat unit.

\[
\left( -\text{CH}_3\text{C}\text{C}_2\text{H}_4\text{O}\text{O} - \right)_n
\]

Figure 2.2: PC repeat unit.
2.1.1 Thermal Characterization

Thermogravimetric analysis

Thermogravimetric analysis (TGA) can be used to determine the onset temperature for thermal degradation and the degradation temperature, which is defined as the temperature where the absolute value of the slope of the weight loss as a function of temperature curve is a maximum. The degradation onset temperature provides an upper limit for the temperature range over which further characterization, such as DSC and rheology, should be conducted. Additionally, knowledge of the degradation characteristics provides a realistic temperature limit for the temperature in the powder bed. Short exposure to the onset temperature should not result in substantial degradation, however, if the degradation temperature is reached or exceeded, some degradation should be expected. A Perkin Elmer TGA-7 was used in this research. The temperature ranges used were: 25-700°C for PC and PEO M_v=1x10^5 g/mol and 25-500°C for PEO M_v=1x10^6 and 8x10^6 g/mol. For all samples, the heating rate was 10°C/min and the atmosphere used was nitrogen. Because the heating rates during LS are well outside the range of standard thermogravimetric analyzers, the exact values of the onset and degradation temperatures, which are rate dependent, are not of high importance; thus only single TGA experiments were conducted for each material.

Figure 2.3 shows the percent weight loss as a function of temperature for the three different molecular weights of PEO; the inset in the figure shows the temperature range where the onset of degradation occurs. Figure 2.4 shows the absolute value of the derivative of the weight loss with respect to temperature for the PEOs. The maximum value of the derivative is the degradation temperature. Figure 2.5 is the weight loss as a function of temperature for PC. Figure 2.6 is the absolute value of the derivative of the weight loss with respect to temperature for PC. The values of the onset temperature and the degradation temperature are summarized in Table 2.1. The degradation onset temperature for the PEOs lie in the range from 175-200°C and the degradation temperatures are in the range of 289-333°C. The 5% weight loss temperature for all the PEO molecular weights is 230°C for 10°C/min heating rate. PC is stable at temperatures approximately 200°C higher than PEO. The degradation onset temperature for PC is 405°C and the degradation temperature is 543°C. The 5% weight loss temperature is 475°C.
Figure 2.4: TGA of PEO $M_v = 1 \times 10^5$, $1 \times 10^6$, and $8 \times 10^6$ g/mol; derivative of weight with respect to temperature as a function of temperature.

Figure 2.5: TGA of PC.
Table 2.1: TGA data.

<table>
<thead>
<tr>
<th>material</th>
<th>degradation onset temperature, °C</th>
<th>degradation temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO $M_v= 1 \times 10^5$ g/mol</td>
<td>175</td>
<td>333</td>
</tr>
<tr>
<td>PEO $M_v= 1 \times 10^6$ g/mol</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>PEO $M_v= 8 \times 10^6$ g/mol</td>
<td>192</td>
<td>289</td>
</tr>
<tr>
<td>PC</td>
<td>405</td>
<td>543</td>
</tr>
</tbody>
</table>

**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) is a thermal analysis technique that is used to investigate thermally-induced phase transitions. Semi-crystalline polymers exhibit a first order solid/liquid phase transition; differential scanning calorimetry can be used to determine the melting temperature range, the enthalpy or latent heat of melting, the recrystallization temperature range and the enthalpy of fusion for semi-crystalline polymers. The temperature at which the phase transition occurs and the breadth of the transition are both heating rate dependent; the higher the heating rate the higher the transition temperature and the wider the temperature range of the transition. Differential scanning calorimetry can be used to determine the glass transition temperature for amorphous polymers, which is also heating rate dependent.

In this work, a Perkin Elmer Pyris 1 DSC was used. For all samples the heating rate was 10°C/min and the atmosphere was nitrogen. Figure 2.7 is a DSC curve for PEO $M_v=1 \times 10^5$ g/mol. The heating method used was as follows: hold for one minute at 25°C, heat from 25°C to 100°C at 10°C/min (same rate for all temperature scans), hold for one minute at 100°C, cool from 100°C to 25°C, hold for one minute at 25°C, and heat from 25°C to 100°C. The thermal cycle can be summarized as: hold, heat, hold, cool, heat. Typically the data collected from second heating are reported, however, the solid/liquid transition in the first heating is important in this research because the range and breadth of the transition observed in the first heating is assumed to correspond to the transition which occurs during LS because the powders will be melted and cooled only once during the LS experiments conducted in this research. Figure 2.8 and Figure 2.9 are the DSC curves for PEO $M_v=1 \times 10^6$ g/mol and $M_v=8 \times 10^6$ g/mol,
respectively. The melt and re-crystallization data from the three PEO DSC curves are summarized in Table 2.1. An increase in the melting and re-crystallization temperature of PEO is observed as the molecular weight increases. However, the enthalpy of melting is approximately equal for all three molecular weights. Each of the PEO DSC curves are representative for the given molecular weight and the melting temperatures and enthalpies are in agreement with literature values for PEO². Only one DSC measurement was made for each material because the data is conformational in nature, not investigative.

Figure 2.7: DSC curve for PEO 1x10⁵ g/mol.

Figure 2.8: DSC curve for PEO 1x10⁶ g/mol.
Table 2.2: PEO DSC data.

<table>
<thead>
<tr>
<th>PEO M, (g/mol)</th>
<th>melt onset temp. °C</th>
<th>melt temp. °C</th>
<th>ΔH melting, J/kg</th>
<th>re-xtal onset temp. °C</th>
<th>re-xtal temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10⁷</td>
<td>61</td>
<td>69</td>
<td>1.7x10⁵</td>
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<td>42</td>
</tr>
<tr>
<td>1x10⁸</td>
<td>62</td>
<td>72</td>
<td>1.6x10⁶</td>
<td>49</td>
<td>45</td>
</tr>
<tr>
<td>8x10⁶</td>
<td>66</td>
<td>73</td>
<td>1.6x10⁶</td>
<td>52</td>
<td>47</td>
</tr>
</tbody>
</table>

Since PC is amorphous the solid-to-liquid transition occurs at the glass transition temperature, T_g. Figure 2.10 is the DSC curve for PC; the glass transition temperature is 146°C.
2.1.2  Powder Sizing and Characterization

The as-received PC and PEO powders were separated into the size distributions listed in Table 2.3 using standard sieving methods and utilizing a Ro-tap sieve shaker. The mesh designation –A/+B, where A and B are mesh sizes, refers to particles which fall through an A-mesh sieve but do not fall through a B-mesh sieve. Thus, after sufficient sieving, the particles on top of the B-mesh sieve will have a particle size distribution which lies primary between the opening sizes of the A- and B-mesh sieves. A sufficient amount of powder for testing in the lab-scale LS unit was collected from all four of the powders in all four of the size ranges with the exception of PC, which had only a trace amount of powder smaller than 25µm or -500 mesh.

Table 2.3: Particle size distributions, mesh and opening sizes.

<table>
<thead>
<tr>
<th>mesh sizes</th>
<th>opening sizes (µm)</th>
<th>average diameter of distribution, (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100/+170</td>
<td>150-90</td>
<td>120</td>
</tr>
<tr>
<td>-170/+325</td>
<td>90-45</td>
<td>67.5</td>
</tr>
<tr>
<td>-325/+500</td>
<td>45-25</td>
<td>35</td>
</tr>
<tr>
<td>-500</td>
<td>&lt;25</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Powder Density**

In powder processing methods, the initial packing density of the particles being consolidated is of significant importance; the higher the initial packing density the smaller the change in volume and amount of energy required to reach the desired relative density. The pour and tap densities of a powder bound the range of initial packing densities for a given powder and are dependent on the degree of interparticle friction. Interparticle friction increases with increasing particle irregularity (deviation from smooth spherical geometry). The pour and tap densities of the different particle size distributions of PC and PEO were measured using standard techniques. The mass of 20-30 ml of powder poured into a 50 ml graduated cylinder was measured and the pour density of the powder was determined by dividing the powder mass by the poured volume. The graduated cylinder was then secured in a ring-stand and tapped by the side of a shaker-table oscillating at approximately 500RPMs for two minutes. Figure 2.11 shows the setup used to tap the graduated cylinder. The apparatus and method for determining the tap density are similar to ASTM B527-93. Figure 2.12 shows the pour and tap density as a function of the average particle size of each of the distributions in Table 2.3 for all four materials, less PC -500 mesh. Each of the pour and tap density values plotted in Figure 2.12 is the average of three values; the error bars on each of the data points are plus and minus one standard deviation.

The average pour and tap densities for all the materials and distributions fall between 0.30-0.40 and 0.40-0.50, respectively. The pour and tap densities of PC decreases with decreasing particle size. In the two larger-particle size distributions, the pour and tap densities of PEO are inversely proportional to the molecular weight; the lower molecular weights have higher densities. However, for the smallest-particle size distributions, the pour and tap densities of PEO are proportional to the molecular weight; higher molecular weight powders have higher densities. PC has the highest tap density for the two larger-particle size distributions. PEO 1x10^6 g/mol has the highest tap density for the distribution with 35µm average size. PEO 8x10^6 g/mol has the highest tap density for the smallest-particle size distribution. The ratio of the tap-to-pour density of a powder, known as the Hausner Ratio, provides a more quantitative comparison of the interparticle friction in a given powder. Interparticle friction increases as the aspect ratio of the particles increases, the size of the particles decreases, the surface roughness of the particles increases, the moisture content of the powder increases and the surface tack of the particles increases.

Interparticle friction is a catch-all term encompassing all factors which reduce the packing density of a powder from close-packing. Interparticle friction has a greater effect on the pour density because gravity is the only driving force for packing. Interparticle friction plays a lesser role in the tap density because the mechanical energy put into the powder provides more energy to overcome interparticle friction. Because the Hausner Ratio is the quotient of the tap and pour densities, the closer the ratio is to unity, the lower the interparticle friction. Figure 2.13 is a plot of the Hausner Ratio as a function of the average particle size of each distribution for PC and PEO powders. The error bars on the data points are plus and minus one standard deviation, as calculated using propagation of errors for division of two averages. PC has the highest interparticle friction for all particle sizes. For PC and PEO the general trend is: the smaller the particle size, the higher the interparticle friction. Of the PEO powders, 1x10^5 g/mol has the highest
interparticle friction. For the two smaller-particle size distributions, PEO $8 \times 10^6$ g/mol has the lowest interparticle friction and for the two larger-particle distributions, $1 \times 10^6$ g/mol has the lowest interparticle friction. All of the powders used in this research have relative tap densities below that of simple cubic packing, which is 0.52.

Figure 2.11: Tap density setup.

Figure 2.12: Pour and tap density as a function of average particle size.
Scanning Electron Microscopy

Scanning electron microscopy (SEM) was conducted using a LEO 1550. All of the powders were coated with gold-platinum to provide a conductive surface for imaging. The SEM images provide qualitative explanations for the packing characteristics observed in the previous section. In this section, two images are presented for each particle size distribution for all four materials. Figure 2.14 shows the SEM images for all three particle size distributions of PC. Figure 2.15, Figure 2.16 and Figure 2.17 are the SEM images of the PEO particle size distributions in order of increasing molecular weight. The following bullets summarize the observations which can be made from the SEM images of the powder.

- Sieving the powder produced noticeably different particle size distributions with relatively few fines remaining in the larger particle size distributions.
- For PC, as the particle size decreases, the fraction of high aspect ratio particles with jagged surfaces is observed to increase.
- The shape of PC particles is less equiaxed than the PEO particles.
- The highest aspect ratio particles in the PC are approximately 3:1.
- For PEO, the particles in all of the distributions and molecular weights are agglomerates of smaller particles which display some level of porosity.
- In all molecular weights of PEO the particles become increasingly equiaxed as the particle size decreases.

The observation that the PC particles are less equiaxed than the PEO particles supports the fact that PC had the highest Hausner Ratio. The observed increase in the number of high aspect ratio particles as the particle size of PC powder decreases supports the measured decrease in tap density as the particle size decreases. The observation that the PEO particles become more equiaxed as the particle size decreases supports the observed increase in tap density as the particle size decreased. Generally, the shape and surface roughness of the particles supports the fact that all of the particles have relative tap densities below simple cubic packing.
Figure 2.14: SEM images of PC powders distributions.
Figure 2.15: SEM images of PEO $1 \times 10^5$ g/mol particle size distributions.
Figure 2.16: SEM images of PEO 1x10^6 g/mol particle size distributions.
Figure 2.17: SEM images of PEO $8 \times 10^6$ g/mol particle size distributions.
2.1.3 Rheologic Characterization

The rheologic properties of liquid PC and the three molecular weights of PEO were measured using a small amplitude oscillatory shear method. The measurements were made using a Rheometrics RMS-800 rheometer in a parallel plate configuration; Figure 2.18 shows a schematic of parallel plate configuration for rheologic measurements. Storage and loss shear moduli, \( G' \) and \( G'' \) respectively, were obtained as a function of frequency for a set temperature. Measuring the rheologic response of a polymeric liquid at several temperatures allows for construction of a time-temperature master curve which can be used to predict the response of the polymeric liquid for time-temperature combinations that were not measured. Construction and use of master curves for describing the behavior of polymeric materials is based on the principal of time-temperature equivalence; a short exposure to a high temperature will yield the same changes in properties as a longer exposure to a lower temperature.

![Figure 2.18: Schematic of oscillatory shear apparatus.](image)

Table 2.4 lists the temperatures and frequency ranges over which rheologic measurements were made for each of the materials. The testing temperatures were chosen to span the temperature range over which the polymeric liquid is chemically stable; this range is based on knowledge of the melting or glass transition temperature from DSC and the degradation onset temperature from TGA. Plaques, approximately 1.5mm thick, of each of the materials were compression molded at appropriate temperatures and pressures. From the plaques, 25mm disks were punched for testing in the rheometer. The strain amplitude used was 1% or less and the purge gas was nitrogen. *Due to limited access to the rheometer, one sample was run at each of the conditions.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions: Testing temperature (°C) / frequency range (rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>170 / 0.1-100; 230/ 0.1-100; 270/ 0.1-100</td>
</tr>
<tr>
<td>PEO 1x10⁵ g/mol</td>
<td>80 / 0.1-100; 115 / 0.1-100; 135/ 0.1-100; 150 / 0.01-100</td>
</tr>
<tr>
<td>PEO 1x10⁶ g/mol</td>
<td>80 / 0.1-100; 150 / 0.1-100; 190 / 0.01-100</td>
</tr>
<tr>
<td>PEO 8x10⁶ g/mol</td>
<td>80 / 0.1-100; 150 / 0.1-100; 190 / 0.01-100</td>
</tr>
</tbody>
</table>

The rheologic characteristics of interest in this work were obtained from knowledge of the tensile creep compliance, discussed in the previous chapter. The following discussion steps through the procedure which was used to approximate the tensile creep compliance from small amplitude oscillatory shear data for PC; the procedure was also used to determine/approximate the desired rheologic characteristics for the PEOs. Figure 2.19 is a plot of the shear storage and loss moduli as a function of frequency, \( G' \) and \( G'' \) respectively, for PC at three different temperatures.

First, based on the assertion of the Cox-Merz rule\(^3\), the angular frequency, \( \omega \), was converted to time per \([2.1]\). Next, the shear storage and loss moduli were converted to shear storage and loss compliances per \([2.2]\) and \([2.3]\), respectively. The shear storage compliance as a function of time for the three testing temperatures is shown in Figure 2.20. Using the time-temperature superposition principal, the low and high temperature curves were shifted along the time axis, by multiplying the time by an appropriate shift factor, to produce a master curve of the shear

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storage compliance. The shift factors were determined by visually matching the slopes of the curves. The shift factor values will be reported later when the WLF parameters are determined. Using the Alfrey approximation, [2.4], the retardation spectrum, L(τ), were determined from shear storage compliance. Figure 2.22 shows the retardation spectrum for PC determined using the Alfrey approximation. From the retardation spectrum and shear storage and loss compliances, the shear compliance was approximated. Finally, the shear compliance was used to approximate the tensile compliance. Although several assumptions/approximations were required to approximate the tensile creep compliance from the small amplitude oscillatory shear data, the difficulty in experimentally measuring the tensile creep compliance yields this approach necessary.

![Figure 2.19: Storage and loss moduli for PC as a function of frequency for three temperatures.](image)

\[ t \approx \frac{2\pi}{\omega} \]  

\[ J' = \frac{G'}{G'_{\infty}^2 + G''_{\infty}^2} \]  

\[ J'' = \frac{G''}{G'_{\infty}^2 + G''_{\infty}^2} \]
Figure 2.20: Shear storage compliance as a function of time for three temperatures for PC.

Figure 2.21: PC storage creep compliance master curve.
\[ L(t) = \frac{dJ'}{d \ln(t)} \approx \frac{\Delta J'}{\Delta \ln(t)} \] \[ \text{[2.4]} \]

Figure 2.22: PC retardation spectrum.

The shear compliance was calculated from the retardation spectrum using [2.5], however, \( J_0 \) and \( \eta_0 \) were determined first by fitting [2.6] and [2.7] to the shear storage and loss compliances, respectively. As shown in Figure 2.22 the retardation spectrum calculated from the shear data is a series of points, not a continuous function, therefore, a linear interpolating function was fit to the data points, as shown in Figure 2.23, to allow for numerical integration of the terms containing \( L(\tau) \) in [2.5], [2.6] and [2.7]. Figure 2.24 shows the shear storage compliance as a function of time calculated using [2.6] and determining an appropriate value for \( J_0 \). For times less than one second [2.6] provides an excellent fit to the values calculated directly from experimental data, however, for times greater than one second the fit deviates from the data as a result of the over-emphasis of the contribution of the elements in the retardation spectrum with longer relaxation times. The plateau value of the shear storage compliance at long times approximates the value of the long-time elastic compliance, \( J_e \). Figure 2.25 shows shear loss compliance as a function of time as predicted using [2.7] after determination of an appropriate value for \( \eta_0 \) and the values calculated directly from experimental data. The value of \( \eta_0 \) was determined by matching the slope of the \( J'' \) curve at long-times or calculating the average slope of the \( J'' \) data when the data do not converge to a single slope. The shear loss compliance calculated using [2.7] fits the data calculated from experimental results well.
\[ J(t) = J_0 + \int_{-\infty}^{\infty} L(\tau)(1 - e^{-t/\tau})d\ln \tau + \frac{t}{\eta_0} \quad [2.5] \]

\[ J' = J_0 + \int_{-\infty}^{\infty} L(\tau) \frac{1}{1 + \frac{\tau^2}{t^2}} d\ln \tau \quad [2.6] \]

\[ J'' = \frac{t}{\eta_0} + \int_{-\infty}^{\infty} L(\tau) \frac{\tau}{1 + \frac{\tau^2}{t^2}} d\ln \tau \quad [2.7] \]

**Figure 2.23**: Interpolating function and discrete data points of the PC retardation spectrum.

**Figure 2.24**: Experimental and calculated shear storage compliance for PC.
Knowing \( J_0 \), \( L(\tau) \) and \( \eta_0 \), the shear creep compliance \( J(t) \) was calculated using [2.5]. The shear creep compliance for PC calculated using [2.5] is shown in Figure 2.26. Also shown in Figure 2.26 are the experimental and calculated shear storage compliances, the viscous component of the compliance, \( t/\eta_0 \), and the inverse shear storage modulus, \( 1/G' \). Without experimental shear creep compliance data, assessment of the validity of the calculated shear creep compliance was not possible. However, the shear creep compliance should be bounded by \( 1/G' \) and \( J^{1.5} \) as shown in Figure 2.26; thus the calculated creep compliance function should provide a reasonable approximation of the shear creep compliance. Finally, an approximation of the tensile creep compliance, \( D(t) \), was made assuming that [2.8] applies. Equation [2.8] assumes that Poisson’s ratio is very close to \( \frac{1}{2} \) which physically means that the change in volume caused by an applied stress is negligible compared to the change in shape; the bulk modulus is much greater than the shear modulus. The mathematical model of the tensile creep compliance used in Lin et al’s long-time limit of viscoelastic contact growth is a power law fluid. As previously mentioned, the Lin et al’s model was used to model viscoelastic contract growth prior to the onset of viscous flow which occurs at the characteristic relaxation time, \( \tau \). Figure 2.27 is a plot of the tensile creep compliance approximated using the assumptions described previously; also shown on the plot are the power law fluid fit and the viscous component of the tensile creep compliance.

**Figure 2.25:** Experimental and calculated shear loss compliance for PC.

**Figure 2.26:** Shear compliance functions and experimental data for PC.
The method described above for approximating the tensile creep compliance from the small amplitude oscillatory shear for PC was also used to determine the tensile creep compliance for the three molecular weights of PEO. A power law fit to the tensile creep compliance was also made for the PEOs. Figure 2.28 shows the shear creep compliance functions (left) and the tensile creep compliance with the power law fit (right) for all three molecular weights of PEO. The trends observed in the changes in rheologic characteristics as the molecular weight increases are:

- a slight increase in the initial elastic component, $J_0$, with increasing molecular weight; this value should be independent of molecular weight because it does not involve long range cooperative chain motion.
- a significant increase in the viscosity, which also results in a significant increase in the relaxation time, is observed as the molecular weight increases; however, the viscosity does not increase as the molecular weight to the 3.4 power as suggested by the theory of de Gennes.
- the shear creep compliance curves for the two higher molecular weight PEOs calculated using the aforementioned approximations do not fall between the $1/G'$ and $J'$ values calculated directly from the experimental data at long times. This deviation suggests that the simple rheologic model does not accurately describe the behavior of high molecular weight PEOs.

All of the relevant rheologic quantities are summarized later in the chapter. The rheologic data and the calculations used for determining the rheologic parameters used in this work can be found in the Appendix.
Figure 2.28: PEO shear creep compliance functions (left), tensile creep compliance and power law fit (right).
**Time temperature superposition**

In Sperling\(^8\), Figure 10.14 is an example of a stress relaxation master-curve which is constructed by shifting stress relaxation data for different temperatures along the time axis to produce a continuous curve. To produce a stress relaxation master-curve from stress relaxation data at various temperatures, a reference temperature is selected, the curve labeled “0” in the “Stress Relaxation Data” frame, then the stress relaxation curves for all of the other temperatures are shifted left or right to overlap the reference temperature curve or other curves that have already been shifted to the reference temperature. The data sets for temperatures above and below the reference temperature are shifted left and right, respectively, using [2.9], where \(a_T\) is the shift factor to shift from a temperature \(T_1\) to the reference temperature. The temperature difference between each data set and the reference temperature is also calculated, this difference labels each of the curves shown in the right frame. Having constructed the master curve of the stress relaxation modulus as a function of time for the reference temperature, as shown in the primary frame, predictions of the stress relaxation modulus over a wide range of times at the reference temperature can be made. Furthermore, the log of the shift factor for each of the different temperatures can be plotted as a function of the deviation from the reference temperature, as shown in the upper right corner of the example master curve in Sperling\(^8\). Often, the WLF equation, [2.10], provides an adequate description of the temperature-difference dependence of the log of the shift factor. After determining \(C_1\) and \(C_2\) in the WLF equation, the master curve can be shifted to correspond to any temperature. Extrapolating to temperatures outside the temperature range of the experiments can lead to significant error in the prediction of polymer behavior, specifically if the extrapolation is to temperatures below the glass transition or melting temperature. Master-curves of other time- and temperature-dependent polymer mechanical properties can also be constructed using the same methodology.

\[
t_{\text{ref}} = \frac{t_{T_1}}{a_T}
\]  

[2.9]

The PC compliance functions discussed above were constructed by using the principal of time-temperature superposition to shift the 170°C and 270°C shear data to match the slope of the 230°C as shown in Figure 2.21; the unshifted data is shown in Figure 2.20. Equation [2.9] was used to shift the independent variable, time. Figure 2.29 is a plot of the log of the shift factor as a function of the temperature difference; the line on the graph is the best fit to the WLF equation. Having constructed tensile creep compliance master-curve, as described above and shown in Figure 2.27, and knowing the parameters for the WLF equation, an approximation of the tensile creep compliance can be made over a wide range of times and temperatures using equations [2.9] and [2.10]. The upper left plot in Figure 2.30 shows a plot of the log of the shift factor as a function of the temperature difference for PEO 1x10^3 g/mol; the line on the graph is the best fit to the WLF equation.

\[
\log(a_T) = \frac{-C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})}
\]  

[2.10]
The log of the shift factor as a function of temperature difference for the two higher molecular weight PEOs does not match the concavity of the WLF equation, therefore an equation which matched the concavity, concave down, of the shift factor data was selected, [2.11]. Equation [2.11] was chosen because it provided an adequate description of the data, and is not based on any previous work in the literature. The upper right and bottom plots in Figure 2.30 are plots of the log of the shift factor as a function of the temperature difference for PEO 1x10^6 g/mol and PEO 8x10^6 g/mol, respectively; the lines on the graphs are the best fits to [2.11]. As previously mentioned, due to limited access to the rheometer, one sample was run at each of the conditions.

\[
\log(a_T) = B_0 (1 - e^{-B_1 (T - T_{ref})})
\]  

[2.11]
Figure 2.30: Log shift factor as function of temperature difference for PEOs.

2.2 SUMMARY OF MATERIAL PROPERTIES

2.2.1 Thermal Conductivity Approximation

A literature value for the thermal conductivity of PEO was not available; therefore, the empirical equation, [2.12], proposed by Zhong et al \(^9\) for determining the thermal conductivity polymeric liquids was used. Where \(k\) is the thermal conductivity, \(C_\rho\) is the specific heat, \(T_m\) is the melting temperature of the polymer, and \(M\) is the mer molecular weight.

\[
k = \frac{6.833 C_\rho \rho^{0.793}}{T_m^{0.666} M^{1.022}} \quad [2.12]
\]

The values of the relevant material properties for PEO are: \(C_\rho = 75 \text{ J/(mol K)} \(^10\), \(\rho = 1.18 \text{ g/cm}^3 \(^11\), \(T_m = 338\text{K}, \) and \(M = 44\text{g/mol}.\) The thermal conductivity, as predicted by [2.12], of PEO liquid is \(k = 0.25 \text{ W/(m K)}\).

Table 2.5 lists the physical, thermal and rheologic properties for the materials used in this research. Aside from the transition temperatures, the thermal and physical properties of all four of the materials are approximately equivalent. The majority of the thermal and physical properties are assumed to be independent of the molecular weight and the
same value is used for all three molecular weights of PEO. The major difference between PC and PEO is that the former is amorphous and the latter is semi-crystalline. This difference allows for comparison of the behavior of the two polymer forms during LS. The relaxation times of the three molecular weights of PEO span three orders of magnitude and the zero-shear viscosities also span three orders of magnitude. These ranges will allow for investigation of the effect of the rheologic properties, and subsequently the molecular weight, on densification during LS.

Table 2.5: Summary of material properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>PC</th>
<th>PEO 1x10^5 g/mol</th>
<th>PEO 1x10^6 g/mol</th>
<th>PEO 8x10^6 g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (ρ), g/cm³</td>
<td>1.20 ± 2</td>
<td>1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>glass transition temperature (T_g), °C</td>
<td>146</td>
<td>-65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>melting temperature (T_m), °C</td>
<td>N/A</td>
<td>69</td>
<td>72</td>
<td>73</td>
</tr>
<tr>
<td>re-crystallization (T_r), °C</td>
<td>N/A</td>
<td>42</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td>degradation temperature (T_d), °C</td>
<td>543</td>
<td>333</td>
<td>300</td>
<td>289</td>
</tr>
<tr>
<td>surface energy (γ), J/m²</td>
<td>35x10^-14 ± 13</td>
<td>42x10^-14 ± 14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thermal conductivity (k), W/(m K)</td>
<td>0.20 ± 2</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>specific heat (cₚ), J/(kg K)</td>
<td>1.7x10^3 ± 153</td>
<td>1.7x10^3 ± 157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>enthalpy of melting (ΔH_m), J/kg</td>
<td>N/A</td>
<td>1.7x10^7</td>
<td>1.6x10^7</td>
<td>1.6x10^7</td>
</tr>
<tr>
<td>reference temperature (T_ref), °C</td>
<td>230</td>
<td>115</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>zero-shear viscosity (η₀), Pa-s⁻¹</td>
<td>9.0x10⁴</td>
<td>3.4x10⁴</td>
<td>1.1x10⁴</td>
<td>6.5x10⁴</td>
</tr>
<tr>
<td>long-time viscoelastic compliance (D₂₀), Pa⁻¹* Pa⁻¹*</td>
<td>1.4x10⁻⁶</td>
<td>6.7x10⁻⁹</td>
<td>5.3x10⁻⁷</td>
<td>9.2x10⁻⁷</td>
</tr>
<tr>
<td>relaxation time (τ), s⁻¹</td>
<td>0.13</td>
<td>2.3</td>
<td>59</td>
<td>600</td>
</tr>
<tr>
<td>power law intercept (A₀), Pa⁻¹* Pa⁻¹*</td>
<td>1.6x10⁻⁷</td>
<td>3.5x10⁻⁷</td>
<td>4.4x10⁻⁷</td>
<td>8.5x10⁻⁷</td>
</tr>
<tr>
<td>power law slope (A₁), Pa⁻¹* Pa⁻¹* Pa⁻¹*</td>
<td>8.5x10⁻⁶</td>
<td>8.8x10⁻⁶</td>
<td>3.8x10⁻¹²</td>
<td>4.6x10⁻⁹</td>
</tr>
<tr>
<td>power law exponent, m⁻¹</td>
<td>0.65</td>
<td>0.46</td>
<td>2.72</td>
<td>0.82</td>
</tr>
<tr>
<td>WLF C₁*</td>
<td>15.7</td>
<td>9.5</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>WLF C₂*</td>
<td>408</td>
<td>995</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>alt. t-T eqn. B₀*</td>
<td>N/A</td>
<td>N/A</td>
<td>0.55</td>
<td>0.097</td>
</tr>
<tr>
<td>alt. t-T eqn. B₁*</td>
<td>N/A</td>
<td>N/A</td>
<td>-0.018</td>
<td>-0.077</td>
</tr>
</tbody>
</table>

*: tensile deformation;  #: at T_ref; †: value at part bed temperature; ‡: at T_melt

2.3 LASER SINTERING MODELING AND EXPERIMENTATION

In this work, modeling and experimentation focused more on PC and PEO 1x10^5 because both of these materials exhibit rheologic behavior which is easily characterized using standard models. The two higher molecular weight PEOs exhibit rheologic characteristics which are not well described using the simplified rheologic model used in this work. Additionally, the time-temperature superposition data for these two materials does not fit the standard WLF model. Figure 2.31 shows matrices which detail the modeling and experiments which were undertaken in this work. The matrices show the combinations of laser power and average particles that were modeled using the approached outlined in the next two chapters and which samples were made using the lab-scale LS unit. For all three molecular weights of PEO, the bed temperature was 25°C. However, two different bed temperatures were investigated for PC through modeling and experimentation as shown in Figure 2.31. Microstructural investigation of the samples made using the lab-scale LS unit was done using scanning electron microscopy.

The samples made using the lab-scale LS for the microstructural investigation were a single scan vector, 25.4mm in length, scanned at 25.4 mm/s. A small powder volume insert for the lab-scale LS was used to limit the amount of powder needed for each experiment. In all of the modeling work, the density of the powder bed was assumed to be equal to the tap density, as measured and described above, for the given average particle size of the material. To be consistent with the models, the small powder volume insert, filled with powder, was tapped for two minutes prior to sintering to pack the powder to its tap density. At least three samples were made for all of the PEO molecular weights and conditions and at least two samples were made for each of the PC average particle size – process parameter combinations. A representative sample from each of the experimental permutations was selected for microstructural investigation using SEM.
2.4 MICROSTRUCTURAL INVESTIGATION OF SINTERED SAMPLES USING SEM

Representative samples from each of the experimental permutations listed in Figure 2.31 were sputtered with 10nm of gold-palladium to provide a conductive surface to allow for microstructural investigation using SEM. Again, the LEO 1550 field emission scanning electron microscope was used. A full-width image of each of the specimens was taken in addition to images at 500x, 1000x and 2000x. These images provide a means of qualitatively investigating the ability of the model developed herein to predict the behavior of viscoelastic polymers consolidated using LS. Evidence of viscoelastic contact growth, viscous contact growth and bulk surface flow was sought.

2.5 CHAPTER 2 REFERENCES

3 THERMAL MODEL

Lasers offer a means of rapidly inducing local thermal gradients that can be used to induce thermally driven changes such as chemical reactions, melting, sintering or ablation. Controlling the rates and extents of said physical and chemical changes during laser heating requires special consideration because (1) no isothermal dwell, where constant material properties and reaction rates can be assumed, is present in the thermal profile and (2) the heating and cooling rates in laser processing are typically higher than in traditional processes and as such the rates of change in the system are much higher. Additionally, laser processing does not lend itself to closed loop temperature control which is typically employed to control thermal processes. As such, thermal models are of prime importance in understanding and subsequently controlling rapid thermally induced processes that result from laser heating. Therefore, laser sintering is a process in which a heightened understanding of the thermal phenomenon would provide the basis for further process-structure-property understanding.

Most thermal models of LS presented in the literature employ a numerical technique, such as finite element or finite difference, to determine the powder-bed temperature. The thermal models presented/developed in this work will be closed-form analytical solutions. Unlike numerical models, analytical solutions provide direct cause/effect relationships between independent and dependent variables. Analytical solutions typically require substantially less computing power and processor time. Developing and validating a thermal model is not the primary object of this research. Thermal modeling is a means to an end; the end being obtaining thermal data which can be used to investigate the mechanisms by which polymeric powders coalesce during LS. Thoughtful consideration will be given to balancing model complexity and accuracy.

In addition to the primary goal of providing thermal data for coalescence modeling, the thermal modeling effort will also investigate two hypotheses: (1) convective heat loss through the upper boundary of the powder-bed has a significant effect on the powder temperature in the LS process, (2) the mathematical representation of the beam is important to obtaining accurate thermal data.

3.1 MODEL DEFINITION

As discussed in the Review of Thermal Models, a closed-form three-dimensional solution to laser heating of a substrate by a moving beam flux, which accounts for convective heat loss, temperature dependent material properties and phase change, does not exist. In this work three approximations to the aforementioned thermal process will be investigated. All of the solutions presented are based on Fourier’s Law of heat transfer in one-dimension, \[3.1\]. A semi-infinite approximation of the substrate is utilized to obtain closed-form solutions. A general schematic of the proposed problem is given in Figure 3.1. Variable definitions are given in Table 3.1.

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad [3.1]
\]

![Figure 3.1: Thermal model schematic.](image)
Table 3.1: Variable definitions for thermal models.

