The Effect of Temperature on the Solvent Removal from Solution-Cast Thin Polymer Films

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by
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ABSTRACT

An apparatus has been designed and assembled to study the solvent removal from solution-cast thin polymer films. The computer interfacing of a thermogravimetric analyzer, spectrophotometer, electronic flowmeters and control valves for the apparatus enabled the preprogramming of the carrier gas velocity, carrier gas solvent content, and temperature profiles to simulate the environment experienced in large parallel flow industrial driers. The apparatus has also been designed to enable the visual observation of the drying film with an optical microscope.

Initial experimental studies conducted with the apparatus studied the effect of temperature on the solvent removal. The results indicate that high temperatures can cause skinning of the film surface resulting in slower solvent removal rates. The skin formation can be suppressed with higher solvent concentration in the carrier gas. The visual observations revealed the formation of standing waves in the film surface during drying at high gas velocities (>200 cm/min). The wave formation overcomes the effect of skinning by increasing the surface area of the film.
1. INTRODUCTION

This thesis represents work done as a continuation of research concerning the drying of solvent-cast polymer films conducted in the Ohio University Polymer Engineering Laboratory [1-4]. Specifically the purpose of this work was to design and assemble an experimental apparatus capable of simulating the environment experienced by solvent-cast films in large industrial driers. The completed design allowed for the control of the operating conditions, and the measurement and recording of the appropriate variables. Additionally, the apparatus was designed to allow for visual observation of the drying film with an optical microscope. Initial experiments conducted with this apparatus studied the effect of drying temperature on the solvent removal process.

This thesis presents an introduction to solution casting with more in-depth background information on the drying process. Also included in the background is a literature review of the effect of solvent and its removal on the final film properties. A review of past experimental techniques along with a complete description of the apparatus and procedures developed for this thesis is also presented. Finally the results and conclusions from the initial experiments are presented.
2. BACKGROUND

The solution casting process is a continuous process as shown in Figure 1. Initially a polymer is dissolved by a solvent or solvents and then the solution is spread into a film. The film is formed by casting the solution from a casting die onto a carrier such as a conveyor belt, large drum, or casting substrate. The removal of the solvent starts immediately after casting. The film then travels through a drier where most of the solvent is removed. The film then continues on for further processing, or is separated from the carrier, or in the case of composites, another layer can be applied. A thorough description of the process is given in the references [5-9].

Inside the drier the solvent is removed by direct contact with a carrier gas. The carrier gas can flow parallel, countercurrent, or it can be impinging flow. The gas velocity, temperature, pressure along with its vapor composition make up the drying conditions in the drier. These driers can be up to 300 ft long and 16 ft wide with the conditions changing along the length. These environmental differences can be imposed or a natural result of the drying process in the film. The drying conditions do affect the final film properties as will be shown and are the motivation for this study.
POLYMER FILM SOLUTION-CASTING

Figure 1. The Solution Casting Process
Solution casting is used when the properties desired or the polymers used are not compatible with the faster and cheaper melt extrusion and calendering processes [6]. Solution casting differs from extrusion and calendering in that solvents, not heat, are used to lower viscosity of the polymer. A lower viscosity is needed to form thin continuous films, and lower temperatures allow the use of thermally degradable polymers. Solution processing has also been used to produce films from polymer blends that can be achieved in solution but not in the melt [6].

The solution processing of polymers also results in different final film properties. Properties like surface tension are not the same for a polymer solution at a given viscosity and a melt at the same viscosity. This permits the formation of thinner, and higher quality films with solution casting [5-6]. Removal of the solvent in the drying stage enables larger changes in the film thickness during casting. The solution properties also vary with the choice of solvents which in turn can affect the film properties. The choice of solvents is therefore also very important in manipulating the resultant properties.

2.1. Drying Theory

The solvent removal from polymer films has been studied by several investigators [10-14]. They have confirmed that solvent removal occurs in two phases. The first phase occurs when the film surface is wet with
solvent and the interphase transport of solvent between the film and the carrier gas is the rate controlling factor. The second phase occurs when the solvent content near the film surfaces approaches zero and internal diffusion of solvent to the film surface is the rate controlling factor. The solvent removal rates in the different phases is dependent on the solvent and solution properties, the sample geometry, and the drying conditions.

Plots of the log of the weight ratio of solvent to polymer in the film during drying \((m_1/m_2)\) vs. the log of time divided by the thickness \((t/L)\) or the thickness squared \((t/L^2)\) are used to distinguish between the drying phases \([10,12,14,15]\). The thickness is \(L\) and \(t\) is the time. Figure 2 is an example of such a plot. The first phase appears as the first straight portion of the plot followed by a transition where the solvent content in the film surface rapidly goes to zero then the second straight portion is the second phase. Plots vs. \(\log(t/L)\) for films dried at the same conditions but of varying thicknesses will show the curves converging to one curve if interphase transport is the overall controlling factor \([10,14]\). Plots vs. \(\log(t/L^2)\) for different film thicknesses will show a single curve if internal diffusion is the overall controlling factor \([10,14]\).

The film surface during the first phase is considered
Figure 2. Typical Plot for Solvent Removal from Thin Films [6]
to be wet with solvent so that the interphase transport of the solvent is then an evaporative process. The solvent properties of volatility, and heat of vaporization have large effects on the solvent removal rate during the first phase. The drying conditions, like the gas temperature and velocity, also have large effects on the removal rate in the first phase. The internal diffusion is relatively rapid during the first phase, because of the high solvent concentration, and the solvent concentration is considered uniform in the film [8].

It is in the transition between the first and second phases that the solvent concentration at the surface approaches zero, and this takes place very rapidly. Hansen [10] states that the transition occurs when the solvent concentration is such that it raises the glass transition temperature, \( T_g \), of the solution, to the actual film temperature at this time in the drying process. Therefore solvents with high heats of vaporization causing lower film temperatures will also cause an earlier start of the slower second phase.

The second phase is controlled by the internal diffusion of the solvent to the film surface. Diffusion in polymers is a complex subject and is treated in depth by Crank and Park [16], but there are essentially three different mechanisms that can occur. The first mechanism is characterized by the polymer molecules rearranging
after the passing of a solvent molecule. This occurs in diffusion above the $T_g$ and obeys Fick's law. Fick's law is given by

\[ F = D \frac{\partial c}{\partial x} \quad (1) \]

where $F$ is the mass flux per unit area, $c$ is the concentration, $x$ is the position, and $D$ is the diffusion coefficient which may be a function of concentration and temperature. In the second case the polymer molecules do not rearrange behind vacating solvent molecules, but are frozen in place. The second case occurs below the $T_g$ and it also obeys Fick's Law. The third case occurs near the $T_g$ and exhibits non-Fickian behavior. The third case is a combination of the other two cases.

Vrentas and Duda use a Deborah number to predict which mechanism is occurring [17-18]. The Deborah number is defined as

\[ D_b = \frac{\lambda}{\Theta} \quad (2) \]

where $\lambda$ is the characteristic polymer relaxation time, and $\Theta$ is the characteristic solvent diffusion time. For $D_b<<1$ the first mechanism is observed, that is the polymer molecules rearrange relatively quickly after solvent molecules move. For $D_b>>1$ the second mechanism is observed and the polymer molecules are frozen in place. For $D_b=1$ the third mechanism is observed.
In the first two cases the diffusion was said to be Fickian, but the diffusion coefficients are complex functions of concentration and temperature. Vrentas and Duda have developed the free volume theory to explain and predict the diffusion coefficients in polymer solutions with \( D_b \ll 1 \) \(^{[17-18]}\). The statistical mechanical theory has been developed by Daytner and Pace for diffusion coefficients in solutions with \( D_b \gg 1 \) \(^{[19-20]}\). During the drying process all three of the mechanisms may operate in different regions of the film or at different times. Hansen \(^{[10]}\) states as a general rule solvents with the greatest minimum cross sectional area will be retained in the film longer and at higher concentrations.

Previously at Ohio University a mathematical model of the drying process was developed by Roehner \(^{[1,2]}\). The model was based on the equations of energy and change and solved by a finite difference technique. The model predicts the temperature and concentration profiles in the film during drying. The results show that at high carrier gas temperatures or high gas velocities a thin layer of virtually solvent-free polymer can develop at the film surface. This is caused by the rapid evaporation of solvent at the surface and is usually associated with a subcooling of this layer. The diffusion coefficient in this layer is several orders of magnitude lower than in the rest of the film. The lower diffusion coefficient and
the subcooling cause a significant reduction in the overall solvent removal rate. The apparatus used in the present study was designed to enable the visual inspection of the film surface during drying in order to search for any observable change in the film surface characteristics.

