

# Polymer Film Deposition by a New Vacuum Process

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## ABSTRACT

In recent years a number of papers have been written concerning vacuum web coating of acrylate films onto a variety of substrates, for a variety of applications, utilizing the Polymer Multi-Layer (PML) process for flash evaporation of monomer fluids [1-12]. While of interest to many, widespread implementation of the PML process has not occurred, in part due certain process limitations and stability issues. With traditional PML deposition a relatively long time is required for the process to reach equilibrium once liquid monomer flow to the evaporator is initiated, and a much longer time is required for gaseous monomer output from the evaporator to subside once the liquid monomer flow is terminated. This lack of instant-on/instant-off capability will be seen to be particularly problematic for in-line batch coaters. Further, control of the traditional PML process becomes increasingly difficult as web speeds decrease. This makes it difficult to match in-line deposition rates and line speeds with slower processes such as sputtering. There is also a tendency, with traditional PML evaporators, for the rate to decrease steadily with time as monomer polymerizes inside the evaporator and interferes with heat transfer between the walls and the freshly injected liquid monomer. A new Vacuum Monomer Technique (VMT), which utilizes a new low temperature source design to produce gaseous monomer, has been developed that allows vacuum deposition of acrylate films with the same properties (ultra smooth and pinhole-free) as PML deposited films. The new VMT process should permit sub-micron or multiple-micron thick films to be deposited at web speeds in excess of 100 meters per minute as in the PML process. However, unlike the PML process, the VMT process should also permit controlled deposition of very thin films at very low web speeds (100s of Angstroms thick at a fraction of a meter per minute). The VMT process should also be far more applicable to in-line batch coating processes than is the PML process since, for practical purposes, it can be turned on and off instantly. There is a large overlap between the classes of starting monomers used in the PML and VMT processes so a great deal of insight into the VMT process can be gleaned from the PML literature. The VMT process will be described, a complete mathematical description and model for the process will be developed, and data relevant to barrier films and optical coatings will be presented.

## INTRODUCTION

The PML deposition process, while potentially commercially useful and capable of high rate deposition, could be improved if some process limitations were removed and some process stability issues were addressed. This work began as an effort to address some of these PML process issues. In this effort to reduce the background monomer pressure during PML deposition, reduce the time required to start and stop the PML flash evaporator, and eliminate monomer polymerization within the flash evaporator, a fundamental study of the processes involved was undertaken. As a result a new technique for vacuum deposition of polymer films was developed. This technique does not rely on flash evaporation of the monomer material. Instead, this new Vacuum Monomer Technique (VMT) uses a low temperature monomer source/reservoir (generally less than 80°C) and relies on the vapor pressure difference between liquid within the monomer source and liquid condensed onto the surface of the cooled substrate.

The PML process will be discussed briefly to illustrate the limitations that this work set out to overcome. This will lead into the mathematical analysis employed to describe the evaporation process in order to understand the process more completely. From the mathematical analysis a new approach to the evaporation, and subsequent condensation onto a surface, of monomer fluids will naturally emerge.

## Review of the PML Process

The PML flash evaporation web coating process begins with degassing a monomer fluid to a suitable base pressure. The degassed monomer is then continuously atomized to a fine mist and sprayed over as large an area as possible on the interior of a very hot enclosure that has a heated pressure baffling expansion nozzle at one end. By "very hot", it is meant that the enclosure walls are hot enough to instantly vaporize the monomer mist, without a pool of liquid forming, yet, hopefully, not hot enough to pyrolyze and/or polymerize the monomer on contact (typically between 150°C and 450°C, depending on the monomer in use). Under these conditions the monomer evaporates as quickly as it is introduced into the enclosure. Thus, the mass flow of monomer gas exiting the nozzle should be directly calculable from the monomer fluid feed rate. In a web coating process the monomer gas exits the

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evaporator through a narrow slit as a uniform line source, condenses as a liquid film on the cooled substrate that is moving past the slit, and the liquid film is subsequently polymerized when the substrate passes an ultraviolet or electron beam radiation source. Since the evaporator/slit can be constructed so as to emit a uniform density line of gas then, as long as the total fluid input is steady in time, the coated web will be uniform in thickness along both its length and width.