<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>direction of beam travel; heat conduction is not considered in this direction</td>
</tr>
<tr>
<td>y</td>
<td>surface dimension normal to beam travel; heat conduction is not considered in this direction</td>
</tr>
<tr>
<td>z</td>
<td>direction of heat conduction into the powder-bed</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>T</td>
<td>substrate temperature</td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat</td>
</tr>
<tr>
<td>h</td>
<td>convective heat transfer coefficient</td>
</tr>
<tr>
<td>T_infinity</td>
<td>convective boundary temperature</td>
</tr>
<tr>
<td>ρ</td>
<td>density</td>
</tr>
<tr>
<td>ε</td>
<td>porosity</td>
</tr>
<tr>
<td>α</td>
<td>thermal diffusivity, ((k/(ρ c_p)))</td>
</tr>
<tr>
<td>Q</td>
<td>surface flux</td>
</tr>
<tr>
<td>T_0</td>
<td>initial temperature</td>
</tr>
<tr>
<td>V</td>
<td>beam velocity in x direction</td>
</tr>
<tr>
<td>P</td>
<td>beam power</td>
</tr>
<tr>
<td>ω</td>
<td>beam radius</td>
</tr>
</tbody>
</table>

3.1.1 Boundary Conditions and Bed Properties

The physical situation being modeled is heating of a powder-bed by a laser beam moving in the positive x-direction. Heat imparted to the surface by the laser beam flux is dissipated by conduction into the powder-bed and by convection to the atmosphere through the upper surface. The two boundary conditions and the initial condition are specified in [3.2], [3.3] and [3.4], respectively. The material properties used for the powder-bed will be assumed constant and be calculated as described below.

\[-k \frac{\partial T}{\partial z} = Q + h(T_\infty - T(0,t)) \quad [3.2]\]

\[T(z,t) = T_0 \text{ as } z \to \infty \quad [3.3]\]

\[T(z,0) = T_0 \quad [3.4]\]

The effective thermal conductivity, \(k_{\text{eff}}\), of the powder-bed will be calculated using the Maxwell-Eucken model, [3.5] and [3.6]; the factors in the equation are dependent on the relative density of the powder, \(ρ_{\text{rel}}\). The density of the powder-bed is equal to the product of the relative density and the polymer density, and the specific heat is equal to that of the polymer. The air contribution to the bed density and specific heat is negligible.

\[k_{\text{eff}} = k_1 \frac{1 - \left(1 - \frac{k_2}{k_1}\right) \psi}{1 + (a-1)\psi} \]

If \(ρ_{\text{rel}} > 0.5\) then \(k_1 = k_{\text{poly}}, k_2 = k_{\text{air}}\) and \(ψ = ε\)

If \(ρ_{\text{rel}} < 0.5\) then \(k_1 = k_{\text{air}}, k_2 = k_{\text{poly}}\) and \(ψ = 1 - ε\) \[3.5\]

\[a = \frac{3k_1}{2k_1 - k_2} \quad [3.6]\]

3.2 Beam Energy Calculation

Figure 3.2 is a plot of the normalized intensity (W/m²) of a Gaussian beam, such as the beam produced by a CO₂ laser. The functional form of the intensity is described by [3.7]. In this work the coordinate system is defined such that the beam moves across the bed in the positive x-direction while maintaining a constant y position, see Figure 3.1. To mathematically account for motion in the intensity equation, [3.7] can be transformed into a moving front by substituting, \(-vt+x+x_0\) for \(x\), as in [3.8]. Figure 3.3 shows the beam intensity as a function of position for three
different times calculated using the transformed beam intensity function, [3.8]. Note: the starting position of the beam, \(x_0\) will be zero in this work.

\[
I(x, y) = \frac{2P}{\pi \sigma^2} e^{-\frac{2(x^2 + y^2)}{\sigma^2}} \quad [3.7]
\]

\[
I(x, y, t) = \frac{2P}{\pi \sigma^2} e^{-\frac{2((-\sigma^2 + x^2 + y^2)}{\sigma^2}} \quad [3.8]
\]

The total energy absorbed, \(q_{\text{total}}\) by any point \((x, y)\) can be calculated by integrating [3.8] from \(-\infty \leq t \leq \infty\) as shown in [3.9].

\[
q_{\text{total}} = \int_{-\infty}^{\infty} I(x, y, t) \, dt = \frac{2P}{\pi \sigma^2} e^{-\frac{2y^2}{\sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{2((-\sigma^2 + x^2 + y^2)}{\sigma^2}} = e^{-\frac{2y^2}{\sigma^2}} \sqrt{2} \frac{P}{\pi V \omega} \quad [3.9]
\]

In this work the effect of three different approximations of the Gaussian beam shape on the temperature profile of the powder-bed will be investigated. The total energy incident on a point \((x, y)\) in any of the models investigated will be equal to the total energy incident on a point \((x, y)\) as calculated in [3.9] for the Gaussian intensity distribution.

### 3.2.1 Beam Approximations

Figure 3.2 and Figure 3.3 are cross-sections of beam intensities, however the Gaussian beam has 2 normal spatial components \(x\) and \(y\) which can be considered separately with regard to their effect on heating of the powder-bed. There are no limitations on the functional form of the \(y\)-component of the beam intensity because heat transfer is only in the \(z\)-direction and beam motion is only in the \(x\)-direction. Thus, the \(y\)-component of the beam approximation can be the ideal Gaussian form. The functional form of the \(x\)-component of the beam intensity,
however, must be of a form that allows for a solution of Fourier’s Law of heat transfer in one-dimension, [3.1].

Recalling the transformation of the beam intensity to a moving front, the functional form of the x-component dictates the functional form of the flux component, $Q$, in the $z=0$ boundary condition.

The first approximation of the beam assumes that the total beam energy, [3.9], is imparted to the substrate by a line flux, a moving front of zero thickness. The second and third approximations of the beam geometry are a square and a triangle, respectively. Figure 3.4 shows a graphical representation of the three beam approximations and the ideal Gaussian beam. Notes: (1) the line flux is a given finite thickness for illustration purposes only; (2) all of the units are arbitrary and size relationships should not be inferred.

3.3 DISCUSSION OF MODEL ASSUMPTIONS

Pursuit of a closed-form analytical solution to the heat transfer problem posed above puts several constraints on the solution. The major assumptions are discussed below.

(1) Temperature-independent material properties must be used to maintain the linearity of the partial differential equation. Discussions about the temperature dependence of properties specific to materials in this work are discussed in the Materials and Methods chapter.

(2) Phase change cannot be considered because the presence of a moving boundary condition would introduce a nonlinearity which can not be dealt with analytically under the specified boundary conditions. However, dividing the enthalpy of melting by the heat capacity, [3.10], gives the temperature rise, $\Delta T_{\text{melt}}$, that is equivalent to the energy required for melting. Thus, the phase boundary can be approximated by the surface contour with a temperature equal to the sum of the melting temperature and $\Delta T_{\text{melt}}$.

\[
\frac{\Delta H_{\text{melt}}}{c_p} = \Delta T_{\text{melt}} \tag{3.10}
\]

(3) The assumption of one-dimensional heat conduction was required to obtain a closed-form analytical solution to the outlined problem. However, this assumption can be rationalized by the fact the energy distribution in a Gaussian beam changes as a function of position in a manner similar to the functional form of thermal diffusion in a semi-infinite medium. Both Gaussian functions and solutions to heating of a semi-finite body approach zero at infinity and both have functional forms which are approximately exponential for $x>0$.

3.4 THEORY OF SOLUTIONS

One of the hypotheses investigated in the thermal modeling portion of this work is that convective heat loss has a significant effect on the temperature profile of the powder-bed. To quantify this difference, at least mathematically, the solutions considered in this work will account for convective heat transfer from the surface. The most direct means of solving transient heat transfer problems with convective boundaries is the Laplace transform. As such the
solutions to laser heating which account for convective heat loss will be derived using Laplace transforms. To obtain a solution using the Laplace transform technique the approximation of the x-component of the beam intensity must be of a form which will afford inversion of the Laplace transform solution. The three beam intensity approximations mentioned above yield invertible solutions.

3.5 MATERIAL AND HEAT TRANSFER PROPERTIES

The material properties of a nylon 12 powder-bed with relative density of 0.55, which is a typical bed density for nylon 12, are enumerated in Table 3.2 and used in the presentation of heat transfer solutions in this chapter. The values of the boundary condition components and the initial condition are outlined in Table 3.3.

Table 3.2: Properties of nylon 12 powder-bed.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative density, $\rho_{\text{rel}}$</td>
<td>0.55</td>
</tr>
<tr>
<td>density of polymer, $\rho_{\text{poly}}$</td>
<td>1.034 g/cm$^3$</td>
</tr>
<tr>
<td>thermal conductivity of polymer, $k_{\text{poly}}$</td>
<td>0.25 W/(m K)</td>
</tr>
<tr>
<td>thermal conductivity of air, $k_{\text{air}}$</td>
<td>0.03 W/(m K)</td>
</tr>
<tr>
<td>effective thermal conductivity calculated using [3.5] and [3.6], $k_{\text{eff}}$</td>
<td>0.13 W/(m K)</td>
</tr>
<tr>
<td>specific heat of polymer, $c_p$</td>
<td>1.26 x 10$^3$ J/(kg K)</td>
</tr>
<tr>
<td>enthalpy of melting of polymer, $\Delta H_{\text{melt}}$</td>
<td>95 x 10$^3$ J/kg</td>
</tr>
<tr>
<td>$\Delta T_{\text{melt}}$ calculated using [3.10]</td>
<td>75$^\circ$C</td>
</tr>
<tr>
<td>melting temperature of polymer, $T_{\text{melt}}$</td>
<td>185$^\circ$C</td>
</tr>
<tr>
<td>phase boundary temperature</td>
<td>260$^\circ$C</td>
</tr>
</tbody>
</table>

Table 3.3: Values of boundary components and initial condition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>laser power, $P$</td>
<td>1.125 W</td>
</tr>
<tr>
<td>beam radius, $\omega$</td>
<td>1.5 x 10$^{-3}$ m</td>
</tr>
<tr>
<td>scan velocity, $V$</td>
<td>25.4 x 10$^{-3}$ m</td>
</tr>
<tr>
<td>convective heat transfer coeff., $h$</td>
<td>10 J/K</td>
</tr>
<tr>
<td>convective boundary temperature, $T_{\text{eff}}$</td>
<td>171$^\circ$C</td>
</tr>
<tr>
<td>initial and semi-infinite boundary temperature, $T_0$</td>
<td>171$^\circ$C</td>
</tr>
</tbody>
</table>

3.6 LINE FLUX SOLUTION

The line flux solution is mathematically the simplest solution considered. In this solution the energy flux, $Q$, is imparted into the powder-bed as a moving line heat flux in the form, [3.11]. $\delta(t-\tau)$ is the Dirac Delta function which is zero for all times $t \neq \tau$; at $t = \tau$ the total energy, $q_{\text{total}}$, is imparted to the powder-bed along the line $x=\tau V$ in the $z=0$ plane. $T_b$ [3.14] is the powder-bed temperature as a function of time and position assuming a line flux. The detailed solution to one-dimensional heating by a line flux which considers convective heat loss is detailed in the Appendix, only the resulting temperature equation is presented in this chapter.

$$Q = q \delta(t - \tau)$$  

$$q = q_{\text{total}} = e^{\frac{-2\tau^2}{\omega^2}} \frac{\sqrt{2}}{\pi} \frac{P}{V\omega}$$  

$$\tau = \frac{x}{V}$$
\[ T_i(x, y, z, t) = T_0 + (T_0 - T_0) \left( \frac{1}{\sqrt{\alpha}} e^{-H \sqrt{\alpha t}} - H \sqrt{\alpha} \frac{z}{2 \sqrt{\alpha t}} \right) + \frac{1}{\sqrt{\pi (t - \tau)}} e^{-H \sqrt{\alpha t}} \left( H \sqrt{\alpha}\sqrt{t - \tau} + \frac{z}{2 \sqrt{\alpha(t - \tau)}} \right) \]

The simplicity of the line flux approximation results in a solution with a relatively simple functional form. The temperature as a function of time at \((x=0.315 \text{ s} \times 25.4\times10^{-3} \text{ m/s}, y = 0)\), as predicted by [3.14], is plotted for several different bed-depths in Figure 3.5. At \(t=0.315 \text{ s}\) the line flux is incident on the line \(x=0.315 \text{ s} \times 25.4\times10^{-3} \text{ m/s}\), in the \(z=0\) plane. The phase boundary temperature \(T=260 \degree C\) is also plotted in Figure 3.5. The major short fall of the line flux solution is the instantaneous delivery of the total beam energy which results in prediction of an infinite surface temperature at \(t=\tau (z=0, \text{ shown in red in Figure 3.5})\). The instantaneous energy delivery neglects the time dependent effect of energy delivery. When a beam of finite width pass over a point heat dissipates into the bulk while energy is still being delivered, thus heat diffuses further into the bulk. The temperature at the surface is lower and the temperature gradient from the surface into the bulk is smaller.

![Figure 3.5: Temperature as function of time for several depths calculated using the line flux solution.](image)

The two-dimensional representation of the thermal profile presented in Figure 3.5 provides insight, however, it is not an ideal means of visualizing the four-dimensional problem of heating by a moving laser beam. Figure 3.6, Figure 3.7 and Figure 3.8 are alternative means of visualizing the temperature distribution in the powder-bed at \(t=0.315 \text{ s}\), as predicted by [3.14]. Figure 3.6 is the temperature distribution in the \(y=0\) plane at \(t=0.315 \text{ s}\). At \(t=0\) the line flux is at \(x=0\), for \(t>0\) the beam moves in positive \(x\)-direction with a velocity of 25.4\times10^{-3} \text{ m/s}. At the instant in time captured in Figure 3.6 the beam position is \(x=8.001 \text{ mm}\), the right edge of the temperature gradient. The two black contours are \(T_l=260 \degree C\) and \(T_l=400 \degree C\). The \(T_l=260 \degree C\) contour represent the approximate phase boundary between liquid and solid. The maximum depth of this contour is approximately 200 µm which is a realistic value for the laser power assumed in this solution. 400°C is approximately the onset of degradation for nylon 12; short exposure to this temperature will lead to minimal degradation, however, as the temperature increases above 400°C the rate and extent of degradation increase. The \(T_l=400 \degree C\) contour in Figure 3.6 is 0.6 mm long and approximately 100 µm deep. Material on the higher temperature side of this contour could be subject to degradation depending on the duration of its exposure.

Figure 3.7 is a three-dimensional plot of the approximate phase boundary contour, \(T_l=260 \degree C\). The contour is concave up; material above the contour is liquid, material below is solid. The leading edge of the contour is not a
realistic facsimile of the phase boundary (melt pool) that would be expected from laser heating. Real melt pools are comet shaped, i.e. a spherical head leading a conical tale. The shape of the leading edge of the contour mimics the shape of the flux distribution, thus, the unrealistic shape of the phase boundary results from approximating the beam as in instantaneous line flux. Figure 3.8 shows the phase boundary and the beam intensity. The dependence of the phase boundary on the shape of the flux is apparent by the parallelism of the flux intensity and the leading edge of the phase boundary. The trailing portion of the phase boundary is realistic since the effect of instantaneous energy delivery is dimensioned as heat transfer minimizes the thermal gradient.
Figure 3.6: Temperature distribution calculated using line flux solution; contours at \( T_i=260 \, ^\circ C, T_f=400 \, ^\circ C \).

Figure 3.7: Phase boundary contour \( T_i=260 \, ^\circ C \).

Figure 3.8: Phase boundary contour \( T_i=260 \, ^\circ C \) and current beam intensity.
3.7 SQUARE FLUX SOLUTION

The instantaneous energy delivery of the line flux approximation neglected the time dependence of energy input. The square flux solution does however consider the time dependence of energy input into the powder bed. [3.15] is the square flux term used in this solution. \( U(t-t) \) is the unit step function; for \( (t-t)>0 \) \( U(t-t) = 1 \), for \( (t-t)<0 \) \( U(t-t) = 0 \). Energy is delivered at a constant rate to a surface point \((x,y)\) between times \( \tau_{on} \) and \( \tau_{off} \). The total energy input into the powder bed, \( q_{total} \), is equal to that of the Gaussian beam, as calculated in [3.19].

\[
Q = q' (U(t-\tau_{on}) - U(t-\tau_{off}))
\]

\[
q' = \frac{P}{\omega^2 \pi} e^{-\frac{2\pi^2}{\omega^2 x^2}}
\]

\[
\tau_{on} = \frac{x}{V}
\]

\[
\tau_{off} = \frac{x}{V} + \frac{2\omega}{V} \sqrt{\frac{\pi}{2}}
\]

\[
q'(\tau_{on} - \tau_{off}) = \frac{P}{\omega^2 \pi} e^{-\frac{2\pi^2}{\omega^2 x^2}} \frac{2\omega}{V} \sqrt{\frac{\pi}{2}} = e^{-\frac{2\pi^2}{\omega^2 x^2}} \frac{2}{\pi} \frac{P}{V \omega} = q_{total}
\]

Figure 3.1 shows the intensity distributions of the Gaussian and square beams. Determination of the beam width/diameter is subjective and a source of possible of error. Since the Gaussian distribution extends to \( \pm \infty \) there is no mathematically obvious choice for the beam width. The limiting cases are: as the beam width approaches zero the square flux collapses to a line flux; conversely as the beam width approaches infinity the beam intensity would approach zero and no heating would occur. The width of the square beam chosen for this work is \((\pi/2)^{1/2} 2\omega/V\), as shown in Figure 3.9. The intensity of the Gaussian beam is approximately 5% of its maximum at the chosen beam diameter.

![Figure 3.9: Square intensity and Gaussian intensity.](image)

The detailed solution to one-dimensional heating of a powder-bed by a moving square flux is detailed in the Appendix; the resulting equation for the bed temperature as a function of position and time, \( T_{sq} \), is [3.20]. \( T_{sq} \) has a similar but slightly more complex functional form than \( T_l \). Figure 3.10 shows the temperature as a function of time, calculated using \( T_{sq} \), at several bed-depths (z-positions) for the x,y-coordinates \((x=0.315 \text{ s} \times 25.4 \times 10^{-3} \text{ m/s}, y=0)\). At \( t=0.315 \text{ s} \), the leading edge of the square flux is incident on the line \( x = 0.315 \text{ s} \times 25.4 \times 10^{-3} \text{ m/s}=8.001 \text{mm} \), in the z=0 plane. The trailing edge of the square flux is incident on the line \( x = 8.001 \text{ in} \) at \( t=0.463 \text{ s} \). The phase boundary temperature \( T=260^\circ C \) is also plotted in Figure 3.10. The temperatures predicted for the depths plotted in Figure 3.10 by \( T_{sq} \) are reasonable for the laser power used in the calculation. However, the discontinuities in the slope of the \( z=0 \) curve are an artifact of the step changes in the beam energy delivered to the bed surface. Figure 3.10 and Figure 3.5 are the temperature as a function of time, calculated using the square flux approximation and the line flux approximation for the same locations. The major difference between the predictions of the two flux approximations is: a finite temperature is predicted at the surface for all times by the square flux approximation.
while the line flux approximation predicts an infinite surface temperature at \( t=\tau \). Visualizing the temperature distribution using three-dimensional graphics will allow for further discussions of the differences between \( T_l \) and \( T_{sq} \).

The total energy delivered to the bed is equal in the square and line flux approximations. The difference between the square and line flux approximations solutions is the rate of energy delivery, and it is apparent from the comparison of the two solutions that the approximation of the energy delivery rate used has significant effects on the calculated temperature distributions. To further investigate the square flux solution and compare it to the line flux solution, three-dimensional plots identical in range and time to those presented in the line flux solution are presented in Figure 3.11, Figure 3.12 and Figure 3.13.

Figure 3.11 shows the thermal distribution in the \( y=0 \) plane at \( t=0.315 \) s. The leading edge of the square flux is at \( x=8.001 \) mm and the trailing edge is at \( x=4.241 \) mm. The black contour in the thermal distribution is the phase boundary \( T=260^\circ C \), the depth of the contour/phase boundary is approximately 200 µm which is realistic for the laser power used in this calculation. Contrary to the prediction of the line flux solution, the square flux solution does not predict any temperatures of 400 \( ^\circ C \) or above. Figure 3.12 is a three-dimensional contour plot of the phase boundary at \( t=0.315 \) s. The phase contour is concave-up; material above the phase contour is liquid, material below is solid. The shape of the phase boundary is realistic with exception of the discontinuity in the slope of the contour at the trailing edge of the beam. Figure 3.13 shows the phase boundary and the beam intensity at \( t=0.315 \) s. As was previously noted, the leading edge of the phase boundary mimics the beam intensity which has a finite width in the square flux approximation. The finite width results in time dependent delivery of energy to the powder bed thus the depth of the phase boundary increases as the beam passes a given point as shown in Figure 3.13 and Figure 3.11.

The total energy delivered to the bed is equal in the square and line flux approximations. The difference between the square and line flux approximations solutions is the rate of energy delivery, and it is apparent from the comparison of the two solutions that the approximation of the energy delivery rate used has significant effects on the calculated temperature distributions. To further investigate the square flux solution and compare it to the line flux solution, three-dimensional plots identical in range and time to those presented in the line flux solution are presented in Figure 3.11, Figure 3.12 and Figure 3.13.
Figure 3.11: Temperature distribution calculated using square flux solution; contours at $T_{sq} = 260\, ^\circ C$, $T_{sq} = 400\, ^\circ C$.

Figure 3.12: Phase boundary contour $T_{sq} = 260\, ^\circ C$.

Figure 3.13: Phase boundary contour $T_{sq} = 260\, ^\circ C$ and current beam intensity.
3.8 **TRIANGULAR FLUX SOLUTION**

The line flux solution considered only the effect of the total energy input on the thermal profile of the powder-bed. The square flux solution considered time dependent energy delivery by inputting a constant flux over a specified time; the total energy input was equal to that of the line flux. The triangular flux solution delivers the same total energy but will consider the effect of the shape of the energy distribution on the bed temperature. The triangular flux approximation, shown in Figure 3.14 is the simplest non-constant-intensity approximation of the Gaussian intensity. The triangular intensity was determined by equating the maximum intensity of the triangle to that of the Gaussian distribution and then equating the total energy of the triangular intensity to that of the Gaussian distribution. [3.21] is the equation of the triangular flux distribution and [3.26] verifies that the total energy delivered by the beam is equal to $q_{total}$, the total energy of the Gaussian beam and the line and square beam approximations.

![Figure 3.14: Triangular and Gaussian intensities.](image)

The detailed solution to one-dimensional heating of a powder-bed by triangular flux which considers convective heat transfer can be found in the Appendix. The solution for heating by a triangular flux is more complex than the line and square flux solutions which are found by direct inversion of the Laplace transform solutions. Inversion of the Laplace transform solution of the triangular flux problem requires convolution of two inverse transforms. $T_{tri}$, [3.27], is the equation for the temperature of the powder-bed as a function of time and location assuming a moving triangular flux. $\tau_1$, $\tau_2$ and $\tau_3$, in [3.23], [3.24] and [3.25], are the times the leading edge, maximum intensity and trailing edge are incident on a line with constant $x$-component in the $z=\theta$ plane.

\[
Q = q''((t-\tau_1)U(t-\tau_1) - 2(t-\tau_2)U(t-\tau_2) + (t-\tau_3)U(t-\tau_3))
\]  \[3.21\]

\[
q'' = \frac{V}{\omega \sqrt{\frac{\pi}{2}}} \frac{2P}{\omega^2 \pi} e^{\frac{2y^2}{\omega^2}} \quad \quad \quad \quad \quad [3.22]
\]

\[
\tau_1 = \frac{x}{V} + \frac{2\omega}{V} \sqrt{\frac{\pi}{2}}
\]  \[3.23\]

\[
\tau_2 = \frac{x}{V} + \frac{\omega}{V} \sqrt{\frac{\pi}{2}}
\]  \[3.24\]

\[
\tau_3 = \frac{x}{V}
\]  \[3.25\]

\[
q''(\tau_1 - \tau_2)^2 = \frac{V}{\omega \sqrt{\frac{\pi}{2}}} \frac{2P}{\omega^2 \pi} e^{\frac{2y^2}{\omega^2}} \left( \frac{\omega}{V} \sqrt{\frac{\pi}{2}} \right)^2 = e^{\frac{2y^2}{\omega^2}} \frac{2P}{\sqrt{\pi} \omega V} = q_{total}
\]  \[3.26\]
temperatures exhibit smooth slope transitions as would be expected if the bed were heated by a Gaussian beam. At

Figure 3.15 shows the temperature as a function of time calculated using $T_{tri}$, at several bed-depths ($z$-positions) for the $x,y$-coordinates ($x = 0.315 \, m/s$). Note: $T_{tri}$ is not defined for $z=0$, therefore a finite depth of 10 nm is used to approximate $z=0$. At $t=0.315 \, s$, the leading edge of the triangular flux is incident on the line $x = 0.315 \, m/s = 8.001 \, mm$, in the $z=0$ plane. The maximum beam intensity is incident on $x=8.001 \, m/s$ plane at $t=0.389 \, s$. The trailing edge of the triangular flux is incident on $x=8.001 \, m/s$ plane at $t=0.463 \, s$. The phase boundary temperature $T=260 \, C$ is also plotted in Figure 3.15. The powder-bed temperatures calculated using $T_{tri}$ are reasonable given the laser power assumed. The shape of the temperature versus time curves for all temperatures exhibit smooth slope transitions as would be expected if the bed were heated by a Gaussian beam. Figure 3.15 shows the temperature as a function of time for the same time and locations as shown in Figure 3.5 and Figure 3.16. Of the three beam approximations investigated in this work $T_{tri}$ results in the most realistically shaped temperature as a function of time curves.

Figure 3.16 shows the thermal distribution in the $y=0$ plane at $t=0.315 \, s$. The leading edge of the triangular flux is at $x=8.001 \, mm$, the maximum intensity is at $x=6.121 \, mm$ and the trailing edge is at $x=4.241 \, mm$. The black contours in the thermal distribution are the phase boundary $T=260 \, C$ and the degradation onset temperature $T=490 \, C$. The depth of the phase boundary is approximately 200 $\mu m$ and the depth of the degradation boundary is 20 $\mu m$ which are realistic for the laser power used in this calculation. Figure 3.17 is a three-dimensional contour plot of the phase boundary calculated using $T_{tri}$ at $t=0.315 \, s$. The phase contour is concave-up; material above the phase contour is liquid, material below is solid. The shape of the phase boundary is realistic; no discontinuities in the slope are observed. Figure 3.18 shows the phase boundary and the beam intensity at $t=0.315 \, s$. The triangular beam intensity is a relatively accurate approximation of the ideal Gaussian intensity and as such the phase boundary contour has a nearly ideal shape.

The major short coming of the triangular flux solution is the complexity of the solution. Complexity is a minor issue when the alternative approach is considered; a numerical technique which would require repeated calculations and substantially greater time to converge to $T_{tri}$. The beam approximation, which accounts for the shape of the beam intensity and the total energy input, results in realistic temperature predictions over the entire range of time and position, a realistic phase boundary and a continuous slope in the temperature as a function of time at all bed depths.
Figure 3.15: Temperature as function of time for several depths calculated using the triangular flux solution.

Figure 3.16: Temperature distribution calculated using line flux solution; contours at $T_{tri}=260\, ^\circ C$, $T_{tri}=400\, ^\circ C$.

Figure 3.17: Phase boundary contour $T_{tri}=260\, ^\circ C$. 
3.9 COMPARISON OF SOLUTIONS

The three different beam intensity approximations presented represent three levels of complexity which can be considered in modeling laser surface heating. First, the line flux solution only considers the total energy of the beam. Second, the square flux solution considers the total energy of the beam and the time-dependence of the energy input into the surface. Third, the triangular flux solution accounts for the total energy, the time-dependence of the energy input and the shape of the beam intensity. As the complexity of the beam approximation increased the temperature distribution in the powder-bed approached what would be expected for a Gaussian beam. From the comparison of the solutions shown in Figure 3.19, Figure 3.20 and Figure 3.21, the following observations can be made for this particular set of process parameters and material properties: (1) all three solutions converge as the time and/or bed-depth increase; (2) the square and triangular flux solutions produce similar results for the square beam width chosen with the exception of the deviation in the maximum temperature; (3) deviations between the line flux and triangular flux exceed 100°C just after energy input.

The major shortfall of the line flux approximation is the infinite temperature predicted at the surface which results in unrealistic temperatures at and just below the bed surface at the instant of energy delivery and immediately after. Since the surface temperature decreases from infinity, using the line flux solution temperature predictions for further calculations requires a subjective selection of the time and dimensional ranges over which the solution is physically realistic. The temperatures predicted by the square flux solution, for the laser power used in this chapter, are finite and realistic over the range investigated. However, the subjectivity in determining the beam width/diameter, which will directly affect the thermal profile, is a significant issue; as the beam diameter decreases the predicted surface temperature will increase until the solution converges to the line flux solution. The only drawback to the triangular flux solution is its complexity.

The advantage of the line flux solution is its simplicity. For modeling circumstances where surface or near-surface temperatures at or just following energy input are not the primary interest, this solution could find application. However, in this work surface and near surface (~200µm) temperatures are of primary interest. The temperatures predicted by the model will be used to predict the coalescence/densification of the particles near the powder-bed surface. The near-surface temperatures predicted by the square flux solution are realistic and the solution is less complex than the triangular source. However, the absolute temperature predicted by the square flux is dependent on the choice of beam diameter which introduces an unnecessary source of error. The major benefits of the triangular flux approximation are that the determination of the beam intensity is objective and the predictions are representative of what would be expected from a Gaussian beam.

Figure 3.18: Phase boundary contour $T_{\text{tri}}=260^\circ\text{C}$ and current beam intensity.
Figure 3.19: Temperature as function of time for several depths for solutions.

Figure 3.20: Temperature difference between triangular flux and line flux solutions.

Figure 3.21: Temperature difference between triangular flux and square flux solutions.
3.10 IMPORTANCE OF CONVECTIVE HEAT LOSS

It was hypothesized that convective heat loss from the powder-bed surface has a significant effect on powder-bed temperature during laser heating. The triangular flux approximation is used exclusively in this discussion of convective heat loss since the triangular flux approximation yields the most probable surface temperature curves. To test the hypothesis, the surface (z=10 nm) temperature as a function of time for a point (x=8.001 m, y=0) was plotted, in Figure 3.22 for three conditions: no convective heat loss and convective heat loss with two different convective heat transfer coefficients. \( h=25 \) is the upper limit and \( h=10 \) is a median value for the convective heat transfer coefficient for free convection\(^2\). The detailed solution to one-dimensional heating by a moving triangular flux that does not consider convective loss is presented in the Appendix, [3.28] is the resulting equation for the temperature as a function of time and position.

The maximum temperature difference predicted between the solution considering no convective heat loss and the solution representing the upper limit of free convective heat transfer is 10°C over the time range plotted in Figure 3.22. 10°C is approximately 5% of the average temperature therefore convective heat loss is not a significant factor in laser heating of a powder bed for the processing conditions and material properties considered. In modeling other processes such as laser cutting, laser surface alloying, or laser surface hardening the inclusion of convective heat loss in the thermal model could be more beneficial.

---

Figure 3.22: Surface temperature as a function of time for three different values of the convective heat transfer coefficient.

\[
T_{\text{pow}}(x, y, z, t) = \begin{cases} 
U(t - t_0) \left( \frac{e^{-\frac{x^2}{a^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{(x-l)^2}{a^2}}}{2\sqrt{\pi t}} - 2\frac{e^{-\frac{(x-l)^2}{a^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{x^2}{a^2}}}{2\sqrt{\pi t}} \right) \left( \frac{e^{-\frac{y^2}{b^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{(y-l)^2}{b^2}}}{2\sqrt{\pi t}} - 2\frac{e^{-\frac{(y-l)^2}{b^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{y^2}{b^2}}}{2\sqrt{\pi t}} \right) \right) \left( \frac{e^{-\frac{z^2}{c^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{(z-l)^2}{c^2}}}{2\sqrt{\pi t}} - 2\frac{e^{-\frac{(z-l)^2}{c^2}}}{2\sqrt{\pi t}} + \frac{e^{-\frac{z^2}{c^2}}}{2\sqrt{\pi t}} \right) \right) \right) \right)
\]

[3.28]
3.11 CHAPTER 3 REFERENCES


4 SINTERING MODEL

In the LS process, selected regions of the powder bed are rapidly heated through a phase transition into the liquid state, where long-range cooperative molecular motion occurs and the powder sinters. The degree of sintering depends on the properties of the material, the powder packing, and the amount of energy input by the laser beam in excess of what is required to induce the phase change. To predict the degree of sintering at a point in the powder bed during LS, a process model should consider the temperature at that point as a function of time, the sintering mechanisms and the material properties relevant to the mechanism. Sintering by viscoelastic contact growth, sometimes referred to as zipping mode sintering, can contribute significantly to polymer densification prior to densification by viscous flow. Regardless of the sintering time the contribution of viscoelastic contact growth to densification increases with decreasing particle size.

Following the transition to the liquid state, the onset of viscous flow occurs at $\tau$, the characteristic relaxation time of the polymeric liquid. Generally speaking, sintering before $\tau$ occurs by viscoelastic contact growth because the contribution of the viscosity to the creep compliance is small compared to the viscoelastic contribution. Sintering after 2$\tau$ is by viscous means because the viscoelastic contribution to the creep compliance is small compared to the viscous contribution. Between $\tau$ and 2$\tau$ the zipping and stretching modes of contact growth between particles both contribute to densification. However, these mechanisms are competitive; contact growth by zipping closes the gap at the front of the crack tip, while contact growth by stretching opens the gap at the crack tip. Figure 4.1 is schematic of contact growth by zipping and stretching: Note, how A and A' and B and B' converge in the zipping mode and remain separated in the stretching mode.

Numerical crack closing models have been suggested which balance the energy at the crack tip to determine the contribution of sintering from both mechanisms. A simpler approach is switching sintering mechanisms from viscoelastic contact growth to viscous sintering at $\tau$. The difference in the density predicted by the crack closing approach and the simpler approach is assumed to be small because the mechanisms are competing and the time over which both mechanisms are acting together is small. Therefore, it is usually sufficient to assume that for times less than or equal to $\tau$ sintering will occur via viscoelastic contact growth and for times greater than $\tau$ sintering will occur by viscous sintering. The model for viscoelastic contact growth of spheres developed by Lin et al will be used to predict sintering up to $\tau$. After $\tau$, the well-known final stage sintering model of Mackenzie and Shuttleworth will be used to model sintering. As the time in liquid phase decreases from the time that is required to reach full density, the contribution of viscoelastic sintering to the total density increases. During LS a polymer is in the liquid phase for a relatively short period of time, compared to the time in liquid phase during traditional sintering of polymer. Additionally, imparting enough energy into the powder bed that full density is achieved adversely affects part tolerances. Therefore parts made by LS are typically ~95% of full density. Accurate determination of the time in the liquid state is important because it is during this period of time that sintering occurs. An accurate thermal model should be the basis for determining the time in the liquid state.