2.2. The Effect of Solvent on the Final Film Properties

Previously it was shown that the choice of solvent can greatly affect the drying process. The solvent volatility has the most significant influence in the first stage and diffusion coefficient in the second phase. The choice of solvents can also influence the final film properties, as has been shown by several investigators [21-26].

Kurbanaliyev et al. [21] studied the effect of different casting solvents on the final film strength, density, and microporosity. They studied films of cellulose triacetate (CTA), polyvinylcholride (PVC), and polymethylmethacrylate (PMMA) cast from several different solutions with the same compositions. The set of solvents used for one polymer was not the same for the other polymers. All of the solutions were cast onto polished glass and allowed to dry at room conditions for two days and then further drying took place under a vacuum.

Mechanical tensile tests were conducted on the films. The tests were done at constant stress and the
time to break and the strain at break was measured. The strain at break was found to vary up to 50% of the highest value with the use of different solvents. The time to break in seconds was several orders of magnitude different, but varied in the same pattern as the strain values with respect to solvent used. Their data was then plotted with respect to the intrinsic viscosity of the solution as shown in Figure 3. The strength was found to go through a minimum with the highest strengths found with the "good" and "bad" solvents. The reason for this behavior is not yet understood, but it is evident that the choice of solvents is important to the final film properties.

Most published research has been concerned with the effect of the casting solvent on films of polymer blends and copolymers [22-26]. The study by Bagrodia and Wilkes used styrene-butadiene-styrene triblock copolymers cast from seven different solutions [22]. The molar content of the copolymer was also varied for this study. The Young's moduli of the films were measured and plotted vs. the solubility parameter, $\delta$, of the solvent used. It was found that as $\delta$ increases, towards the value of $\delta$ for styrene, the modulus also increases. This effect is most evident in copolymers with 30-40% styrene.

Styrene-butadiene-styrene triblock copolymers naturally form a domain structure where the like
Figure 3. Strength of Films Poured from Solutions in Different Solvents as a Function of the Value of the Intrinsic Viscosity for CTA(a), PVC(b) and PMMA(c) at 293 K [21]
segments of the polymer chains aggregate. Low styrene content copolymers form a structure with spherical styrene domains and a continuous butadiene domain. High styrene content copolymers form a continuous styrene domain with spherical butadiene domains. Polystyrene has a higher modulus than polybutadiene and copolymers with a continuous styrene domain also have higher moduli. Therefore as the \( \phi \) of the solvent approaches that of styrene during film formation the styrene domains are swollen more than the butadiene domains as the film shrinks, and this leads to greater connectivity of the styrene domains and higher modulus. Copolymers with a styrene content of 30-40% are affected more because these are approaching the content needed to form a continuous styrene domain.

Kalfoglou [25-26] made similar studies with the same styrene-butadiene-styrene triblock copolymers. Kalfoglou cast films from three different solvents: cyclohexane, a selective solvent for the butadiene phase; methylethylketone (MEK), a selective solvent for the styrene phase; and toluene which is a solvent for both phases. The films cast from MEK had higher moduli as would be suspected from Bagrodia and Wilkes' study, but it was also found that the films cast from toluene possessed higher tensile strength and mechanical hysteresis. Kalfoglou concluded that there is more effective load transfer between phases if a
solvent for both phases is used.

Eastmond and Haraguchi [23] were concerned with the dynamic mechanical properties of polycarbonates, polystyrene, and blends and block copolymers of the two when cast from different solutions. The properties of the blends were found to be a simple combination of the two single polymers cast from the same solvent. The copolymers were more greatly affected by different solvents. This was argued to be caused by the development of excess free volume near the interfaces of the two phases. The excess free volume is developed when a solvent preferentially dissolves one of the phases. As solvent evaporates one phase hardens faster and the chain ends in the dissolved phase are stuck at one end, and when the remainder of the solvent is removed the chains in the dissolved phase are not free to move and completely fill all voids caused by the solvent removal. This phenomenon does not take place in blends because the two phases are not interconnected in the same manner as in copolymers.

2.3. Molecular Orientation Induced by Solvent Removal

As the choice of solvent affects the film properties so does the manner in which it is removed. In solution casting of polymer films molecular orientation is caused by the polymer movement induced by solvent removal or diffusion in polymer films. Molecular orientation in polymer films results in the enhancement of mechanical
Collier [29] has shown that solvent removal from solution cast films on solid substrates can cause elongational flow of the polymer resulting in molecular orientation. Unlike most orienting processes where the elongational forces are externally applied forces, in solvent removal the elongational forces are caused by constraining the naturally occurring contracting forces. Solvent removal from an unconstrained polymer solution results in the three dimensional volumetric shrinkage without the development of orientation. Solvent removal from a solution film constrained in two dimensions by a substrate results in one dimensional thickness reduction with or without orientation. The orientation is caused by the polymer flow in the planar directions during thickness reduction and is dependent on the speed at which the solvent is removed. At slow solvent removal the relaxation of the polymer molecules can occur with little or no orientation, and at fast solvent removal the molecules are in effect frozen into oriented positions by an increasing viscosity. The competing forces, molecular relaxation and solvent removal are best compared by the Deborah number, now defined as:

$$D_b = \frac{\lambda}{T_{1/2}}$$  \hspace{1cm} (3)

where $\lambda$ is the polymer relaxation time, and $T_{1/2}$ is the
time for removal of one half of the solvent. The Deborah number still represents the same phenomenon as when used by Vrentas and Duda. For constrained processes with $D_b >> 1$ orientation occurs and for $D_b << 1$ solvent removal results in only thickness reduction. This is best shown schematically by Collier [29] in Figure 4.

Collier also shows in case of very large $D_b$ the resulting polymer deformation is equivalent to a simple elongational flow, the Stephan Squeeze with no sticking at the wall. Collier also notes that during solvent removal the $D_b$ is not the same through the thickness of the film. That is, solvent is removed faster from the upper regions of the film resulting in larger $D_b$ at the film surface than at the substrate. An orientation gradient can be expected to result from this, with higher orientation occurring at the film surface.

Prest and Luca [30-32] studied the orientation of solvent cast films as a function of film thickness, polymer molecular weight, plasticizer content, casting solvent, and coating temperature. The studies included films of polystyrene, polycarbonate, and poly-n-vinyl carbazole made from solution in methylene chloride, benzene, THF, and chloroform. Prest and Luca described the mechanism for producing orientation as a competition between the relaxation times of the concentrating solution and the time scale for the collapse of the film. This is
SLOW SOLVENT REMOVAL OF UNCONSTRAINED SYSTEM

POLYMER MOLECULES IN SOLUTION

SLOW SOLVENT REMOVAL FROM A SYSTEM CONSTRAINED BY A SUBSTRATE BASE

ONE DIMENSIONAL COMPACTION

ONE DIMENSIONAL COMPACTION AND PLANAR EQUIVALENT STRETCH DUE TO ENTANGLEMENT

RESTRAINT ON PLANAR CONTRACTION AND LACK OF RELAXATION TIME

FAST PROCESSES ARE THOSE WITH HIGH DEBORAH NUMBERS, $D_b = \frac{\lambda}{\tau_{1/2}}$

$\lambda$ = FLUID RELAXATION TIME
$\tau_{1/2}$ TIME FOR REMOVAL OF ONE HALF THE SOLVENT (PROCESS TIME)

Figure 4. Time Dependent Solvent Removal in Constrained Systems [29]
essentially the same as Collier's use of the Deborah number.

Using optical properties like birefringence and refractive index, they were able to make relative comparisons of orientation in different films. Solutions were drawn on glass slides to produce the films. Then the films were dried under vacuum at room temperature.

The first comparisons made were between films of different molecular weight polymer and different film thicknesses. They note two effects. The first is that orientation increases with decreasing film thickness. Secondly that increasing molecular weight produces increased anisotropy in the films. This is shown in Figure 5 [32]. The dependence of orientation on film thickness may be a result of the orientation gradient described by Collier. They found the orientation increases with molecular weight up to an effective entanglement network molecular weight. This is shown in Figure 6 [32]. The authors suggest that this means that the orientation is caused by orientation of the whole molecules and/or the entanglement networks and not just the alignment of segments of molecules. This assumes that the films were dried at the same rates and not just the same drying conditions.