The reason that monomer fluid is atomized to a fine mist and sprayed over as large an area as possible on the interior of a very hot enclosure is to reduce the cooling affects of the liquid on the hot interior surface of the evaporator. If the rate of monomer mass impingement per unit area is too high, and the surface cools too much, then monomer liquid may build up on the interior surfaces of the evaporator. If such liquid build up occurs, and the monomer resides on the surface for too long, the monomer will polymerize inside the evaporator. When the monomer polymerizes inside the evaporator the resultant polymer film interferes with the heat transfer between the surface and the subsequently atomized liquid. Gradually more and more polymerization occurs, causing the heat transfer to continuously degrade, and the rate of monomer retention within the evaporator continuously increases over the duration of the run. Thus, typically the PML deposition rate is not constant, but slowly decreases with time for constant flow of liquid monomer to the atomizer. Ultrasonic atomizers are also prone to produce pulsed outputs, particularly under low flow conditions, which also causes film thickness variations along the length of the web.

Due to the mechanical limitations of the monomer delivery/atomization step it takes a “while” for the gaseous monomer output to reach its quasi-steady state value once liquid flow begins, and it takes a much longer “while” for the gaseous monomer output to stop once the liquid flow is terminated. The time between initiating the liquid flow and quasi-steady state gaseous output can range from tens of seconds to minutes depending on the exact nature of the plumbing. The time between terminating the liquid flow and zero gaseous output (even near enough zero gaseous output for practical purposes) ranges from minutes to much longer. In fact, on shut-off, the monomer lines are typically purged through the atomizer/evaporator systems with an inert gas in order to prevent the residual liquid, which continuously seeps into the atomizer, from polymerizing and clogging the atomizer. These limitations are not too severe for a continuous web coating process where a substrate leader and trailer section (even run at lower speed) can be used. However, they will be shown to be highly problematic when discrete parts are coated in an in-line batch processing tool.

With an in-line batch coater, if a line source evaporator is used and left on continuously, the part can simply be moved past the line source to obtain a coating of uniform thickness. With

such a source cold shutters would be required to condense all monomer gas, except when the part passes directly over the slit, or else large volumes of monomer would build up inside of the vacuum chamber and create a severe housekeeping problem. Since the PML source takes such a long time to turn on and shut off, during most of the monomer “on-time” the monomer would be collected on the shields and only a small fraction of the “on-time” would actually be used for deposition. Under such circumstances, if cold shutters are used, the shutters will quickly reach saturation and limit the run duration. Instead of a slit, a shower-head evaporator outlet nozzle could be designed to give uniform areal coverage over the entire part. The part could then be positioned prior to injection/atomization of a known volume of liquid monomer and moved on to the cure station once the gaseous output dies down and the source is shuttered. Unfortunately, from the moment any monomer condenses on the part the condensed monomer is also re-evaporating from the part. The thickness of the resulting polymer film will depend not only on the total monomer flow through the evaporator but also on the temperature versus time profile of the substrate over the entire time between the start of the monomer flow through the final polymerization step. It is very difficult to cool the substrates in such a batch coater, except prior to beginning to move them through the system. As will be seen, the film thickness errors resulting from process control errors under these circumstances are daunting. It will be seen that deposition of 10s to 100s of microns of material may be needed in order to have 1 micron of polymer after the cure step. Compounding this, it will also be seen that the variations in resultant film thickness, due to process variations, can be up to 10s of microns per second of transit time, and 10s of microns per °C in substrate temperature. Thus, it can be a nearly impossible task to control film thickness to any reasonable accuracy in a PML batch coater.