The previous chapter explored several approximate solutions to heating of a powder-bed by a moving laser beam. The solution which approximated the shape of the beam intensity as a triangle produced thermal profiles that closely resembled what would be expected for heating by an ideally shaped Gaussian beam. In this work, the triangular flux solution that included convective heat loss from the surface is used to approximate the thermal distribution in the
powder-bed during laser sintering. This solution uses constant material properties and no phase change is accounted for. Because the temperature and density dependence of material properties are ignored, the bed temperature can be determined prior to calculating the change in density of the powder-bed. For semi-crystalline polymers such as PEO ignoring the energy associated with the enthalpy of melting results in a significant over estimation of the bed temperature. To account for the enthalpic energy associated with the phase change a reduction in the temperature of the liquid phase is made. Time-temperature superposition will be used to shift the average temperature of a point during the liquid state to a reference temperature with a known creep compliance.

4.1 **MODEL DEFINITION**

The LS process constructs three-dimensional shapes by consecutively sintering powder layers; the bottom of the layer n is sintered to the top of the layer n-1. Individual layers are sintered by raster-scanning the powder surface with the laser beam, Figure 4.2. The raster pattern is comprised of individual scan lines, each overlapping the previous to form a continuous layer. The fundamental process unit of the LS process is a single scan line. Understanding the process-structure-property relationships which define powder sintering resulting from a single laser scan line will aid in process advancement. Because the laser beam is axis-symmetric, the temperature changes and sintering induced by the laser beam are assumed to be symmetric about the path traced by the beam center-line on the powder surface, the red lines shown on the rater pattern. Additionally, if the quasi-stationary approximation of a moving heat source is used, then the thermal and physical changes resulting from laser heating are the same for all planes parallel to the y-z plane inside the raster pattern.

The axis-symmetric nature of the beam and the quasi-stationary approximation afford reduction of the geometry needed to capture the sintering behavior resulting from a single scan line to the cross-section depicted in Figure 4.3. The cross-section lies in a plane normal to the x-direction and is in the middle of the scan line, such that the beam is scanning at a constant velocity when it crosses over the plane. The red curve represents half of the beam intensity which is symmetric about the plane (x, y=0, z). Below the beam intensity is the powder bed which has been divided into a grid with spacing in the y and z directions of \( \Delta y \) and \( \Delta z \) respectively. The grid geometry is also symmetric about the plane (x, y=0, z).

The presence of the co-error function and exponential function in the triangular flux solution prohibits analytically solving for contours of equal temperature. Therefore, determining equa-temperature contours, such as the solid/liquid boundary in the powder bed, is done by comparing temperatures at specific points to the contour temperature. By comparing the maximum temperature at a point to the phase transition temperature it can be determined whether the powder at this point changed from solid to liquid during LS. Points which did not reach the liquid state are of no interest since the solid powder will not exhibit any significant sintering on the time-scale of scanning a single line. Determining if a point reached the liquid state before calculating the density allows for limiting the number of density calculations to only those points in the liquid state. The blue contour over-laying the grid in Figure 4.3 is a representative phase boundary. *Note: The blue contour is not exactly representative of the phase contour as it would be determined as described above since it does not follow grid intersection points.*
Figure 4.3: Model geometry.

Figure 4.4 is a flow chart which details the algorithm used to calculate data at each intersection point which reaches the liquid state. The specific data calculated at each point is discussed later in this chapter. The algorithm is based on two while loops. Initial values of y and z-coordinates are input, \( y=y_0=0 \) and \( z=z_0 \). \( z_0 \) must be a non-zero number due to the limitations of the triangular flux solution. The value of \( z_0 \) is sufficiently small that it approximates the surface temperature of the bed. After initializing the coordinates, the time at which the maximum temperature is reached for the surface point \( (y=0, z=z_0) \) is calculated by setting the derivative of the temperature with respect to time equal to zero and solving for the time. Knowing the time at which the maximum temperature occurs affords calculation of the maximum temperature. If the maximum temperature is above the phase transition temperature then the point \( (y=0, z=z_0) \) is liquefied by the energy from the laser beam. If the maximum temperature is below the phase transition temperature, then the powder remains solid and the algorithm ends since none of the powder-bed will be liquefied. Because the surface point \( (y=0, z=z_0) \) is exposed to the maximum laser intensity, it is obvious that if the maximum temperature at this point does not exceed the phase transition temperature then no other point’s temperature exceeds the phase transition temperature. If the phase transition temperature is exceeded at \( (y=0, z=z_0) \), the inner loop advances by increasing the depth into the powder-bed (z-direction) by \( \Delta z \) until the maximum temperature for the coordinate \( (y=0, z=z_0+n\Delta z) \) does not exceed the phase transition temperature. The maximum temperature at each z-coordinate is determined in the same manner as it was for \( (y=0, z=z_0) \): determine the time of the maximum temperature by finding the time when the derivative of the temperature with respect to time is equal to zero and then calculate the temperature for this time.

For any y coordinate once the maximum temperature of a z-coordinate \( (z=z_0+n\Delta z) \) does not exceed the phase transition temperature the process returns to the outer loop. The outer loop adds \( \Delta y \) to the previous y-coordinate and again tests whether the maximum surface temperature exceeds the phase transition temperature; if the temperature is in excess of the phase transition temperature the z-coordinate values are incremented until the maximum temperature does not exceed the phase transition temperature. Once a surface coordinate \( (y=m\Delta y, z=z_0) \) does not reach the phase transition temperature the algorithm ends. At each point which exceeds the phase transition temperature relevant data is calculated.
The goals of the sintering model presented in this research are to: 1) investigate the contribution of viscoelastic contact growth to densification during heating of a polymeric powder bed by a moving laser beam, 2) develop a tool that affords investigation of the LS process and material parameter space and 3) investigate viscoelastic sintering for times less than the characteristic relaxation time, $\tau$. Mazur, Lin and other have presented theories for coalescence of viscoelastic spheres. However, testing these theories for times on the order of the characteristic relaxation time or less is difficult because the relaxation time of most polymer liquids is generally too short for testing to be conducted using standard furnaces. The rapid thermal cycles of the LS process allow for testing in this time range.

As discussed in the introductory chapter, the two major classes of polymers are amorphous and semi-crystalline. The solid-liquid phase transition occurs at different types of transitions for these two classes. An amorphous polymer becomes liquid above its glass transition temperature, while a semi-crystalline polymer becomes liquid above its melting temperature. Prior to being scanned by the laser beam, the powder-bed is at a temperature below that of the solid-liquid phase transition, thus for sintering to occur the polymer must be heated through a phase transition. Because the glass transition is a quasi-second-order phase transition there is no enthalpy specifically associated with the transition. However, the melt transition is a first-order phase transition which has the enthalpy of melting/fusion associated with it. The triangular flux solution of laser heating developed in the previous chapter did not account for the solid/liquid phase change. The lack of a phase change does not pose a problem when using the solution for approximating the temperature of an amorphous polymer powder-bed during LS. However, disregarding the enthalpy of melting for a semi-crystalline polymer will result in significantly over estimating the bed temperature and thus over estimating the density or underestimating the time required to reach full density.
4.2 THERMAL APPROXIMATION OF PHASE CHANGE

Semi-crystalline polymers do not exhibit long-range cooperative molecular motion on a time-scale applicable to the LS process below the melting temperature. Thus, for sintering to occur the heat imparted to a point must be sufficient to melt the polymer. Melting is an endothermic process; to melt a material an excess of heat (negative enthalpy of fusion) is required over the heat needed to raise the material to its melting temperature. The temperatures predicted by the triangular flux solution do not account for phase change, thus the enthalpic energy which would be absorbed during melting, instead contributes to heating. Figure 4.5 is the temperature as a function of time for a powder bed of PEO100k at $y=0$, $z=1\mu m$, as predicted by the triangular flux solution. The material properties for a PEO100k powder bed and the LS process parameter used to generate the temperature distribution in Figure 4.5 are given in Table 4.1 and Table 4.2. Also plotted in Figure 4.5 are the melting temperature, the approximate phase boundary and the re-crystallization temperature.

![Figure 4.5: Temperature as a function of time predicted by triangular flux solution and the three relevant transition temperatures.](image)

**Table 4.1:** Properties of PEO100k powder bed. *(PEO100k, the model material used in this chapter, has the same thermal properties as PEO M=1x10^5 g/mol but slightly different rheologic properties)*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative density, $\rho_{rel}$</td>
<td>0.55</td>
</tr>
<tr>
<td>density of polymer, $\rho_{poly}$</td>
<td>1.1 g/cm³</td>
</tr>
<tr>
<td>thermal conductivity of polymer, $k_{poly}$</td>
<td>0.25 W/(m K)</td>
</tr>
<tr>
<td>thermal conductivity of air, $k_{air}$</td>
<td>0.03 W/(m K)</td>
</tr>
<tr>
<td>effective thermal conductivity of powder, $k_{eff}$</td>
<td>0.13 W/(m K)</td>
</tr>
<tr>
<td>specific heat of polymer, $c_p$</td>
<td>$1.7 \times 10^3$ J/(kg K)</td>
</tr>
<tr>
<td>enthalpy of melting of polymer, $\Delta H_{melt}$</td>
<td>$168 \times 10^3$ J/kg</td>
</tr>
<tr>
<td>temperature change equivalent to enthalpy of melting, $\Delta T_{melt}$</td>
<td>99°C</td>
</tr>
<tr>
<td>melting temperature of polymer $T_{melt}$</td>
<td>65°C</td>
</tr>
<tr>
<td>phase boundary temperature, $\Delta T_{melt} + T_{melt}$</td>
<td>164°C</td>
</tr>
</tbody>
</table>

**Table 4.2:** Values of boundary components and initial conditions.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>laser power, P</td>
<td>1.125 W</td>
</tr>
<tr>
<td>beam radius, (\omega)</td>
<td>$1.5 \times 10^{-3}$ m</td>
</tr>
</tbody>
</table>
As discussed in the previous chapter, $\Delta T_{\text{melt}}$ is defined as the temperature rise resulting from the amount of energy equivalent to the enthalpy of melting. To approximately account for the phase transformation, $\Delta T_{\text{melt}}$ is added to the melting temperature, $T_{\text{melt}}$, and this sum is termed the approximate phase boundary; material with a temperature exceeding that of the approximate phase boundary melts. Because first-order phase changes are ideally isothermal, the temperature of the material for the duration of the phase change is equal to the melting temperature. Therefore the temperature of the material that exceeds the approximate phase boundary can be reduced by $\Delta T_{\text{melt}}$ and an isothermal section inserted for the powder temperature between $T_{\text{melt}}$ and $T_{\text{melt}} + \Delta T_{\text{melt}}$. The dashed magenta line in Figure 4.6 is the reduced temperature as a function of time which approximately accounts for phase change.

As was mentioned in the Materials chapter semi-crystalline polymers do not begin to re-crystallize on the time-scale of seconds until some undercooling has occurred, the temperature at which re-crystallization occurs is $T_{\text{recrystal}}$. As depicted in Figure 4.6 the polymer will remain at the re-crystallization temperature until the phase change is complete. In this research the time duration of interest is the time between the completion of the melting transition and the onset of re-crystallization. In Figure 4.6 the melting transition is complete at approximately 0.37 seconds and the onset of re-crystallization is at approximately 0.5 seconds, the time in the liquid state is the difference of the two times, 0.13 seconds. Using the completion of melting and the onset of re-crystallization assumes that no significant contribution to sintering occurs during either of the phase changes.

To allow for use of the same model code for amorphous and semi-crystalline polymers the value of $\Delta T_{\text{melt}}$ is set equal to zero and the glass transition temperature, $T_g$, substituted for $T_{\text{melt}}$ and $T_{\text{recrystal}}$.

![Figure 4.6: Temperature as a function of time as predicted by the triangular flux, relevant transition temperatures and the temperature as a function of time with a reduction for melting.](image)

4.3 **TIME-TEMPERATURE SUPERPOSITION**

For each intersection point on the powder-bed grid, Figure 4.3, which is above the phase transition temperature the time at which the phase transition from solid-to-liquid is complete and the time at which the phase transition from liquid-to-solid begins are calculated numerically. In the temperature profile shown in Figure 4.6, the solid-to-liquid phase transition is complete at approximately 0.38 seconds and liquid-to-solid phase transition begins at
approximately 0.50 seconds. Knowing the liquid temperature as a function of time, affords the use of time-temperature superposition to determine the time in the liquid state at the reference temperature, which is a temperature where the rheologic characteristics are known. The WLF equation, [4.1], can be used to determine the shift factor which is used scale the time durations at one temperature to the reference temperature. In [4.1], \( a_T \) is the shift factor, \( T_{\text{ref}} \) is the reference temperature to which the time is being shifted, and \( C_1 \) and \( C_2 \) are material constants determined by fitting the shift factors obtained from construction of a master curve to the WLF equation, as described in the Materials and Methods chapter. Figure 4.7 is a plot of \( \log(a_T) \) as a function of the deviation from the reference temperature for PEO100k. The black squares are experimentally determined shift factors and the red line is a best fit of the data to the WLF equation. The WLF parameters for PEO100k are: \( C_1 = 9.5 \) and \( C_2 = 995^\circ C \) and \( T_{\text{ref}} = 115^\circ C \).

\[
\log(a_T) = \frac{-C_1(T(t) - T_{\text{ref}})}{C_2 + T(t) - T_{\text{ref}}} \quad [4.1]
\]

Given a temperature and duration of exposure to that temperature, \( \Delta t \), the WLF equation can be used to determine the shift factor and then the equivalent exposure time at the reference temperature, \( \Delta t_{\text{ref}} \), can be determined using [4.2]. However, during LS process the temperature of liquid is not constant and thus the shift factor changes as a function of time. A first-order approximation would be to calculate the shift factor based on the average liquid temperature. However, previous work by the author determined that calculating a shift factor based on the average temperature of the liquid was not a suitable approximation because faster cooling rates (achieved by lowering the initial powder-bed temperature) resulted in higher average temperatures and a thus lower shift factors. When the shift factor determined from the average temperature is used in the model the following is observed: for a given laser power lowering the initial powder-bed temperature increases the density predicted by the model. Obviously, lowering the initial powder-bed temperature should lower the density.

\[
\Delta t_{\text{ref}} = \Delta t a_T \quad [4.2]
\]
The mathematically correct solution to determining the duration of exposure at the reference temperature from a non-isothermal exposure is to integrate $1/\alpha T$ with respect to time. Using the WLF equation and the temperature as a function of time, $1/\alpha T$ as a function of time can be determined for the time the polymer is in liquid state, as shown on the right in Figure 4.8. Numerical integration of $1/\alpha T$ with respect to time is employed in the model developed herein to determine the time at the reference temperature for each point on the powder-bed grid which reaches the liquid state. In the temperature profile shown in Figure 4.6, the non-isothermal time in liquid state is 0.12 seconds and the time in the liquid state shifted to the reference temperature is 0.11 seconds. The calculated time at the reference temperature is reasonable given that the liquid temperature only slightly exceeds the reference temperature for approximately 0.03 seconds.

**Figure 4.8**: The shift factor (right) and inverse shift factor (left) as functions of time.

### 4.4 RHEOLOGIC PROPERTIES

Polymer liquids exhibit all or some combination of three regimes of flow, instantaneous elastic, viscoelastic and viscous. The tensile creep compliance $D(t)$, $[4.3]$, is a material property which characterizes polymeric liquid flow. $D_0$ is the instantaneous elastic contribution. $D_v$ is the viscoelastic contribution which dominates over intermediate times. $t/\eta_0$ is the viscous term which dominates at long times. Realistically, the time ranges for viscous and viscoelastic flows overlap, however, in this sintering model the viscoelastic component is only considered for $t \leq \tau$ and the viscous component is only considered for $t > \tau$. For a discussion of the properties of polymeric liquids see the Materials chapter. The sintering model developed in this work considers the viscoelastic and viscous nature of polymeric liquids and their effects on sintering of polymeric powders. For times less than or equal to $\tau$ the viscoelastic contact growth model developed by Lin is used. Lin’s model is based on a power law fluid with a tensile creep compliance of the form of equation $[4.4]$. Therefore the components of the tensile creep compliance, $[4.3]$, which are dominate for times less than $\tau$, $D_0$ and $D_v$, are fit to $[4.4]$, as shown in Figure 4.9. In the combined-mechanism sintering model presented herein, the sintering mechanism changes at the characteristic relaxation time, $\tau$, to sintering by viscous flow which is modeled by the Mackenzie-Shuttleworth (MS) model. As the MS model predicts sintering by viscous flow, the material property of interest is $\eta_0$, the zero-shear viscosity. The green line in Figure 4.9 is the viscous contribution to the tensile creep compliance. Table 4.3 lists the relevant material properties for PEO100k for the Lin and MS sintering equations.

$$D(t) = D_0 + D_v + \frac{t}{\eta_0}$$  \[4.3\]

$$D(t) = A_0 + A_1 t^m$$  \[4.4\]
Table 4.3: Rheologic properties of PEO100k.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero-shear viscosity, ( \eta_0 )</td>
<td>12000 Pa-s</td>
</tr>
<tr>
<td>long time viscoelastic compliance, ( J_e )</td>
<td>0.00014 Pa(^{-1} )</td>
</tr>
<tr>
<td>relaxation time, ( \tau )</td>
<td>0.54 s</td>
</tr>
<tr>
<td>power law intercept, ( A_0 )</td>
<td>1.12\times10^{-6}</td>
</tr>
<tr>
<td>power law slope, ( A_1 )</td>
<td>1.2\times10^{-4}</td>
</tr>
<tr>
<td>power law exponent, ( m )</td>
<td>0.63</td>
</tr>
</tbody>
</table>

4.5 DENSIFICATION

The two sintering mechanisms considered in this model are viscoelastic contact growth and viscous contact growth which result in zipping and stretching of the contact region respectively. For times less than the characteristic relaxation time, \( \tau \), viscoelastic contact growth will be the sintering mechanism and for times greater than \( \tau \) viscous contact growth will be the sintering mechanism. Figure 4.10 is schematic of two spherical particles before sintering and after sintering has begun. During sintering the contact radius, \( a \), increases and the distance between the centers of the spheres, \( l_0 - \Delta l \), decreases. The ratios of \( a/R \) and \( \Delta l/l_0 \) are approximately related by [4.5]\(^7\) and the density is related by [4.6]\(^8\), where \( \rho_0 \) is the initial packing density of the powder. The ratio of \( a/R \) needed to achieve full density, \( \rho = 1 \), is related to the initial density by [4.7]. The major assumption of the sintering model presented herein is that the particles being sintered are all spherical and have the same radius, \( R \).
\[ \frac{\Delta l}{l_0} = \left( \frac{a}{R} \right)^2 \]  

\[ \rho = \frac{\rho_0}{\left( 1 - \frac{\Delta l}{l_0} \right)^3} = \frac{\rho_0}{\left( 1 - \left( \frac{a}{R} \right)^2 \right)^3} \]  

\[ \left( \frac{a}{R} \right)_{\text{at full density}} = \sqrt{1 - \rho_0^{1/3}} \]  

4.5.1 Viscoelastic Contact Growth

Viscoelastic contact growth will be modeled using the equations presented by Lin et al\(^9\), [4.8]. \( \gamma_m \) and \( c_m \) are defined in [4.9] and [4.10] respectively; \( \Gamma \) is the gamma function. \( m \) and \( A_1 \) are parameters of the power law fluid fit to the tensile creep compliance before time \( \tau \). \( W \) is twice the surface energy of the polymer: \( W=2\gamma \). \( \delta_c \) is the range of the adhesive surface force assumed to be 50nm in this work\(^10\). Discussion of Lin's development of this model can be found in the literature review in the introductory chapter.

\[ a_0 = \left( \frac{9\pi}{2} \right)^{\frac{1}{m+1}} \left( \frac{4m+3}{m} \right)^2 \left( \frac{\delta_c}{c_m} \right)^2 \left( \frac{\gamma_m A_1 W}{c_m R} \right)^{\frac{1}{m+1}} t^{\frac{1}{m+1}} \]  

\[ c_m = \frac{2m+1}{m+1} \]  

\[ \gamma_m = \left( \frac{\pi}{4} \right)^{\frac{1}{2}} \frac{\Gamma(m+1)}{\Gamma(m+1.5)} \]  

4.5.2 Viscous Contact Growth

After the characteristic relaxation time the sintering mechanism is assumed to change to contact growth by viscous flow. The Mackenzie-Shuttleworth (MS) sintering model will be used to model viscous sintering. Equation [4.11]\(^11\) is a form of the differential equation which governs sintering as predicted by MS. \( a_0 \) is the pore size when viscous sintering begins. The solution to the differential equation is [4.12].
\[
\frac{d\rho}{dt} = \frac{3\gamma}{2a_0\eta_0}(1 - \rho) \tag{4.11}
\]

\[
\rho(t) = 1 + e^{\frac{-3\gamma t}{2a_0\eta_0}}(\rho_0 - 1) \tag{4.12}
\]

At time \(\tau\), viscoelastic contact growth is assumed to cease and give way to viscous contact growth. To transition from one mechanism to the other, the relative density of the powder bed at \(\tau\) must be determined in order to calculate the initial pores size for use in the Mackenzie-Shuttleworth model. The intermediate density is calculated using equations [4.8] and [4.6]. Knowing the intermediate density and assuming simple cubic bed packing, where the characteristic length, \(l\), is the unit-cell dimension, the initial pore size pore size, \(a_0\), can be calculated as follows. The initial volume of the cubic unit cell is \(l_0^3\), where \(l_0=2R\) and the volume of the unit cell occupied by solid material at any time is \((4\pi/3)R^3\). Equations [4.8] and [4.5] can be used to determine \(\Delta l\) at time \(\tau\), and thus \(l(t)=\Delta l(t)-l_0\). Subtracting the solid volume of the unit-cell, \((4\pi/3)R^3\), from \(l(t)^3\) yields the pore volume per unit cell. Assuming one pore per unit-cell the pore radius is given by [4.13].

The procedure described in the previous paragraph to calculate the initial pore size is valid if the powder being considered has a relative density of approximately 0.52, which the relative density for simple cubic packing. Recall from the Materials and Methods chapter that the tap densities of all the materials used in this work are less than simple cubic packing. However, simple cubic packing is the lowest density periodic packing and periodic packing must be assumed to calculate an initial pore size for the MS model based only on the particle size and relative density. Therefore, for powders which have packing densities less than simple cubic an average separation between the particles will be assumed, \(l_0=2R+\delta\), to afford a periodic structure which can be used to calculate an initial pore size. The value of \(\delta\) can be calculated knowing the particle size and the tap density.

\[a_0 = \left(\frac{3}{4\pi}\left(l(t)^3 - \frac{4\pi}{3}R^3\right)\right)^{1/3} \tag{4.13}\]

### 4.5.3 Combining Densification Mechanisms

Coupling the initial viscoelastic contact growth with viscous contact growth at time \(\tau\) is done using equation [4.13] and equating the density at \(\tau\) due to viscoelastic contact growth with the starting density for viscous contact growth. For \(t<\tau\) equations [4.8] and [4.6] can be used to calculate the density. For \(t>\tau\) equation [4.12] can be used to calculate the density. However for repeated calculations a single sintering equation is useful. The combined sintering equation which accounts for both mechanisms is [4.14], where \(U(t)\) is the unitstep function. Figure 4.11 is a plot of the relative density predicted by the combined-mechanism sintering model for 50\(\mu\)m PEO100k powder at \(T=115^\circ\text{C}\) (the reference temperature for equation [4.1]). The two contributing components to [4.14] and the MS sintering equation are also shown in Figure 4.11. The black dashed curve was calculated using equation [4.14], the red curve is the contribution to [4.14] by the first term in the equation which is viscoelastic contact growth and the blue curve is the contribution to [4.14] by the second term in the equation which is viscous contact growth. The solid black curve is the density predicted by the MS model of viscous contact growth only. The initial and full densities are also shown. The step changes in the individual contributions to [4.14] result in a vertical line on the graph at \(t=\tau\). The combined-mechanism model and the MS model predict full density at approximately 3 seconds for \(T=115^\circ\text{C}\). Agreement between the two models at the time that full density is reached indicates that for PEO100k particles with \(R=50\mu\)m viscous contact growth is the majority contributor to densification.
\[ \rho(t) = U(t - \tau) \left\{ \frac{1}{1 - \left( \frac{2 \pi}{2} \frac{m+1}{m} \frac{\pi}{4 \text{ cm}^2} \left( \frac{d_0}{R} \right)^2 \frac{m}{2 \text{ m}^3} \left( \frac{l}{4 \text{ m}^3} \right)^2 \right)^2} \right\} + \]

\[ U(t - \tau) \left\{ \frac{1}{1 + e^{-\frac{2^2 \pi}{2} \tau}} \right\} \frac{\rho_0}{1 - \left( \frac{2 \pi}{2} \frac{m+1}{m} \frac{\pi}{4 \text{ cm}^2} \left( \frac{d_0}{R} \right)^2 \frac{m}{2 \text{ m}^3} \left( \frac{l}{4 \text{ m}^3} \right)^2 \right)^2} = 1 \]

\[ [4.14] \]

---

**Figure 4.11:** Sintering curves for \( R = 50\mu m \) PEO100k powder.

Time-temperature superposition allows for use of the reference temperature sintering curve for all temperatures; this assumes only the rates of molecular motion change with temperature not the mechanisms. For a given set of LS processing parameters the time in the liquid state and the average temperature during the time in the liquid state are calculated at each intersection point on the powder-bed grid which is liquid. The average temperature is used to calculate the shift factor per [4.1] and the shift factor is then used to shift time in the liquid state to the reference temperature per [4.2]. The shifted time in the liquid state is then used as the sintering time. The shifted time in the liquid state and the average temperature in the liquid state can be increased by increasing the laser power, \( P \), decreasing the scan speed, \( V \), or increasing the bed temperature. All process and material properties being equal, reducing the particle size results in an increase in the sintering rate as can be observed by comparing Figure 4.11 \( (R=50\mu m) \) and Figure 4.12 \( (R=25\mu m) \). Note the difference in time scales for the two aforementioned figures.
Comparing Figure 4.11 and Figure 4.12, an increase in the densification rate and an increase in the amount of sintering attributable to viscoelastic contact growth are observed for the smaller particle size. Additionally, the difference between sintering by viscous contact growth only, MS sintering model, and the combined-mechanism-sintering model increases for the smaller particle size. Figure 4.13 and Figure 4.14 are sintering curves for R=15µm and R=10µm; the same trends are again observed as the particle size decreases. For PEO100k particles with R=15µm viscoelastic contact growth accounts for the majority of the densification as predicted by the combined-mechanism model. The MS model for viscous contact growth predicts full density will be reached over a decade later than the combined-mechanism model does. Reducing the particle size to R=10µm, Figure 4.14, the combined mechanism-model predicts that all sintering will occur by viscoelastic contact growth and full density will be reached at approximately 0.015 seconds, two decades before full density is predicted for viscous contact growth only.

Figure 4.12: Sintering curves for R=25µm PEO100k powder.
One of the major flaws of Lin’s model of viscoelastic contact growth is displayed in Figure 4.14, the lack of an asymptotic approach to full density. As the sintering time approaches infinity, the predicted density approaches infinity. Any density above unity is physically meaningless and should be assumed to be unity. For a hand calculation or a small number of computations substituting unity for the erroneous predictions of Lin’s model would suffice. However, in the combined-mechanism model presented herein, the density predicted by Lin’s equation at $\tau$ is used as the starting density for viscous sintering and a density above unity will result in computational errors in the program when calculating the starting density and pore size for the viscous sintering portion of the model, even if the viscous contribution is zero. To avoid these errors, the logic presented in flowchart format in, Figure 4.15 is added to the model code. If the time in the liquid state shifted to the reference temperature is less than $\tau$, then process proceeds down the left leg of the first decision. Then, if full density is not reached in the shifted time, then the first term in equation [4.14] is the only non-zero term. Or, if the shifted time is less than $\tau$ and full density reached at or before $\Delta t_{ref}$ then a density of unity is returned. If $\Delta t_{ref}$ is greater than $\tau$ and full density is reached at or
prior to \( \tau \) then a density of unity is returned. If the time is greater than \( \tau \) and full density is not reached prior to \( \tau \) and then process follows the right most path and both terms in [4.14] contribute to contact growth.

![Density calculation flow chart.](image)

At each intersection point on the grid shown in Figure 4.3 which is heated to the liquid state by the energy from the laser beam a series of calculations are made and relevant data is stored. The individual calculations have been described in greater detail in previous sections and are listed below in order of occurrence.

1. Input relevant material and process data, as in Table 4.1, Table 4.2, and Table 4.3.
2. Define the temperature as a function of time and position using the triangular flux solution.
3. Define the combined-mechanism sintering curve for the given particle size as in Figure 4.12 for PEO100k, \( R=25\mu m \).
4. Iterate through the while-loops shown in Figure 4.4; at each intersection point with maximum temperature above the phase transition temperature the following steps are carried out:
   a. Calculate the time at which the phase transition from solid-to-liquid is complete.
   b. Calculate the time at which the phase transition from liquid-to-solid begins.
   c. Calculate the shifted time, \( \Delta t_{\text{ref}} \), at the reference temperature by integrating \( 1/aT \) with respect to time for the duration of time the polymer is in the liquid state.
   d. Compare \( \Delta t_{\text{ref}} \) to \( \tau \), and flow through the if-statements in Figure 4.15.
   e. Calculate and store: maximum temperature, time in the liquid state, average temperature in the liquid state, shifted time in the liquid state, ratio of shifted time to \( \tau \), density contribution by viscoelastic contact growth, the density contribution by viscous contact growth, the total density, the fraction of viscoelastic contribution to the total density, and the ratio \( a/R \).

The model code is executed in Mathematica and can be found in the Appendix.

4.6 **EXAMPLE OF MODEL RESULTS**

In this section the combined-mechanism sintering model is demonstrated for LS of PEO100k powder with a radius of 25\( \mu m \) and an initial relative packing density of 0.55. The thermal properties of the powder bed are given in Table 4.1, the LS process parameters are given in Table 4.2 and the rheologic properties for PEO100k are given in Table 4.3. The grid spacings, \( \Delta y \) and \( \Delta z \) shown in Figure 4.3, used in the model are both 5\( \mu m \). The combined mechanism sintering curve for PEO100k particles with a 25\( \mu m \) radius is shown in Figure 4.12. The temperature distribution in
the y=0 plane of the PEO100k powder-bed for a scan-in-progress is shown in Figure 4.16. The temperature is predicted by the triangular flux solution for the LS process parameters in Table 4.2. The black contour in Figure 4.16 is the phase boundary temperature. The temperature of the liquid material will be reduced by $\Delta T_{\text{melt}}$ to approximately account for the melting transition. Figure 4.17 shows the three-dimensional phase boundary contour and the beam intensity for the same time depicted in Figure 4.16. The diameters of the major and minor axes of the liquid pool shown are 2.5mm and 1.5mm. The major diameter of the liquid pool is similar to the beam diameter (3.2mm) and the minor diameter of the liquid pool is approximately half the diameter of the beam.

Figure 4.16: Temperature distribution in the y=0 plane for PEO100k, phase boundary contour shown.

Figure 4.17: PEO100k liquid pool and beam intensity.

Figure 4.16 and Figure 4.17 show the temperature distribution in powder for a single instant, however, to calculate the amount of sintering resulting from LS the temperature as a function of time over the entire process is required. Recall Figure 4.6 showed the temperature as a function of time for a single point in the bed. Also shown in Figure 4.6 was the reduced temperature which approximately accounted for the melting transformation. Calculating the temperature distribution in the powder-bed is the first step of the combined-mechanism sintering model. From the temperature distribution at a given point the density can be calculated using the strategy outlined in the previous sections.

Figure 4.18 is a plot of the relative density of laser-sintered PEO100k particles, with a 25µm radius, predicted by the combined-mechanism sintering model for the process conditions in Table 4.2; a short list of process conditions is given above the plot. The combined-mechanism model predicts a maximum sintering depth (z-direction) of 56µm.
and maximum width (y-direction) of 685µm. The maximum predicted relative density is 0.83, the average relative density is 0.76 and the minimum relative density is 0.70. Of locations on the powder-bed grid which reached the liquid state, all exhibit at least a 27% increase in density. Because the density is only calculated at points which were heated to the liquid state, points below and to the right of the liquefied points are predicted to remain at the initial packing density, 0.55. Note the aspect ratio of the plot is not 1:1.

Figure 4.18: Density of R=25µm PEO100K, LS processing conditions in Table 4.2.

Sintering data generated using the combined mechanism model will be compared to specimens laser sintered using the same process parameters which were modeled. Scanning electron microscopy will be used to investigate the sintered structures. It is difficult to determine the density of an entire specimen or a given location in a specimen from a micrograph, but it is often easy to measure the ratio of the contact radius to the particle radius, $a/R$, between to particles. Thus the model results also include $a/R$ for each point as shown in Figure 4.19. For an initial relative packing density of 0.55, the $a/R$ ratio for full density is 0.425.

Figure 4.19: Ratio of the contact radius to the particle radius for PEO100k R=25µm.

Also included in the model output is the average temperature in the liquid state, $T_{avg}$. Figure 4.20 is a plot of this data. Points near the edge of the phase boundary have an average temperature lower than the melting temperature, which is 65°C. Average temperatures below the melting temperature result from the fact that the liquid does not re-crystallize until it is under-cooled to the re-crystallization temperature, thus areas with just enough thermal energy to reach the liquid state can sinter during time required to reach the re-crystallization temperature. The under-cooling phenomenon is the reason that even points near the edge of the liquid boundary still had at least a 27% increase density, as shown in Figure 4.18. From a process-structure-property stand point the larger the undercooling required to reach the re-crystallization temperature the larger the difference between the minimum sintered density and the initial powder bed density, which is also the density of the adjacent unsintered powder.
The ratio of the shifted time in the liquid state, $\Delta t_{\text{ref}}$, to the characteristic relaxation time $\tau$, is output by the model; this ratio is termed the $\tau$-fraction. For PEO100k laser sintered using the conditions in Table 4.2 the maximum value of the $\tau$-fraction is 0.153 and the minimum value is 0.019. This ratio is of interest for two reasons: 1) if the $\tau$-fraction is less than or equal to unity, then all of the densification predicted by the model is from viscoelastic contact growth and 2) the degree sintering for times less $\tau$ is not well investigated and knowing the fraction of the characteristic relaxation time that the polymer was in the liquid state provides a measure for comparison of different processing conditions and different materials. Reptation theory of polymer adhesion predicts that the properties of the contact region will not be equal to those of the bulk until the chains from the surfaces of the individual particles have formed a fully interpenetrating network. The time for formation of a fully interpenetrating network is typically known as the reptation time, $t_R$, and is approximately equal to the characteristic relaxation time $\tau$. Prior to formation of a fully interpenetrating network, minor chains diffuse across the contact region resulting in particle adhesion. Thus for $\tau$-fractions much less than unity very weak or no particle adhesion may be observed in the contact area. As the $\tau$-fraction approaches unity the strength of the contact area should approach that of the bulk.
fraction is greater than or equal to unity, then the properties of the contact area should be equal to those of the bulk because the polymer remains above the re-crystallization temperature for a time exceeding \( \tau \) allowing for formation of a fully interpenetrating network.