The authors also studied the effect on orientation due to the temperature difference between the casting
Figure 5. Birefringence vs. Film Thickness for Different Weight Averaged Molecular Weights [32]

Figure 6. Birefringence vs. Weight Averaged Molecular Weight for 3 m Thick Film [32]
temperature, \( T_C \), and the glass transition temperature, \( T_g \), of the final film. The results are shown in Figure 7 [32]. They found that the larger the difference between \( T_C \) and \( T_g \) the greater the resultant orientation produced. Since in their studies \( T_C \) was lower than \( T_g \) decreasing the difference meant increasing \( T_C \). Using Collier's [29] analysis raising \( T_C \) would decrease the relaxation time of the polymer, \( \lambda \), and therefore decrease \( D_b \). So Prest and Luca's findings regarding temperature are consistent with Collier's analysis. Another way to look at it is that the initial \( T_g \) of the solution is usually lower than \( T_C \), so with solvent removal \( T_g \) of the solution rises until it passes \( T_C \) when the molecules are frozen into place. Prest and Luca do not consider the effect of temperature and concentration gradients in the drying films.

Figure 7. Birefringence vs. Casting Temperature [32]
Since the glass transition temperature is molecular weight dependent, Prest and Luca tried to decouple the temperature and weight effects. The $T_g$ can be manipulated by using plasticizers and a broader molecular weight distribution without much effect on molecular weight average if care is taken. Doing this Prest and Luca were able to estimate the contribution to orientation by the entangled network is equal to 30% of the total orientation for high molecular weight polymers cast at room temperature.

Studying the effect of casting solvent on orientation of the films, Prest and Luca find that choice of solvent has little effect on the orientation produced, and imply that the initial molecular dimensions in solution have little effect on the final orientation.

In their concluding remarks, Prest and Luca [32] state that the orientation reflects both the stresses supported by the entanglement network and the alignment of localized segments; and that orientation is a function of temperature difference between casting and the final glass transition temperature of the film.

Solvent removal causes orientation due to the volumetric shrinkage and resulting polymer flow, but molecular orientation can also be caused by the swelling of polymer films by solvent molecules. In 1953 Dreschel, Hoard, and Long [33], and Long and Kokes [34] found
orientation developed normal to the plane of polymer films subjected to repeated sorption-desorption cycles.

Dreschel, Hoard, and Long [33] studied cellulose nitrate films cast from an acetone solution on glass and mercury surfaces. The dried films were removed from the substrates and suspended in an acetone vapor chamber and the weight gain due to the sorption was measured vs. time and then the chamber was evacuated while measuring weight loss due to desorption. The sorption and desorption was assumed to take place through the two film surfaces and not the edges because of the relative sizes. They found that in the glass-cast films the sorption and desorption of acetone was much faster than the mercury-cast films. This was expected because the diffusion of solvent molecules into an oriented polymer is faster than diffusion in unoriented polymers if polymer molecules are oriented normal to the direction of diffusion [16], and the glass-cast films were so oriented. The glass-cast films were oriented by the process already described and the mercury-cast films were not because casting on mercury allows the area of the film to shrink with the thickness. Also as expected after repeated sorption-desorption cycles the sorption rates decreased because of the loss of orientation in the glass-cast films. What was not expected was that the unoriented mercury-cast also experienced a decrease in sorption rates with repeated
sorption-desorption cycles.

Using birefringence techniques they discovered that the films were developing orientation normal to the film plane. They hypothesized that this orientation was developed when acetone starts to enter the dried film and the swelling of the film is restricted to the thickness direction because of the still dried film core. The swelling causes polymer to flow and orientate normal to the film plane. The decrease in sorption rates was a result of the orientation normal to the plane. Diffusion is slower in oriented polymers than in unoriented polymers when the diffusion direction is parallel to the orientation [16]. Since the diffusion coefficient increases with concentration, during desorption the deswelling of the film approaches an isotropic character so that orientation produced during sorption is essentially not disturbed. They found that the values of the birefringence data of the glass-cast films changed in sign after enough cycles, that is orientation changed 90° from planar to normal.

Long and Kokes [34] also reported similar results to that of Dreschel, Hoard, and Long [33]. This phenomena should be dependent on $D_b$, as is the polymer orientation with solvent removal, but was not discussed by the authors. A possible application for orientation normal to the plane would be for the control of permeability of
films, since this orientation does slow diffusion of penetrants. By manipulation of the duration of the sorption cycles, temperature, and vapor concentration, films could be produced with reduced permeability.

2.4. Strains Induced by Solvent Removal

Solution casting is often used to produce composite films of thin layered polymers, but strains caused by subsequent solvent removal can cause film curling or delamination failures. This problem has been studied by Chow and Penwell [35-38]. They have analyzed the problem by considering the film shrinkage caused by solvent removal as equivalent to applying a compressive load in the plane of the film as shown in Figure 8. In Figure 8 $P$ represents the compressive force per unit width, $S$ is the interfacial force, and $\rho$ is the radius of curvature caused by the interfacial strain, $e_s$, between the two components, 1 and 2.

Using fracture mechanics with Griffith's energy criterion [39] they were able to derive the following expressions for $S$, $\rho$, $e_s$:

\[
e_s = - \left[ \frac{1}{C_2 h_2} + \frac{h_1 h_2}{4(D_1+D_2)} \right] S \hspace{1cm} (4)
\]

\[
\frac{1}{\rho} = \frac{h S}{2(D_1+D_2)} \hspace{1cm} (5)
\]
Figure 8. Illustration of Coordinates, Loading, and Deformation in the Solvent Drying of Two Layer Systems [35]
\[
S = - \frac{P}{C_2 h_2 \Delta}
\]  
where
\[
\Delta = \frac{1}{C_1 h_1} + \frac{1}{C_2 h_2} + \frac{h^2}{4(D_1 + D_2)}
\]  
\[
C_i = \frac{E_i}{(1 - \nu_i^2)}
\]  
\[
D_i = \frac{C_i h_i^3}{12}
\]

and \(E_i\) is the Young's modulus of component \(i\), and \(\nu_i\) is the Poisson's ratio.

Experiments were then conducted by casting solutions of poly-N-vinyl carbazole (PVK) onto 2 in. by 2 in. films of Mylar and Kapton. The solutions were then dried at room temperature in a ventilated hood for several hours followed by vacuum drying for another 16 hours. The radius of curvature, \(\rho\), of the resultant films was measured by tracing the shadow of the films when placed under a parallel light source. Using equations 4-6 the interfacial force and strains can be calculated. The results of varying thickness and using films of different moduli, Mylar and Kapton, corresponded well to the predictions of equations 4-6. An interesting result of the study was that the additional vacuum drying had little effect on the curvature, and the strains are built into
the film during the initial stages of drying.

Chow and Penwell [37] then extend their analysis to composite films of multiple layers. Equations 4-6 now become

\[ e_i = \varepsilon_i + \frac{S_{i+1} - S_i}{C_i h_i} + \frac{Y_i}{\rho}; (i=1, \ldots N) \]  

\[ \frac{1}{\rho} = \frac{N-1}{j=1} \frac{(h_j + h_{j+1}) S_{j+1}}{j=1} \]  

\[ \frac{1}{C_i h_i} + \frac{1}{C_i h_i + 1} S_{i+1} - \left( \frac{S_i}{C_i h_i} + \frac{S_{i+2}}{C_i h_i + 1} \right) \]

\[ + \frac{h_i + h_{i+1}}{4} \sum_{j=1}^{N-1} (h_j + h_{j+1}) S_{j+1} = \varepsilon_{i+1} - \varepsilon_i; (i=1, \ldots N-1) \]  

where

\[ \varepsilon_i = \frac{P_i}{C_i h_i} \]  

for the system defined in Figure 9. In addition they also derived a thermal elastic relation for the stress and strain given by

\[ \frac{\sigma_i}{C_i} = - (1+\nu_i) \alpha_i \Delta T + e_i \]  

where \( \sigma_i \) is the stress caused by thermal and elastic forces, \( \alpha_i \) is the linear expansion coefficient and \( \Delta T \) is
Figure 9. Illustration of the Local Coordinates of the N-layered Composite [37]
a temperature change. Using these newly derived equations, 10-14, they attempted to predict the curling behavior of composite solvent-cast films [38].