Lastly, it is very difficult to prevent monomer from polymerizing inside of the evaporator and causing a gradual decrease in gaseous output over the duration of any deposition process. Generally, the higher the molecular weight of the liquid monomer, the higher the evaporator temperature required for flash evaporation and the more severe the problem of polymerization within the evaporator.

## **THEORY AND MATHEMATICAL DEVELOPMENT**

### **Evaporation Theory**

It has long been known that the vapor pressure of any liquid in equilibrium with its vapor can be calculated by equating the molar Gibbs free energies of the liquid and vapor phases and rearranging terms, with the assumption that there are no chemical reactions or flux losses [13]. The resulting expression for vapor pressure (known as Hildebrand’s Rule [13]) depends only on the Kelvin temperature, the molar enthalpy of vaporization, and the molar volume of the gas.

Thus, for systems of known materials in equilibrium, it is only necessary to know the temperature in order to determine impingement rates from the gas to the liquid surface, or emission rates from the liquid to the gaseous volume. This last statement pre-supposes knowledge of the molar enthalpy of vaporization for the material in question. There is much literature devoted to tabulations of the vapor pressure versus temperature characteristics of organic liquids and the fitting of these data to Hildebrand's rule [14]. Similar tabulations and analyses have been published for solids, such as metals, that have been melted and the resultant liquid is in equilibrium with its vapor [15]. Recent work has shown that Hildebrand's rule can be extended to situations where metals are evaporated onto substrates and there is both flux lost from the system and the liquid, gas, and system walls are at different temperatures [16, 17].

Following the development of Hildebrand's rule in Hirschfelder [13] it is seen that, for any single component evaporation process, the equilibrium vapor pressure of the gas above the liquid is given as:

$$P = 10^{\left(A - \frac{B}{T}\right)} \quad (\text{milliTorr}) \quad \text{Equation 1}$$

where A and B are constants which depend upon the material that is evaporating, and T is the Kelvin temperature of the liquid, gas, and enclosure surfaces. Please note that, while many units and experimental temperatures will be given in °C throughout the text, one must always use °K when performing calculations with any of the equations. The thermal equilibrium conditions, under which Equation 1 was first derived, are equivalent to the liquid being in a sealed enclosure, with no chemical reactions and with the liquid, vapor and all surfaces at the same temperature ( $T_{\text{gas}} = T_{\text{liq}} = T_{\text{surfaces}}$ ). The Hildebrand's Rule analysis is extended in Dushman and Lafferty [15] to yield the areal mass evaporation/impingement rate from/to a liquid surface in equilibrium with its vapor as:

$$W = 10^{\left(C - 0.5 \log(T) - \frac{B}{T}\right)} \quad \left(\frac{\text{g}}{\text{cm}^2 \cdot \text{s}}\right) \quad \text{Equation 2}$$

where C and B are constants which depend upon the material that is evaporating. B is the same B as in Equation 1, and C is a function of A and molecular weight. Equation 2 still assumes thermal equilibrium.

### Non-Equilibrium Evaporation Process Analysis

Moltech's Vacuum Group has extended this analysis [16, 17] to non-equilibrium situations. The Moltech work has shown that Equations 1 and 2 (with either the surface or gas tempera-

ture) can be applied to any evaporation situation, and any surface, in which the species entering the gas phase from a surface is the same as the species impinging on that surface from the gas phase. In other words, Equations 1 and 2 will always apply when only thermal processes are important (i.e. as long as there are no chemical reactions or non-thermal physical bombardment processes taking place in the gas or liquid phases, or on the surfaces).

This relaxation of the constraint on the applicability of Equations 1 and 2 permits modeling of real systems. It allows for species to condense, for practical purposes, permanently onto surfaces. Species can escape from the evaporation enclosure entirely, and the realistic situation where  $T_{\text{gas}} \neq T_{\text{liq}} \neq T_{\text{surfaces}}$  can now be modeled. Extension of this analysis to modeling monomer evaporation and condensation process allows engineering and construction of evaporators for which the film thickness, chamber pressure, and all relevant rates of change can be calculated strictly from Equations 1 and 2, system geometry, and the elementary principles of Kinetic Theory.