![Graph showing depth and viscoelastic fraction](image)

**Figure 4.22:** Fraction of the total densification attributed to viscoelastic deformation.

4.7 **CLOSING REMARKS ABOUT THE COMBINED-MECHANISM SINTERING MODEL**

In this chapter a sintering model applicable to LS which combines contact growth by viscoelastic and viscous means was presented. The sintering model is based on the triangular flux solution to heating of a powder-bed by a moving laser heat source. The major geometric differences between the sintering model presented and LS practice are presented in Table 4.4. As the model results are compared to experimental data in the following chapters the validity of the assumptions will be addressed and will vary from system to system.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Model</th>
<th>LS practice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution</td>
<td>mono-dispersed</td>
<td>(~100\mu m) size range</td>
</tr>
<tr>
<td>Particle shape</td>
<td>spherical</td>
<td>varies: spherical to oblique spheroid</td>
</tr>
<tr>
<td>Particle roughness</td>
<td>perfectly smooth</td>
<td>varies: smooth to course</td>
</tr>
<tr>
<td>Pore geometry (as in MS)</td>
<td>spherical</td>
<td>non-spherical</td>
</tr>
<tr>
<td>Powder-bed geometry</td>
<td>continuum</td>
<td>discrete particles</td>
</tr>
</tbody>
</table>

4.8 **CHAPTER 4 REFERENCES**

5 LAB-SCALE LS UNIT

The laser sintering unit, shown in Figure 5.1 was designed and built as part of this research to test the applicability of materials to processing by LS and to provide a means of producing single scan vector samples to compare with the results of the thermal/sintering model developed in this work. The laser, mounted vertically in the LS unit, is a Synrad 48-1 CO₂ laser with a nominal power of 10W. The Parker translation stage, mounted in the bottom of the enclosure, has a travel of 152 mm x 152 mm and is driven by two stepper motors. The build area, shown in Figure 5.2, is a typical configuration in that the powder-bed is indexed down after each layer is scanned. The powder-bed depth is adjusted via a micrometer-driven vertical translation stage. Additional powder is delivered via a counter-rotating roller driven by a gear-motor. The powder-bed surface is heated from above by a set of infrared (IR) heating lamps. The temperature of the bed surface is measured using a non contact IR temperature sensor. Additional heating at the powder base is done via a strip heater. The build area is enclosed in a controlled atmosphere chamber which allows for sintering powders prone to oxidative degradation. The front of the chamber, not shown in Figure 5.1, has glove box arms to allow the user to manipulate powder in the build area while maintaining a controlled atmosphere. A portable oxygen sensor is used to measure the oxygen content in the chamber.

![Figure 5.1: Lab-scale LS unit.](image)

![Figure 5.2: Build area.](image)
For each sintered layer, a motion program must be created and downloaded to the motion controller by the Parker Motion Architect software. The Parker AT 6200 motion controller sends motion commands to the two Zeta micro-stepper drives which generate pulses to move the Zeta stepper motors. Additionally, the motion controller sends a +5V digital signal to a NAIS FP0-C16T programmable logic controller (PLC) to initiate lasing during motion of the translation stage. The PLC sends an analog signal, proportional to the desired laser power, to the Synrad UC-1000 laser power controller when the motion controller signals the beginning of a scan vector. Figure 5.3 shows the calibration curve for the laser power as a function of the PLC control variable. The laser power was measured using a Synrad Laser Power Wizard. A ladder logic program, which includes the laser power to be used, is created and downloaded to the PLC using FPSoft (software provided with PLC). Figure 5.4 is a control flow chart for operation of the lab-scale LS unit. Figure 5.5 shows the various controllers for lab-scale LS unit.

Prior to sintering powder, the powder-bed is preheated via the IR heating lamps and the silicone strip heater. The powder-bed temperature control is crucial if geometrically accurate multi-layer specimens are desired. The powder-bed surface is heated by two Research Inc. 4184 IR lamps which are powered by a Research Inc. 5620 IR heater power controller. The power output by the IR heater power controller is proportional to the 4-20 mA signal which is output from an Omega CN1166 PID temperature controller. The powder-bed surface temperature control loop is completed by a Raytek MID non-contact IR temperature sensor which is connected to the Omega CN1166 temperature controller. The base of the powder-bed is heated using silicone strip heater with a power density of 10W/in². The powder-bed base temperature is measured by a K-type thermocouple. A Teco/Sigma MDC4E PID temperature controller measures the thermocouple temperature and controls the power to the strip heater. Once the powder-bed temperature has stabilized, sintering commences.

![Figure 5.3: Laser power calibration curve.](image-url)
Dimensions and Process Parameters

- Computer
- Motion Control Software
- PLC Software
- Motion Controller
- Programmable Logic Controller
- Micro-stepper Drives
- Stepper Motors
- Translation Stage
- Laser
- Laser Power Controller
- PID Temperature Controller
- IR Heater Power Supply/Controller
- IR Heating Lamps
- IR Temperature Sensor
- Silicone Strip Heater
- Thermocouple

Figure 5.4 Control flow chart for lab-scale LS unit.

Tensile specimens were fabricated from nylon 12 in the lab-scale LS unit to benchmark the capabilities of the unit and guide the design improvements. The average ultimate tensile strength (UTS) of nylon 12 sintered in the lab-scale LS unit was 38.5±3 MPa and the average strain at maximum stress was 9%. 3D Systems reports a UTS of 44 MPa and a strain to failure of 9% for parts built using a Sinterstation® 2500plus®. Because the mechanical properties of nylon 12 samples made using the lab-scale LS unit and commercial unit were similar (~15% difference in UTS), the performance of the lab-scale LS unit was deemed comparable to commercial LS units. Note: The nylon 12 samples made for comparison to commercially made samples were made prior to the addition of the IR temperature sensor and powder-bed surface temperature controller. These additions should result in samples with properties closer to those of commercially made samples.

Figure 5.5: Controllers for lab-scale LS unit.
Notes on single scan vector fabrication in the lab-scale LS unit.

- Fabrication of single scan vector samples (a representative sample is shown on the left in Figure 5.6) which are one beam diameter wide and 25.4mm long, requires only a very small amount of powder. Therefore, to conserve powder, a metal insert (shown on the right in Figure 5.6) with a small rectangular depression in the mid-section was fabricated to fill the majority of the build volume when single scan vectors are being fabricated.

![Figure 5.6: Single scan vector sample and insert for single scan vector fabrication.](image)

- PC and PEO single scan vectors were fabricated in air.
- During fabrication of the PC samples with bed temperatures of 100°C and 130°C, the powder-bed was heated to the desired bed temperature using very conservative PID parameters; the heating rate over the last 10°C was approximately 1°C per minute.

5.1 CHAPTER 5 REFERENCES

1 http://www.synrad.com/products/overview.htm; information for all Synrad products
2 http://www.parker.com/products/EPD/; information all Parker motion control products
3 http://www.aromat.com/acsd/product//plc/fp0/fp0.html
4 http://www.researchinc.com/thermal/th_products.htm; information for all Research Incorporated products
5 http://www.omega.com/pptst/CN1166.html
6 http://www.raytek-northamerica.com/tools/products/view.html?phase=show&id=1013539420&tool_id=14&cat_id=2.2.1.1
7 no information available
9 http://www.3dsystems.com/products/datafiles/lasersintering/datasheets/DURAFORMHigh.pdf
6 RESULTS AND DISCUSSION

In this chapter, the results of the modeling and experimental aspects of this work will be presented and qualitatively compared. Laser sintering of four materials was investigated in this work, PC and three molecular weights of PEO. The materials selected for this work allow for comparison of the effects of material form, amorphous or semi-crystalline, and comparison of the effect of molecular weight which directly affects the rheologic characteristics on laser sintered structures. The primary focus of this work is to investigate LS of PC and PEO \( M_v=1 \times 10^5 \) g/mol; these two materials exhibit rheologic characteristics which are described well using a standard model of the tensile creep compliance and the WLF equation. The rheologic characteristics of the two higher molecular weight PEOs, \( M_v=1 \times 10^6 \) g/mol and \( M_v=8 \times 10^6 \) g/mol, are not well described by the standard model used in this work. Also, the concavity of the \( \log(a_T) \) as a function of temperature difference data for the two higher molecular weight polymers is concave down which does not match the concavity of the WLF equation, therefore a function which matched the concavity and form of the data was selected.

The results will be presented in the following order: 1) PEO \( M_v=1 \times 10^5 \) g/mol, 2) PEO \( M_v=1 \times 10^6 \) g/mol and \( M_v=8 \times 10^6 \) g/mol, 3) PC. The results and discussion section for each material will be presented in the following order: 1) presentation and discussion of the maximum and average temperatures as a function of position as predicted by the thermal model, 2) presentation and discussion of the densification profiles predicted by the combined-mechanism sintering model and the Mackenzie-Shuttleworth model, 3) presentation and discussion of the sintered microstructures as observed using scanning electron microscopy, 4) comparison of the model predictions and the observed microstructure. Discussion of the effect of molecular weight on the sintering behavior will follow the PEO \( M_v=8 \times 10^6 \) g/mol section. Following the PC section, the effect of the polymer form (semi-crystalline or amorphous) on the densification process during LS will be discussed.

All of the thermal model results presented in this section were obtained using the triangular flux approximation solution and the temperature recovery method to account for the enthalpy of melting when appropriate. The temperature as a function of time for the points in the powder bed which reach the liquid state was determined using the aforementioned thermal model. The temperature as a function of time was used in conjunction with a time-temperature superposition model to determine the time in the liquid state at the reference temperature as a function of bed position. From knowledge of the tensile creep compliance at the reference temperature, the density as a function of position was predicted using the combined mechanism sintering model and the Mackenzie-Shuttleworth sintering model. Recall, from the Sintering Model chapter, that a cross-section of the \( y-z \) plane is divided into a grid with uniform spacing and the temperature profile and final density are determined at each intersection point on the grid. Detailed model results are presented for each particle size/processing parameter combination for which a sample was fabricated using the lab-scale LS unit. In addition to the density distributions predicted by the combined-mechanism sintering model and the Mackenzie-Shuttleworth sintering model, the ratio of the time at the reference temperature to the relaxation time at the reference temperature, termed the \( \tau \)-fraction is also presented in the detailed model results.

As discussed in the Materials and Methods chapter, samples were fabricated from selected particle size distributions of four materials using various process parameters. Sample microstructure was then investigated using scanning electron microscopy. Representative images of sample microstructures are shown for four magnifications: a full-width image of the sample and images at magnifications of 500x, 1000x and 2000x. Key microstructural features will be noted; these include: non-viscous particle contact, particle necking, bulk surface flow and changes in particle shape and/or surface characteristics as compared to the powder. The bulk images of the samples were made using a secondary electron detector, which is at an angle of approximately 45° to the sample surface, therefore the structure in open pores is not shown and the surface features are more distinguishable. The additional three images of each sample were obtained for an in-lens detector which provides a more detailed image of the porous microstructure.

6.1 PEO \( M_v=1 \times 10^5 \) G/MOL

As discussed in the Materials and Methods chapter, Figure 6.1 details the LS process parameters and particle sizes of PEO \( M_v=1 \times 10^5 \) g/mol which were modeled and for which samples were fabricated and the microstructure investigated. The initial powder-bed temperature for all models and experiments was 25°C for PEO \( M_v=1 \times 10^5 \) g/mol. The \( y \) and \( z \) grid spacing used for all of the PEO \( M_v=1 \times 10^5 \) g/mol models was 5 µm. In this chapter, when detailed results are presented, the data marker for each intersection point on the grid is scaled so that a continuous
distribution in the y-z cross-sections is produced, as opposed to isolated squares on a grid which was the manner in which detailed y-z cross-sections were shown in the Sintering Model chapter.

<table>
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<th>Laser power, W</th>
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<th>1.5</th>
<th>2</th>
<th>3.5</th>
<th>4.9</th>
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<td>model and experiment</td>
<td>model only</td>
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**Figure 6.1:** Modeling and experimentation matrix for PEO M_v=1x10^5 g/mol.

### 6.1.1 Thermal Model Results

Figure 6.2 and Figure 6.3 are plots of the maximum and average temperatures, respectively, as a function of position for PEO M_v=1x10^5 g/mol, R=60µm sintered using laser powers from 1.0W to 4.9W, as predicted by the triangular flux approximation solution. The heat associated with the enthalpy of melting has been accounted for using the temperature recovery method. Only points in the powder bed which reached the liquid phase during LS are plotted in the figures. From the figures it is evident that the width and depth of the powder bed volume, which reaches the liquid phase during LS, increases as the laser power increases. In Figure 6.2, the range of the temperature scales on the left side of each of the plots is identical. The minimum value of the temperature scale, which corresponds to blue, is 25°C (the initial powder-bed temperature). The maximum value of the temperature scale, which corresponds to red, is 1200°C. In Figure 6.2, the highest maximum temperature in the powder bed, which occurs at the point (y=0, z=0), increases from 177°C for P=1.0W to 1158°C for P=4.9W. The lowest maximum temperature, which occurs everywhere along the bottom surface, is 69°C (which is the melting temperature of PEO M_v=1x10^5 g/mol) for all laser powers. The mean maximum temperature is 108°C for P=1.0W and increases to 283°C for P=4.9W.

In Figure 6.3, the range of the temperature scales on the left side of each of the plots is identical. The minimum value of the temperature scale, which corresponds to blue, is 25°C (the initial powder-bed temperature). The maximum value of the temperature scale, which corresponds to red, is 170°C. In Figure 6.3, the highest average temperature, which also occurs at the same location (y=0, z=0), is 111°C for P=1.0W and increases to 167°C for P=4.9W. The lowest average temperature, which occurs everywhere along the bottom surface, is 57°C for all laser powers; 57°C is 12°C below the melting temperature and 15°C above the re-crystallization temperature. The mean of the average temperatures for all the points in the bed which reached the liquid phase is 81°C for P=1.0W and increases to 102°C for P=4.9W.
Figure 6.2: Maximum temperature profiles PEO $M_w=1\times10^5$ g/mol, $R=60\mu$m for various laser powers.
Figure 6.3: Average temperature profiles PEO $M_v=1\times10^5$ g/mol, $R=60\mu$m for various laser powers.
Figure 6.4 and Figure 6.5 are plots of the maximum and average temperatures for PEO $M_s=1\times10^5$ g/mol, $R=10\mu$m sintered using laser powers from 1.0W to 4.9W. The ranges of temperature scales used in Figure 6.4 and Figure 6.5 are identical to those of the previous maximum and average temperature plots, respectively. Again, the width and depth of the powder bed volume, which reaches the liquid phase, increases as the laser power increases. In Figure 6.4, the highest maximum temperature in the powder bed, which occurs at the point $(y=0, z=0)$, increases from 182°C for $P=1.0W$ to 1183°C for $P=4.9W$. The lowest maximum temperature, which occurs everywhere along the bottom surface, is 69°C for all laser powers. The mean maximum temperature is 110°C for $P=1.0W$ and increases to 286°C for $P=4.9W$. In Figure 6.5, the highest average temperature also occurs in the same location $(y=0, z=0)$, is 112°C for $P=1.0W$ and increases to 167°C for $P=4.9W$. The lowest average temperature, which occurs everywhere along the bottom surface, is 57°C for all laser powers. The mean of the average temperatures for all the points in the powder bed which reached the liquid phase is 82°C for $P=1.0W$ and increases to 103°C for $P=4.9W$. 
Figure 6.4: Maximum temperature profiles PEO $M_r=1 \times 10^5$ g/mol, $R=10 \mu$m for various laser powers.
6.1.2 Thermal Model Discussion

The maximum and average temperature distributions are essentially identical for PEO $M_v = 1 \times 10^5$ g/mol $R = 10 \mu m$ and $R = 60 \mu m$ with the exception of minor temperature shifts. The temperature distributions should be approximately...
equal because the only differences in the thermal properties are minor difference in the thermal conductivity of the powder bed due to differences in the tap densities of the two powders. Since there is a factor of six difference in the particle size, a significant difference in the rate of change in the thermal conductivity in the region being sintered could be expected. Thus, significant differences in the thermal profiles of the two powders would be expected during sintering. However, in the model developed herein, the thermal conductivity and specific heat are assumed to be independent of temperature and density. Thus the thermal profiles are not significantly different.

The average temperatures predicted by the thermal model are realistic. The average temperatures are well below the degradation temperature of PEO 1x10⁵ g/mol, which is 333°C, for the laser powers investigated. However, the maximum temperatures predicted by the thermal model are hundreds of degrees above the degradation temperature to depths of approximately 100µm for laser powers of 3.5W and 4.9W. Without specific knowledge of the degradation kinetics for temperatures and heating rates comparable to those of the LS process, it cannot be definitively stated that degradation should occur. However, if the model assumptions are correct, it would be reasonable to assume that some degradation would occur when laser powers of 3.5W or greater are used.

The major model approximation that could result in unrealistically high surface temperatures is the use of a surface heat flux to describe the absorption of photons by the polymer. As previously noted, laser heating is a volumetric phenomenon; the absorption of photons decays exponentially from the material’s surface. Also, the assumptions of one-dimensional heat transfer and temperature- and density-independent thermal properties could also lead to unrealistically high temperatures. All of the aforementioned assumptions lead to excess surface temperatures.

In the thermal model results presented above, the average temperature of the liquefied PEO near the liquefied/unliquefied interface is below the melting temperature. This observation was also made in the Sintering Model chapter. The fact that the average temperature is below the melting temperature is significant because it leads to the following conclusion. The difference between the melting and re-crystallization temperature (the undercooling required for solidification) allows material, which has imparted to it exactly the amount of energy required to reach the liquid phase, to remain in the liquid phase for a finite period of time before solidifying. During the time required for the material to cool from the melting temperature to the re-crystallization temperature, densification can occur. If a material exhibited no undercooling, then material which has imparted to it exactly the amount of energy required to reach the liquid phase would instantaneously solidify upon melting and densification would not occur. Thus, the undercooling phenomena allows for a step-change in the density across the liquefied/unliquefied interface to develop during LS if the densification kinetics are such that significant contact growth can occur during the time required to cool to the re-crystallization temperature. Previous researchers have stated that the amount of undercooling is important in the layer-addition process during LS¹. However, the potential to develop a step-change in the density across the liquefied/unliquefied interface has never been reported.

6.1.3 Sintering Model Results

The figures spanning Figure 6.6 through Figure 6.10 show the densification profiles (relative density as a function of position) predicted by the combined-mechanism model (CMM) and by the Mackenzie-Shuttleworth (MS) model for laser powers of 1W, 1.5W, 2.0W, 3.5W and 4.9W for R=60µm PEO 1x10⁵ g/mol. The bottom graph in each of the figures is the ratio of time in the liquid phase at the reference temperature to the characteristic relaxation time at the reference temperature; this ratio is termed the t-fraction by the author. Recall that the relaxation time, τ, is the time when viscous flow becomes the dominant deformation mode of the polymeric liquid. The relaxation time is also the time that densification mode is switched in the combined-mechanism model from viscoelastic contact growth to viscous contact growth. The thermal model used to predict the maximum and average temperatures as a function of position, shown above, was used in conjunction with the WLF fit to the log(αₜ) as a function of temperature data to approximate the time in the liquid state at the reference temperature. For each of the model results presented below there is a corresponding maximum and average temperature plot in the previous section.

The relative density and t-fraction plots in the sintering model results figures are the predictions for a single pass at the specified laser power for the defined particle size. The average, maximum and minimum densities predicted by the CMM and the MS model are stated on the respective plots along with the initial density. Recall that only positions in the powder bed which are heated into the liquid phase are shown in the plots. The relative density scale on each density plots ranges from the initial relative density, which is assumed to be the tap density of the powder, to full relative density, which is equal to unity. The t-fraction scale is the same for all of the results in this section and ranges from 5x10⁻³, which is significantly less than the time required for viscous flow to occur, to 2x10⁻¹, which
is significantly longer than the time required for viscous flow to occur. Detailed model results are shown for all the particle size/processing parameter combinations for which samples were fabricated. The detailed model results provide specific predictions for the density as a function of position. The model results are presented in order of decreasing particle size. For each particle size, the results are presented in order of increasing laser power.

Figure 6.6: Sintering model results for PEO $1\times10^5$ g/mol, $P=1.0$ W, $R=60\mu$m.
Figure 6.7: Sintering model results for PEO $1 \times 10^5$ g/mol, $P=1.5W$, $R=60\mu m$. 
Figure 6.8: Sintering model results for PEO $1 \times 10^5$ g/mol, P=2.0W, R=60µm.
Figure 6.9: Sintering model results for PEO $1\times10^5$ g/mol, $P=3.5W$, $R=60\mu m$. 
The results shown in Figure 6.6 through Figure 6.10 are for laser sintering of PEO 1x10^5 g/mol, R=60µm powder at laser powers from 1.0W to 4.9W, respectively. Recall that the profiles shown are the cross-sections of the volume of powder which the thermal model predicts will reach the liquid phase. The average relative density as predicted by the combined-mechanism model ranges from 0.51 for P=1.0W to 0.59 for P=4.9W. The average relative density as predicted by the Mackenzie-Shuttleworth model ranges from 0.46 for P=1.0W to 0.51 for P=4.9W. The maximum relative density as predicted by the combined-mechanism model ranges from 0.53 for P=1.0W to 1.0 for P=4.9W. The maximum relative density as predicted by the Mackenzie-Shuttleworth model ranges from 0.46 for P=1.0W to 1.0 for P=4.9W. The minimum relative density as predicted by the combined-mechanism model is 0.50 for all laser powers. The minimum relative density as predicted by the Mackenzie-Shuttleworth model is 0.46 for all laser powers. The initial powder bed relative density is 0.46. No significant increase (significant being greater than 0.1 increase in the relative density) in the relative density is observed at depths comparable to the particle diameter, 120µm, until the laser power is increased to 3.5W. In comparing the combined-mechanism model results to the Mackenzie-Shuttleworth model results for the two higher laser powers, a deviation band in the density predictions is observed. Specifically, areas where the \( \tau \)-fraction is greater than approximately 0.1 and less than approximately 100, the density predictions of the combined-mechanism model and the MS model are different by an average of approximately 0.05; the CMM results are the larger of the two. For lower and higher values of the \( \tau \)-fraction the CMM and MS density predictions are in good agreement.

Figure 6.11 and Figure 6.12 show the model results for LS of PEO 1x10^5 g/mol, R=34µm powder at laser powers of 3.5W and 4.9W, respectively. The average relative density as predicted by the combined-mechanism model is 0.61.
for $P=3.5\text{W}$ and 0.65 for $P=4.9\text{W}$. The average relative density as predicted by the Mackenzie-Shuttleworth model is 0.47 for $P=3.5\text{W}$ and 0.51 for $P=4.9\text{W}$. The maximum relative density as predicted by the combined-mechanism model is 0.99 for $P=3.5\text{W}$ and 1.0 for $P=4.9\text{W}$. The maximum relative density as predicted by the Mackenzie-Shuttleworth model is 0.97 for $P=3.5\text{W}$ and 1.0 for $P=4.9\text{W}$. The minimum relative density as predicted by the combined-mechanism model is 0.50 for both laser powers. The minimum relative density as predicted by the Mackenzie-Shuttleworth model is 0.44 for both laser powers. The initial powder bed relative density is 0.44. With the exception of the MS model predictions for $P=3.5\text{W}$, significant densification is predicted by both sintering models to depths of at least one particle diameter in the center of the liquid volume. As was observed in the previous set of model results, comparing the combined-mechanism model results to the Mackenzie-Shuttleworth model results for the two laser powers, a deviation band in the density predictions is observed. Specifically, areas where the $\tau$-fraction is greater than approximately 0.01 and less than approximately 100, the density predictions of the combined-mechanism model and the MS model are different by an average of approximately 0.1; the CMM results are the larger of the two. For lower and higher values of the $\tau$-fraction the CMM and MS density predictions are in good agreement.

**Figure 6.11:** Sintering model results for PEO $1\times10^5 \text{ g/mol}$, $P=3.5\text{W}$, $R=34\mu\text{m}$. 
Figure 6.12: Sintering model results for PEO 1x10^5 g/mol, P=4.9W, R=34µm.

Figure 6.13 and Figure 6.14 show the model results for LS of PEO 1x10^5 g/mol, R=18µm powder at laser powers of 3.5W and 4.9W, respectively. The average relative density as predicted by the combined-mechanism model is 0.75 for P=3.5W and 0.79 for P=4.9W. The average relative density as predicted by the Mackenzie-Shuttleworth model is 0.50 for P=3.5W and 0.54 for P=4.9W. The maximum relative density as predicted by the combined-mechanism model is 1.0 for both laser powers. The maximum relative density as predicted by the Mackenzie-Shuttleworth model is 1.0 for both laser powers. The minimum relative density as predicted by the Mackenzie-Shuttleworth model is 0.45 for both laser powers. The initial powder bed relative density is 0.45. Significant densification is predicted by both sintering models to depths of at least one particle diameter in the center of the liquid volume for both laser powers. The CMM predicts significant densification even at the bottom edge of the liquefied volume. In the previous sets of model results, comparing the combined-mechanism model results to the Mackenzie-Shuttleworth model results, a deviation band in the density predictions is observed. At the extreme in the τ-fraction, the two models predicted similar densities. However, no lower bound of equivalent predictions is observed between the combined-mechanism model and the Mackenzie-Shuttleworth model for PEO 1x10^5 g/mol, R=18µm. In areas where the τ-fraction is less than approximately 100, the density predictions of the combined-mechanism model and the MS model are different by an average of approximately 0.2. For values of the higher τ-fraction higher than 100, the CMM and MS density predictions are in good agreement.
Figure 6.13: Sintering model results for PEO $1\times 10^5$ g/mol, $P=3.5$ W, $R=18$ µm.
The results shown in Figure 6.15 through Figure 6.19 are for laser sintering of PEO $1 \times 10^5$ g/mol, $R=10\mu m$ powder at laser powers from 1.0W to 4.9W, respectively. The average relative density as predicted by the combined-mechanism model ranges from 0.72 for $P=1.0W$ to 0.96 for $P=4.9W$. The average relative density as predicted by the Mackenzie-Shuttleworth model ranges from 0.45 for $P=1.0W$ to 0.56 for $P=4.9W$. The maximum relative density as predicted by the combined-mechanism model ranges from 0.85 for $P=1.0W$ to 1.0 for $P=4.9W$. The maximum relative density as predicted by the Mackenzie-Shuttleworth model ranges from 0.45 for $P=1.0W$ to 1.0 for $P=4.9W$. The minimum relative density as predicted by the combined-mechanism model is 0.63 for all laser powers. The minimum relative density as predicted by the Mackenzie-Shuttleworth model is 0.45 for all laser powers. The initial powder bed relative density is 0.45. The CMM predicts significant densification will occur throughout the entire liquefied volume at all laser powers and approximately full density will be reached for the entire liquefied volume for laser powers of 3.5W and 4.9W. The MS model, however, does not predict a significant increase in the relative density to depths comparable to a particle diameter, 20µm, until the laser power reaches 3.5W. As was observed in the previous $R=18\mu m$ model results, no lower bound of equivalent predictions is observed between the combined-mechanism model and the Mackenzie-Shuttleworth model for PEO $1 \times 10^5$ g/mol, $R=10\mu m$. Additionally, the density ranges predicted by the CMM and the MS model do not even overlap for laser powers of 2W or less. In areas where the $\tau$-fraction is less than approximately 100, the density predictions of the combined-mechanism model and the MS model are different by an average of approximately 0.35. For values of the higher $\tau$-fraction higher than 100, the CMM and MS density predictions are in good agreement.
Figure 6.15: Sintering model results for PEO $1 \times 10^5$ g/mol, $P=1.0W$, $R=10\mu m$. 
Figure 6.16: Sintering model results for PEO $1 \times 10^5$ g/mol, $P=1.5$ W, $R=10$ µm.
Figure 6.17: Sintering model results for PEO 1x10^5 g/mol, P=2.0W, R=10µm.
Figure 6.18: Sintering model results for PEO $1 \times 10^5$ g/mol, P=3.5W, R=10µm.
Figure 6.19: Sintering model results for PEO $1 \times 10^5$ g/mol, $P=4.9$ W, $R=10\mu$m.

The average relative density of laser sintered PEO $1 \times 10^5$ g/mol scan vectors predicted by the CMM and the MS model for all of the particle size/process parameter combinations in Figure 6.1 are summarized in the graph in Figure 6.20, which is a plot of the relative density as a function of the particle radius. The following trends are observed in the graph of the CMM and MS model results:

- For laser powers of 2W and below the MS model predicts essentially no increase in the average relative density of the volume of powder which was liquefied;
- For all laser powers, the CMM predicts an increase in the average relative density of at least 0.5;
- For all laser powers, the CMM predicts that the average relative density increases as the particle radius decreases;
- Taking into consideration the slight differences in the initial densities of the powders, the MS model predicts that change in average density increases as the particle radius decreases; and
- The average densities predicted by the CMM are higher than those predicted by the MS model and the deviation between the two models increases as the particle radius decreases.
The graph in Figure 6.21 is a plot of the relative density as a function of the particle radius; plotted on this graph are
the minimum densities predicted by the CMM and the average densities predicted by the MS model. The minimum
density predicted by the MS model is the initial density of the powder bed in all cases. For the two smaller particle
radii the minimum density predicted by the CMM is greater than the average density predicted by the MS model.
The minimum density predicted by the CMM for a given particle is higher than initial density and independent of
laser power. The minimum density predicted by the MS model is also independent of laser power; however, the
minimum density is also equal to the initial density.

Figure 6.20: Relative density as a function of particle size for various laser powers.

Figure 6.21: Relative density as a function of particle size for various laser powers.
6.1.4  Sintering Model Discussion

When interpreting the results of the sintering models presented above, it is important to remember that the densification models used in this work, Lin et al’s viscoelastic contact growth approximation and the Mackenzie-Shuttleworth model, are based on consolidation of discrete geometries and are assumed to accurately describe densification of a continuum with average properties approximately equal to those of the discrete particles. When the volume of the region undergoing densification is large compared to the volume of the particle then using a continuum approach is reasonable. In this work, specifically for low laser powers and large particle sizes, the results of the continuum-based models are questionable. For example, Figure 6.6 shows the model results for laser sintering R=60µm PEO powder, melting is predicted, a minor increase in the powder is predicted by the CMM and no densification is predicted by the MS model. The maximum depth of the region predicted to melt is approximately equal to the radius of the powder. Since a fraction of the powder particles are predicted to melt then it should be assumed that no densification will occur. Considering the R=60µm powder, the CMM does not predict significant densification for an entire particle volume for laser powers less than 2.0W.

The most notable result from the combined-mechanism model is the prediction of densities significantly higher than the initial bed density adjacent to the liquefied–unliquefied boundary, as shown in Figure 6.19. As mentioned in the discussion of thermal modeling results for PEO 1x10^5 g/mol, material at the bottom of the liquefied volume, which receives just enough thermal energy to reach the liquid state, remains in the liquid state for a finite period of time because solidification does not occur until the liquid is cooled to the re-crystallization temperature. The combined-mechanism model predicts that an increase in the relative density can occur over the time required to cool from the melting temperature to the re-crystallization temperature. The amount of densification which occurs during cooling is dependent on the particle size because the cohesive surface attraction forces act over a larger fraction of the total particle surface for smaller particles. The MS model does not predict that any densification can occur during the aforementioned cooling time. 0.005 is the minimum increase in relative density that would be observed in the analysis herein.

The minimum density predicted by the CMM was observed to be independent of laser power. The minimum density for all samples occurs on the right-most edge of the liquefied volume. The lack of dependence on the laser power suggests that the cooling rate at the right edge is approximately the same for all laser powers. Therefore, the period of time in the liquid state required to cool from the melting temperature to the re-crystallization temperature and thus the τ-fraction are independent of laser power. The position where minimum density occurs does, however, move further from the center of the liquefied volume as the laser power increases. Starting at the location of minimum density and moving along the bottom boundary of the liquefied volume, the density is observed to increase. As the depth of the points on the bottom of the liquefied volume increases, the cooling rate decreases and thus a longer period of time is required to cool from the melting temperature to the re-crystallization temperature. Therefore the density along the bottom edge of the liquefied volume predicted by the CMM will increase as the depth of liquefied volume increases. However, heat conduction in the thermal model is considered only in the z-direction so the cooling rate will be slower than if heat conduction were considered in all three directions.

The deviation gap observed in the density predictions of the CMM and the MS model in the R=60µm and the R=34µm particles can be explained by reviewing plots of the relative density as a function of time for different particle sizes which were presented in the Sintering Model chapter. Figure 6.22 contains three representative plots of the relative density as a function of time for different particle size as predicted by the CMM and the MS model. The initial relative density and full relative density are shown on the plots. The material properties and processing parameters used to make these plots were detailed in the Sintering Model chapter. The deviation gap in the agreement of the predictions of the two models arises because for very short times or small τ-fractions the CMM and MS model are approximately equal, as shown in the R=50µm plot in the upper left corner of Figure 6.22. As the sintering time increases the deviation between the models increases in the intermediate time range and then begins to decrease until the models finally converge for multiple τ-fractions. For the smaller particle sizes, the CMM predicts significant increases in density for relatively short times or τ-fractions less than one. Thus, the two models will predict significantly different densities even for τ-fractions multiple orders of magnitude less than 1. The two models will always converge as the τ-fraction approaches infinity.
6.1.5 Observed Microstructures of Sintered Samples

As previously mentioned, scan vector samples were fabricated using the lab-scale LS unit. For PEO 1x10^5 g/mol, the particle sizes/process parameter combinations for which samples were fabricated are detailed in the modeling and experimentation matrix in Figure 6.1. SEM was then used to investigate the sintered microstructure. The microstructure of laser sintered PEO 1x10^5 g/mol is presented in this section. The SEM micrographs are presented in order of decreasing particle size. For each particle size the results are presented in order of increasing laser power. Four micrographs are presented for each sample. The orientation of the scan vector samples is such that the micrographs show the top surface of the sample which is where the laser beam was incident. The top left micrograph for each sample shows the full width of the sintered scan vector. The other three micrographs are representative images of the laser sintered microstructure at specific magnifications: 500x, 1000x and 2000x. Micrographs at specific magnifications focus on the microstructure around the centerline of the scan vector, mid-width of the region of the top of the scan vector. However, when noted, the location of the microstructure depicted in the micrograph may not be in the central region of the scan vector. For example, if the surface in the central region has undergone bulk flow then the micrographs will focus on the microstructure adjacent to the region of bulk flow. Because interpretation of the laser sintered microstructures is qualitative, defining some terms which will be used to characterize the microstructures is helpful.

- **Bulk liquid flow**- coalescence of the individual particles has proceeded to the point at which continuous structures are multiple times larger (at least 2x) than the particle size of the powder, individual particles are no longer observed in these areas.
- **Viscous contact**- particle to particle contact which exhibits the hour glass shape characteristic of viscous sintering.

Figure 6.22: Density as a function of time for three particle sizes.
Non-viscous contact - particle to particle contact which does not exhibit a characteristic hour glass shape but significant contact between particles is observed.