They considered the composite film shown in Figure 10 where a plasticized polycarbonate (PPC) solution is cast on one side of a Mylar film, with a thin interfacial layer (IL) between them. The removal of solvent from the PPC film results in a curl, \( V(x) \). A fourth layer, the anticurl layer, made of a polycarbonate (PC) solution is then cast on the other side of the Mylar film to counteract the curl. Notice that the coated films do not reach the edge of the supporting film; this is desired in many applications [38]. The distance, \( a \), is half the width of the PPC layer and the PC layer varies a distance \( \epsilon \) from that. Chow and Penwell were able to derive a set of equations relating the material parameters, geometry, and process parameter to the curl, \( V(x) \). The first set is for \( \epsilon > 0 \):

\[
\frac{V(x)}{V(a)} = \begin{cases} 
\frac{x^2}{a^2}, & -1 \leq \frac{x}{a} \\
\frac{2x}{1+\gamma(-1-1)^2}, & 1<\frac{x}{a} \leq 1+1 \\\n\frac{\epsilon \epsilon^2}{(1+2+\gamma-\gamma+2(1+\gamma(-1-(1+\gamma(-1))))}, & \frac{x}{a} \leq \frac{\epsilon}{a} \leq \frac{\epsilon \times L}{a}
\end{cases}
\]  

(15)

where

\[
\gamma = \frac{\sum_{i=1}^{2} A_i}{\sum_{i=1}^{4} B_i} \cdot \frac{\sum_{i=1}^{4} B_i}{\sum_{i=1}^{2} A_i}
\]  

(16)
Figure 10. Figure 10(a) Illustrates the Layers of the Composite. Figure 10(b) Illustrates the Position of the PC Layer Relative to the PPC. $V(x)$ Represents the Curl of the Composite [38]
\[ A_i = \frac{1}{2} \Theta_i c_i h_i (d_i + d_{i+1}) \]  
(17)

\[ B_i = \frac{1}{3} c_i (d_{i+1}^3 - d_i^3) \]  
(18)

\[ \epsilon_1 = -\epsilon_i + (1 + \nu_i) \alpha_i \Delta T \]  
(19)

\[ d_i = H_i - \bar{\nu} \]  
(20)

\[ H_i = \sum_{k=1}^{i-1} h_k \]  
(21)

\[ \bar{\nu} = \frac{1}{2h} \bar{c} \sum_{i=1}^{4} c_i h_i (H_i + H_{i+1}) \]  
(22)

\[ \bar{c} = \frac{1}{h} \sum_{i=1}^{4} c_i h_i \]  
(23)

For \( \epsilon < 0 \):

\[ V(x) = \begin{cases} 
\frac{x^2 x \epsilon}{a^2}, & -1 < x \leq 0 \\
\frac{x \epsilon (1-\delta)(2+\epsilon-1) + \delta(1+\epsilon-1)^2}{a}, & 1 < x \leq 1 \\
\frac{x \epsilon (1-\delta)(2+\epsilon-1) + \delta(1+\epsilon-1)^2}{a}, & 1 < x \leq 1 \\
\frac{x^2 x \epsilon [1-(1-\delta)^2] \cdot (1+\epsilon-1)}{a^2}, & 1 < x \leq 1 
\end{cases} \]  
(24)

where

\[ \delta = \frac{\sum_{i=2}^{4} A_i}{\sum_{i=1}^{4} B_i} \]  
(25)
These equations are further complicated by the fact that \( C, \nu, \alpha \) and \( \gamma \) can be dependent on temperature, solvent content, and time, but the authors claim that they can be used to minimize curling by manipulating the geometry and the drying conditions. This analysis does not consider the effect of orientation on the development of strains.

2.5. **Experimental Techniques**

The ability to measure the weight of a drying sample is essential when studying the drying behavior of solution cast films. The means to measure the weight vs. time is central to most apparatus designed to study drying. This section reviews the apparatus used by past investigators.

First in 1969 Robinson et al. [40] used a device shown in Figure 11. They were interested in the effect of high pressures and temperatures, and their apparatus was built in a 3 foot section of 8 in. sch. 40 steel pipe. In the center a sample tray was suspended from a transducer which could be used to measure weight. One end of the pipe was fed with compressed air with an outlet at the other end. This system allowed for the control of the carrier gas flowrates, temperature, and pressure at constant values, but not changing values, and no solvent content in the carrier gas. The main drawback of this system is that it required that the carrier gas be temporarily shut off to get accurate weight readings.

A year later, 1970, G.M. Sletmoe used an apparatus
Figure 11. Cutaway View of High Pressure Drying Container. Experiment Apparatus Used by Robinson et al. [40]
pictured in Figure 12 [11]. This system used a Shell Thin Film Evaporometer which measured weight and time. There is no temperature control, control of the solvent content in the carrier gas, or pressure. All experiments done with this system were done at room temperature and pressure. The Evaporometer did provide accurate and continuous weight readings. The solvent was also measured by determining the solvent picked up by the carrier gas by means of gas liquid chromatography (GLC) in order to confirm the weight readings.

Figure 12. Experimental Apparatus Used by Sletmoe [11]
In 1972 Toei et al. used the apparatus shown in Figure 13 [13]. In this apparatus a flat plate is used for casting the film. The plate is held by a cantilever in air duct. The deflection of the cantilever is measured by a differential transformer whose signal is converted to weight readings. This system also operated at constant flowrates and temperatures, and the pressure was restricted to atmospheric and the carrier gas was dry.

![Figure 13. Drying Apparatus of Coated Film. Experimental Apparatus of Toei et al. [13]](image)

More recently, 1983 and 1984, Boucif [3] and Tso [4] have used a thermogravimetric analyzer to study drying behavior (the use of a thermogravimetric analyzer will be discussed later in this thesis). Boucif and Tso were able to control solvent content in the carrier gas. Boucif did
this by direct injection of measured amounts of solvent into the gas stream, and Tso accomplished this by mixing dry and saturated gas streams. This was an improvement as in many industrial situations there is solvent present in the carrier gas, but this was still restricted to constant values of solvent content. The next section describes the system set up for this thesis that allows for varying flowrates and solvent content which is closer to actual applications.
3. EXPERIMENTAL

Experimental studies of solvent removal from a PMMA-toluene, polymer-solvent, solution that was cast into thin films were conducted for this research effort. The process variables controlled include temperature, carrier gas velocity, and vapor concentration in the carrier gas. The effect of temperature on the solvent removal was studied by varying the temperature of experimental runs at different sets of conditions.

Polymer solutions were injected into small flat aluminum pans that were held in a thermogravimetric analyzer (TGA). The TGA measured and recorded the weight loss due to solvent removal and also controlled and recorded the temperature of the sample. An optical microscope positioned above the TGA enabled visual observations during solvent removal. Control valves and electronic flowmeters were used to control flowrate and vapor composition of the carrier gas passing through the TGA sample furnace. The actual vapor composition in the carrier gas was measured by a spectrophotometer. These instruments were all linked with a IBM PC-XT with the help of an analog processor and a multiplexer.

The following sections describe and give an explanation of the function of each piece of equipment
followed by a description of the overall process. Finally the operating procedure is explained in detail.

3.1. Equipment

3.1.1. Thermogravimetric Analyzer with Thermal Analyzer

A du Pont model 951 TGA was used to measure the weight loss and control the temperature of a sample solution. The TGA allows for the continuous recording of the sample weight, the derivative of the weight loss, and the sample temperature. The sample solution was held in a furnace with a gas stream passing through. The TGA, pictured in Figure 14, consists of a Hahn microbalance whose balance arm extends into a quartz furnace tube where the sample is held. The balance and furnace tube are mounted on guides that allow the furnace tube to slide in and out of an electric furnace. The furnace tube was modified to have two openings to allow the entrance and exit of the carrier gas. The balance housing is also purged with a dry N₂ gas stream.

A du Pont model 1090 Thermal Analyzer (TA) with 1091 Disk Memory attachment is used to program and control the TGA and record data from the TGA. The 1090 and 1091 are pictured in Figure 15. The TA is a microprocessor based instrument that allows for the preprogramming of the temperature in the TGA furnace. During an experimental run the TA reads and records the sample temperature, weight, and time elapsed. The TA displays the real time
Figure 14. Thermogravimetric Analyzer
Figure 15. The 1090 Thermal Analyzer and The 1091 Disk Memory
data on a plasma display unit and plots the data on a built-in plotter. The recorded data is stored on a floppy disk by the 1091 memory attachment. The TA is also equipped with a RS-232 communication port which allows for the transfer of data and external control of the instrument.