The Moltech publications [16, 17] use a mass balance analysis to develop equations of constraint that connect all of the evaporated flux streams within the system. The basis of the analysis is that the mass flux, in g/s, leaving any surface is given, from Equation 2, as  $W(T_{\text{surface}})$  times the area of that surface while the mass flux impinging upon any surface is given by  $W(T_{\text{gas}})$  times the area of that surface. The constraint arises by requiring that the total flux that enters the gas phase (due to emission from all surfaces) must exactly match the total flux that condenses onto all surfaces plus the flux that escapes from the system—in other words, conservation of flux. Given that the liquid temperature and all surface temperatures are known, the analysis requires a specific temperature distribution of the gas within the evaporator in order to balance all of the flux. In a wide variety of situations the gas turns out to be isothermal [16, 17]. An isothermal gas distribution is represented by a single temperature, and allows a simple algebraic solution of the constraint equation for a single value of  $T_{\text{gas}}$ . If the gas is not isothermal then a self-consistent boundary value problem must be solved in order to determine  $T_{\text{gas}}$  as a function of position. In either situation the local value of  $T_{\text{gas}}$  determines the local impingement rate, and the local value of  $T_{\text{liq}}$  or  $T_{\text{surface}}$  determines the local emission rate. The Moltech publications [16, 17] demonstrate the validity of this approach for the specific case of Li evaporation from a complex geometry evaporator under non-equilibrium conditions. The following analysis draws upon, and extends, Moltech's prior Li work [16, 17].

## Engineering Analysis Of Monomer Evaporator Construction

In units of  $\text{g}/\text{cm}^2 \cdot \text{s}$ ,  $W(T)$  in Equation 2 allows calculation of the areal mass impingement rate onto, or emission from, any surface as long as  $T_{\text{gas}}$ , for impingement, or  $T_{\text{surface}}$  for emission, is known. If the surface has area  $A \text{ cm}^2$  then the total mass flux rate (emission or impingement) in  $\text{g}/\text{s}$  is given as:

$$\text{Total Mass Flux Rate} = W(T) \cdot A \left( \frac{\text{g}}{\text{s}} \right) \quad \text{Equation 3a}$$

If the total time  $t$  (in s) that the area  $A$  is emitting or receiving the flux is also known, then the total mass flux can be calculated as:

$$\text{Total Mass} = W(T) \cdot A \cdot t \quad (\text{g}) \quad \text{Equation 3b}$$

If the density  $\rho$  (in  $\text{g}/\text{cm}^3$ ) of the impinging/condensing material is known then  $d$ , the total accumulation of thickness on the surface (for impingement), or depletion (for emission), can be calculated as:

$$d = 10^4 \cdot \frac{W(T) \cdot A \cdot t}{\rho \cdot A} = 10^4 \cdot \frac{W(T) \cdot t}{\rho} \quad (\text{um}) \quad \text{Equation 3c}$$

If the substrate is not stationary, and the exposure time  $t$  actually results from the substrate moving past an aperture of width  $w \text{ cm}$  at velocity  $V \text{ m}/\text{min}$ , then the thickness is given as:

$$d = 10^4 \cdot \frac{W(T) \cdot w}{\rho \cdot V} \cdot \left( \frac{60}{100} \right) \quad (\text{um}) \quad \text{Equation 3d}$$

In steady state, flux must be continually both impinging on, and be emitted from, all surfaces in the system. Further, for any particular surface, if  $T_{\text{gas}} > T_{\text{surface}}$  there will be a net accumulation of material on that surface. Contrawise, for any particular surface, if  $T_{\text{gas}} < T_{\text{surface}}$  there will be a net loss of material from that surface. Thus, under steady state conditions, surfaces at temperatures below  $T_{\text{gas}}$  will act as flux sinks while surfaces at temperatures above  $T_{\text{gas}}$  will be depleted of species through emission.