Figure 6.23 contains micrographs of PEO $1 \times 10^5$ g/mol, R=60µm laser sintered at 4.9W. Attempts at fabricating samples at lower laser powers for this particle size were unsuccessful. The scan vectors for the lower laser powers had insufficient strength to be removed from the powder bed. The microstructure in the central region of the scan vector shown in Figure 6.23 can be characterized by viscous contact; the particles are connected by necks which are indicative of viscous sintering. Particles in the center of the upper right micrograph exhibit smoother surfaces and more rounded features as compared to the un-sintered powder (micrographs of the un-sintered powder were shown in the Materials and Methods Chapter 2). Particles closer to the edges of the scan vector have shape and surface characteristics similar to those of the un-sintered powder. No bulk liquid flow is observed on the particle scan vector surface.

Figure 6.23: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, P=4.9W, R=60µm.

Figure 6.24 and Figure 6.25 are micrographs PEO $1 \times 10^5$ g/mol, R=34µm laser sintered at 3.5W and 4.9W respectively. The microstructure of the two scan vectors both exhibit viscous contact in the center of the sample and non-viscous contact at the edges of the scan vector. Particles in the center of the scan vector exhibit a smoother surface and more rounded features as compared to the un-sintered powder. Particles closer to the edges of the scan vector have shape and surface characteristics similar to those of the un-sintered powder.
Figure 6.24: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=3.5W$, $R=34 \mu m$.

Figure 6.25: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=4.9W$, $R=34 \mu m$. 
Figure 6.26 and Figure 6.27 are micrographs PEO 1x10^5 g/mol, R=18µm laser sintered at 3.5W and 4.9W respectively. Both samples curled significantly around the centerline of the scan vector. The microstructure of the P=3.5W scan vector exhibits viscous contact over the majority of the sample surface. The ratio of the neck diameter to the particle diameter is qualitatively observed to be larger for the R=18µm scan vector laser sintered at 3.5W as compared to the R=34µm scan vector sintered at the same laser power. The microstructure of the P=4.9W sample exhibited bulk viscous flow on the center of the scan vector surface. Outside the region of bulk viscous flow, the viscous contact characterizes the nature of the particle connectivity.

**Figure 6.26:** SEM micrographs of laser sintered PEO 1x10^5 g/mol, P=3.5W, R=18µm.
The figures which span Figure 6.28 through Figure 6.32 are micrographs of scan vectors sintered at laser powers ranging from 1.0W to 4.9W, respectively, for PEO 1x10^5 g/mol, R=10µm. The microstructures of the scan vectors sintered at 1.0W, shown in Figure 6.28, and 1.5W, shown in Figure 6.29, are both composed of a mixture of viscous and non-viscous particle contact. No bulk viscous flow is observed in either sample. Figure 6.30 shows a scan laser sintered at 2.0W. A significant increase in the fraction of viscous contact is observed and an increase in the ratio of the neck diameter to the particle diameter is observed, as compared to the two scan vectors sintered at lower laser powers. No bulk viscous flow is observed for LS at 2.0W. Figure 6.31 and Figure 6.32 are micrographs of scan vectors of PEO 1x10^5 g/mol, R=10µm sintered laser powers of 3.5W and 4.9W. Both of the aforementioned scan vectors have well defined strips of bulk viscous flow in the middle. The width of the strip is proportional to the laser power. Viscous contact dominates the particle to particle contact in the areas at the edges of the sample where bulk viscous flow is not observed.
Figure 6.28: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=1.0\text{W}$, $R=10\mu\text{m}$.

Figure 6.29: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=1.5\text{W}$, $R=10\mu\text{m}$.
Figure 6.30: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=2.0$W, $R=10\mu$m.

Figure 6.31: SEM micrographs of laser sintered PEO $1 \times 10^5$ g/mol, $P=3.5$W, $R=10\mu$m.
6.1.6 Discussion of Sintered Sample Microstructures

No conclusive evidence for the presence of viscoelastic contact growth was observed. Non-viscous contact is present in the samples sintered at lower laser powers, however, definitively stating that these contacts result from viscoelastic deformation driven by attractive surface forces is not warranted because viscous neck growth is also observed in these samples in close proximity to particles which appear to be joined by non-viscous contact. Therefore, the contacts perceived as being non-viscous could be particles which are not in good contact or have not been in contact from the beginning of the sintering process and are just starting to develop viscous necks.

6.1.7 Comparison of Model Predictions and Experimental Results

The maximum temperatures predicted by the thermal model for laser sintering at PEO $1 \times 10^5$ g/mol at 3.5W and 4.9W are hundreds of degrees above the degradation temperature of the polymer. However, no smoking or major color changes were observed during fabrication of the samples at the aforementioned laser powers. This leads to the conclusion that temperatures predicted by the thermal model are most likely erroneously high. Reasons for the excessive temperatures were proposed above in the Discussion of Thermal Model Results section. Over estimation of the temperatures has a trickle down effect because the temperature of the liquid as a function of time is used in the calculation for the time in the liquid state at the reference temperature. Over estimating the temperature of the liquid results in an overestimation of the time in the liquid phase at the reference temperature and, subsequently, an overestimation of the density.

Detailed model results were presented for each of the particle size/processing conditions for which micrographs were presented. Quantitative determination of the relative density is not possible from SEM micrographs, however, qualitative observations such as if the surface of the sample appears to be sintered to full density, bulk liquid flow has occurred on the surface, or the particles appear to be relatively unchanged from the un-sintered powder. Table 6.1 cross-references the model results and the SEM micrographs for equivalent particle size/processing condition combinations.
Table 6.1: PEO 1x105 g/mol cross-references for model results and SEM micrographs.

<table>
<thead>
<tr>
<th>Particle size, Laser Power</th>
<th>Model results figure number</th>
<th>Micrograph figure number</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=60µm, P=1.0W</td>
<td>Figure 6.6</td>
<td>laser sintered sample had no strength</td>
</tr>
<tr>
<td>R=60µm, P=1.5W</td>
<td>Figure 6.7</td>
<td>laser sintered sample had no strength</td>
</tr>
<tr>
<td>R=60µm, P=2.0W</td>
<td>Figure 6.8</td>
<td>laser sintered sample had no strength</td>
</tr>
<tr>
<td>R=60µm, P=3.5W</td>
<td>Figure 6.9</td>
<td>laser sintered sample had no strength</td>
</tr>
<tr>
<td>R=60µm, P=4.9W</td>
<td>Figure 6.10</td>
<td>Figure 6.23</td>
</tr>
<tr>
<td>R=34µm, P=3.5W</td>
<td>Figure 6.11</td>
<td>Figure 6.24</td>
</tr>
<tr>
<td>R=34µm, P=4.9W</td>
<td>Figure 6.12</td>
<td>Figure 6.25</td>
</tr>
<tr>
<td>R=18µm, P=3.5W</td>
<td>Figure 6.13</td>
<td>Figure 6.26</td>
</tr>
<tr>
<td>R=18µm, P=4.9W</td>
<td>Figure 6.14</td>
<td>Figure 6.27</td>
</tr>
<tr>
<td>R=10µm, P=1.0W</td>
<td>Figure 6.15</td>
<td>Figure 6.28</td>
</tr>
<tr>
<td>R=10µm, P=1.5W</td>
<td>Figure 6.16</td>
<td>Figure 6.29</td>
</tr>
<tr>
<td>R=10µm, P=2.0W</td>
<td>Figure 6.17</td>
<td>Figure 6.30</td>
</tr>
<tr>
<td>R=10µm, P=3.5W</td>
<td>Figure 6.18</td>
<td>Figure 6.31</td>
</tr>
<tr>
<td>R=10µm, P=4.9W</td>
<td>Figure 6.19</td>
<td>Figure 6.32</td>
</tr>
</tbody>
</table>

In general, for PEO 1x105 g/mol, the CMM and the MS model both over estimate the density of the laser sintered scan vectors as observed using scanning electron microscopy. Since both the CMM and the MS models overestimate densification, it can be concluded that overestimation of the temperature in the liquid phase is the primary source of error. If the CMM over predicted and the MS model did not then the primary source of error would be most likely be overestimation of the range over which adhesive surface forces act to close the gap adjacent to the area of particle contact. Also, the error in the model results increases as the particle size decreases and the laser power increases. The bulk viscous flow observed in some of the samples sintered at higher laser powers is outside the realm of what would be defined as densification by sintering.

6.2 PEO $M_c = 1 \times 10^6$ g/mol and $M_v = 8 \times 10^6$ g/mol

As discussed in the Materials and Methods chapter, Figure 6.33 details the LS process parameters and particle sizes of PEO $M_c = 1 \times 10^6$ g/mol and $M_v = 8 \times 10^6$ g/mol which were modeled and for which samples were fabricated and the microstructure investigated.

6.2.1 Thermal Model Results Discussion

In the Thermal Model Results and Thermal Model Discussion presented for PEO 1x10^5 g/mol, the temperature distributions in the powder bed were shown to be essentially independent of the particle size because the thermal model used to predict the temperature does not consider density and temperature dependent material properties. The thermal properties are assumed constant throughout the sintering process. The only differences in the thermal properties of PEO 1x10^5 g/mol, PEO 1x10^6 g/mol and PEO 8x10^6 g/mol which would affect the thermal profile predicted by the thermal model are the differences in melting and re-crystallization temperatures which span a 4°C range and a 5°C range respectively. Thus, there is not a significant enough difference between the thermal profiles of PEO 1x10^6 g/mol, PEO 1x10^6 g/mol and PEO 8x10^6 g/mol to warrant presenting detailed thermal model results for the later two PEOs.
6.2.2 Sintering Model Results

The sintering model results (both CMM and MS) for PEO $1 \times 10^6$ g/mol and PEO $8 \times 10^6$ g/mol are all completely unreasonable or incomplete for all laser powers with three exceptions. The results for PEO $1 \times 10^6$ g/mol, $R=10\mu$m sintered at laser powers of 1W and 1.5W, which are shown in Figure 6.34 and Figure 6.35 respectively, are reasonable. Also, the results for PEO $8 \times 10^6$ g/mol, $R=10\mu$m sintered at laser powers of 1W, shown in Figure 6.39 are reasonable. The results shown in Figure 6.36 through Figure 6.38 and Figure 6.40 are incomplete in the higher temperature regions of the liquefied volume because errors were generated in these locations. The higher laser power results for PEO $8 \times 10^6$ g/mol $R=10\mu$m were omitted for this chapter. Note: All of the model results presented in this section will be moved to the appendix in the final document.

Figure 6.34: Sintering model results for PEO $1 \times 10^6$ g/mol, $P=1.0W$, $R=10\mu$m.
Figure 6.35: Sintering model results for PEO $1\times10^6$ g/mol, $P=1.5W$, $R=10\mu m$. 
Figure 6.36: Sintering model results for PEO $1\times10^6$ g/mol, $P=2.0W$, $R=10\mu m$. 
Figure 6.37: Sintering model results for PEO $1 \times 10^6$ g/mol, $P=3.5W$, $R=10\mu m$. 
Figure 6.38: Sintering model results for PEO $1 \times 10^6$ g/mol, $P=4.9$ W, $R=10\mu$m.
Figure 6.39: Sintering model results for PEO 8x10^6 g/mol, P=1.0W, R=10µm.
6.2.3 Sintering Model Discussion
The results of the CMM and the MS model for LS of PEO 1x10^6 g/mol and PEO 8x10^6 g/mol are grossly errant for all but the P=1W and P=1.5W models for PEO 1x10^6 g/mol and P=1W for PEO 1x10^6 g/mol. The errors stem from two problems. First, the time-temperature superposition data and the equation selected to fit that data both exhibit a rapid decrease in log(aT) as the temperature increases above the reference temperature. Thus, for temperatures at the high end of the experimental rheology data and outside the range of the experimental data, the shift factor decreases to unrealistically small values. These unrealistically small shift factors result in unrealistically large times in the liquid phase at the reference temperature. Further, when the temperature reaches some large value, the shift factor becomes numerically equal to zero because the machine precision is not large enough to calculate a finite value. Division by zero is then attempted during calculation of the time in the liquid state and an error is generated for such grid points, which causes the lack of data in the higher temperature areas of the liquefied volume. The second problem, which exacerbates the first problem, is the excessively high temperatures predicted by the thermal model for the higher laser powers.

6.2.4 Observed Microstructures of Sintered Samples
The figures which span Figure 6.41 through Figure 6.45 are micrographs of scan vectors sintered at laser powers ranging from 1.0W to 4.9W, respectively, for PEO 1x10^6 g/mol, R=10µm. The figures which span Figure 6.46
through Figure 6.49 are micrographs of scan vectors sintered at laser powers ranging from 1.5W to 4.9W, respectively, for PEO 8x10^6 g/mol, R=10µm. Evidence of viscous contact growth between particles is not observed in any of the scan vectors for either molecular weight, at any laser power. However, evidence of bulk liquid flow is evident at laser powers of 3.5W and 4.9W for PEO 1x10^6 g/mol and at a laser power of 4.9W for PEO 8x10^6 g/mol. Particles which were not involved in bulk liquid flow exhibit shape and surface characteristics similar to the unsintered powder. The volume of liquid which participates in the bulk liquid flow is observed to be proportional to the laser power for PEO 1x10^6 g/mol. The volume of the liquid participating in bulk liquid flow is observed to decrease with increasing molecular weight at P=4.9W. Adhesion of the particles not participating in bulk liquid flow is observed to be by non-viscous contact.

Figure 6.41: SEM micrographs of laser sintered PEO 1x10^6 g/mol, P=1.0W, R=10µm.
Figure 6.42: SEM micrographs of laser sintered PEO 1x10^6 g/mol, P=1.5W, R=10µm.

Figure 6.43: SEM micrographs of laser sintered PEO 1x10^6 g/mol, P=2.0W, R=10µm.
Figure 6.44: SEM micrographs of laser sintered PEO 1x10^6 g/mol, P=3.5W, R=10µm.

Figure 6.45: SEM micrographs of laser sintered PEO 1x10^6 g/mol, P=4.9W, R=10µm.
Figure 6.46: SEM micrographs of laser sintered PEO 8x10^6 g/mol, P=1.5W, R=10µm.

Figure 6.47: SEM micrographs of laser sintered PEO 8x10^6 g/mol, P=2.0W, R=10µm.
**Figure 6.48:** SEM micrographs of laser sintered PEO 8x10^6 g/mol, P=3.5W, R=10µm.

**Figure 6.49:** SEM micrographs of laser sintered PEO 8x10^6 g/mol, P=4.9W, R=10µm.
6.2.5 Discussion of Sintered Sample Microstructures

The only evidence of viscous deformation in any of the scan vector micrographs shown above for PEO 1x10^6 g/mol and PEO 8x10^6 g/mol is in the regions where bulk viscous flow occurred. No viscous neck growth is observed in any of the scan vectors. No distinctive difference in the amount of contact growth is observed for LS of the two different molecular weights at a given laser power. All of the particle adhesion appears to have occurred by non-viscous means. However, without sintering model result and experimentally calculated densities, estimating whether or not the contact growth occurred by viscoelastic deformation driven by attractive surface forces is not possible. Contact growth by small unobservable regions of viscous flow cannot be ruled out as the mechanism of particle adhesion in the results presented above.

6.3 DISCUSSION OF MOLECULAR WEIGHT EFFECTS

Viscous neck formation is observed for PEO 1x10^5 g/mol and not for the two higher molecular weights. Particle adhesion is observed in the two higher molecular weights, however, no necks indicative of viscous flow are observed. Evidence of bulk viscous flow is observed during laser sintering of 10µm particles of all three molecular weights using a laser power of 4.9W. The volume of material participating in bulk viscous flow is observed to decrease as the molecular weight increases.

Values of the long-time viscoelastic component of the tensile creep compliance, D_e, for the three molecular weights of PEO are, in order of increasing molecular weight, 6.7x10^{-6} Pa^{-1}, 5.3x10^{-7} Pa^{-1} and 9.2x10^{-7} Pa^{-1}. The approximate zero-shear viscosities, η_0, are, in order of increasing molecular weight, 3.4x10^5 Pa-s, 1.1x10^8 Pa-s and 6.5x10^8 Pa-s. The range of zero-shear viscosities spans approximately three orders of magnitude and the range of the long-time viscoelastic component of the tensile creep compliance spans only one order of magnitude. The difference in the ranges of these two components of the tensile creep compliance indicates that the major difference in the deformation characteristics of these three molecular weights of PEO is in the viscous flow regime. Therefore, it can be assumed that rate of non-viscous contact growth is similar for all three molecular weights. However, because the zero-shear viscosities increase with molecular weight, the amount of time that non-viscous contact growth is the dominant contact growth mechanism increases as the molecular weight increases. Even if non-viscous contact growth is not present at all, the rate of viscous contact will depend on the molecular weight. Increasing the molecular weight will reduce the amount of viscous contact growth observed for a given particle size/processing parameter combination. The observation of viscous neck formation in the lower molecular weight polymer and not in the two higher molecular weights is in agreement with the trend of increased viscous flow as the molecular weight decreases. However, no significant distinction is observed in the contact growth characteristics of the two higher molecular weight PEOs as would be expected based on the aforementioned discussion. A possible explanation could be that the equilibrium amount of non-viscous contact has been reached and the time period in the liquid state was not long enough for viscous flow to occur for either molecular weight. From the discussion of non-viscous contact growth presented in the Introduction, it could be concluded that the equilibrium amount of non-viscous contact should be approximately equal because the D_e values are similar and the surface energies are approximately equal.

Due to the highly erroneous predictions of the time in the liquid state at the reference temperature for PEO 1x10^6 g/mol and PEO 8x10^6 g/mol, comparison of the model results for three molecular weights is not warranted.

6.4 PC

As discussed in the Materials and Methods chapter, Figure 6.50 details the LS process parameters and particle sizes of PC which were modeled and for which samples were fabricated and the microstructure investigated. The grid-spacing used in some of the PC models increased to 50µm to decrease the computing time. The higher laser power PC models with a grid spacing of 5µm required several to days to complete, thus the grid spacing was reduced.
6.4.1 Thermal Model Results

Figure 6.51 shows the maximum temperature distribution of liquefied volume predicted by the thermal model for PC powders with radii of 60 μm, 34 μm and 18 μm laser sintered at 4.9 W at bed temperatures of 100°C and 130°C. The liquefied volume predicted for the lower bed temperature (plots on the left) is significantly smaller than for the higher bed temperature (plots on the right) for all particle sizes. The maximum temperatures increase as the particle size decreases. However, direct comparisons of the temperature distributions should only be made between like models of equal particle size because relative densities of the different particle sizes are not equal, thus there are slight differences in the thermal properties of the powder bed which results in differences in bed temperatures. The maximum temperature for any location in the powder bed which has an initial temperature of 100°C is exactly 30°C lower than the maximum temperature of the same location in the powder bed which has an initial temperature of 130°C. The highest maximum temperatures predicted for the model results shown in Figure 6.51 range from 1271°C to 1500°C.
Figure 6.51: Maximum temperature distribution for PC powders laser sintered at 4.9W for three particle sizes and at two different bed temperatures.

Figure 6.52 contains plots of the distribution of average temperatures of liquefied volume, while in the liquid state, predicted by the thermal model for PC powders with radii of 60 µm, 34 µm and 18µm laser sintered at 4.9W at bed temperatures of 100°C and 130°C. The maximum average temperature for all three particles sizes falls in the range of 160°C to 210°C. The average temperatures for the lower initial powder-bed temperature are higher than for the powder bed with a higher initial temperature.
Figure 6.52: Average temperature while in the liquid state for PC powders laser sintered at 4.9W for three particle sizes and at two different bed temperatures.

6.4.2 Thermal Model Discussion

As was observed in the model predictions for PEO $1 \times 10^5$ g/mol, the temperatures predicted for sintering using a laser power of 4.9W are significantly above the degradation temperature of the polymer, which is approximately 540°C for PC. The same explanation for the excessive temperatures predicted by the model discussed in the PEO $1 \times 10^5$ g/mol section apply to PC. The temperatures predicted for PC are higher than PEO for a given laser power. The temperatures predicted for PC are higher for three reasons. First, the initial powder-bed temperatures are higher for PC. Second, the specific heat of PC is lower than PEO; thus, the temperature increase per unit of energy for equal mass will be larger for PC. Third, the enthalpy of melting reduces the temperature of PEO because energy is expended via the phase change without increasing the temperature.
Comparison of the model predictions for the two different bed temperatures leads to the conclusion that the powder-bed temperature is linearly additive; increasing the initial temperature by a given amount results in an equivalent increase in the temperature at any time. The aforementioned linear additivity of the initial bed temperature to the temperature distribution results from the use of temperature and density-independent material properties. A quantifiable, although possibly insignificant, departure from linearly additive bed temperatures would be expected if temperature and density-dependent material properties were used.

The relationship between the initial bed temperature and the average temperatures in the liquefied state is reversed from what would most likely be expected. Intuitively, one would expect that raising the initial temperature should increase the average temperature. However, the opposite is observed. Raising the initial bed temperature lowers the average temperature. The explanation for the observed effect is that a lower bed temperature results in a higher cooling rate from the maximum temperature to the liquid-to-solid phase transition temperature. Thus, the period of time the polymer is in the liquid state is longer for higher bed temperatures because the cooling rate is lower and the temperature is always decreasing, therefore the average temperature will be lower.

6.4.3 Sintering Model Results

The figures spanning Figure 6.53 through Figure 6.60 show the densification profiles (relative density as a function of position) predicted by the combined-mechanism model (CMM) and by the Mackenzie-Shuttleworth (MS) model for laser sintering of PC powders ranging in size from 60µm to 18µm at laser powers spanning the range of 1W to 4.9W and with initial bed temperatures of 100°C and 130°C. Results are not presented for all permutations of particle size/processing parameter combinations. Results are presented for permutations for which micrographs of the sintered structure are presented. The bottom graph in each of the figures is the ratio of time in the liquid phase at the reference temperature to the characteristic relaxation time at the reference temperature; this ratio is termed the $\tau$-fraction by the author.

The average, maximum and minimum densities predicted by the CMM and the MS model are stated on the respective plots along with the initial density. Recall that only positions in the powder bed which are heated into the liquid phase are shown in the plots. The relative density scale on each density plot ranges from the initial relative density, which is assumed to be the tap density of the powder, to full relative density, which is equal to one. The $\tau$-fraction scale is the same for all of the results in this section and ranges from $5 \times 10^{-6}$, which is significantly less than the time required for viscous flow to occur, to $3 \times 10^{11}$, which is significantly longer than the time required for viscous flow to occur. The model results are presented in order of decreasing particle size. For each particle size the results are presented in order of increasing laser power. For each laser power the results are presented in order of increasing initial bed temperature.

Figure 6.53 and Figure 6.54 show the densification profiles predicted by the CMM and the MS model for LS of PC R=60µm powder at P=4.9W and with initial bed temperatures of 100°C and 130°C. As mentioned in the thermal model results for PC, the major effect observed by increasing the initial bed temperature is the increase in the liquefied volume. Comparison of the average densities predicted by the two sintering models for all particle size/processing parameter combinations will be done later in this section. The penetration depth of the full density region into the bed is approximately equal for both bed temperatures. Also the CMM and the MS model are in good agreement for both initial bed temperatures.

Figure 6.55 and Figure 6.56 show the densification profiles predicted by the CMM and the MS model for LS of PC R=60µm powder at P=4.9W and with initial bed temperatures of 100°C and 130°C. Comparing the results to the R=60µm results, only a minor increase in the penetration depth of the full density region is observed for the smaller particle size. Also, as observed in the R=60µm results, the CMM and MS models are in good agreement.
Figure 6.53: Sintering model results for PC, \( R=60\mu m \), \( T_0=100^\circ C \) \( P=4.9W \).
Figure 6.54: Sintering model results for PC, $R=60\mu m$, $T_0=130^\circ C$, $P=4.9W$. 

$\rho_{\omega}=0.57$, $\rho_{\omega_{max}}=1.0$, $\rho_{\omega_{min}}=0.50$, $\rho_{\omega_{f}}=0.59$
Figure 6.55: Sintering model results for PC, $R=34\mu m$, $T_0=100^\circ C$, $P=4.9\,W$. 
Figure 6.56: Sintering model results for PC, $R=34\mu m$, $T_0=130^\circ C$, $P=4.9 W$.

Figure 6.57 and Figure 6.58 show the CMM and MS model results for laser sintering $18\mu m$ PC powder with an initial bed temperature of $130^\circ C$ at laser powers of 1.0W and 3.5W, respectively. Both models predict a limited densification for sintering at 1.0W. The agreement between the CMM and MS model is good for laser sintering at 3.5W. The predicted penetration depth of the full density region is deeper for the $R=18\mu m$ PC powder than for the larger particle sizes. Figure 6.59 and Figure 6.60 show the CMM and MS model results for laser sintering $18\mu m$ PC powder with initial bed temperatures of $100^\circ C$ and $130^\circ C$, respectively, at laser powers of 4.9W. Again the CMM and MS model results are in good agreement.
Figure 6.57: Sintering model results for PC, $R=18\mu$m, $T_0=130^\circ$C, $P=1.0$W.
Figure 6.58: Sintering model results for PC, R=18µm, T₀=130°C P=3.5W.
Figure 6.59: Sintering model results for PC, R=18µm, T₀=100°C P=4.9W.
Figure 6.61 shows plots of the average relative density as a function of particle size as predicted by the CMM and the MS model for laser sintering PC at various laser powers. Both models predict higher average relative densities for the lower initial powder-bed temperature. Taking into account the differences in the initial relative density, the average relative density of the liquefied volume is observed to increase with decreasing particle size. As was observed in the PEO 1x10^5 g/mol model results, a critical laser power is observed, below which no increase in the average relative density is predicted by the MS model. The critical laser power is approximately 0.75W for both of the initial bed temperatures. The average relative densities predicted by the CMM are larger than the predictions by the MS model. The deviation between the predictions of the two models is observed to increase as the particle size decreases.
6.4.4 *Sintering Model Discussion*

The decrease in the average density predicted by both models for the higher bed temperature results from the fact the liquefied volume is larger for the higher bed temperatures. The observed agreement in the CMM and MS model results for PC is attributed to the short relaxation time of PC and the lack of undercooling exhibited by PC.

6.4.5 *Observed Microstructures of Sintered Samples*

Table 6.2 provides a brief summary of the features of the laser sintered PC microstructures observed in the SEM micrographs presented in Figure 6.62 through Figure 6.70.
Table 6.2: General description of PC microstructure.

<table>
<thead>
<tr>
<th>Material</th>
<th>Avg. Particle Size, µm</th>
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</tr>
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<td></td>
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<td>no</td>
</tr>
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<td>Viscous neck formation</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>non-viscous contact</td>
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<td>no</td>
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</table>

Figure 6.62: SEM micrograph of laser sintered PC, R=60µm, P=4.9W, T₀=100°C.
Figure 6.63: SEM micrograph of laser sintered PC, R=60µm, P=4.9W, T₀=130°C.

Figure 6.64: SEM micrograph of laser sintered of PC, R=34µm, P=4.9W, T₀=100°C.
Figure 6.65: SEM micrograph of laser sintered of PC, $R=34\mu m$, $P=4.9W$, $T_0=130^\circ C$.

Figure 6.66: SEM micrograph of laser sintered of PC, $R=18\mu m$, $P=1.0W$, $T_0=130^\circ C$. 
Figure 6.67: SEM micrograph of laser sintered of PC, $R=18\mu m$, $P=2.0W$, $T_0=130^\circ C$.

Figure 6.68: SEM micrograph of laser sintered of PC, $R=18\mu m$, $P=3.5W$, $T_0=130^\circ C$. 
Figure 6.69: SEM micrograph of laser sintered PC, R=18µm, P=4.9W, T₀=100°C.

Figure 6.70: SEM micrograph of laser sintered PC, R=18µm, P=4.9W, T₀=130°C.
6.4.6 Discussion of Sintered Sample Microstructures

No evidence of viscoelastic contact growth was observed for LS of PC. Viscous necks were observed at all but the lowest two laser powers, 1.0W and 2.0W.

6.4.7 Comparison of Model Predictions and Experimental Results

The thermal model results predicted excessively high temperatures for sintering using laser powers of 3.5W and 4.9W, however, no smoking or degradation was observed during laser sintering of PC scan vectors for any laser power. As was the case for PEO 1x10^5 g/mol, both of the sintering models, CMM and MS, overestimate the density of laser sintered PC scan vectors as compared to the microstructures observed by SEM. The possible explanations for the overestimation of the densities by both the combined-mechanism model and the MS model, which were presented in the PEO 1x10^5 g/mol Comparison of Model Predictions and Experimental Results, apply here also.

6.5 COMPARISON OF LASER SINTERING OF SEMI-CRYSTALLINE AND AMORPHOUS POLYMERS

Previous work presented in the literature states that semi-crystalline polymers are favored over amorphous polymers because semi-crystalline polymers exhibit a more drastic decrease in viscosity at the solid-liquid phase transition than amorphous polymers. Parts fabricated from semi-crystalline polymers typically have tighter tolerances than parts fabricated from amorphous polymers. This has been attributed to the more drastic decrease in the viscosity of semi-crystalline polymers at the solid-to-liquid phase change as compared to amorphous polymers. Semi-crystalline polymers do have a more drastic decrease in viscosity at the phase transition, however, the results of the modeling effort herein lead to the conclusion that the enthalpy of melting associated with the phase change is the property which makes semi-crystalline polymers better suited for LS. An attractive feature of semi-crystalline polymers is the enthalpy associated with the solid-to-liquid phase change which acts as an energy barrier and significantly decreases the volume of material which reaches the liquid phase as compared to an amorphous material. When comparing the liquid volume predicted for any of the PC models with a bed temperature of 100°C, Figure 6.59 for example, to the liquid volume predicted for any PEO models, Figure 6.14 for example, for the same laser power, a significant difference in the size of the liquid volume is observed. The temperature change required to heat PC from 100°C to above the glass transition temperature is approximately 45°C and the temperature change required to heat PEO from 25°C to its melting temperature is approximately 45°C. The specific heats used for both materials were equal and the relative densities of the two powders are approximately equal. Thus, approximately the same fraction of the laser power is expended to heat the two polymers from the bed temperature to the solid-to-liquid phase transition. Therefore, the difference in the liquefied volumes must be attributed to the enthalpy associated with melting the semi-crystalline polymer. Additionally, qualitative comparison of PC samples fabricated using a bed temperature of 100°C and PEO samples fabricated using the same laser power supports the model prediction of a smaller liquefied volume for PEO. It can be concluded that the tighter tolerance observed for parts fabricated from semi-crystalline polymers results from the enthalpy of melting which acts as an energy barrier, thus limiting the liquefied volume.

6.6 PROPOSED APPLICATIONS OF THE OBSERVATIONS MADE TO PRACTICE

Based on the conclusion made from the model and experimental results, if one were to design or select materials for LS applications, it would be prudent to select materials with particle sizes on the order of a 1µm to enhance non-viscous contact growth and minimize the viscous flow required to reach an acceptable density. Flow additives would most likely be needed for a powder of this size to achieve sufficient powder bed densities. If the particle size is small enough that viscous flow is not needed for densification, the LS process parameters should be selected so that the polymer remains in the liquid phase for a time just longer than the relaxation time to relieve thermal stress which could lead to curling. Ideally, the relaxation time should be short enough so that excessive heating, which could lead to degradation, isn’t required to reach the relaxation time on the time scale of LS processing. The discussion just above is applicable to amorphous and semi-crystalline polymers. As discussed above the enthalpic energy barrier makes semi-crystalline polymers better suited for LS processing. Increasing the enthalpy of melting for semi-crystalline polymers is desirable for LS processing because increasing the energy barrier to liquid formation should improve part tolerances. Also, increasing the amount of under-cooling required for recrystallization to occur allows for increasing the minimum sintered density. Future efforts could benefit from using the thermal model and the combined-mechanism sintering model developed in this work to predict and/or understand the behavior of materials during LS.
1 Personal communication with Rick Booth, Austin TX, 1999.
7 CONCLUSIONS AND FUTURE WORK

7.1 THERMAL MODEL CONCLUSIONS
A one-dimensional closed-form analytical solution for heating of a semi-infinite body, with a convective boundary condition, by a moving surface heat flux was developed. The solution approximates the shape of a Gaussian energy distribution of the laser beam more accurately than previous solutions in the literature. The thermal modeling effort also showed that convective heat loss from the surface during LS has a negligible effect on the temperature distribution in the powder-bed. The average temperatures predicted by the thermal model for liquid PEO and PC during the LS process are well below the degradation temperatures of the two polymers. However, the maximum temperatures predicted by the thermal model for LS of PEO and PC are questionably high for laser powers above approximately 3.5W. The maximum temperatures predicted by the thermal model for laser powers of 3.5W and above are hundreds of degrees above the degradation temperature and no smoking or visible degradation was observed, as would be expected from the model predictions, when samples were fabricated at 3.5 and 4.9W.

7.2 THERMAL MODEL FUTURE WORK
To further improve the thermal model, an analytical solution should be developed which treats the laser energy imparted to the powder as a volumetric internal heat source as opposed to a surface heat flux as was done in this work. The use of a volumetric internal heat source should result in lower surface temperatures.

7.3 SINTERING MODEL CONCLUSION
A sintering model that combines the effects of viscoelastic deformation driven by attractive surface forces and viscous flow driven by curvature-based forces was developed. The powder-bed temperature was approximated using the thermal model developed herein. The effect of the enthalpy of melting for semi-crystalline polymers was accounted for using a temperature recovery approach. Time-temperature superposition was used to account for the temperature dependence of the tensile creep compliance. The combined-mechanism sintering model predicts higher densities than are observed experimentally. Two probable causes of the over prediction are: 1) the excessively high temperature predicted by the thermal model lead to over estimating the time in the liquid state at the reference temperature and 2) the long interaction length used for the attractive surface force results in an over estimation of the contact growth associated with viscoelastic deformation. Density predictions made using the thermal model results and the Mackenzie-Shuttleworth sintering model also over estimate the density at the higher end of the laser powers investigated. Over estimation by the Mackenzie-Shuttleworth model suggests that the excessively high temperatures are a likely cause of the over estimation by both models. As the particle size decreased, the deviation in the densities predicted by the combined-mechanism sintering model and the Mackenzie-Shuttleworth model increased. As would be expected, the densities predicted by the combined-mechanism sintering model and the Mackenzie-Shuttleworth model were observed to: increase with increasing laser power, increase with decreasing particle size and increase with increasing bed temperature. Model results for the two higher molecular weight PEOs were incomplete because of difficulties in modeling the time-temperature superposition characteristics of the materials. Thus, the dependence of the density on the molecular weight was not directly evident from model results.

Evaluation of the sintering model results leads to several conclusions about the effects of the material properties on the nature of densification during LS. First, the attractive feature of semi-crystalline polymers with respect to LS is not the drastic change in viscosity at the melting point as stated in previous work. The attractive feature is the enthalpy associated with the solid-to-liquid phase change which acts as an energy barrier and significantly decreases the volume of material which reaches the liquid phase as compared to an amorphous material. Second, the liquid-to-solid phase change for semi-crystalline polymers does not occur until some amount of under-cooling (approximately 25°C for PEO) has occurred, therefore, material which has the minimum energy required to reach the liquid state can still undergo some level of densification, most likely by non-viscous means. The combined-mechanism sintering model predicts that for an ideal system of significantly small particles, a step change in the density across the boundary between the liquefied and un-liquefied powder should exist. The step change in the density across the boundary could be as drastic as: fully dense in the region that liquefied, to loose powder in the un-liquefied region. The sintering model also shows that for a given semi-crystalline polymer, the minimum density of the sintered region is independent of laser power for a given particle size.