3.1.2. Optical Microscope

A Wild model MPS 15/11 microscope was used to visually inspect the sample while it was drying. The microscope was mounted over the TGA and the sample could be watched through the quartz furnace tube. A camera can be attached to the microscope thereby permitting photographing the drying samples.

3.1.3. Control Valves and Flowmeters

Three sets of Matheson model 8100 mass flowmeters and flow controllers were used to monitor and control the carrier gas stream flowrate and vapor composition, and also the purge gas stream for the TGA balance housing. Figure 16 is a drawing of the flowmeters with control valve attached, and the pin assignments for the wiring harness are also given.

The flowmeters measure the mass flowrate and generate a DC voltage signal proportional to the flowrate. The flowmeters were factory calibrated for $N_2$ flowrates of 0-2000 cc/min generating a 0-5 volt direct current voltage
Figure 16. Flowmeters and Control Valves with Wiring Connections
(VDC) signal directly proportional to the flowrate. Inside the flowmeter the gas stream is split and heat is added to a small stream, whose size is proportional to the total stream. From the amount of heat added, the temperature rise, and the heat capacity the mass flowrate inside the flowmeter is calculated and a DC signal generated.

The control valves operate on an electromagnetic principle. A DC voltage is applied to an electromagnet inside the valve, and the magnet lifts the valve open and allows gas flow. The valve operates on a 0-15 VDC signal with a nonlinear relationship between percent open and voltage. A simple proportional control algorithm was used to control the valves, and the Fortran program (VALVE) that executed the algorithm is given in APPENDIX B. The voltage to the valves was increased or decreased an amount proportional to the difference between the desired flowrate and the flowmeter readings.

Operating the flowmeters and control valves required the reading of the 0-5 VDC signal from the flowmeters, and the ability to generate a 0-15 VDC signal to the control valves. This was accomplished with an analog processor to be discussed later.

3.1.4. Spectrophotometer

A Perkin-Elmer model 330 spectrophotometer was used to measure the actual solvent content in the carrier gas
stream. The spectrophotometer measures the absorbance of light, at a specific wavelength, by the gas stream. A special flow through sample cell was used to allow continuous monitoring of the gas stream. Figure 17 shows the spectrophotometer. In order to utilize the flow through cell the door from the sample compartment must be removed and the gas line connected to the cell. Then the sample compartment must be resealed to prevent interference from light sources in the surroundings. In this investigation cardboard and duct tape were used to reseal the sample compartment. The spectrophotometer is also equipped with a RS-232 communication port. The RS-232 port allows the PC to read and record the absorbance value registered by the spectrophotometer.

Figure 17. Model 330 Spectrophotometer
3.1.5. Computer Equipment

An IBM PC-XT was used along with an Omega model OM-900 data acquisition and control processor and a RS-232 multiplexer. The PC was used to collect and analyze the data from the TA-TGA, spectrophotometer, and flowmeters, and also used to control the control valves. Fortran programs were developed and used to communicate between the PC and the other instruments and execute the control algorithm for the valves.

The Omega control processor is itself a microprocessor. The Omega is equipped with 4 analog input channels and 4 analog output channels. These analog channels read or send -10 to +10 DC voltage signals. Three of the input channels are used to read the signals generated by the 3 flowmeters and 3 of the output channels are used to control the valves. A signal amplifier is used to increase the 0-10 VDC signal of the Omega to the 0-15 VDC signal needed by the valves. The wiring connections are shown in Figure 18. The Omega converts the analog signals to digital ones and vice-versa. The Omega has its own command language and the commands are received from the PC through a RS-232 communication port.

The multiplexer is used to access all three of the instruments used, the TA-TGA, spectrophotometer, and Omega processor from the single communication port of the PC. The multiplexer has 5 RS-232 ports. When the host port is
Omega Processor

Analog input                   Analog output

Valve #1     ±1
Valve #2     ±2
Valve #3     ±3
Pins #5 and #6 on valves     ±4

1 ± 2 ± 3 ± Amplifier ±

Valve #1     Valve #2     Valve #3

Pins #14 and #15 on valves

Figure 18. Wiring Connections for the Omega Analog Channels
wired to the PC, the PC then has access to the other four. The pin connections are shown in Figure 19. The other four ports do not have access to each other. Each port has its own selectable communication parameters, e.g. baud rate, parity, and word size. This allows each instrument to communicate at its optimum speed. Only one port can be accessed at a time by using commands, from the PC, intercepted by the multiplexer.

3.2. Chemicals

A du Pont E22495-125 PMMA resin was used in this research. The resin had a intrinsic viscosity of 0.40, but it should be noted that the polymer was several years old and the viscosity may have changed. The toluene was supplied by Fisher Scientific.

3.3. Setup

The complete setup of the apparatus is shown in Figure 20. The gas from the cylinder is split into two streams. One stream is bubbled through two flasks of the solvent in order to saturate it with the solvent. The other line remains dry. Each line has a flowmeter and control valve. The lines are then rejoined, and the vapor concentration of the carrier gas is fixed by the relative flowrates of the two lines. The total flowrate of the carrier gas is equal to the sum of the flowrates in the feed lines. After rejoining the gas line passes through
Figure 19. Wiring Connections for RS-232 Lines
Figure 20. Schematic View of Experimental Apparatus
the spectrophotometer and the special flow through sample cell, and the actual concentration is measured. The gas stream then enters the TGA where it passes over the polymer solution on the balance arm and exits the system. It should be noted that Figure 20 does not show the purge gas line for the balance housing. The purge gas line is also split off from the cylinder and controlled and monitored by the third flowmeter and valve. The purge gas lines enters the back of the TGA and does not pass over the sample.

The computer connections start at the PC. From the communication port of the PC one line goes to the host port of the multiplexer. Three lines leave the multiplexer and go to the RS-232 ports of the Omega processor, TA, and spectrophotometer. The TA has its own wiring to connect the TGA. From the output terminals of the Omega processor two wires go to each valve via the amplifier. Two leads from each flowmeter go to separate input channels of the Omega.

3.4. Procedure

3.4.1. Preparation of Polymer Solution

1. Weigh some toluene in a sample bottle of known weight. Then add the PMMA into the solvent until the weight ratio is 80% by weight solvent.

2. The sample bottle should be glass and sealed with cork, because plastic or rubber materials may absorb
toluene.

3. Wait about one week until the solution is clear and of homogeneous consistency. Agitation is helpful especially for the first hour and then periodically the following days.

3.4.2. Power Up the Equipment

1. The TGA is powered up through the TA. The power switch, heater switch, and the power switch on the Disk Memory Attachment must all be turned on. The TA-TGA should warm up for half an hour.

2. The spectrophotometer is powered up by a single switch. The spectrophotometer performs self diagnostic tests and self calibration for about 20 minutes and is then ready for use.

3. The valves require about 15 minutes to warm up. They are powered up by turning on the power supply box.

4. The PC must be turned on and booted up. The Omega must be turned on and the multiplexer and signal amplifier must be plugged in.

3.4.3. Starting the Carrier Gas Flow and Measuring Vapor Concentration

1. Set the spectrophotometer wavelength to 212 nm, and in the absorbance mode. 212 nm is used because it is suitably absorbed by toluene.
2. Start the VALVE program on the PC and set the dry gas flowrate equal to the total flowrate to be used for this experimental run. A listing of the VALVE program is given in APPENDIX B.

3. Read the absorbance value on the spectrophotometer display. When this value reaches a steady state, zero the Spectrophotometer. This will take about 30 minutes.

4. Stop the VALVE program, restart, and set the wet gas flowrate equal to the total flowrate.

5. Read and record absorbance value on the spectrophotometer when it reaches steady state.

6. Stop VALVE program and restart setting the wet and dry gas line to the desired flowrates.

7. Read and record the absorbance value when it reaches steady state. The solvent content in the carrier gas is given by Beer's Law,

\[
C = C_s \frac{a}{a_s}
\]

where \( C \) and \( C_s \) are the vapor concentration of solvent in the carrier gas and at saturated conditions, and \( a \) and \( a_s \) are the absorbance readings.

3.4.4. Preparing the TA

The TA displays a series of screens on the plasma display which prompt the user for input. The following
steps show the input provided for this investigation, but others are possible.

1. First the TA displays the time and date and asks for confirmation. The user then supplies the correct date and time.

2. Enter 7 for the module type this corresponds to the GA module.

3. The percent weight recording mode should be selected.

4. 5.0 seconds per data point are sufficient for the sampling interval.