A simplified spreadsheet model for a monomer evaporator has been developed. This model assumes a rectangular liquid surface of area  $A_{\text{liq}} = L_{\text{liq}} \cdot w_{\text{liq}}$  and a rectangular evaporator aperture of area  $A_{\text{e}} = L_{\text{e}} \cdot w_{\text{e}}$ . The substrate is taken as  $T_{\text{sub}} < T_{\text{liq}}$  and all evaporator surfaces are taken equal to  $T_{\text{liq}}$ . From the mass balance constraint analysis one finds that if any flux is

lost, or if any of the evaporator walls (or the substrate) are at lower temperature than  $T_{\text{liq}}$ , while no surfaces exceed  $T_{\text{liq}}$ , then  $T_{\text{gas}}$  must be less than  $T_{\text{liq}}$ . In the case of the spreadsheet model, some flux can escape at the aperture opening and some flux can build up on the substrate (while the substrate is over the aperture) since  $T_{\text{sub}} < T_{\text{liq}}$ . Since all other surfaces are at  $T_{\text{liq}}$ , which is higher than  $T_{\text{gas}}$ , flux does not build up on any other surfaces. Thus, in the spreadsheet model, the rate that flux is emitted from any non-substrate surface is greater than the rate at which it impinges upon that surface (because  $T_{\text{surface}} > T_{\text{gas}}$ ). Therefore, the walls can be neglected in the analysis and the only parameters needed to calculate  $T_{\text{gas}}$  are  $T_{\text{liq}}$ ,  $T_{\text{sub}}$ ,  $A_{\text{liq}}$  and  $A_{\text{e}}$  (actually,  $A_{\text{liq}}$  and  $A_{\text{e}}$  are not independent and only the ratio  $A_{\text{e}}/A_{\text{liq}}$  is really needed). Note that the assumption that all evaporator surfaces are at  $T_{\text{liq}}$  is only a computational convenience. The Moltech publications [16, 17] include walls that are not only less than  $T_{\text{liq}}$ , but have a  $100^\circ\text{C}$  gradient across them, but those calculations were done in MathCad and are not readily performed in a spreadsheet. Further, and not shown here, we have demonstrated that any complex geometry, and gradient containing, evaporator can be mathematically mapped into an equivalent simplified (rectangular with all walls at  $T_{\text{liq}}$ ) evaporator and then analyzed with the simplified spreadsheet model.

$T_{\text{gas}}$  is determined by solving the constraint equations which, in essence, amounts to summing all of the  $W(T) \cdot A$  products at all surfaces in the system (using  $T_{\text{gas}}$  for impingement and  $T_{\text{surface}}$  for emission) and then finding the value of  $T_{\text{gas}}$  that makes the sum go to zero.

The thickness accumulated on the substrate is then calculated as a sum from as many as three sources. The flux that condenses onto the substrate as the substrate passes the aperture yields, by Equation 3d, the maximum thickness that can actually accumulate on the substrate. If the substrate is so cold that, for practical purposes, no condensed flux is ever re-emitted then this is the only term of the sum that must be considered. This is the case for Li condensing onto a moving web below about  $300^\circ\text{C}$ . If the substrate temperature is high enough to allow substantial re-emission then more terms are needed. For deposition of liquid acrylate monomers, onto a near room temperature substrate, the condensed liquid monomer will be re-emitted constantly, both while the substrate is over the evaporator aperture and after the substrate has left the region above the evaporator aperture. Thus, unless the liquid acrylate monomer condensed onto the substrate is polymerized by some means, all of the liquid acrylate monomer will eventually evaporate from the surface of the substrate. If the acrylate is polymerized to form a solid at a position  $w_{\text{p}} \text{ cm}$  after passing the evaporator aperture then the total accumulated polymer thickness can be calculated. This is done, through use of Equation 3d, by calculating the monomer thickness condensed over the evaporator aperture minus the monomer

thickness re-emitted over the evaporator aperture minus the monomer thickness re-emitted as the substrate travels from the evaporator aperture to the cure position.