For both semi-crystalline and amorphous polymers, the relaxation time acts as a pseudo-energy barrier to viscous flow because for viscous flow to occur a sufficient amount of thermal energy must be input to maintain the polymer
in the liquid state for a time greater than the relaxation time. The relaxation time is dependent on the molecular weight therefore controlling the molecular weight of the polymer can control the propensity for viscous sintering. The effect of the molecular weight and subsequently the relaxation time was evident from the combined-mechanism model results, the Mackenzie-Shuttleworth model results and the PEO experimental results which all showed that viscous flow decreased as the molecular weight increased.

7.4 SINTERING MODEL FUTURE WORK
An immediate improvement in the sintering model would be to experimentally determine the interaction length of the attractive surface forces. The improvements in the thermal model should lead to improvements in the sintering model results since the temperatures from the thermal model directly affect the sintering kinetics. A more long-range goal is to develop a contact growth model which explicitly accounts for contact growth driven by attractive surface forces and curvature-based forces and considers both viscoelastic and viscous deformation.

The combined-mechanism sintering model could also be used to model oven sintering of polymer powder. Comparing density predictions made using the model to the density of samples sintered in an oven using the processing conditions model would allow for quantitative evaluation of the ability of the combined-mechanism sintering model to predict experimental behavior.

7.5 EXPERIMENTAL INVESTIGATION CONCLUSIONS
Conclusive evidence of viscoelastic contact growth driven by attractive surface forces was not observed. However, non-viscous contact growth was observed to bind the majority of the particles in samples sintered at the lower laser powers used in this work and the particles near the edges of all the samples. Qualitative investigation of the microstructure of the PEO samples using SEM showed that as the molecular weight increased for a given laser power, the amount of bulk surface flow decreased and the amount of non-viscous contact increased. Qualitatively speaking a better-developed network of viscous necks was observed in PC as compared to the PEOs. Viscous neck growth and bulk surface flow were observed to: increase with increasing laser power, increase with decreasing particle size and increase with increasing bed temperature.

7.6 EXPERIMENTAL INVESTIGATION FUTURE WORK
The contribution of viscoelastic contact growth driven by attractive surface forces to densification during LS is most easily investigated by observing of the sintered microstructure of a single scan vector. Future investigations should use spherical particles with a diameter on the order of 1 µm to allow for more definitive determinations of the contact growth mechanisms; results similar to Mazur et al’s would be desirable. Future experimental work should also investigate the microstructure of powders sintered in an oven. The microstructure of oven-sintered samples should be compared to LS samples which have an equivalent time in the liquid state at the surface as predicted by time-temperature superposition. Oven sintering would also allow for fabrication of larger samples which could be characterized using Archimedes density testing. The oven-sintered sample densities should be compared to the predictions by the combined-mechanism sintering model. If the oven-sintered samples exhibited microstructures similar to LS samples with equivalent times in the liquid state, then the contact growth mechanism for the oven-sintered and LS samples could be assumed to be the same. Thus, indirectly determining whether the contribution of viscoelastic contact growth driven by attractive surface forces to densification during LS is significant.

Future investigation into the differences between LS of amorphous and semi-crystalline polymers should include a comparison of scan vectors which result from laser sintering an amorphous polymer and a semi-crystalline polymer, of approximately the same particle size and shape and with similar rheologic properties, using conditions where the thermal energy required to heat the polymers from the initial bed temperature to the liquid state is equal. The energy required to liquefy the amorphous polymer would just be the energy associated with the specific heat, however, the thermal energy required to liquefy semi-crystalline polymer would include the enthalpy of melting and the energy associated with the specific heat. Comparing the dimensions of the two sintered samples would show whether or not the enthalpy of melting acts as an energy barrier which limits the liquefied volume in semi-crystalline polymers.

7.7 LAB-SCALE LS UNIT CONCLUSIONS
A lab-scale LS unit was constructed to fabricate test specimens for model validation and to test the applicability of materials to LS. The mechanical properties of nylon 12 samples made in the lab-scale LS unit were similar to the mechanical properties of nylon 12 samples made using a commercial LS unit.
7.8 **LAB-SCALE LS UNIT FUTURE WORK**

If the lab-scale is to be effectively used for repeated fabrication of multi-layer samples, then a fully automated powder delivery system should be built to replace the current set-up. Additionally, the beam diameter should be reduced to less than a millimeter to improve the resolution of the sintered parts. If the beam diameter is reduced, the laser power must also be reduced by using partially reflective optics so that the ratio of laser power to scan speed is in the same range as the current configuration.
Appendix A  PC Shear Creep Compliance Fit

\[\text{Off[NIntegrate::"slwcon"]}\]
\[\text{Off[General::spell]}\]
\$
\text{TextStyle} = \{\text{FontFamily} \rightarrow \text{"Arial"}, \text{FontSize} \rightarrow 12, \text{FontWeight} \rightarrow \text{Bold}\};
\]
\$\text{<< Graphics`Graphics`}

- **Input L values**

\[\text{Lt} = \{(0.00016232400, 0.00000011408),\]
\[\quad (0.00025725900, 0.00000010890), (0.00040772900, 0.000000111368),\]
\[\quad (0.00064620600, 0.00000012186), (0.00102000000, 0.00000013803),\]
\[\quad (0.00162000000, 0.00000015886), (0.00257000000, 0.00000018788),\]
\[\quad (0.00408000000, 0.00000022512), (0.00646000000, 0.00000026503),\]
\[\quad (0.01024000000, 0.00000032411), (0.01623000000, 0.00000039241),\]
\[\quad (0.02573000000, 0.00000047869), (0.04078000000, 0.00000057860),\]
\[\quad (0.06462000000, 0.00000070853), (0.08116000000, 0.00000076835),\]
\[\quad (0.1024200000, 0.00000086372), (0.1286300000, 0.00000086649),\]
\[\quad (0.2038600000, 0.00000093550), (0.3231000000, 0.00000094780),\]
\[\quad (0.5120800000, 0.00000086719), (0.8116000000, 0.00000090896),\]
\[\quad (1.2863000000, 0.00000074593), (2.0290500000, 0.00000126293),\]
\[\quad (5.0966200000, 0.00000238379), (8.1163700000, 0.00000481226),\]
\[\quad (20.2899000000, 0.00003400940), (32.15753, 0.00005740260)\};\]
\[\text{tmin} = 0.00016232400;\]
\[\text{tmax} = 32.15753;\]
Calculate and plot interpolating function

\[ p_1 = \text{LogLogListPlot}[\text{Log}[L(t), \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}]]; \]
\[ L = \text{Interpolation}[[t, \text{InterpolationOrder} \rightarrow 1], \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \]
\[ p_2 = \text{LogLogPlot}[L[t], \{t, \text{Min}, .01\}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \]
\[ p_3 = \text{LogLogPlot}[L[t], \{t, .01, \text{Max}\}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \]
\[ \text{Show}[p_1, p_2, p_3, \text{DisplayFunction} \rightarrow \$$\text{DisplayFunction}, \text{PlotRange} \rightarrow \text{All}, \text{AxesLabel} \rightarrow \{\text{"time, s"}, \text{"L (Pa s)\(^{-1}\)"}\}]; \]

Calcallate and plot \( J' \)

\[ p_4 = \text{LogLogListPlot}[\text{Table}\left(\begin{array}{c}
\text{Log}[L[\text{Int}], 3.8 \times 10^{-7} + \text{NIntegrate}\left(\frac{L[\text{Int}]}{1 + \left(\frac{\text{Int}}{\text{Min}}\right)^2 (\text{Int})^2}, \\{\text{Min}, \text{Log}[\text{Min}], \text{Max}[\text{Max}], .1\}],
\\text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100]\right), \{\text{Int}, \text{Log}[\text{Min}], \text{Log}[\text{Max}], .1\}\right], \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow 100, \text{PlotJoined} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 0]; \]
- Input experimental J' values

\[
\text{Jprimereal} = \{(0.1256000, 0.000002585548935), (0.07924790, 0.0000021877853805), (0.0500199, 0.000001861494936), (0.03154907, 0.000001595038502), (0.01990586, 0.000001478148843), (0.0125591, 0.000000659198547), (0.00499996, 0.000000472514406), (0.0019905, 0.000000384850725), (62.8000, 0.000002803610741), (39.6239510, 0.0000025621256298), (25.0009953, 0.0000015972574615), (9.9529296, 0.0000007172241846), (6.2798116, 0.0000004956064986), (3.9622451, 0.0000003395039140), (2.4999801, 0.0000002852036894), (1.5773663, 0.0000004809649773), (0.995236, 0.0000004466124960), (0.6279560, 0.0000004047541267), (0.3962120, 0.0000003648183723), (0.2499940, 0.0000003211711153), (0.1577354, 0.0000002780896377), (0.0995236, 0.0000002381859000), (0.0628000, 0.00000020879435), (62.4995024, 0.00000023916463380), (39.4341575, 0.00000049072661003), (24.8809045, 0.0000002636962747), (15.6989011, 0.00000026975920856), (9.9053003, 0.0000008243328724), (6.2498507, 0.0000007404), (3.9433860, 0.0000006306), (2.4880904, 0.0000005785), (1.5700000, 0.0000005203)) \%
\]

\[\text{p5} = \text{LogLogListPlot[Jprimereal, PlotRange \rightarrow All, DisplayFunction \rightarrow Identity, PlotStyle \rightarrow RGBColor[0, 0, 0]]};\]
show[p4, p5, plotrange -> all,
displayfunction -> $displayfunction, axeslabel -> {"time, s", "j', pa^{-1}"}]

\begin{align*}
  J_0 &= 3.8 \times 10^{-7} \text{ Pa}^{-1} \\
  J_e &= 4.1 \times 10^{-6} \text{ Pa}^{-1}
\end{align*}
Calulate and plot J'' values

Input experimental J'' values

\[ J_{\text{DP}} = \{ \{0.12560000, 0.000004370446683\}, \{0.07924790, 0.000001317616331\}, \{0.03154907, 0.000000269780616\}, \{0.01255962, 0.00000012330653\}, \{0.00792449, 0.000000072552334\}, \{0.00499996, 0.00000004815253\}, \{0.00315473, 0.000000024057432\}, \{0.00199047, 0.000000012443982\}, \{0.00125591, 0.000000006237384\}, \{0.00079242, 0.000000003246439\}, \{0.00049999, 0.000000001382486\}, \{0.00031547, 0.000000000792449\}, \{0.00019905, 0.000000000499996\}, \{0.00012560, 0.000000000315473\}, \{0.00007924, 0.000000000199047\}, \{0.00004999, 0.000000000125591\}, \{0.00003155, 0.000000000079242\}, \{0.00001991, 0.000000000049999\} \} \]

\[ \text{p6} = \text{LogLogListPlot}[J_{\text{DP}}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}] \]

\[ \text{p7} = \text{LogLogListPlot}[\text{Table} \left\{ e^{\text{int}}, \frac{e^{\text{int}}}{30000} + \text{NIntegrate}\left[ \frac{L[e^{\text{int}}]}{1 + \left( \frac{1}{e^{\text{int}}} \right)^2 \left( e^{\text{int}} \right)^2} \right], \{\ln \lambda, \log[t_{\text{min}}], \log[t_{\text{max}}} \right\} \right\}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}, \text{PlotJoined} \to \text{True}, \text{PlotStyle} \to \text{RGBColor}[0, 0, 1]] \]
Show[p6, p7, PlotRange → All, DisplayFunction → $DisplayFunction, AxesLabel → {"time, s", "J''", Pa^{-1}}}, AxesOrigin → {-4, -7}]

η₀ = 30000 Pa s

- Calculate and Plot J(t) -

p8 = LogLogListPlot[Table[{e^int, 3.8 * 10^{-7} + \frac{e^{int}}{30000} + \text{NIntegrate}[L[e^{ln}], -\frac{1}{1-e^{int}}],

{lnλ, Log[tmin], Log[tmax], .1}, MinRecursion → 7, MaxRecursion → 100}],

{lnλ, Log[tmin], Log[tmax], .1}], PlotRange → All, DisplayFunction → Identity,

PlotJoined → True, PlotStyle → RGBColor[1, 0, 1];
Show[p8, PlotRange → All, DisplayFunction → Identity,

AxesLabel → {"time, s", "J(t), Pa^{-1}"}];

Jtable = Table[{e^int, 3.8 * 10^{-7} + \frac{e^{int}}{30000} + \text{NIntegrate}[L[e^{ln}], -\frac{1}{1-e^{int}}],

{lnλ, Log[tmin], Log[tmax], .1}, MinRecursion → 7, MaxRecursion → 100}],

{lnλ, Log[tmin], Log[tmax], .1}];
Export["PCJtable.dat", Jtable]
Input $G'$ inverse

\[
G_{\text{pinv}} = \{(0.12560000, 0.0000099731), (0.07924790, 0.0000066304),
\{0.05000199, 0.0000045874\}, \{0.03154907, 0.0000012752\}, \{0.01255962, 0.0000009232\}, \{0.00792449, 0.0000007178\}, \{0.00499996, 0.0000006468\}, \{0.00199047, 0.0000005473\}, \{0.00125591, 0.0000005182\}, \{0.00079242, 0.0000005182\}, \{0.00049999, 0.0000005182\}, \{0.00019905, 0.0000005182\}, \{0.00007924, 0.0000005182\}, \{0.00003155, 0.0000005182\}, \{0.00001256, 0.0000005182\}, \{0.00000499, 0.0000005182\}, \{0.00000199, 0.0000005182\}, \{0.00000079, 0.0000005182\}, \{0.00000049, 0.0000005182\}, \{0.00000020, 0.0000005182\}, \{0.00000010, 0.0000005182\}, \{0.00000005, 0.0000005182\}, \{0.00000002, 0.0000005182\}, \{0.00000001, 0.0000005182\}, \{0.00000000, 0.0000005182\}\};
\]

\[p9 = \text{LogLogListPlot}[G_{\text{pinv}}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[0, 1, 0]];\]

\[p10 = \text{LogLogPlot}\left[\frac{t}{30000}, \{t, t_{\text{min}}, t_{\text{max}}\}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[0,1,1]\right];\]
Show[p4, p5, p8, p9, p10, PlotRange -> All, DisplayFunction -> $DisplayFunction, AxesOrigin -> {-4, -8.5}, AxesLabel -> {"time, s", "Compliance functions, Pa^{-1}"}]

Compliance functions, Pa^{-1}

- Graphics -
Appendix B  PEO 1 x10^5 g / mol Shear Creep Compliance Fit

Off[NIntegrate::"slwcon"]
Off[General::spell]
$TextStyle = {FontFamily -> "Arial",FontSize -> 12, FontWeight -> Bold};
<< Graphics`Graphics`

Input L values

Lt = {
{0.0365200, 0.00000177}, {0.0578800, 0.00000227},
{0.0811600, 0.00000262}, {0.0917400, 0.00000287}, {0.1258000, 0.00000323},
{0.1286300, 0.00000337}, {0.1454000, 0.00000361}, {0.1704400, 0.00000376},
{0.1704401, 0.00000384}, {0.1993800, 0.00000418}, {0.2038600, 0.00000430},
{0.2304400, 0.00000462}, {0.2701200, 0.00000499}, {0.2701201, 0.00000488},
{0.3159900, 0.00000538}, {0.3231000, 0.00000553}, {0.3652200, 0.00000603},
{0.4281200, 0.00000626}, {0.4281201, 0.00000658}, {0.5008100, 0.00000691},
{0.5120800, 0.00000723}, {0.5788400, 0.00000760}, {0.6785200, 0.00000831},
{0.6785201, 0.00000820}, {0.7937300, 0.00000901}, {0.8116000, 0.00000921},
{0.9174000, 0.00000998}, {1.0753800, 0.00001092}, {1.0753801, 0.00001058},
{1.2579700, 0.00001162}, {1.2863000, 0.00001184}, {1.4540000, 0.00001246},
{1.7043500, 0.00001381}, {1.7043501, 0.00001425}, {1.9937700, 0.00001517},
{2.0386700, 0.00001546}, {2.3044600, 0.00001644}, {2.7012300, 0.00001837},
{2.7012301, 0.00001861}, {3.1599400, 0.00002012}, {3.2311100, 0.00002041},
{3.6523700, 0.00002140}, {4.2812100, 0.00002495}, {4.2812101, 0.00002362},
{5.0082200, 0.00002609}, {5.1210300, 0.00002626}, {5.7868000, 0.00002763},
{6.7853400, 0.00002940}, {6.7853401, 0.00003015}, {7.9375900, 0.00003397},
{8.1163700, 0.00003407}, {9.1744900, 0.00003572}, {10.7541600, 0.00003971},
{10.7541601, 0.00004112}, {12.5837000, 0.00004484}, {12.8637300, 0.00004435},
{14.5061000, 0.00004608}, {17.0442100, 0.00005157}, {17.0443800, 0.00005286},
{19.9387800, 0.00005789}, {20.3877600, 0.00005861}, {23.0453900, 0.00006014},
{27.0132600, 0.00006710}, {27.0138400, 0.00007005}, {31.6010400, 0.00007773},
{32.3124700, 0.00007517}, {42.8128500, 0.00008826}, {42.8143100, 0.00008983},
{50.0843300, 0.00010264}, {51.2119800, 0.00010243}, {67.8551500, 0.00011473},
{67.8561900, 0.00011876}, {79.3785600, 0.00013515}, {107.5451500, 0.00015850},
{107.5451501, 0.00014964}, {170.4407900, 0.00019044},
{270.1375700, 0.00024842}, {428.1367700, 0.00025262},
{678.5252400, 0.00060362}, {1075.4252400, 0.00039499}};

tmin = 0.0365200;
tmax = 1075.4252400;
Calculate and plot interpolating function

```
p1 = LogLogListPlot[Lt, PlotRange -> All, DisplayFunction -> Identity];
L = Interpolation[Lt, InterpolationOrder -> 1];
p2 = LogLogPlot[L[t], {t, tmin, .5},
PlotRange -> All, DisplayFunction -> Identity, PlotDivision -> 1000];
p3 = LogLogPlot[L[t], {t, .5, 5}, PlotRange -> All,
DisplayFunction -> Identity, PlotDivision -> 1000];
p31 = LogLogPlot[L[t], {t, 5, tmax}, PlotRange -> All,
DisplayFunction -> Identity, PlotDivision -> 1000];
Show[p1, p2, p3, p31, DisplayFunction -> $DisplayFunction,
PlotRange -> All, AxesLabel -> {"time, s", "L, (Pa s)^{-1}"}];
```