5. Then sample identity must be entered along with the rate and operator's identity.

6. Select any method 10-12. The different method numbers allow for different heating programs to be run sequentially.

7. Set initial temperature to room temperature. Set temperature step size between 0 and 250. A zero step size will run experiment at room temperature. A 250 step size will set the furnace to 250°C over room temperature, but the actual sample temperature will be about 100°C since the sample is held outside the furnace to facilitate observations. Since the gas is flowing out of the furnace before passing the sample there is a significant temperature drop between the furnace and the sample. The TGA does record the actual sample temperature. Set the step time to 100
minutes. Set the final temperature to the initial temperature plus the step size. These settings will start the TGA at room temperature and go as quickly as possible to the final temperature and hold for 100 minutes. When the next method is set to zero and the TGA stops after completing the aforementioned method.

8. Set the x-axis signal to time.
9. Set the x-axis range to 5 min/cm.
10. Set the x-axis shift to zero.
11. Set the y-axis signal to signal A. Signal A is percent weight loss.
12. Set the y-axis range to 5%/cm.
13. Set the y-axis shift to zero.

3.4.5. Preparing the TGA

1. Install a ring holder balance arm and ring pan according to the TGA manual. Then place a DSC sample pan in the ring pan. The DSC pan will hold the polymer solution.

2. Press the Display Axis key on the TA. The bottom line of the plasma display will give the weight on the balance arm.

3. If the weight reading is not within ±15 mg remove the pyrex bell over the balance housing and add or subtract counterweights from that end of the balance arm until the reading is within 15 mg.

4. Once the reading is within ±15 mg press the Signal
Zero key and then the Enter key on the TA. The weight reading will now be zero.

3.4.6. Starting the Run

1. Use a syringe to withdraw polymer solution from the sample bottle. Withdraw slowly to avoid cavitation in the syringe.

2. Inject about 45 mg into a DSC sample pan and close the furnace tube immediately. Position the furnace tube so that the sample pan is just outside the furnace.

3. On the TA press the Standby, Store Data, and Start keys and the Start key again and the TGA will start recording.

4. Adjust and focus the microscope in order to make and record visual observations during the run.

3.4.7. After the Run

1. Remove and save the sample from the TGA.

2. Press the Playback key on the TA and enter time for the x-axis, and temperature, weight, and derivative of weight for curves 1, 2, and 3 respectively.

3. Stop the valve program on the PC, and start the TAFILE program to automatically transfer the TA data to the PC. The TAFILE program listing is given in APPENDIX B.
4. RESULTS

Experimental runs were made at five different sets of conditions. At each set of conditions runs were made at several different temperatures. The conditions set consisted of the gas velocity and the solvent content of the gas. The conditions are listed in Table 1 below:

Table 1. Experimental Conditions

<table>
<thead>
<tr>
<th>Set Number</th>
<th>Gas Velocity (cm/min)</th>
<th>Solvent content ( \frac{P_s - P_g}{P_s} \times 100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>115.5</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>115.5</td>
<td>45.0</td>
</tr>
<tr>
<td>3</td>
<td>115.5</td>
<td>79.0</td>
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<td>4</td>
<td>202.1</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>288.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The gas velocity is calculated from the mass flowrates recorded by the flowmeters under the ideal gas assumption ignoring the presence of solvent vapor. The solvent content is represent by the value,
Table 2. Experimental Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Starting Wt.</th>
<th>Gas Velocity</th>
<th>Solvent Content</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution</td>
<td>(1-Ps/Pg) x 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg</td>
<td>cm/min</td>
<td>Ps-Pg</td>
<td>°C</td>
</tr>
<tr>
<td>1</td>
<td>39.21</td>
<td>115.5</td>
<td>0.0</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>47.58</td>
<td>115.5</td>
<td>0.0</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>28.54</td>
<td>115.5</td>
<td>0.0</td>
<td>73</td>
</tr>
<tr>
<td>10</td>
<td>36.02</td>
<td>288.7</td>
<td>0.0</td>
<td>22</td>
</tr>
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<td>11</td>
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<td>288.7</td>
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</tr>
<tr>
<td>12</td>
<td>36.43</td>
<td>288.7</td>
<td>0.0</td>
<td>38</td>
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<tr>
<td>13</td>
<td>48.82</td>
<td>288.7</td>
<td>0.0</td>
<td>62</td>
</tr>
<tr>
<td>14</td>
<td>45.61</td>
<td>288.7</td>
<td>0.0</td>
<td>74</td>
</tr>
<tr>
<td>15</td>
<td>34.33</td>
<td>115.5</td>
<td>0.0</td>
<td>31</td>
</tr>
<tr>
<td>17</td>
<td>45.02</td>
<td>115.5</td>
<td>46.0</td>
<td>20</td>
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<tr>
<td>18</td>
<td>46.77</td>
<td>115.5</td>
<td>45.7</td>
<td>33</td>
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<td>115.5</td>
<td>45.8</td>
<td>48</td>
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<td>54.23</td>
<td>115.5</td>
<td>44.0</td>
<td>66</td>
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<tr>
<td>21</td>
<td>64.04</td>
<td>115.5</td>
<td>43.0</td>
<td>97</td>
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</tr>
<tr>
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<td>38.33</td>
<td>115.5</td>
<td>0.0</td>
<td>53</td>
</tr>
<tr>
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<td>59.27</td>
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<td>25</td>
<td>41.11</td>
<td>115.5</td>
<td>77.6</td>
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<tr>
<td>26</td>
<td>57.00</td>
<td>115.5</td>
<td>78.0</td>
<td>31</td>
</tr>
<tr>
<td>27</td>
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<td>115.5</td>
<td>77.7</td>
<td>45</td>
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<td>28</td>
<td>41.86</td>
<td>202.1</td>
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<tr>
<td>29</td>
<td>51.94</td>
<td>202.1</td>
<td>0.0</td>
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<tr>
<td>30</td>
<td>46.22</td>
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<td>72</td>
</tr>
<tr>
<td>32</td>
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<td>202.1</td>
<td>0.0</td>
<td>37</td>
</tr>
<tr>
<td>34</td>
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<td>202.1</td>
<td>0.0</td>
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<tr>
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<td>82</td>
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<td>29.79</td>
<td>115.5</td>
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<td>84</td>
</tr>
<tr>
<td>37</td>
<td>42.89</td>
<td>115.5</td>
<td>45.0</td>
<td>76</td>
</tr>
</tbody>
</table>
where $P_s$ is the vapor pressure of the solvent at saturation, and $P_g$ is the vapor pressure at the experimental conditions. This value can be calculated by

$$ (1 - \frac{P_s - P_g}{P_s}) \times 100 $$

(27)

where $a_s$ is the absorbance reading on the spectrophotometer for a saturated gas stream, and $a_g$ is the absorbance reading at the environmental conditions. Figures 21 through 25 show the solvent loss vs. time for five experimental runs at five different temperatures for the operating conditions of sets 1 through 5 respectively, as the sets are listed in Table 1. The data are taken directly from the date recorded by the TA. The solvent loss is recorded as the weight percentage of the initial sample.

Figures 26 through 30 plot evaporation flux vs. temperature at different stages during the run for sets 1 through 5 respectively. The evaporation flux is calculated when the sample is 75%, 65%, 55%, and 45% by weight solvent and plotted vs. temperature. The values of the flux at each stage are connected to the other runs for that set of conditions to show effect of temperature. The evaporation flux is calculated from the derivative of the
Figure 21. Experimental for Runs in Set 1, Gas Velocity = 115.5 cm/min and Solvent Content = 0% for Several Temperatures. A = Run 1 at 23°C, B = Run 15 at 31°C, C = Run 23 at 53°C, D = Run 9 at 73°C, and E = Run 22 at 94°C
Figure 22. Experimental for Runs in Set 2, Gas Velocity = 115.5 cm/min and Solvent Content = 45% for Several Temperatures. A=Run 17 at 20°C, B=Run 18 at 33°C, D=Runs 19 and 20 at 48°C and 66°C, Respectively, and E=Run 21 at 97°C.
Figure 23. Experimental for Runs in Set 3, Gas Velocity = 115.5 cm/min and Solvent Content = 79% for Several Temperatures. A=Run 25 at 20°C, B=Run 26 at 31°C, C=Run 7 at 45°C, D=Run 31 at 72°C, and E=Run 30 at 98°C
Solvent loss vs. Time

Figure 24. Experimental for Runs in Set 4, Gas Velocity = 202.1 cm/min and Solvent Content = 0% for Several Temperatures. A=Run 28 at 25°C, B=Run 29 at 32°C, C=Run 32 at 37°C, D=Run 34 at 69°C, and E=Run 35 at 82°C
Figure 25. Experimental for Runs in Set 5, Gas Velocity = 288.7 cm/min and Solvent Content = 0% for Several Temperatures. A=Run 10 at 22°C, B=Run 11 at 30°C, C=Run 12 at 38°C, D=Run 13 at 62°C, and E=Run 14 at 74°C
Evaporation flux vs. Temp.