Note that, for purposes of the total thickness calculation, it is not actually necessary to artificially decompose the re-emission process into a portion over the evaporator and a portion outside of the evaporator. However, some portion of the gas that is re-emitted over the evaporator actually returns to the evaporator and must be accounted for when calculating  $T_{\text{gas}}$ . The portion that is re-emitted over the evaporator that does not return to the evaporator, plus the monomer re-emitted outside of the evaporator, goes into the vacuum chamber at large and contributes to the total gas load on the pumps and raises the chamber pressure. Thus, for these other reasons, it is convenient to decompose the re-emitted flux into these two contributions.

When liquid acrylate monomer of density  $\rho$  g/cm<sup>3</sup> condenses from gas at  $T_{\text{gas}}$  °K, onto a web at  $T_{\text{sub}}$  °K, through an aperture  $w_e$  cm wide, with the web moving at  $V$  m/min, and is polymerized a distance  $w_p$  cm after exiting the evaporator, the resultant polymer thickness is either

$$d = \frac{10^4}{\rho \cdot V} [W(T_{\text{gas}}) \cdot w_e - W(T_{\text{sub}}) \cdot w_e - W(T_{\text{sub}}) \cdot w_p] \cdot \left(\frac{60}{100}\right) \quad (\text{um})$$

Equation 4a

OR

$$d = \frac{10^4 \cdot w_e}{\rho \cdot V} \left[ W(T_{\text{gas}}) - W(T_{\text{sub}}) \cdot \left\{ 1 + \frac{w_p}{w_e} \right\} \right] \cdot \left(\frac{60}{100}\right) \quad (\text{um})$$

Equation 4b

Note that, in Equations 4a and 4b, the duration, for each step of the process, is given as (60/100)·(WIDTH/V) seconds, where WIDTH is the width of the particular process zone under consideration. Thus,  $d$  may also be written in terms of elapsed time as:

$$d = \frac{10^4}{\rho} [W(T_{\text{gas}}) \cdot t_e - W(T_{\text{sub}}) \cdot t_e - W(T_{\text{sub}}) \cdot t_p]$$

$$= \frac{10^4}{\rho} \left[ \{W(T_{\text{gas}}) - W(T_{\text{sub}})\} \cdot t_e - W(T_{\text{sub}}) \cdot t_p \right] \quad (\text{um})$$

Equation 4c

### Process Stability and Gradients

While Equations 4 will yield the polymer thickness obtained after polymerization, it is also important in any manufacturing process to understand the stability of the process with respect to fluctuations in the hardware, material, and process parameters. The resultant polymer film thickness, as given by

Equations 4, is a function of  $T_{\text{gas}}$ ,  $T_{\text{sub}}$ ,  $V$ ,  $w_e$ ,  $w_p$ ,  $\rho$  and indirectly, through  $W(T)$  in Equation 2, B and C. The first three variables are process parameters, the middle two are evaporator design parameters and the last three are material parameters. Differentiation of Equations 4 with respect to each of these parameters in turn will yield the Gradients of  $d$  with respect to each parameter—i.e. you find the change in  $d$  per unit change in the parameter of differentiation. The magnitudes of these gradients reveal the stability of the process with respect to fluctuations in the variables. For instance, a gradient of  $10^6$  um per degree °C change in  $T_{\text{gas}}$  would mean that if the temperature set point varied by only 1 °C the thickness would vary by 1 meter and the process, to say the least, would be unstable. A change of  $10^{-3}$  um per degree °C in  $T_{\text{gas}}$ , on the other hand, would be very stable with a variation of only 10 Å for a 1 °C change in  $T_{\text{gas}}$ . The gradients used in the spreadsheet model are listed in the APPENDIX.