L, (Pa s)^{-1}

Calcuulate and plot J'

```
p4 = LogLogListPlot[Table[
{e^{ln[t]*4*10^{-6} + NIntegrate[
L[e^{ln[t]}], {ln[t], Log[tmin], Log[tmax], .1}],
1 + (1/e^{ln[t]})^2 * (e^{ln[t]})^2}
MinRecursion -> 7, MaxRecursion -> 100}],
{ln[t], Log[tmin], Log[tmax], .1}],
PlotRange -> All, DisplayFunction -> Identity, PlotJoined -> True,
PlotStyle -> RGBColor[1, 0, 0]];```
Input experimental $J'$ values

$$J_{\text{primereal}} = \{(1318.8, 0.00107651), (832.0504732, 0.00089458), (525, 0.00061662), (331.2735494, 0.00050030), (209.0015848, 0.00038587), (131.88, 0.00029819), (83.21029718, 0.00022928), (52.5, 0.00017644), (33.12569075, 0.00013580), (20.90082095, 0.00010489), (13.18760437, 0.00008115), (8.320714718, 0.00005065), (5.249958201, 0.00000189), (4.13870769, 0.00000148), (3.0248746, 0.00000119), (2.08999597, 0.00000097), (1.3188, 0.00003092), (0.832045224, 0.00001864), (0.52498746, 0.00001484), (0.33124447, 0.00001198), (0.208999597, 0.00000999), (0.13188, 0.00000999), (0.09734, 0.00000999), (0.0628, 0.00000999), (0.02826, 0.00000999), (0.0178295405, 0.00000999), (0.0070980949, 0.00000630), (0.044785628, 0.00000526), (0.02826, 0.00000444));$$

\[p5 = \text{LogLogListPlot}[J_{\text{primereal}}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}, \text{PlotStyle} \to \text{RGBColor}[0,0,0]];\]
Show[p4, p5, PlotRange -> All,
DisplayFunction -> $DisplayFunction, AxesLabel -> {"time, s", "J', Pa^{-1}"}]

- Graphics -

\[ J_0 = 4 \times 10^{-6} \text{ Pa}^{-1} \]
\[ J_e = 2.0 \times 10^{-5} \text{ Pa}^{-1} \]
Calulate and plot J'' values

Input experimental J'' values

\[ J_{dp} = \{(131.8, 0.00701949), (832.0504732, 0.00427735), \]
\{(525, 0.00273568), (331.2735494, 0.00183280), (209.0015848, 0.00122900), \}
\{(131.88, 0.00083829), (83.21029718, 0.00058029), (52.5, 0.00040558), \}
\{(33.12569075, 0.00028595), (20.90082095, 0.00020368), \}
\{(13.18760437, 0.00014647), (8.320714718, 0.00010617), \}
\{(5.249958201, 0.00007762), (3.312469231, 0.00005764), \}
\{(2.08995975, 0.00004214), (1.31870769, 0.00003139), (0.832045224, 0.00002353), \}
\{(0.52498746, 0.00001778), (0.331244427, 0.00001348), (0.208999597, 0.00001030), \}
\{(0.13188, 0.00000796), (83.21029718, 0.00065150), \}
\{(52.50209005, 0.00044924), (33.12652282, 0.00031338), \}
\{(20.90115219, 0.00022158), (13.18760437, 0.00015791), \}
\{(8.320714718, 0.00011365), (5.249958201, 0.00008260), \}
\{(3.312469231, 0.00006037), (2.08995975, 0.00004458), \}
\{(1.31870769, 0.00003297), (0.832045224, 0.00002465), (0.52498746, 0.00001851), \}
\{(0.331244427, 0.00001402), (0.208999597, 0.00001070), (0.13188, 0.00000824), \}
\{(97.34, 0.00072483), (61.41124211, 0.00049561), \}
\{(24.45052875, 0.0002169), (15.42704091, 0.00017204), \}
\{(9.733707989, 0.00012375), (6.141479911, 0.00008971), \}
\{(3.874969148, 0.00006560), (2.444917766, 0.00004818), \}
\{(1.542616077, 0.00003571), (0.973331867, 0.00002659), \}
\{(0.614126817, 0.00001518), (0.387490745, 0.00001507), \}
\{(0.244889934, 0.00011146), (0.154261608, 0.00000878), \}
\{(0.09734, 0.00000678), (0.628, 0.00047896), (39.62395104, 0.00032992), \}
\{(25.00099526, 0.00023285), (15.77453468, 0.00016632), \}
\{(9.952929616, 0.00011998), (6.279811606, 0.00008754), \}
\{(3.962245104, 0.00006437), (2.499980096, 0.00004756), \}
\{(1.57736301, 0.00003542), (0.995236178, 0.00002654), \}
\{(0.627956043, 0.00002003), (0.396212011, 0.00001518), \}
\{(0.249994029, 0.00001115), (0.157735441, 0.00000888), \}
\{(0.099523618, 0.00000688), (0.0628, 0.00000538), \}
\{(28.26, 0.00023217), (17.83077797, 0.00016575), \}
\{(11.25044787, 0.00012073), (7.098540604, 0.00008861), \}
\{(4.478818327, 0.00006541), (2.825915223, 0.00004878), \}
\{(1.783010297, 0.00003655), (1.124991043, 0.00002758), \}
\{(0.709814835, 0.00002090), (0.44785628, 0.00001591), \}
\{(0.282580219, 0.00001218), (0.178295405, 0.00000796), \}
\{(0.112497313, 0.00000724), (0.070980949, 0.00000566), \}
\{(0.044785628, 0.00000444), (0.02826, 0.00000353)\};

\[ p6 = \text{LogLogListPlot}[J_{dp}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}]; \]

\[ p7 = \text{LogLogListPlot}[\text{Table}\left[\frac{e^{\text{int}}}{114000} + \text{NIntegrate}\left[\frac{L[e^{\text{int}}] \left( \frac{1}{e^{\text{int}}} \right) (e^{\text{int}})}{1 + \left( \frac{1}{e^{\text{int}}} \right)^2 (e^{\text{int}})^2} \right], \{\ln \lambda, \text{Log[tmin]}, \text{Log[tmax]}, .1\}, \text{MinRecursion} \to 7, \text{MaxRecursion} \to 100\}\}, \]
\[ \{\text{Int, Log[tmin]}, \text{Log[tmax]}, .1\}\}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}, \]
\[ \text{PlotJoined} \to \text{True}, \text{PlotStyle} \to \text{RGBColor}[0, 0, 1]; \]
Show[p6, p7, PlotRange → All, DisplayFunction → $DisplayFunction, AxesLabel → {"time, s", "J''", Pa\textsuperscript{-1}}}, AxesOrigin → {-1.65, -5.5}]

\[ \eta_0 = 114000 \text{ Pa s} \]

- Calculcate and Plot J(t) -

\[
p8 = \text{LogLogListPlot}\left[\text{Table}\left[\left\{ e^{\text{int}}, 4 \times 10^{-6} + \frac{e^{\text{int}}}{114000} + \text{NIntegrate}\left[ L[e^{\text{int}}] \left( 1 - e^{-\frac{e^{\text{int}}}{114000}} \right) \right], \{\ln(\lambda), \text{Log}[\text{tmin}], \text{Log}[\text{tmax}], .1\}\right], \text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100}\right], \{\text{int}, \text{Log}[\text{tmin}], \text{Log}[\text{tmax}], .1\}\}\right], \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotJoined} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 1]\right];
\]

Show[p8, PlotRange → All, DisplayFunction → Identity, AxesLabel → {"time, s", "J(t), Pa\textsuperscript{-1}"}]

- Graphics -
Appendix B: PEO 1x10^5 Shear Creep Compliance Fit

Jtable = Table[{{e^{int}, 4 \times 10^{-6} + e^{int}, 114000},
NIntegrate[L[e^{int}] (1 - e^{-\frac{\lambda t}{114000}}), (ln\lambda, Log[tmin], Log[tmax], .1),
MinRecursion \rightarrow 7, MaxRecursion \rightarrow 100}, {int, Log[tmin], Log[tmax], .1}];
Export["PEO100kJtable.dat", Jtable]

PEO100kJtable.dat

- Input G' inverse

Gpinv = {{1318.8, 0.0468478}, (832.0504732, 0.0213463),
(525, 0.0127537), (331.2735494, 0.0072146), (209.0015848, 0.0043002),
(131.88, 0.0026549), (83.21029718, 0.0016980), (52.5, 0.0011087),
(33.12564975, 0.0007380), (20.90082095, 0.000504),
(13.18760437, 0.0003455), (8.32071418, 0.0002422), (5.249985201, 0.0001715),
(3.312469231, 0.0001249), (2.089995975, 0.0000893), (1.31870769, 0.0000377),
(0.832045224, 0.0000483), (0.52498746, 0.0000361), (0.33124427, 0.0000271),
(0.208999597, 0.0000195), (0.13188, 0.0000159), (0.0628, 0.0000108),
(0.044785628, 0.0000090), (0.02826, 0.0000072)};

p9 = LogLogListPlot[Gpinv, PlotRange -> All,
DisplayFunction -> Identity, PlotStyle -> RGBColor[0, 1, 0]];
Appendix B: PEO $1 \times 10^5$ Shear Creep Compliance Fit

Show[p4, p5, p8, p9, p10, PlotRange -> All, DisplayFunction -> $\$DisplayFunction,
AxesOrigin -> {-1.65, -6.5}, AxesLabel -> {"time, s", "Compliance functions, Pa$^{-1}$"}]

Compliance functions, Pa$^{-1}$

- Graphics -
Appendix C  PEO 1x10^{6} g / mol Shear Creep Compliance Fit

Off[NIntegrate::"slwcon"]
Off[General::spell]
$TextStyle = \{FontFamily \rightarrow "Arial", FontSize \rightarrow 12, FontWeight \rightarrow Bold\};
<< Graphics`Graphics`
<< Statistics`DataSmoothing`

- Input L values

Lt = \{\{0.0243500, 0.000000087\}, \{0.0385900, 0.000000112\},
\{0.0611600, 0.000000126\}, \{0.0811600, 0.000000116\}, \{0.0969300, 0.000000133\},
\{0.1286300, 0.000000150\}, \{0.1536300, 0.000000161\}, \{0.2038600, 0.000000174\},
\{0.2434800, 0.000000178\}, \{0.3231000, 0.000000192\}, \{0.3858900, 0.000000205\},
\{0.4058100, 0.000000198\}, \{0.5120800, 0.000000226\}, \{0.6160000, 0.000000238\},
\{0.6431500, 0.000000241\}, \{0.6816000, 0.000000260\}, \{0.9693300, 0.000000326\},
\{1.0193200, 0.000000323\}, \{1.2863000, 0.000000302\}, \{1.5363100, 0.000000302\},
\{1.6155200, 0.000000322\}, \{2.0386700, 0.000000360\}, \{2.4391000, 0.000000364\},
\{2.5604200, 0.000000379\}, \{3.2311100, 0.000000436\}, \{3.5891200, 0.000000445\},
\{4.0579800, 0.000000440\}, \{5.1210300, 0.000000488\}, \{6.1163300, 0.000000529\},
\{6.4315100, 0.000000514\}, \{8.1163700, 0.000000593\}, \{9.6937400, 0.000000646\},
\{10.1933700, 0.000000618\}, \{12.8637300, 0.000000729\},
\{15.3635900, 0.000000807\}, \{16.1555600, 0.000000732\},
\{20.3877600, 0.000000871\}, \{25.6051400, 0.000000890\},
\{32.3124700, 0.000001066\}, \{40.5814600, 0.000001038\},
\{51.2119800, 0.000001335\}, \{64.3172800, 0.000001297\},
\{101.9353500, 0.000001572\}, \{161.5598800, 0.000001931\},
\{256.5059880, 0.000002395\}, \{405.8114100, 0.000003116\},
\{643.1846800, 0.000003952\}, \{1019.3732700, 0.000005197\},
\{1615.5362800, 0.000007400\}, \{2560.5362800, 0.000011610\}\};
tmin = 0.03147;
tmax = 2088.04;
LtAvg = MovingAverage[Lt, 2];
- Calculate and plot interpolating function

\[
p_1 = \text{LogLogListPlot}[L_t, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}];
\]
\[
p_{11} = \text{LogLogListPlot}[\text{LtAvg}, \text{PlotRange} \rightarrow \text{All},
\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 0]];
\]
\[
L = \text{Interpolation}[\text{LtAvg}, \text{InterpolationOrder} \rightarrow 1];
\]
\[
p_2 = \text{LogLogPlot}[L[t], \{t, \text{tmin}, .5\},
\quad \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000];
\]
\[
p_3 = \text{LogLogPlot}[L[t], \{t, .5, 5\}, \text{PlotRange} \rightarrow \text{All},
\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000];
\]
\[
p_{31} = \text{LogLogPlot}[L[t], \{t, 5, 100\}, \text{PlotRange} \rightarrow \text{All},
\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000];
\]
\[
p_{32} = \text{LogLogPlot}[L[t], \{t, 100, 1000\}, \text{PlotRange} \rightarrow \text{All},
\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000];
\]
\[
p_{33} = \text{LogLogPlot}[L[t], \{t, 1000, \text{tmax}\}, \text{PlotRange} \rightarrow \text{All},
\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000];
\]
\[
\text{Show}[p_1, p_{11}, p_2, p_3, p_{31}, p_{32}, p_{33}, \text{DisplayFunction} \rightarrow \$\text{DisplayFunction},
\quad \text{PlotRange} \rightarrow \text{All}, \text{AxesLabel} \rightarrow \{"time, s", "L, (Pa s)^{-1}"\}];
\]

\[L, (\text{Pa s})^{-1}\]
\section*{Calcular and plot $J'$}

\begin{verbatim}
p4 = LogLogListPlot[
  Table[
    {e^int, 1.05 \times 10^{-6} + NIntegrate[
        L[e^{ln}] / (1 + (\frac{1}{\lambda_{max}})^2 (e^{ln})^2),
        {ln \lambda, Log[tmin], Log[tmax], .1}, MinRecursion \rightarrow 7, MaxRecursion \rightarrow 100}
    ],
    {int, Log[tmin], Log[tmax], .1}], PlotRange \rightarrow All, DisplayFunction \rightarrow Identity, PlotJoined \rightarrow True, PlotStyle \rightarrow RGBColor[1, 0, 0];
\end{verbatim}

\section*{Input experimental $J'$ values}

\begin{verbatim}
Jprimereal =
  
  {{18.84, 0.000003184}, {11.88718531, 0.000002812}, {7.500298579, 0.000002515},
   {4.732360403, 0.000002271}, {2.985878885, 0.000002066},
   {1.883943482, 0.000001899}, {1.186673531, 0.000001760},
   {0.749994029, 0.000001610}, {0.47320989, 0.000001500},
   {0.298570854, 0.000001406}, {0.188386813, 0.000001324},
   {0.118863603, 0.000001250}, {0.074998209, 0.000001189},
   {0.047320632, 0.000001131}, {0.029857085, 0.000001079},
   {0.01884, 0.000001039}, {0.0628, 0.000001039}, {0.099523618, 0.000001177},
   {0.25009526, 0.000001379}, {0.1577453468, 0.000002977},
   {9.95292616, 0.000002642}, {6.279811606, 0.000002369},
   {3.962245104, 0.000002144}, {2.499980096, 0.000001943},
   {1.577366301, 0.000001777}, {0.995236178, 0.000001638},
   {0.627956043, 0.000001519}, {0.396212011, 0.000001415},
   {0.249994029, 0.000001326}, {0.157735441, 0.000001246},
   {0.099523618, 0.000001177}, {0.0628, 0.000001124}, {3140, 0.0000322004},
   {1981.072555, 0.000016656}, {1250, 0.000013249}, {788.7465461, 0.000010856},
   {497.6228209, 0.000009306}, {314, 0.000007601}, {198.1197552, 0.000006498},
   {125, 0.000005609}, {78.87069225, 0.000004885}, {49.76385939, 0.000004288},
   {31.39905803, 0.000003810}, {19.81122552, 0.000003401},
   {12.49990048, 0.000003063}, {7.886831503, 0.000002779},
   {4.976180892, 0.000002542}, {3.139780215, 0.000002340},
   {1.981060056, 0.000002165}, {1.249970144, 0.000002017},
   {0.7886777207, 0.000001887}, {0.497618089, 0.000001775}, {0.314, 0.000001684};

\end{verbatim}

\begin{verbatim}
p5 = LogLogListPlot[Jprimereal, PlotRange \rightarrow All, DisplayFunction \rightarrow Identity, PlotStyle \rightarrow RGBColor[0, 0, 0];
\end{verbatim}
Show[p4, p5, PlotRange -> All, DisplayFunction -> $DisplayFunction, AxesLabel -> {"time, s", "J', Pa^{-1}"}, AxesOrigin -> {-1.8, -6}]

- Graphics -

\[ J_0 = 1.05 \times 10^{-6} \text{ Pa}^{-1} \]
\[ J_e = 1.6 \times 10^{-6} \text{ Pa}^{-1} \]
Calulate and plot J'' values

Input experimental J'' values

\[ \text{JDp} = \{(18.84, 0.00001699), (11.88718531, 0.000001385), (7.500298579, 0.00001140), (4.732360403, 0.000000946), (2.98578885, 0.000001073), (1.88673531, 0.000000568), \} \]

\[ \text{JDp} = \{(0.47320989, 0.000001441), (0.298570854, 0.000000313), (0.18836813, 0.000000274), \} \]

\[ \text{JDp} = \{(0.074998209, 0.000000243), \} \]

\[ \text{JDp} = \{(6.279811606, 0.0000001286), \} \]

\[ \text{JDp} = \{(39.62395104, 0.0000000736), \} \]

\[ \text{JDp} = \{(314.0, 0.0000000242), \} \]

\[ \text{p6} = \text{LogLogListPlot}[\text{JDp}, \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}] \;

\[ \text{p7} = \text{LogLogListPlot}[\text{Table}\left[\left\{\frac{e^{\text{Int}}}{3.54 \times 10^7} + \text{NIntegrate}\left[\frac{L[e^{\text{Int}}]}{1 + \left(\frac{1}{e^{\text{Int}}}\right)^2 \left(e^{\text{Int}}\right)^2} \right] \right\}, \right\{\text{ln} \lambda, \text{Log}[\text{tmin}], \text{Log}[\text{tmax}], .1\}, \text{MinRecursion} \to 7, \text{MaxRecursion} \to 100\}]), \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity}, \text{PlotJoined} \to \text{True}, \text{PlotStyle} \to \text{RGBColor}[0, 0, 1]] \;

Appendix C: PEO 1x10^6 g/mol Shear Creep Compliance Fit
Show[p6, p7, PlotRange → All, DisplayFunction → $DisplayFunction, AxesLabel → {"time, s", "J\''', Pa^{-1}}}, AxesOrigin → {-1.65, -7}]

$\eta_0 = 3.54 \times 10^7 \text{ Pa s}$

- Graphics -

$p8 = \text{LogLogListPlot[Table[\{e^{int}, 1.05 \times 10^{-6} + \frac{e^{int}}{3.54 \times 10^7} + \text{NIntegrate}[L[e^{ln}] \left(1 - \frac{e^{int}}{3.54 \times 10^7}\right), \\
\{ln\lambda, \text{Log[tmin]}, \text{Log[tmax]}, .\1}, \text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100]\}], \\
\{int, \text{Log[tmin]}, \text{Log[tmax]}, .1\}], \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \\
\text{PlotJoined} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 1];}$

Show[p8, PlotRange → All, DisplayFunction → Identity, AxesLabel → {"time, s", "J(t), Pa^{-1}"}];
Appendix C: PEO 1x10^6 g/mol Shear Creep Compliance Fit

\[ J_{\text{table}} = \text{Table}\left\{ \left\{ e^{t_{\text{int}}}, 1.05 \times 10^{-6} + \frac{e^{t_{\text{int}}}}{3.54 \times 10^7} \right\} \text{NIntegrate}[L[e^{t_{\text{int}}}], \{\ln\lambda, \text{Log}[t_{\text{min}}], \text{Log}[t_{\text{max}}], .1\}, \text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100\}], \{t_{\text{int}}, \text{Log}[t_{\text{min}}], \text{Log}[t_{\text{max}}], .1\}\right\];
\text{Export["PEO1000kJtable.dat", } J_{\text{table}}] \]

- **Input G' inverse**

\[ G_{\text{pinv}} = \{\{18.84, 0.000004090\}, \{11.88718531, 0.000003494\}, \{7.500298579, 0.000003032\}, \{4.732360403, 0.000002665\}, \{2.985788885, 0.000002370\}, \{1.883943482, 0.000002134\}, \{1.188673531, 0.000001943\}, \{0.749994029, 0.000001755\}, \{0.47320989, 0.000001615\}, \{0.298570854, 0.000001498\}, \{0.188386813, 0.000001398\}, \{0.118863603, 0.000001310\}, \{0.074998209, 0.000001239\}, \{0.047320632, 0.000001174\}, \{0.029857085, 0.000001117\}, \{0.01884, 0.000001075\}, \{25.00099526, 0.000004492\}, \{20.77453468, 0.000003805\}, \{9.952929616, 0.000003267\}, \{6.279811606, 0.000002844\}, \{3.962245104, 0.000002504\}, \{2.49980096, 0.000002222\}, \{1.577366301, 0.000001992\}, \{0.995236178, 0.000001806\}, \{0.627956043, 0.000001650\}, \{0.396212011, 0.000001519\}, \{0.249994029, 0.000001410\}, \{0.157735441, 0.000001315\}, \{0.099623618, 0.000001236\}, \{0.0628, 0.000001176\}, \{3140, 0.0000042706\}, \{1981.072555, 0.000003052\}, \{1250, 0.000023322\}, \{788.7465461, 0.000001828\}, \{497.6228209, 0.000014547\}, \{314, 0.000011693\}, \{198.1197552, 0.000009524\}, \{125, 0.000007865\}, \{78.87069225, 0.000006576\}, \{49.76385939, 0.000005558\}, \{31.39905803, 0.000004763\}, \{19.81122552, 0.000004126\}, \{12.49990048, 0.000003616\}, \{7.886831503, 0.000003201\}, \{4.976180892, 0.000002869\}, \{3.139780215, 0.000002592\}, \{1.981060056, 0.000002364\}, \{1.249970144, 0.000002174\}, \{0.788677207, 0.000002013\}, \{0.497618089, 0.000001880\}, \{0.314, 0.000001772\}\};

\[ p9 = \text{LogLogListPlot}[G_{\text{pinv}}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[0, 1, 0]]; \]

\[ p10 = \text{LogLogPlot}\left[\frac{t}{3.54 \times 10^7}, \{t, \text{tmin, tmax}\}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[0, 1, 1]\right]; \]
Show[p4, p5, p8, p9, p10, PlotRange -> All, DisplayFunction -> $DisplayFunction, AxesOrigin -> {-1.65, -9}, AxesLabel -> {"time, s", "Compliance functions, Pa^{-1}"}]
APPENDIX D: PEO 8x10^6 g/mol Shear Creep Compliance Fit

Appendix D  PEO 8x10^6 g/mol Shear Creep Compliance Fit

Off[NIntegrate::"slwcon"]
Off[General::spell]
$TextStyle = {FontFamily -> "Arial", FontSize -> 12, FontWeight -> Bold};
<< Graphics`Graphics`
<< Statistics`DataSmoothing`

Input L values

Lt = {{0.0325, 0.00000008093}, {0.0515, 0.00000010224},
    {0.0812, 0.00000007863}, {0.0815, 0.00000012537}, {0.129, 0.00000009016},
    {0.1291, 0.00000012224}, {0.204, 0.00000009901}, {0.205, 0.00000015828},
    {0.323, 0.00000011333}, {0.325, 0.00000015988}, {0.512, 0.00000012898},
    {0.515, 0.00000017931}, {0.812, 0.00000014384}, {0.815, 0.00000021714},
    {1.29, 0.00000016278}, {1.291, 0.00000033482}, {2.04, 0.00000019224},
    {2.05, 0.00000023316}, {3.23, 0.00000021565}, {3.25, 0.00000029562},
    {5.12, 0.00000025537}, {5.15, 0.00000034741}, {8.12, 0.00000031214},
    {8.16, 0.00000043186}, {12.2, 0.00000061001}, {12.9, 0.00000038840},
    {12.91, 0.00000054904}, {19.3, 0.00000071412}, {20.4, 0.00000050486},
    {20.5, 0.00000067491}, {30.6, 0.00000081165}, {32.3, 0.00000071353},
    {48.5, 0.00000091232}, {51.2, 0.00000107026}, {76.8, 0.00000103152},
    {122, 0.00000118025}, {193, 0.00000135274}, {306, 0.00000157288},
    {485, 0.00000189147}, {768, 0.00000224092}, {1220, 0.00000273680},
    {1930, 0.00000326019}, {3060, 0.00000403792}, {4850, 0.00000481899},
    {7680, 0.00000652736}, {12200, 0.00000843061}, {19300, 0.00001028080},
    {30600, 0.00001564150}, {48500, 0.00001852000}, {76800, 0.00003405490}};
tmin = 0.042;
tmax = 62650;
LtAvg = MovingAverage[Lt, 2];
Calculate and plot interpolating function

\[
\begin{align*}
  p1 &= \text{LogLogListPlot}[Lt, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}]; \\
  p11 &= \text{LogLogListPlot}[LtAvg, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 0]]; \\
  L &= \text{Interpolation}[LtAvg, \text{InterpolationOrder} \rightarrow 1]; \\
  p2 &= \text{LogLogPlot}[L[t], \{t, \text{tmin}, .5\}, \\
  &\quad \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  p3 &= \text{LogLogPlot}[L[t], \{t, .5, 5\}, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  p31 &= \text{LogLogPlot}[L[t], \{t, 5, 100\}, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  p32 &= \text{LogLogPlot}[L[t], \{t, 100, 1000\}, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  p33 &= \text{LogLogPlot}[L[t], \{t, 1000, 10000\}, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  p34 &= \text{LogLogPlot}[L[t], \{t, 10000, \text{tmax}\}, \text{PlotRange} \rightarrow \text{All}, \\
  &\quad \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotDivision} \rightarrow 1000]; \\
  \text{Show}[p1, p11, p2, p3, p31, p32, p33, p34, \text{DisplayFunction} \rightarrow \$\text{DisplayFunction}, \\
  \text{PlotRange} \rightarrow \text{All}, \text{AxesLabel} \rightarrow \{\"\text{time, s}\", \"L, (Pa s)^{-1}\"\}];
\end{align*}
\]

\[
L, (\text{Pa s})^{-1}
\]
APPENDIX D: PEO 8x10^6 g/mol Shear Creep Compliance Fit

- Calculating and plotting $J'$

$$p4 = \text{LogLogListPlot}[\text{Table}[\{e^{\text{int}}, 2.25 \times 10^{-6} + \text{NIntegrate} \frac{L[e^{\text{int}}]}{1 + (\frac{1}{\text{max}})^2 (e^{\text{int}})^2},
\{\ln \lambda, \text{Log}[\text{tmin}], \text{Log}[\text{tmax}], .1\}, \text{MinRecursion} \to 7, \text{MaxRecursion} \to 100]\},
\{\text{int}, \text{Log}[\text{tmin}], \text{Log}[\text{tmax}], .1\}], \text{PlotRange} \to \text{All}, \text{DisplayFunction} \to \text{Identity},
\text{PlotJoined} \to \text{True}, \text{PlotStyle} \to \text{RGBColor}[1, 0, 0];]
$$

- Input experimental $J'$ values

$$J\text{primereal} = \{(25.12, 0.00000407707), (15.84958042, 0.00000376626),
(10.00039811, 0.00000351342), (6.309813871, 0.00000331453),
(3.981171847, 0.00000315454), (2.511924642, 0.00000301840),
(1.584898042, 0.00000291103), (0.999992038, 0.00000275683),
(0.63094652, 0.00000265683), (0.398094471, 0.00000257426),
(0.251182417, 0.00000250663), (0.158484805, 0.00000242774),
(0.099997612, 0.00000231372), (0.063094177, 0.00000231372),
(0.039809447, 0.00000226663), (0.02512, 0.0000022937),
(62.8, 0.00000435232), (39.62395104, 0.00000385944),
(25.0009526, 0.00000353085), (15.7745346, 0.00000329836),
(9.952929616, 0.00000311949), (6.279811606, 0.00000297574),
(3.962245104, 0.00000285813), (2.499980096, 0.00000275882),
(1.577366301, 0.00000267029), (0.995236178, 0.00000259532),
(0.627956043, 0.00000252908), (0.396212011, 0.00000246968),
(0.249994029, 0.00000241749), (0.157735441, 0.00000237190),
(0.099523618, 0.00000233038), (0.0628, 0.00000229417),
(94.200, 0.000005838275), (59.432.17666, 0.000004269759), (37.500, 0.00000314925),
(23.662 .39638, 0.000002696707), (14928.68463, 0.00000223712),
(9420, 0.000001834985), (59.43 .52656, 0.000001353486),
(37.50, 0.000001312444), (2366.120176, 0.00000126496),
(1492.915882, 0.00000976358), (941.9717408, 0.00000850325),
(594.3367656, 0.00000747124), (374.9971044, 0.00000660016),
(236.6049451, 0.00000587581), (149.2854268, 0.00000525823),
(94.19340646, 0.00000470932), (59.43180169, 0.00000423428),
(37.49910432, 0.00000381405), (23.6031622, 0.00000344037),
(14.92854268, 0.00000311150), (9.42, 0.00000283063));

$$p5 = \text{LogLogListPlot}[J\text{primereal}, \text{PlotRange} \to \text{All},
\text{DisplayFunction} \to \text{Identity}, \text{PlotStyle} \to \text{RGBColor}[0, 0, 0];]$
APPENDIX D: PEO 8x10^6 g/mol Shear Creep Compliance Fit

Show[p4, p5, PlotRange -> All, DisplayFunction -> $DisplayFunction, AxesLabel -> {"time, s", "J', Pa^{-1}"}, AxesOrigin -> {-1.8, -5.7}]

\[ J_0 = 2.25 \times 10^{-6} \text{ Pa}^{-1} \]
\[ J_e = 2.75 \times 10^{-6} \text{ Pa}^{-1} \]
Calulate and plot $J''$ values

Input experimental $J''$ values

$$Jp = \{(25.12, 0.00000158760), (15.84958042, 0.00000128007),
(10.00039811, 0.00000103519), (6.309813871, 0.00000086437),
(3.981171847, 0.00000073690), (2.511924642, 0.00000063215),
(1.584898042, 0.00000056124), (0.999929038, 0.00000047913),
(0.63094652, 0.00000042283), (0.398094471, 0.00000037498),
(0.251182417, 0.00000033568), (0.158484805, 0.00000030561),
(0.099997612, 0.00000027914), (0.063094177, 0.00000025989),
(0.039809447, 0.00000024954), (0.02512, 0.00000024765),
(62.8, 0.00000138265), (39.62395104, 0.00000108982),
(25.0009526, 0.00000089330), (15.77453468, 0.00000074911),
(9.95292616, 0.00000064251), (6.27981160, 0.00000055461),
(3.962245104, 0.00000048643), (2.49980096, 0.00000042787),
(1.57736301, 0.00000038100), (0.995236178, 0.00000034048),
(0.62796043, 0.00000030671), (0.396212011, 0.00000027700),
(0.249994029, 0.00000025443), (0.157735441, 0.00000023398),
(0.099523618, 0.00000022042), (0.0628, 0.00000020839),
(94200, 0.00010818788), (59432.17666, 0.00006602704), (37500, 0.00004473523),
23662.39638, 0.00003244443), (14928.68463, 0.00002403864),
(9420, 0.00001815937), (5943.592656, 0.00001358117),
(3750, 0.00001066484), (2366.120768, 0.00000833100),
(1492.915782, 0.00000662865), (941.9717408, 0.00000530725),
(594.3367656, 0.00000429246), (374.9970144, 0.00000351933),
(236.6049451, 0.00000291855), (149.2854268, 0.00000245608),
(94.19340646, 0.00000209264), (59.43180169, 0.00000179886),
(37.49910432, 0.00000156214), (23.66031622, 0.00000136566),
(14.92854268, 0.00000120091), (9.42, 0.00000105778));

p6 = LogLogListPlot[Jp, PlotRange → All, DisplayFunction → Identity];

p7 = LogLogListPlot[Table[{{eInt, eInt}/2.15*10^8 + NIntegrate[Log[1 + (1/eInt)^2 (eInt)^2], {eInt, Log[tmin], Log[tmax], .1}], MinRecursion → 7, MaxRecursion → 100}],
{Log[tmin], Log[tmax], .1}] PlotJoined → True, PlotStyle → RGBColor[0, 0, 1];
\[ \eta_0 = 2.15 \times 10^8 \text{ Pa s} \]

- Calculate and Plot J(t) -

\[
p^8 = \text{LogLogListPlot[Table[} \{e^{\text{int}}, 2.25 \times 10^{-6} + \frac{e^{\text{int}}}{2.15 \times 10^8} + \text{NIIntegrate}[L[e^{\text{ln}\lambda}] \left(1 - e^{-\frac{e^{\text{int}}}{2.15 \times 10^8}}\right), \{\text{ln}\lambda, \text{Log[tmin]}, \text{Log[tmax]}, .1\}, \text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100]\}, \{\text{int}, \text{Log[tmin]}, \text{Log[tmax]}, .1\}\}, \text{PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity}, \text{PlotJoined} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \text{RGBColor}[1, 0, 1]\};
\]

\[\text{Show[p8, PlotRange} \rightarrow \text{All}, \text{DisplayFunction} \rightarrow \text{Identity, AxesLabel} \rightarrow \{"time, s", "J(t), Pa^{-1}\}];\]
APPENDIX D: PEO 8x10^6 g/mol Shear Creep Compliance Fit

\[ J_{table} = Table\left\{ e^{ln(t)} \cdot 2.25 \times 10^{-6} + \frac{e^{ln(t)}}{2.15 \times 10^8}, \right\}
\]

\[ \text{NIntegrate}[L[e^{ln(t)}\left(1-e^{-e^{ln(t)}}\right)], \{ln(t), \text{Log[tmin]}, \text{Log[tmax]}, .1\}, \]

\[ \text{MinRecursion} \rightarrow 7, \text{MaxRecursion} \rightarrow 100\}], \{ln(t), \text{Log[tmin]}, \text{Log[tmax]}, .1\}; \]

\text{Export["PEO8000kJtable.dat", Jtable]}

---

**Input G' inverse**

\[ \text{Gpinv = \{\{25.12, 0.000004695\}, \{15.84958042, 0.000004201\}, \}
\]

\[ \{10.00039811, 0.000003818\}, \{6.309813871, 0.000003540\}, \]

\[ \{3.981171847, 0.000003327\}, \{2.511924642, 0.000003151\}, \]

\[ \{1.584990482, 0.000003019\}, \{0.999992038, 0.000002840\}, \]

\[ \{0.63094652, 0.000002724\}, \{0.398094471, 0.000002629\}, \]

\[ \{0.251182417, 0.000002546\}, \{0.158484805, 0.000002466\}, \]

\[ \{0.099997612, 0.000002404\}, \{0.063094177, 0.000002343\}, \]

\[ \{0.039809447, 0.000002294\}, \{0.02512, 0.000002257\}, \{62.8, 0.000004792\}, \]

\[ \{39.62395104, 0.000004167\}, \{25.00099526, 0.000003757\}, \]

\[ \{15.77453686, 0.000003468\}, \{9.952929616, 0.000003252\}, \]

\[ \{6.279811606, 0.000003079\}, \{3.962245104, 0.000002941\}, \]

\[ \{2.499980096, 0.000002825\}, \{1.577366301, 0.000002725\}, \]

\[ \{0.995236178, 0.000002640\}, \{0.627956043, 0.000002566\}, \]

\[ \{0.396212011, 0.000002501\}, \{0.249994029, 0.000002444\}, \]

\[ \{0.157735441, 0.000002395\}, \{0.099523618, 0.000002351\}, \]

\[ \{0.0628, 0.000002313\}, \{94200, 0.0000258863\}, \{59432.17666, 0.000144801\}, \]

\[ \{37500, 0.000092738\}, \{23662.39638, 0.000066001\}, \{14928.68463, 0.000048224\}, \]

\[ \{9420, 0.000036321\}, \{5943.592656, 0.000027848\}, \{3750, 0.000021791\}, \]

\[ \{2366.120768, 0.000017426\}, \{1492.915782, 0.000014264\}, \]

\[ \{941.9717408, 0.000011816\}, \{594.3367656, 0.000009937\}, \]

\[ \{374.9970144, 0.000008477\}, \{236.6049451, 0.000007325\}, \]

\[ \{149.2854268, 0.000006401\}, \{94.19340646, 0.000005639\}, \]

\[ \{59.43180169, 0.000004999\}, \{37.49910432, 0.000004454\}, \]

\[ \{23.66031622, 0.000003982\}, \{14.92854268, 0.000003575\}, \{9.42, 0.000003226\}\}; \]

\[ p9 = \text{LogLogListPlot}[\text{Gpinv, PlotRange} \rightarrow \text{All}, \]

\[ \text{DisplayFunction} \rightarrow \text{Identity, PlotStyle} \rightarrow \text{RGBColor[0, 1, 0]}]; \]

\[ p10 = \text{LogLogPlot}\left\{\frac{t}{2.15 \times 10^8}, \{t, \text{tmin}, \text{tmax}\}, \text{PlotRange} \rightarrow \text{All}, \right\]

\[ \text{DisplayFunction} \rightarrow \text{Identity, PlotStyle} \rightarrow \text{RGBColor[0, 1, 1]}]; \]
Show[p4, p5, p8, p9, p10, PlotRange → All, DisplayFunction → $DisplayFunction, AxesOrigin → {-1.65, -9}, AxesLabel → {"time, s", "Compliance functions, Pa⁻¹"}]

Compliance functions, Pa⁻¹

- Graphics -
E SOLUTION TO HEATING BY A MOVING LINE FLUX

The solution presented in this section details the problem outlined in the Thermal Modeling chapter in which the beam energy is assumed to be a moving line flux. Since heat conduction is only being considered in the z-direction, the system is simplified to an instantaneous point flux acting at the boundary of a one-dimensional object. The variable definitions stated in the Thermal Modeling chapter are used in this solution. The partial differential equation, flux/convection boundary condition, infinite boundary condition, and initial condition are defined respectively in, [E.1], [E.2], [E.3] and [E.4].

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{for } z > 0, \quad t > 0 \quad \text{[E.1]}
\]

\[
-k \frac{\partial T}{\partial z} \bigg|_{z=0} = Q + h(T_{\infty} - T(0,t)) \quad \text{for } t > 0 \quad \text{[E.2]}
\]

\[
T(z,t) = T_0 \quad \text{as } z \to \infty \quad \text{[E.3]}
\]

\[
T(z,0) = T_0 \quad \text{[E.4]}
\]

The beam energy, Q, in [E.2] is defined by [E.5]. \( \delta(t-\tau) \) is the Dirac Delta function which is equal to zero for all times not equal to \( \tau \). \( q \) is beam intensity which can vary over the length of the line flux.

\[
Q = q \delta(t-\tau) \quad \text{[E.5]}
\]

The solution of the problem defined above can be obtained by using the Laplace transform technique. The Laplace transform with respect to time, where \( s \) is the transform variable, of Equations [E.1], [E.2], [E.3] and [E.4] results in:

\[
\frac{d^2 \bar{T}}{dz^2} - s \frac{\bar{T}}{\alpha} + \frac{T_0}{\alpha} = 0 \quad \text{[E.6]}
\]

\[
\frac{d \bar{T}}{dz} \bigg|_{z=0} = -q e^{-s\tau} \frac{k}{k} \frac{h T_{\infty}}{k} + \frac{h}{k} \bar{T} \bigg|_{z=0} \quad \text{[E.7]}
\]

\[
\bar{T}(z) = \frac{T_0}{s} \quad \text{as } z \to \infty \quad \text{[E.8]}
\]


\[
\bar{T}(z) = C_1 e^{\frac{\sqrt{s}}{\sqrt{\alpha}}z} + C_2 e^{\frac{-\sqrt{s}}{\sqrt{\alpha}}z} + \frac{T_0}{s} \quad \text{[E.9]}
\]

Boundary condition [E.8] requires that:

\[
C_2 = 0 \quad \text{[E.10]}
\]

Solving for \( C_1 \) using [E.7] results in:
\[ C_1 = \frac{H(T_x - T_0)}{s(\frac{\alpha}{H} + H)} + \frac{qe^{-ts}}{k(\frac{\alpha}{H} + H)} \]  

\[ [E.11] \]

Where,

\[ H = \frac{h}{k} \]  

\[ [E.12] \]

Thus, the solution to the transformed equation is:

\[ \overline{T}(z) = \left( \frac{H(T_x - T_0)}{s(\frac{\alpha}{H} + H)} + \frac{qe^{-ts}}{k(\frac{\alpha}{H} + H)} \right) e^{-\frac{\sqrt{\alpha}z}{s}} + \frac{T_0}{s} \]  

\[ [E.13] \]

To determine the final time dependent solution the inverse Laplace transform of [E.13] must be obtained. The following inverse transforms, [E.14], [E.15], [E.16] and [E.18] are applicable.

\[ \frac{a e^{-k\sqrt{s}}}{s(a + \sqrt{s})}(k \geq 0) \xrightarrow{L^{-1}} -e^{ako} e^{s^2a} \text{Erfc} \left( a\sqrt{t} + \frac{k}{2\sqrt{t}} \right) + \text{Erfc} \left( \frac{k}{2\sqrt{t}} \right) \]  

\[ [E.14] \]

\[ e^{-as} F(s) \xrightarrow{L^{-1}} f(t-a)U(t-a) \]  

\[ [E.15] \]

\[ \frac{e^{-k\sqrt{s}}}{a + \sqrt{s}}(k \geq 0) \xrightarrow{L^{-1}} \frac{1}{\sqrt{\pi t}} e^{-\frac{t^2}{a}} - a e^{ako} e^{s^2a} \text{Erfc} \left( a\sqrt{t} + \frac{k}{2\sqrt{t}} \right) \]  

\[ [E.16] \]

\[ \frac{k}{s} \xrightarrow{L^{-1}} k \]  

\[ [E.17] \]

Inverting the solution yields:

\[ T(z,t) = T_0 + (T_x - T_0) \left( -e^{H^2z} e^{H^2at} \text{Erfc} \left( \frac{H\sqrt{\alpha}t + z}{\sqrt{2\alpha t}} \right) + \text{Erfc} \left( \frac{z}{2\sqrt{\alpha t}} \right) \right) + U(t-\tau) \frac{q\sqrt{\alpha}}{k} \]  

\[ -\frac{1}{\sqrt{\pi (t-\tau)}} e^{-\frac{t^2}{\alpha(t-\tau)}} - H\sqrt{\alpha} e^{H\sqrt{\alpha}(t-\tau)} \text{Erfc} \left( H\sqrt{\alpha}t - \tau + \frac{z}{2\sqrt{\alpha(t-\tau)}} \right) \]  

\[ [E.18] \]

Where \( U(t-\tau) \) is the unit step function at time \( \tau \). \( T(z,t) \) is the solution to heating of a 1-dimensional system by an instantaneous point flux acting at \( t=\tau \) at the \( z=0 \) boundary.

**APPENDIX E REFERENCE**

F. SOLUTION TO HEATING BY A MOVING SQUARE FLUX

The solution presented in this section details the problem outlined in the Thermal Modeling chapter in which the beam energy is assumed to be a moving square flux. Since heat conduction is only being considered in the z-direction, the system is simplified to a square flux acting at the boundary of a one-dimensional system. The variable definitions stated in the Thermal Modeling chapter are used in this solution. The partial differential equation, flux/convection boundary condition, infinite boundary condition, and initial condition are defined respectively in, [F.1], [F.2], [F.3] and [F.4].

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{for } z > 0, \quad t > 0 \tag{F.1}
\]

\[-k \frac{\partial T}{\partial z}_{z=0} = Q + h(T_\infty - T(0,t)) \quad \text{for } t > 0 \tag{F.2}\]

\[T(z,t) = T_0 \quad \text{as } z \to \infty \tag{F.3}\]

\[T(z,0) = T_0 \tag{F.4}\]

The beam energy, Q, in [F.2] is defined by [F.5]. \(U(t-\tau)\) is the unit step function which is equal to zero for all times less than \(\tau\). \(q'\) is beam intensity per unit time acting between \(\tau_{on}\) and \(\tau_{off}\).

\[Q = q'(U(t-\tau_{on}) - U(t-\tau_{off})) \tag{F.5}\]

The solution of the problem defined above can be obtained by using the Laplace transform technique. The Laplace transform with respect to time, where \(s\) is the transform variable, of Equations [F.1], [F.2], [F.3] and [F.4] is:

\[
\frac{d^2 \overline{T}}{dz^2} - \frac{s}{\alpha} \overline{T} + \frac{T_0}{\alpha} = 0 \tag{F.6}
\]

\[
\frac{d \overline{T}}{dz} {z=0} = -q' \left( e^{-\tau_{on} s} - e^{-\tau_{off} s} \right) \frac{h}{s k} T_\infty + \frac{h}{k} \overline{T}_{z=0} \tag{F.7}
\]

\[\overline{T}(z) = \frac{T_0}{s} \quad \text{as } z \to \infty \tag{F.8}\]


\[\overline{T}(z) = C_1 e^{\sqrt{s}z} + C_2 e^{-\sqrt{s}z} + \frac{T_0}{s} \tag{F.9}\]

Boundary condition [F.8] requires that:

\[C_2 = 0 \tag{F.10}\]

Solving for \(C_1\) using [F.7] results in:
C_1 = \frac{H (T_\infty - T_0)}{s \left( \frac{\nu}{\sqrt{\alpha}} + H \right)} + \frac{q(e^{-\tau_{on}^s} - e^{-\tau_{off}^s})}{s k \left( \frac{\nu}{\sqrt{\alpha}} + H \right)} \tag{F.11}

Where,

H = \frac{h}{k} \tag{F.12}

Thus, the solution to the transformed equation is:

\bar{T}(z) = \left( \frac{H (T_\infty - T_0)}{s \left( \frac{\nu}{\sqrt{\alpha}} + H \right)} + \frac{q(e^{-\tau_{on}^s} - e^{-\tau_{off}^s})}{s k \left( \frac{\nu}{\sqrt{\alpha}} + H \right)} \right) \frac{e^{-\frac{\nu z}{\sqrt{\alpha}}} + T_0}{s} \tag{F.13}

To obtain the final time dependent solution the inverse Laplace transform of \[F.13\] must be obtained. The following inverse transforms, \[F.14\]^1, \[F.15\]^2 and \[F.16\]^3 are applicable.

\[
\frac{a e^{-k \sqrt{s}}}{s(a + \sqrt{s})} (k \geq 0) \xrightarrow{L^{-1}} -e^{ak} \text{Erfc} \left( \frac{ak + \frac{k}{2\sqrt{t}}}{\sqrt{t}} \right) + \text{Erfc} \left( \frac{\frac{k}{2\sqrt{t}}}{\sqrt{t}} \right) \tag{F.14}
\]

\[
e^{-as} F(s) \xrightarrow{L^{-1}} f(t - a) U(t - a) \tag{F.15}
\]

\[
\frac{k}{s} \xrightarrow{L^{-1}} k \tag{F.16}
\]

Inverting the solution yields:

\[
T(z,t) = T_0 + (T_\infty - T_0) \left\{ -e^{Hz} e^{H^2 \alpha t} \text{Erfc} \left( H \sqrt{\alpha t} + \frac{z}{2\sqrt{\alpha t}} \right) + \text{Erfc} \left( \frac{z}{2\sqrt{\alpha t}} \right) \right\} \tag{F.17}
\]

\[
+ U(t - \tau_{on}) \frac{q}{h} \left\{ -e^{Hz} e^{H^2 \alpha (t - \tau_{on})} \text{Erfc} \left( H \sqrt{\alpha (t - \tau_{on})} + \frac{z}{2\sqrt{\alpha (t - \tau_{on})}} \right) + \text{Erfc} \left( \frac{z}{2\sqrt{\alpha (t - \tau_{on})}} \right) \right\}
\]

\[
- U(t - \tau_{off}) \frac{q}{h} \left\{ -e^{Hz} e^{H^2 \alpha (t - \tau_{off})} \text{Erfc} \left( H \sqrt{\alpha (t - \tau_{off})} + \frac{z}{2\sqrt{\alpha (t - \tau_{off})}} \right) + \text{Erfc} \left( \frac{z}{2\sqrt{\alpha (t - \tau_{off})}} \right) \right\}
\]

\[T(z,t)\] is the solution to heating of a 1-dimensional system by an square flux acting over \(\tau_{on} < t < \tau_{off}\) at the \(z = 0\) boundary.

APPENDIX F REFERENCES


G  SOLUTION TO HEATING BY A MOVING TRIANGULAR FLUX

The solution presented below is to the problem outlined in the Thermal Modeling chapter in which the beam energy is assumed to be a moving triangular flux. Since heat conduction is only being considered in the z-direction, the system is simplified to a triangular flux acting at the boundary of a one-dimensional system. The variable definitions stated in the Thermal Modeling chapter are used herein. The partial differential equation, flux/convection boundary condition, infinite boundary condition, and initial condition are defined respectively in, [G.1], [G.2], [G.3] and [G.4].

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{for} \ z > 0, \ t > 0 \quad [G.1]
\]
\[-k \frac{\partial T}{\partial z}_{z=0} = Q + h(T_{\infty} - T(0,t)) \quad \text{for} \ t > 0 \quad [G.2]
\]
\[T(z,t) = T_0 \quad \text{as} \ z \to \infty \quad [G.3]
\]
\[T(z,0) = T_0 \quad [G.4]
\]

The beam energy, Q, in [G.2] is defined by [G.5]. \(U(t-\tau)\) is the unit step function which is equal to zero for all times less than \(\tau\). \(q''\) is beam intensity per unit time. The fact that the beam energy term is comprised of three terms of the same functional form, [G.6], allows one to simplify Q used in the solution to the PDE, [G.7], and then use the superposition principal to add the additional terms to the final solution.

\[
Q = q''(t - \tau_{off})U(t - \tau_{off}) - 2(t - \tau_{mid})U(t - \tau_{mid}) + (t - \tau_{on})U(t - \tau_{on}) \quad [G.5]
\]
\[(t - \tau^*)U(t - \tau^*) \quad [G.6]
\]
\[
Q^* = q''(t - \tau^*)U(t - \tau^*) \quad [G.7]
\]

The solution of the problem defined above can be obtained by using the Laplace transform technique. The Laplace transform with respect to time, where \(s\) is the transform variable, of Equations [G.1], [G.2], [G.3] and [G.4] is:

\[
\frac{d^2 \tilde{T}}{dz^2} - \frac{s}{\alpha} \frac{\partial \tilde{T}}{\partial z} + \frac{T_0}{\alpha} = 0 \quad [G.8]
\]
\[
\frac{d \tilde{T}}{dz}_{z=0} = \frac{-q''(e^{-s}\tau^*)}{s^2 k} - \frac{h \frac{T_{\infty}}{k \tau}}{s} + \frac{h T_{z=0}}{k} \quad [G.9]
\]
\[
\tilde{T}(z) = \frac{T_0}{s} \quad \text{as} \ z \to \infty \quad [G.10]
\]


\[
\tilde{T}(z) = C_1 e^{-\frac{s}{\sqrt{\alpha}}} + C_2 e^{\frac{s}{\sqrt{\alpha}}} + \frac{T_0}{s} \quad [G.11]
\]
Boundary condition [G.10] requires that:

\[ C_2 = 0 \]  

[S.12]

Solving for \( C_1 \) using [G.9] results in:

\[ C_1 = \frac{H(T_x - T_0)}{s(\sqrt{s} + H)} + \frac{q''(e^{-\tau s})}{s^2 k(\sqrt{s} + H)} \]  

[G.13]

Where,

\[ H = \frac{h}{k} \]  

[G.14]

Thus, the solution to the transformed problem is:

\[ \overline{T}(z) = \frac{H\sqrt{\alpha}}{s(\sqrt{s} + H\sqrt{\alpha})} e^{\frac{-\sqrt{s}}{\sqrt{\alpha}}} + \frac{q''H\sqrt{\alpha}(e^{-\tau s})}{h s^2(\sqrt{s} + H\sqrt{\alpha})} e^{\frac{-\sqrt{s}}{\sqrt{\alpha}}} + \frac{T_0}{s} \]  

[G.15]

To obtain the final time dependent solution the inverse Laplace transform of [G.15] must be obtained. The following inverse transforms, [G.16]1, [G.17]2 and [G.18]3 are applicable.

\[ \frac{a e^{-k\sqrt{s}}}{s(a + \sqrt{s})}(k \geq 0) \xrightarrow{L^{-1}} -e^{ak} a^{2} \text{erfc}\left(a\sqrt{t} + \frac{k}{2\sqrt{t}}\right) + \text{erfc}\left(\frac{k}{2\sqrt{t}}\right) \]  

[G.16]

\[ e^{-as} F(s) \xrightarrow{L^{-1}} f(t-a)U(t-a) \]  

[G.17]

\[ \frac{k}{s} \xrightarrow{L^{-1}} k \]  

[G.18]

The inverse transforms of the first and third terms in [G.15] can be directly obtained using [G.16] and [G.18], respectively. Obtaining the inverse Laplace transform of the second term is more involved; the first step is convolution, [G.19], of [G.20] and [G.21] for which the inverse transforms are [G.16] and [G.18], respectively. The second step, invoking [G.17] on the result of the convolution gives the inverse transform of the second term. Note: \( \tau \) is a dummy variable used in convolution and is not the same as \( \tau^{*} \).

\[ y(t) = \int_{0}^{t} f(t-\tau) g(\tau) \, d\tau \]  

[G.19]

\[ f(t-\tau) = L^{-1}\left(\frac{1}{s}\right)_{t\rightarrow t-\tau} = 1 \]  

[G.20]
APPENDIX G: Triangular Flux Solution

\[ g(\tau) = L^{-1}\left(\frac{H\sqrt{\alpha}e^{\frac{-\sqrt{s}}{\sqrt{s}+H}}}{s(\sqrt{s}+H\sqrt{\alpha})}\right) = -e^{Hz}e^{\alpha H^2 z}\text{Erfc}\left(H\sqrt{\alpha\tau} + \frac{z}{2\sqrt{\alpha\tau}}\right) + \text{Erfc}\left(\frac{z}{2\sqrt{\alpha\tau}}\right) \]  \[ \text{[G.21]} \]


\[ \int_{0}^{t} -e^{Hz}e^{\alpha H^2 z}\text{Erfc}\left(H\sqrt{\alpha\tau} + \frac{z}{2\sqrt{\alpha\tau}}\right) + \text{Erfc}\left(\frac{z}{2\sqrt{\alpha\tau}}\right) d\tau \]

\[ \text{[G.22]} \]

[G.22] can separated into two terms which be can integrated separately, [G.23] and [G.24]. Integration of the first term is exact, as shown. Exact integration of the second term, [G.24], is not possible; therefore a simplifying assumption will be used to obtain a solution by integration-by-parts, [G.25].

\[ \text{Term1} = \int_{0}^{t} \text{Erfc}\left(\frac{z}{2\sqrt{\alpha\tau}}\right) d\tau = \frac{1}{2\alpha} \left( z^2 - \frac{2z^2}{\sqrt{\pi}} e^{\frac{z^2}{4\alpha t}} + 2\alpha t - (z^2 + 2\alpha t) \text{Erf}\left(\frac{z}{2\sqrt{\alpha t}}\right) \right) \]

\[ \text{[G.23]} \]

\[ \text{For } t > 0 \text{ and } \text{Re}\left(\frac{z}{\sqrt{\alpha}}\right) > 0 \]

\[ \text{Term2} = \int_{0}^{t} -e^{Hz}e^{\alpha H^2 z}\text{Erfc}\left(H\sqrt{\alpha\tau} + \frac{z}{2\sqrt{\alpha\tau}}\right) d\tau \]

\[ \int_{a}^{b} u \, dv = u(b)v(b) - u(a)v(a) - \int_{a}^{b} v \, du \]

\[ \text{[G.25]} \]

To integrate [G.24] \( u \) and \( dv \) are chosen as [G.26] and [G.28] and their respective derivative and integral are [G.27] and [G.29].

\[ u(\tau) = \text{Erfc}\left(H\sqrt{\alpha\tau} + \frac{z}{2\sqrt{\alpha\tau}}\right) \]

\[ \text{[G.26]} \]

\[ du = -2e^{\left(\frac{z}{2\sqrt{\alpha\tau}+H\sqrt{\alpha}}\right)^2} \left( -\frac{z}{4\sqrt{\alpha\tau}^3} + \frac{H\sqrt{\alpha}}{2\sqrt{\tau}} \right) \]

\[ \text{[G.27]} \]

\[ dv = e^{Hz}e^{\alpha H^2 \tau} d\tau \]

\[ \text{[G.28]} \]

\[ v(\tau) = -\frac{e^{Hz+H^2\alpha\tau}}{H^2\alpha} \]

\[ \text{[G.29]} \]
APPENDIX G: Triangular Flux Solution

Difficulty arises due to the fact that $u(0)$ results in division by zero. However the limit of $u(\tau)$ as $\tau$ approaches zero from the left can be investigated.

The value of $u(\tau)$ ranges from 0 to 1 for positive values of $z$ and $t$. Setting $z=0$, the limit of $u(\tau)$ as $\tau$ approaches zero from the left is 1, by L'Hôpital’s rule for forms of the type $0/0$. However, for non-zero values of $z$, $u(\tau)$ approaches zero from the left as is shown in Figure G.1. Since the temperature at $z=0$ is but a single point and will ultimately be outside the range of the final solution, the later limit, $u(0)=0$ will be used. Thus, evaluation of the integral in [G.24] results in [G.30] and the result of convolution is [G.31].

Figure G.1: $u(\tau)$ for several values of $z$. 

\[ Term2 = \int_a^b u \, dv = u(b) \, v(b) - u(a) \, v(a) - \int_a^b v \, du \]

\[ = u(t) \, v(t) - v(0) - \int_0^\tau \left( - \frac{e^{\frac{H^2 \alpha^2 \tau^2}{2}}}{H^2 \alpha} \right) \left( -2e^{-\frac{z^2}{2\sqrt{\pi} \alpha t}} \frac{z}{\sqrt{\pi}} + \frac{H}{2\sqrt{\tau}} \right) \, d\tau \]

\[ = - \frac{2\sqrt{\pi} z - 2H\sqrt{\pi} z^2 + 4H\alpha t e^{\frac{z^2}{2\alpha t}} + 2\sqrt{\pi} z \, + 2\sqrt{\pi} z \, \text{Erf} \left( \frac{\sqrt{\pi}}{2\sqrt{t}} \right) + 2H\sqrt{\pi} z^2 \, \text{Erf} \left( \frac{1}{2} \frac{z^2}{\sqrt{\alpha t}} \right) }{2\alpha^{3/2} H^2 \sqrt{\pi} z^2 \alpha} \]

\[ = \frac{e^{\frac{H^2 \alpha^2 \tau^2}{2}} \text{Erf} \left( \frac{z}{2\sqrt{\alpha t}} + H\sqrt{\alpha t} \right)}{H^2 \alpha} \]

For $t > 0$ and $\text{Re} \left( \frac{z^2}{\alpha} \right) > 0$
\[y(t) = \text{Term1} + \text{Term2} = \]
\[-2\sqrt{\pi}z - 2H\sqrt{\pi}z^2 + 4H\alpha e^{-\frac{z^2}{4H\alpha t}} + 2\sqrt{\pi}z\text{Erf}\left(\frac{z}{2\sqrt{t}}\right) + 2H\sqrt{\pi}z^2\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)\]
\[= \frac{e^{Hz^2+H\alpha t} \text{Erfc}\left(\frac{z}{2\sqrt{t}}\right) + 2\alpha t - \left(z^2 + 2\alpha t\right)\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)}{2\alpha}
\]

The final step in obtaining the inverse Laplace transform of the second term in [G.15] is to apply [G.17] which results in [G.32].

\[L^{-1}\left(\frac{q''H\sqrt{\alpha}e^{-\gamma t}}{h^2(z + H/\sqrt{\alpha})}\right) =
\]
\[-2\sqrt{\pi}z - 2H\sqrt{\pi}z^2 + 4e^{-\frac{z^2}{4H\alpha t}} H(t - \tau^*) \left(\frac{z}{2\sqrt{t}}\right) + 2\sqrt{\pi}z^2\text{Erf}\left(\frac{z}{2\sqrt{t}}\right) + 2H\sqrt{\pi}z^2\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)\]
\[\frac{2H^2\sqrt{\pi}}{\sqrt{\alpha}} \frac{z^2 - 2e^{-\frac{z^2}{4H\alpha t}} \sqrt{\pi} + 2(t - \tau^*)a - (z^2 + 2(t - \tau^*)a)\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)}{2\alpha} - \frac{e^{Hz^2+H\alpha t} (t - \tau^*)a \text{Erfc}\left(\frac{z}{2\sqrt{t}}\right) + H\sqrt{\alpha}(t - \tau^*)}{H^2 \alpha}\]

The partial solution (recall assumption [G.7]) to the temperature as a function of depth into the bed is given by [G.33].

\[T(x,t) = T_b + (T_a - T_b)\left(-e^{Hz^2+H\alpha t} \text{Erfc}\left(H\sqrt{\alpha t} + \frac{z}{2\sqrt{\alpha t}}\right) + \text{Erf}\left(\frac{z}{2\sqrt{t}}\right)\right) + \]
\[-2\sqrt{\pi}z - 2H\sqrt{\pi}z^2 + 4e^{-\frac{z^2}{4H\alpha t}} H(t - \tau^*) \left(\frac{z}{2\sqrt{t}}\right) + 2\sqrt{\pi}z^2\text{Erf}\left(\frac{z}{2\sqrt{t}}\right) + 2H\sqrt{\pi}z^2\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)\]
\[\frac{2H^2\sqrt{\pi}}{\sqrt{\alpha}} \frac{z^2 - 2e^{-\frac{z^2}{4H\alpha t}} \sqrt{\pi} + 2(t - \tau^*)a - (z^2 + 2(t - \tau^*)a)\text{Erf}\left(\frac{z}{2\sqrt{t}}\right)}{2\alpha} - \frac{e^{Hz^2+H\alpha t} (t - \tau^*)a \text{Erfc}\left(\frac{z}{2\sqrt{t}}\right) + H\sqrt{\alpha}(t - \tau^*)}{H^2 \alpha}\]
APPENDIX G: Triangular Flux Solution

Using the superposition principle the full solution to heating of a one-dimensional system by triangular flux is:

\[
T(x,t) = T_0 + (T_u - T_0) \left( -e^{Hx} \text{Erfc} \left( \frac{H \sqrt{\alpha t} + \frac{z}{2 \sqrt{\alpha t}}}{2} \right) + \text{Erf} \left( \frac{z}{2 \sqrt{\alpha t}} \right) \right) + \\
\frac{\varphi}{\kappa} \frac{U(t - \tau_{off})}{2} \left( -2 \sqrt{\frac{\pi}{\alpha}} z - 2H \sqrt{\frac{\alpha}{\pi}} \frac{\varphi}{\kappa} \sqrt{4 \pi (t - \tau_{off})} + 2 \sqrt{\frac{\pi}{\alpha}} \frac{\varphi}{\kappa} z \text{Erf} \left( \frac{1}{2} \sqrt{\frac{t}{\alpha (t - \tau_{off})}} \right) + 2H \sqrt{\frac{\alpha}{\pi}} \frac{\varphi}{\kappa} z \text{Erf} \left( \frac{1}{2} \sqrt{\frac{t}{\alpha (t - \tau_{off})}} \right) \right) + \\
\frac{z^2 - 2 \frac{\varphi}{\kappa} \sqrt{\frac{\alpha}{\pi}} (t - \tau_{off}) + 2(t - \tau_{off}) \alpha \text{Erf} \left( \frac{z}{2 \sqrt{\alpha (t - \tau_{off})}} \right) + H \sqrt{\alpha (t - \tau_{off})} \right) \right) + \\
2U(t - \tau_{on}) \left( -2 \sqrt{\frac{\pi}{\alpha}} z - 2H \sqrt{\frac{\alpha}{\pi}} \frac{\varphi}{\kappa} \sqrt{4 \pi (t - \tau_{on})} + 2 \sqrt{\frac{\pi}{\alpha}} \frac{\varphi}{\kappa} z \text{Erf} \left( \frac{1}{2} \sqrt{\frac{t}{\alpha (t - \tau_{on})}} \right) + 2H \sqrt{\frac{\alpha}{\pi}} \frac{\varphi}{\kappa} z \text{Erf} \left( \frac{1}{2} \sqrt{\frac{t}{\alpha (t - \tau_{on})}} \right) \right) + \\
\frac{z^2 - 2 \frac{\varphi}{\kappa} \sqrt{\frac{\alpha}{\pi}} (t - \tau_{on}) + 2(t - \tau_{on}) \alpha \text{Erf} \left( \frac{z}{2 \sqrt{\alpha (t - \tau_{on})}} \right) + H \sqrt{\alpha (t - \tau_{on})} \right) \right) \right) \right)
\]

\[G.34\]

APPENDIX G REFERENCES

H SOLUTION TO HEATING BY A MOVING TRIANGULAR FLUX

The solution presented below is to the problem outlined in the Thermal Modeling chapter in which the beam energy is assumed to be a moving triangular flux. Since heat conduction is only being considered in the z-direction, the system is simplified to a triangular flux acting at the boundary of one-dimensional system. The variable definitions stated in the Thermal Modeling chapter are used herein. The partial differential equation, flux boundary condition, infinite boundary condition, and initial condition are defined respectively in [H.1], [H.2], [H.3] and [H.4].

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \text{for } z > 0, \quad t > 0 \quad [H.1]
\]

\[-k \frac{\partial T}{\partial z} \bigg|_{z=0} = Q \quad \text{for } t > 0 \quad [H.2]
\]

\[T(z,t) = T_i \quad \text{as } z \to \infty \quad [H.3]
\]

\[T(z,0) = T_0 \quad [H.4]
\]

The beam energy, Q, in [H.2] is defined by [H.5]. \(U(t-\tau)\) is the unit step function which is equal to zero for all times less than \(\tau\). \(q''\) is beam intensity per unit time. The fact that the beam energy term is comprised of three terms of the same functional form, [H.6], allows to simplify Q used in the solution to the PDE, [H.7], and then use the superposition principle to add the additional terms to the final solution.

\[Q = q''((t-\tau_{\text{off}})U(t-\tau_{\text{off}}) - 2(t-\tau_{\text{mid}})U(t-\tau_{\text{mid}}) + (t-\tau_{\text{on}})U(t-\tau_{\text{on}})) \quad [H.5]
\]

\[(t-\tau^*)U(t-\tau^*) \quad [H.6]
\]

\[Q^* = q''(t-\tau^*)U(t-\tau^*) \quad [H.7]
\]

The solution of the problem defined above can obtained by using the Laplace transform technique. The Laplace transform with respect to time, where \(s\) is the transform variable, of Equations [H.1], [H.2], [H.3] and [H.4] is:

\[\frac{d^2 \overline{T}}{dz^2} - \frac{s}{\alpha} \overline{T} + \frac{T_0}{\alpha} = 0 \quad [H.8]
\]

\[\frac{d \overline{T}}{dz} \bigg|_{z=0} = -\frac{q''(e^{-\tau^*})}{s^2 k} \quad [H.9]
\]

\[\overline{T}(z) = \frac{T_0}{s} \quad \text{as } z \to \infty \quad [H.10]
\]


\[\overline{T}(z) = C_1 e^{\frac{\sqrt{s}}{\sqrt{\alpha} z}} + C_2 e^{\frac{-\sqrt{s}}{\sqrt{\alpha} z}} + \frac{T_0}{s} \quad [H.11]
\]

Boundary condition [H.10] requires that:

\[C_2 = 0 \quad [H.12]
\]

Solving for \(C_1\) using [H.9] results in:
Thus, the solution to the transformed problem is:

\[
\overline{T}(z) = \frac{q'' \sqrt{\alpha} (e^{-r z})}{s^{5/2} k} e^{\frac{k^2 z}{s \sqrt{\alpha}}} + \frac{T_0}{s} \tag{H.14}
\]

To obtain the final time dependent solution the inverse Laplace transform of [H.14] must be obtained. The following inverse transforms, [H.15], [H.16] and [H.17] are applicable.

\[
e^{-k \sqrt{s}} (s^{5/2} (k \geq 0) \xrightarrow{L^{-1}} \frac{k}{6} \left( 2 \sqrt{t} e^{\frac{k^2 t}{4t}} (k^2 + 4t) - (k^2 + 6t) \text{Erfc} \left( \frac{k}{\sqrt{2t}} \right) \right) \tag{H.15}
\]

\[
e^{-as} F(s) \xrightarrow{L^{-1}} f(t - a) U(t - a) \tag{H.16}
\]

\[
k \xrightarrow{L^{-1}} k \tag{H.17}
\]

Inversion yields the solution to the simplified Q* flux problem:

\[
T(z, t = T_0 + q'' U(t - r^*) = \begin{cases} 
\frac{e^{-k \sqrt{s}}}{s^{5/2} (k \geq 0)} \left( 2 \sqrt{t} e^{\frac{k^2 t}{4t}} (k^2 + 4t) - (k^2 + 6t) \text{Erfc} \left( \frac{k}{\sqrt{2t}} \right) \right) 
\end{cases} \tag{H.18}
\]

Using the superposition principal the full solution to heating of a one-dimensional system by triangular flux without convective heat loss is:

\[
T(z, t = T_0 + q'' U(t - r_{0a}) = \begin{cases} 
\frac{e^{-k \sqrt{s}}}{s^{5/2} (k \geq 0)} \left( 2 \sqrt{t} e^{\frac{k^2 t}{4t}} (k^2 + 4t) - (k^2 + 6t) \text{Erfc} \left( \frac{k}{\sqrt{2t}} \right) \right) 
\end{cases} \tag{H.19}
\]

\[
\left. \begin{array}{c}
2U(t - r_{0a}) \\
U(t - r_{0a}) \\
\end{array} \right\} \begin{cases} 
\frac{e^{-k \sqrt{s}}}{s^{5/2} (k \geq 0)} \left( 2 \sqrt{t} e^{\frac{k^2 t}{4t}} (k^2 + 4t) - (k^2 + 6t) \text{Erfc} \left( \frac{k}{\sqrt{2t}} \right) \right) 
\end{cases}
\]

APPENDIX H REFERENCES

Appendix I  Example Model Code

Tri. Source Solution

- Front Matter

Clear["\*"]
Off[General::"spell1"]
Off[General::"spell"]
Off[Solve::"ifun"]
Off[FindRoot::"frmp"]
$TextStyle = 
{FontFamily -> "Arial", FontSize -> 12, FontWeight -> Bold};
<< Calculus`VectorAnalysis`
<< Graphics`Legend`
<< Graphics`ContourPlot3D`
<< Graphics`Graphics3D`
APPENDIX I: Example Model Code

Temperature Function and Variable Definition PEO100k PROPERTIES

\[
\begin{align*}
&k_s = 0.25; \\
&k_a = 0.03; \\
&\epsilon = 0.54; \\
&a_2 = \frac{3k_a}{2k_a + k_s}; \\
&k_{\text{eff}} = k_a \frac{1 - (1 - a_2(k_s/k_a))(1 - \epsilon)}{1 + (a_2 - 1)(1 - \epsilon)}; \\
&T_{\text{inf}} = 25; \\
&\rho_{\text{rel}} = 0.46; \\
&\rho_{\text{poly}} = 1180; \\
&\rho = \rho_{\text{poly}} \times \rho_{\text{rel}}; \\
&k = k_{\text{eff}}; \\
&C_p = 1.7 \times 10^3; \\
&\alpha = \frac{k}{\rho C_p}; \\
&h = 10; \\
&T_0 = 25; \\
&V = 0.254; \\
&\omega = 0.0015; \\
&H = \frac{h}{k}; \\
P = 1; \\
&\tau_1 = \left(\frac{x}{V} + \frac{2\omega}{V} \sqrt{\frac{\pi}{2}}\right); \\
&\tau_2 = \left(\frac{x}{V} + \frac{\omega}{V} \sqrt{\frac{\pi}{2}}\right); \\
&\tau_3 = \frac{x}{V}; \\
&q = \frac{V}{\omega \sqrt{\frac{\pi}{2}}} \frac{2P}{\pi \omega^2} \times \text{Exp}\left[-\frac{2y^2}{\omega^2}\right]; \\
&Q(x, y, t) = q((t - \tau_1) \text{UnitStep}[t - \tau_1] - 2(t - \tau_2) \text{UnitStep}[t - \tau_2] + (t - \tau_3) \text{UnitStep}[t - \tau_3]); \\
&\text{plottime} = 0.315; \\
&\text{Null}; \\
&T(x, y, z, t) = \\
&T_0 + (T_{\text{inf}} - T_0) \left(\text{Erfc}\left[\frac{x}{\sqrt{4} \omega} \right] - \text{Erfc}\left[H z + H^2 \alpha t\right] \text{Erfc}\left[H \sqrt{\alpha} t + \frac{z}{\sqrt{4} \alpha}\right]\right) + \\
&\frac{q}{h} \left(-\frac{1}{2H^2 \sqrt{\pi} \sqrt{\frac{\alpha^3}{a}}} \right) \left(-2\sqrt{\pi} z - 2H\sqrt{\pi} z^2 + \right) \\
&4e^{-t^2/2}H^3 \left(t - \tau_1\right) \sqrt{\frac{z^2}{(t - \tau_1) \alpha}} + 2\sqrt{\pi} z \text{Erfc}\left[\frac{\sqrt{\frac{z^2}{\alpha}}}{2\sqrt{(t - \tau_1)}}\right].
\end{align*}
\]
APPENDIX I: Example Model Code

\[
2 \sqrt{\pi} \frac{z^2}{(t - \tau) \alpha} \text{Erf} \left[ \frac{1}{2} \sqrt{\frac{z^2}{(t - \tau) \alpha}} \right] + \frac{1}{2 \alpha} \left( z^2 - \frac{2 e^{-\frac{z^2}{4(t-\tau)\alpha}} \sqrt{(t - \tau) \pi}}{\sqrt{\pi}} + (z^2 + 2(t - \tau) \alpha) \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} \right] \right) - 2(t - \tau) \alpha - (z^2 + 2(t - \tau) \alpha) \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} \right] - \frac{e^{z^2 H^2 (t-\tau)}}{2 H^2 \alpha} \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} + H \sqrt{(t - \tau) \alpha} \right] - 2* \text{UnitStep}[t - \tau - 1]
\]

\[
\frac{1}{2 H^2 \sqrt{\pi} \sqrt{\frac{z^2}{\alpha} \alpha^{3/2}}} \left( -2 \sqrt{\pi} z - 2 H \sqrt{\pi} z^2 + 4 e^{-\frac{z^2}{4(t-\tau)\alpha}} \sqrt{(t - \tau) \pi} \right) \text{Erf} \left[ \frac{1}{2} \sqrt{\frac{z^2}{(t - \tau) \alpha}} \right] + 2 \sqrt{\pi} z \text{Erf} \left[ \frac{1}{2} \sqrt{\frac{z^2}{(t - \tau) \alpha}} \right] + \frac{1}{2 \alpha} \left( z^2 - 2 e^{-\frac{z^2}{4(t-\tau)\alpha}} \sqrt{(t - \tau) \pi} \right) + 2(t - \tau) \alpha - (z^2 + 2(t - \tau) \alpha) \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} \right] - \frac{e^{z^2 H^2 (t-\tau)}}{2 H^2 \alpha} \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} + H \sqrt{(t - \tau) \alpha} \right] + \text{UnitStep}[t - \tau - 2]
\]

\[
\frac{1}{2 H^2 \sqrt{\pi} \sqrt{\frac{z^2}{\alpha} \alpha^{3/2}}} \left( -2 \sqrt{\pi} z - 2 H \sqrt{\pi} z^2 + 4 e^{-\frac{z^2}{4(t-\tau)\alpha}} \sqrt{(t - \tau) \pi} \right) \text{Erf} \left[ \frac{1}{2} \sqrt{\frac{z^2}{(t - \tau) \alpha}} \right] + 2 \sqrt{\pi} z \text{Erf} \left[ \frac{1}{2} \sqrt{\frac{z^2}{(t - \tau) \alpha}} \right] + \frac{1}{2 \alpha} \left( z^2 - 2 e^{-\frac{z^2}{4(t-\tau)\alpha}} \sqrt{(t - \tau) \pi} \right) + 2(t - \tau) \alpha - (z^2 + 2(t - \tau) \alpha) \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} \right] - \frac{e^{z^2 H^2 (t-\tau)}}{2 H^2 \alpha} \text{Erf} \left[ \frac{z}{2 \sqrt{(t - \tau) \alpha}} + H \sqrt{(t - \tau) \alpha} \right] \right);
\]

**Plots**
Bounding Melt Pool and determining melt time and avg. Temp.

**PEO100k**