Figure 26. Solvent Flux vs. Temperature for the Data from Set 1, Gas Velocity = 115.5 cm/min and Solvent Content = 0%. The Solid Lines Connect Data from Several Runs at the Same Stage of Drying, i.e. 75% by Weight Solvent.
Evaporation flux vs. Temp.

Figure 27. Solvent Flux vs. Temperature for the Data from Set 2, Gas Velocity = 115.5 cm/min and Solvent Content = 45%. The Solid Lines Connect Data from Several Runs at the Same Stage of Drying, i.e. 75% by Weight Solvent
Figure 28. Solvent Flux vs. Temperature for the Data from Set 3, Gas Velocity = 115.5 cm/min and Solvent Content = 79%. The Solid Lines Connect Data from Several Runs at the Same Stage of Drying, i.e. 75% by Weight Solvent
Figure 29. Solvent Flux vs. Temperature for the Data from Set 4, Gas Velocity = 202.1 cm/min and Solvent Content = 0%. The Solid Lines Connect Data from Several Runs at the Same Stage of Drying, i.e. 75% by Weight Solvent.
Figure 30. Solvent Flux vs. Temperature for the Data from Set 5. Gas Velocity = 288.7 cm/min and Solvent Content = 0%. The Solid Lines Connect Data from Several Runs at the Same Stage of Drying, i.e., 75% by Weight Solvent.
weight loss with respect to time by

$$E = \frac{dw}{dt} \frac{M_0}{A}$$  \hspace{1cm} (29)$$

where $E$ is the evaporation flux, $dw/dt$ is the derivative of the weight loss as a percentage as recorded by the TA, $M_0$ is the initial weight of the sample, and $A$ is the area of the pan (0.332 cm$^2$).

Figures 31 through 35 plot $\log(m_1/m_2)$ vs. $\log(t/L^2)$ for the runs of sets 1 through 5 respectively. These plots can be used to distinguish between the two phases of drying as mentioned before. The weight of polymer, $M_2$, is a constant for each run and given by

$$M_2 = 0.20 M_0$$  \hspace{1cm} (30)$$

The weight of solvent, $M_1$, at time, $t$, is given by

$$M_1 = (w \times M_0) - M_2$$  \hspace{1cm} (31)$$

where $w$ is the weight percent of the original sample at time, $t$, as recorded by the TA. The thickness of the film, $L$, at time $t$ is given by

$$L = \frac{V}{A}$$  \hspace{1cm} (32)$$

where $V$ is the volume of the solution at time $t$, and is estimated by
Figure 31. Log($m_1/m_2$) vs. Log($t/L^2$) for Set 1, Gas Velocity = 115.5 cm/min and Solvent Content = 0%, ABCDE as in Figure 21
Log-Log Plot of $m_1/m_2$ vs. $t/l^2$

Figure 32. Log($m_1/m_2$) vs. Log($t/L^2$) for Set 2, Gas Velocity = 115.5 cm/min and Solvent Content = 45%, ABCDE as in Figure 22
Figure 33. \( \log(m_1/m_2) \) vs. \( \log(t/L^2) \) for Set 3, Gas Velocity = 115.5 cm/min and Solvent Content = 79%, ABCDE as in Figure 23
Figure 34. $\log(m_1/m_2)$ vs. $\log(t/L^2)$ for Set 4, Gas Velocity = 202.1 cm/min and Solvent Content = 0%, ABCDE as in Figure 24
Log-Log Plot of $m_1/m_2$ vs. $t/1*1$

Figure 35. $\log(m_1/m_2)$ vs. $\log(t/L^2)$ for Set 5, Gas Velocity = 288.7 cm/min and Solvent Content = 0%, ABCDE as in Figure 25
\[ V = \frac{m_1}{V_1} + \frac{m_2}{V_2} \] (33)

where \( V_1 \) and \( V_2 \) are the specific volumes of the solvent and polymer respectively. The specific volume of the toluene is 1.159 cm\(^3\)/gm and the specific volume of the PMMA is 0.8078 cm\(^3\)/gm.
5. DISCUSSION

This section of the thesis is divided into two parts. The first part being a discussion of the performance of the apparatus and suggestions for its improvement. The second part is a discussion of the experimental results and any conclusion drawn from them.

5.1. Performance of Apparatus

The apparatus performed well despite several problems in the initial operation of the apparatus. The mechanical failure of the TA's disk drive resulted in the loss of data for some of the first experimental runs, runs 2-6 and 8. Also in the early runs the final value of the communication parameters (baud rate, word size, and parity) were not yet determined and the communication between the PC and the instruments failed causing the runs to be aborted. Although the instrument and the PC had a wide range of selectable communication parameters the communication between them only worked on a more limited range. The final settings for the parameters were found by trial and error. Even though the communication or the recording of the data failed for some of the initial runs the TA still plotted the real-time data for weight loss vs. time, but those results could not be reproduced for
this thesis. The initial runs were conducted at the same conditions to determine the repeatability of the experiments and the plots showed good agreement. The data for runs 1 and 7 did survive and are plotted in Figure 36.

The apparatus does have some deficiencies. First there is no control over the pressure and all the runs were conducted at atmospheric pressure. The effect of elevated pressures on drying rates has been studied by Robinson et al. [40]. Secondly the start up procedure needs to be improved. Specifically the time between injecting the solution and when the TGA starts recording weight loss should be shortened. Presently the furnace tube has to be removed and then replaced and tightened after injecting the solution and before starting the TA. This takes about 30 seconds. Also the TGA cannot be preheated and it takes about 2-3 minutes to reach the higher temperatures used in this study, but the TA does record the weight loss during this period.

Other possible concerns but yet undetermined effects include the flow over the sample, the edge effect of the sample pan and possible thermal gradients between the upstream and downstream portions of the film. Figure 37 is an enlarged view of the sample pan in the furnace tube. As shown in Figure 37 the gas flow may deviate slightly from a purely parallel flow that would be experienced in a continuous or larger system. Also shown is the meniscus
Figure 36. Experimental Data for Runs 1 and 7 Both at Gas Velocity = 115.5 cm/min, Solvent Content 0%, and the Same Temperature 22°C
that forms along the perimeter of the pan; this becomes more pronounced as volume of the solution shrinks. In Figure 14 the sample is positioned just outside the furnace to enable visual observations, therefore there is a temperature gradient across the sample. The high thermal conductivity of aluminum and the thinness of polymer film minimize this effect.

5.2. Discussion of the Experimental Results

The visual observation made on the drying films showed two phenomena occurring. The two phenomena are bubble formation and the formation of standing waves. Bubble formation occurred in almost all the runs. The waves occurred only on the runs made at higher velocities, the runs of sets 4 and 5. The surface characteristics of the film were hard to observe because the solution is clear and the surface could not be focused in on with the microscope.
Bubble formation started almost within the first few minutes of the runs. The bubbles would grow until about 75% of the solvent had been removed. The number and size of the bubbles increased with increasing temperature. The bubbles coalesced to form larger bubbles and by the end of the run usually only a single bubble remained. The bubbles never broke the surface of the film and never shrunk in size once formed. They did appear to form homogeneously in the solution. The bubble migrated to the center of the samples or around the edge in the meniscus region. In the runs where the waves formed the bubble sometimes moved to the wave peaks. At the highest temperatures for sets 1, 4, and 5 the final bubble was equal to the diameter size of the sample pan. Only runs 25 and 26, the lowest temperature runs of set 3, did not have any bubble formation. Figure 38 parts a through c are sequential micrographs of the bubble growth and combination for run 22, the highest temperature run of set 1. Figure 39 shows the waves that formed during run 12 of set 5, which had the highest gas velocity. The presence of the waves was noticed by observing refracted light patterns on the bottom of the sample pan. For all the runs of sets 4 and 5 standing waves did form. The waves formed perpendicular to the gas flow and along the downstream edge of the sample pan. Generally 2 to 3 waves formed in the downstream half of the film. The magnitude
Figure 38a. Micrograph of Drying Film at 4 min. into Run 22 (Magnified 20x)
Figure 38b. Micrograph of Drying Film at 6 min. into Run 22 (Magnified 20x)
Figure 38c. Micrograph of Drying Film at 10 min. into Run 22 (Magnified 20x)
Figure 39. Micrograph of Drying Film at 15 min. into Run 12 (Magnified 20x)
of the wave appeared to decrease as the volume of the solution decreased.

The effect of temperature on solvent removal rates can be seen in Figures 21 and 22, the weight loss vs. time for several temperatures at the experimental conditions of sets 1 and 2 respectively. Figures 21 and 22 show that increasing temperature results in faster solvent removal rates until some optimum temperature is reached and then the solvent removal rates decrease with increasing temperature. This agrees qualitatively with predictions of Roehner's mathematical model [1-2]. Higher temperatures can result in skin formation and then slower removal rates. The presence of a skin layer is further supported by the fact that bubbles never broke the surface.

Skin formation can be suppressed with increased solvent content in the carrier gas [1-2] This is shown in Figure 23 for experimental set 3 at higher solvent content in the carrier gas. In Figure 23 increasing temperatures result in faster solvent removal rates with no optimum. Figures 24 and 25 also show no optimum between increasing temperature and faster solvent removal rates. The effect of skin formation on the removal rates is most likely caused by the increase surface area of the film due to wave formation. Wave formation could explain the discrepancies between model predictions and actual solvent
removal rates. This effect may go unnoticed in larger industrial driers because the waves in the final film would be reduced due to volumetric shrinkage of the film by solvent removal.

The effect of skin formation on solvent removal rates can also be seen in the plots of the evaporation flux vs. temperature, Figures 26-30. In Figures 26 and 27 for sets 1 and 2, respectively, increasing temperature results in higher solvent fluxes during the initial stages of drying, when the solution is still 75% by weight solvent. After skin formation, increased temperature has no effect on the solvent flux or can actually decrease the solvent flux, as shown by the curves for 65%, 55% and 45%. Figures 28-30 show that when skin formation is suppressed by high solvent content in the carrier gas (set 3) or overcome by wave formation (sets 4 and 5) an increase in temperature results in higher solvent flux at all stages of drying.

The plots of \( \log(m_s/m_p) \) vs. \( \log(t/L^2) \), Figures 31-35, show for the solution concentration and experimental conditions used on this study the drying is in the transition phase. The plots show the first phase is very short and the drying almost immediately enters the transition phase. Only the high temperature runs of sets 4 and 5, Figures 34 and 35, are fully into the second phase of drying.
6. CONCLUSIONS AND RECOMMENDATIONS

The use of high temperatures for the solvent removal from solution-cast polymer film can lead to skin formation resulting in a lower solvent removal rates. High solvent content in the carrier gas will prevent skin formation but may not improve the solvent removal rates. These results agree qualitatively with the predictions of a mathematical model developed by Roehner [1,2]. Disagreement between the experimental results and the model's prediction occur at higher gas velocities where the model predicts skinning and slower removal rates with high temperatures, but experimental results show increasing removal rates with higher temperatures. Visual observations of the drying films revealed the formation of standing waves in the film surface at higher gas velocities. The formation of standing waves will result in larger surface area and therefore fast solvent removal rates. This could explain the disagreement between the experimental results and the model's prediction.

Suggestion for further research include the use of opaque solutions to aid in the visual observations of the film surface. The use of a higher boiling solvent could eliminate any possible effects caused by the bubbles, but may lengthen the time required for experimental runs. A
study of the effect of the sample pan on the gas flow and its relation to wave formation could also prove useful.
REFERENCES


24. K. Arai, C. Veda-Mashima, J. Kotuda, K. Yoshimura,


APPENDIX A - Notation

Roman Letter Symbols

\( a_g \) - Absorbance reading on the spectrophotometer
\( a_s \) - Absorbance reading at the environmental conditions
\( C \) - Concentration
\( D \) - Diffusion coefficient
\( D_b \) - Deborah number
\( E \) - Young's modulus
\( e_s \) - Interfacial strain
\( F \) - Mass flux/area
\( h_i \) - Thickness of component i in composite films
\( L \) - Film thickness
\( M_w \) - Molecular weight (weight average)
\( m_1 \) - Mass of solvent
\( m_2 \) - Mass of polymer
\( P \) - Compressive force
\( P_g \) - Vapor pressure at the experimental conditions
\( P_s \) - Vapor pressure of the solvent at saturation
\( S \) - Interfacial force
\( \Delta T \) - Temperature change
\( T_C \) - Cast temperature
\( T_g \) - Glass transition time
\( T_{1/2} \) - The time to remove half of the solvent
t - Time
V - Curl
W - Film thickness (Figure 5)
x - Position

Greek Letter Symbols

α - Linear expansion coefficient
θ - Characteristic solvent diffusion time
δ - Solubility parameter
σ - Stress-strength
λ - Relaxation time
n - Intrinsic viscosity
Δ - Birefringence
ρ - Radius of curvature
υ - Poisson ratio

Abbreviations

CTA - Cellulose triacetate
GLC - Gas liquid chromatography
IL - Interfacial layer
MEK - Methylethylketone
PMMA - Polymethylmethacrylate
PC - Polycarbonate or personal computer
PPC - Plasticized polycarbonate
PVC - Polyvinylchloride
PVK - Poly-N-vinyl carbazole
TA - Thermal analyzer
TGA - Thermogravimetric analyzer
VDC - Direct current voltage
APPENDIX B - Computer Programs

SPEC PROGRAM

by Gerald W. Powers

Program to read, display and record the absorbance readings from the spectrometer.
Can be made into a subroutine.

real x,y
character*75 word,word2
character a,b,c,d,e,f,g,h
open(unit=1,file='coml',status='old')
open(unit=2,file='corry',status='new')
b='\x44'C

c='\x2c'C
d='\x33'C
e='\x2c'C
f='\x30'C

b,c,d,e,f hexadecimal code for d,3,0 the spectrometer command requesting wavelength and absorbance readings

write(1,100)b,c,d,e,f
100 format(5(a1))

read then display and record wavelength and absorbance reading

read(1,*)x,y
write(*,*)x,y
write(2,*)x,y
stop
end
TAFILE PROGRAM

by Gerald W. Powers

program to transfer data from duPont TA's disk memory to the PC

REAL X,Y,w,z
CHARACTER WORD
OPEN(UNIT=1,FILE='COM1',STATUS='OLD')
OPEN(UNIT=2,FILE='DATA1')

send TA command, @SF, to TA
@SF=send file

WRITE(1,15)
15 FORMAT('@SF')

read first 12 file lines containing
identification

DO 20 I=1,12
READ (1,10)WORD
WRITE (2,10)WORD
10 FORMAT(A80)
20 CONTINUE

read and record data from TA file
x=time
y=temp.
w=weight
z=derivative of weight w.r.t. time

5 READ(1,*)X,Y,w,z
WRITE(2,*)X,Y,w,z
GOTO 5

program terminates with end of file signal from TA

STOP
END
VALVE PROGRAM

by Gerald W. Powers

This program controls the flowrates of three gas lines.

real set(3), vout(3), vcho(3), pr(3), viw(3), diff
open(unit=1, file='com1', status='old')

input the set points for the flowrates of the wet, dry, and purge gas lines.

do 510 i=1, 3
  write(*,500)i
  read(*,*) set(i)
500 format(' input set point for valve', il, ', (cc/min)')

  convert flowrate (cc/min) to millivolts
  2000 cc/min = 500 millivolts

  vcho(i)= set(i)/4.0
505 format('vout', il, '= ', f7.4)
510 continue
  vout(1)=5.5
  vout(2)=5.5
  vout(3)=5.5
100 do 400 i=1, 3

  send voltage out analog output channel i
to control valve i
write(1,505)i, vout(i)

  request and read voltage reading from
  analog input channel i
  for flowmeter i
write(1,120)i
120 format('viw', il)
read(1,60) viw(i)

  convert flowmeter reading from volts to cc/min

  pr(i)= viw(i)*4.0
60 format( 'f10.4')
VALVE program continued...

calculate difference between desired flowrate and actual then calculate new voltage output to valve

diff=vcho(i)-viw(i)
vout(i)=vout(i) + 0.0001*diff

display flowrates

if(i.eq.3)then
write(*,75)pr(1),pr(2),pr(3)
end if
75 format(3(5x,f10.4))
400 continue

goto 100

the program is terminated by entering control C

stop

end