```plaintext
meltTemp = 69;
delHtrans = 170*1000;
HT = delHtrans / Cp;
transtemp = HT + meltTemp;
soltemp = 42;
C1WLF = 9.5;
C2WLF = 995;
Tref = 115;
a[x_, y_, z_, t_] = 10^\{C1WLF*((T[x,y,z] - HT) - Tref)\};
```

APPENDIX I: Example Model Code
Directly below are sintering data PEO100k

\[ De = 6.7 \times 10^{-6}; \]
\[ \eta = 3.4 \times 10^5; \]
\[ \tau = \eta \times De; \]
\[ R = 60 \times 10^{-6}; \]
\[ C_0 = 3.5 \times 10^{-7}; \]
\[ m = .46; \]
\[ Cl = 8.8 \times 10^{-6}; \]
\[ cm = \frac{2m + 1}{m + 1}; \]
\[ \gamma_s = \sqrt{\frac{\pi}{4}} \frac{\Gamma[m + 1]}{\Gamma[m + 1.5]}; \]
\[ \gamma_s = 42 \times 10^{-3}; \]
\[ W = 2 \times \gamma_s; \]
\[ \rho_0 = \rho_{rel}; \]
\[ \delta = \text{Solve}\left[ \rho_0 = \frac{4}{3} \pi R^3 \right] \left( 2x + 2R \right)^{3/2} \left[ 3, 1, 2 \right]; \]
\[ L0 = 2 \left( \delta + R \right); \]
\[ \rho \text{Lin}[t_] = \rho_0 / \left( 1 - \left( \frac{9 \pi}{2} \right)^{n \frac{m - 1}{m}} \left( \frac{4m + 3}{m} \frac{\pi}{4} \frac{cm^2}{R} \right)^{2 \frac{n}{1 + 3}} \left( \frac{Y_m}{cm} \frac{Cl}{W} \right)^{\frac{1}{1 + 3}} t^{\frac{n}{1 + 3}} \right)^3 \]
\[ \Delta \text{Lin} = L0 \left( \frac{9 \pi}{2} \right)^{n \frac{m - 1}{m}} \left( \frac{4m + 3}{m} \frac{\pi}{4} \frac{cm^2}{R} \right)^{2 \frac{n}{1 + 3}} \left( \frac{Y_m}{cm} \frac{Cl}{W} \right)^{\frac{1}{1 + 3}} t^{\frac{n}{1 + 3}} \right)^2 / t \rightarrow t; \]
\[ L@t = L0 - \Delta \text{Lin}; \]
\[ a0 = \left( \frac{3}{4 \pi} \left( \frac{L@t}{3} - \frac{4 \pi R^3}{3} \right) \right)^{\frac{1}{3}}; \]
\[ \rho \text{MS}[t_] = \text{DSolve}\left[ p'[t] = q \text{MS} (1 - p[t]), p[0] = \rho \text{Lin}[t], p[t], t \right] \left[ 1, 1, 2 \right]; \]
\[ q \text{MS} = \frac{3}{2} \pi \gamma_s; \]
\[ \rho \text{visc}[t_] = \text{UnitStep}[t - \tau] \times \rho \text{MS}[t - \tau]; \]
\[ \rho \text{scel}[t_] = \rho \text{Lin}[t] \times \text{UnitStep}[t - \tau]; \]
\[ \rho \text{total}[t_] = \rho \text{visc}[t] + \rho \text{scel}[t]; \]

start loop, use same time, down in z first then step in y

dT(t) is the derivative w/rtn time at a given position. The value of t at dT(t)=0 is used to determine the max temp and the respective bounds for determining for finding the times of the phase transitions.

\[ dT[y_, z_, t_] = \partial_t T[\text{plottime} \times V, y, z, t]; \]
meltTable = {{"y", "z", "Tempmax-HT", "t_melt", "t_fuse", "delta_t", "Tavg-HT", "aT", "delta_t@Tref", "tau_frac", "den_vscel", "den_visc", "den_total", "frac_vscel", "a/R"}};

z0 = 1. * 10^-6;
z = z0;
Δz = 5. * 10^-6;
y = 0;
Δy = 5. * 10^-6;

While[Re[T][plottime + V, y, z0],
FindRoot[dT[y, z0, t] == 0, {t, 1.5 ω/V + plottime, 2.34 ω/V + plottime},
MaxIterations → 100, WorkingPrecision → 16][[1, 2]]] > transtemp,
{While[Re[T][plottime + V, y, z, FindRoot[dT[y, z, t] == 0, {t, 1.5 ω/V + plottime,
2.34 ω/V + plottime}, MaxIterations → 100, WorkingPrecision → 16][[1, 2]]] > transtemp, {tmelt = FindRoot[T[plottime + V, y, z, t] == transtemp,
{t, 0., FindRoot[dT[y, z, t] == 0, {t, 1.5 ω/V + plottime, 2.34 ω/V + plottime},
MaxIterations → 100, WorkingPrecision → 16][[1, 2]]][[1, 2]],
tfuse = FindRoot[T[plottime + V, y, z, t] - HT = soltemp, {t, FindRoot[
dT[y, z, t] == 0, {t, 1.5 ω/V + plottime, 2.34 ω/V + plottime}, MaxIterations →
100, WorkingPrecision → 16][[1, 2]], 5 ω/V + plottime]][[1, 2]],
TavglessHT = NIntegrate[T[plottime + V, y, z, t] - HT, {t, tmelt, tfuse}]/
(tfuse - tmelt), aT = NA, time =
NIntegrate[1/aT[plottime + V, y, z, t], {t, tmelt, tfuse}, MaxRecursion → 20],
If[time ≥ τ, If[ρLin[t] ≥ 1, denlist = {{time τ, 1, 0, 1, 1, 1 - (ρ0 1)^1/3}^1/2},
denlist = {{time τ, vscel[t] - ρ0, ρvsc[time] - ρvsc[t],
ρtotal[time], ρvscel[τ] - ρ0, ρvsc[time] - ρvsc[t],
ρtotal[time], ρvscel[τ] - ρ0, ρvsc[time] - ρvsc[t],
(1 - (ρ0^1/3)) / (ρ0^1/3)}^1/2},
If[ρLin[time] ≥ 1, denlist = {{time τ, 1, 0, 1, 1, 1 - (ρ0 1)^1/3}^1/2},
{time τ, ρLin[time] - ρ0, 0, ρLin[time], 1, 1 - (ρ0^1/3)^1/2}},
{time τ, ρLin[time] - ρ0, 0, ρLin[time], 1, 1 - (ρ0^1/3)^1/2}},
AppendTo[meltTable, {Y/V^10^-6, X/V^10^-6, Re[T[plottime + V, y, z],
FindRoot[dT[y, z, t] == 0, {t, 1.5 ω/V + plottime, 2.34 ω/V + plottime},
MaxIterations → 100, WorkingPrecision → 16][[1, 2]]][[1, 2]]} + HT,
tmelt, tfuse, tfuse - tmelt, TavglessHT, aT, time, denlist[[1]],
denlist[[2]], denlist[[3]], denlist[[4]], denlist[[5]], denlist[[6]]]},
z = z + Δz}}, z = z0, y = y + Δy, Print[y]]}
\[ a_{\text{MSO}} = \left( \frac{3}{4 \pi} \left( \frac{(2 R)^3 - \frac{4 \pi}{3} R^3}{3} \right) \right)^{1/3} ; \]
\[ \rho_{\text{MSO}}[t_] = \text{DSolve}[[p'[t] = q_{\text{MSO}} (1 - p[t]), p[0] = \rho_0], p[t], t][[1, 1, 2]]; \]
\[ q_{\text{MSO}} = \frac{3 \gamma_s}{2 \cdot a_{\text{MSO}} \cdot \eta} ; \]
\[ L = \text{Length}[\text{meltTable}]; \]
\[ \text{meltTable} = \text{Insert}[\text{meltTable}, "\text{den}_{\text{MSO}}", \{1, 16\}]; \]
\[ \text{Do[} \]
\[ \text{meltTable} = \text{Insert}[\text{meltTable}, \rho_{\text{MSO}}[\text{meltTable}[[n, 9]], \{n, 16\}], \{n, 2, L\}] ; \]

The file label is: polymerMW_To_P_vel_R(microns)

\[ \text{Export["PEO100k_P1_R60.dat", \text{meltTable}] } \]
PEO100k_P1_R60.dat

Avg Density

\[ \text{Sum[\text{meltTable}[[i, 13]], \{i, 2, \text{Length[\text{meltTable}]}\}]} / (\text{Length[\text{meltTable}]} - 1) \]
0.51134

Avg MSO

\[ \text{Sum[\text{meltTable}[[i, 16]], \{i, 2, \text{Length[\text{meltTable}]}\}]} / (\text{Length[\text{meltTable}]} - 1) \]
0.460122

Max Density

\[ \text{meltTable}[[2, 13]] \]
0.528084
Vita

Jeffrey P. Schultz is a native of Roanoke, Virginia and is the son of Barbara and Mark Schultz. Jeff received a BS and a MEng from Virginia Tech in Materials Science and Engineering. While finishing his PhD research, Jeff worked at James Madison University as a Research Associate; his primary responsibility was overseeing the operation of the Center for High Performance Manufacturing’s Rapid Prototyping operations. Jeff will remain at Virginia Tech in the Materials Science and Engineering Department as a post-doc for Steve Kampe. His future plans are to continue to working in the area of near-net-shape part fabrication. However, the completion of this work will most likely end his research into LS of polymers. Development of near-net-shape manufacturing processes for metal-matrix composites is a primary interest.