At present the gradients with respect to B and C are not very useful, but they are included for completeness. The time and temperature derivatives, on the other hand, are most useful and insightful. In point of fact, time and temperature tell the entire story. In principle, and pretty much in fact, the physical dimensions can be measured and known with extreme accuracy. However, temperature and time (through velocity) must be experimentally controlled and offer the most chance for uncertainty and human error. For instance, on a 0 °C substrate our calculations show the evaporation rate for HDODA (Hexanediol Diacrylate) is more than 3 um/s. At 10 m/min, with 10 cm between evaporator and cure, 1.82 um of HDODA will be lost (between the evaporator and cure positions) with an error of 675 Å for every 1 °C error in substrate temperature.

Another numerical value that is relevant to system performance is the fraction ( $f$ ) of monomer that evaporates from the substrate between the evaporator and cure positions relative to the amount that is on the substrate as the substrate exits the evaporator. A high value of  $f$  may or may not indicate an unstable process, but it certainly indicates an inefficient process in which most of the monomer ends up as gas in the chamber. Manipulation of Equation 4a gives:

$$f = \frac{w_p}{w_e} \cdot \frac{W(T_{\text{sub}})}{W(T_{\text{gas}}) - W(T_{\text{sub}})} \quad (\text{no units}) \quad \text{Equation 5}$$

Related to the monomer that ends up in the vacuum chamber at large is the pressure rise that this monomer causes and the gas load that it creates for the pumping system. Therefore, it is useful to convert this monomer flux that is escaping to the vacuum chamber, and through the vacuum pumps or onto the walls, to an equivalent flow of monomer gas ( $F$  in sccm) for comparison to other process gas flows and estimation of the resultant rise in chamber pressure.

Before calculating this flow it is important to consider three aspects of the process in this idealized model. First, in the ideal evaporator, some fraction of the monomer re-emitted from the substrate while the web is positioned above the evaporator aperture escapes to the chamber while, after passing the aperture, ALL re-emitted monomer is lost to the chamber. Second, NO monomer can exist on the substrate after the substrate exits the evaporator unless  $T_{sub} < T_{gas}$  because monomer would be re-emitted at a higher rate than it is deposited when  $T_{sub} > T_{gas}$ . Third, when  $T_{sub} < T_{gas}$  there can be no resultant film thickness by the cure position unless a minimum threshold thickness of monomer is deposited onto the substrate as it is over the aperture. Since the monomer is re-emitted at a constant rate, and no more is being deposited outside of the evaporator, a constant thickness (for constant distance and temperature) always evaporates between the evaporator and the cure station. Thus, if the amount on the substrate is less than this constant value it is all evaporated by the time the cure station is reached. What this would look like in an experiment where film thickness is measured as a function of  $w_p$  is as follows. One would measure zero thickness as  $w_p$  is reduced from infinity toward some threshold value of  $w_{pth}$ . As  $w_p$  moves from  $w_{pth}$  to 0 (at the edge of the evaporator aperture) a linear increase in thickness with increasing  $[w_{pth} - w_p]$  would be observed. At  $w_p = 0$ , the maximum thickness, resulting from polymerizing the entire net accumulation of monomer due to traversing the aperture, is measured.

Assume an efficiency,  $0 \leq \epsilon \leq 1$ , for monomer re-emitted over the evaporator to return to the evaporator. If the evaporator were pressed tightly against the substrate with no gaps leading to the chamber, all re-emitted monomer would return, and the efficiency would be  $\epsilon = 1$ . However, as the size of gaps increases, and/or the width of the aperture decreases,  $\epsilon$  tends towards zero and it becomes more likely that re-emitted monomer would escape from the evaporator. The efficiency for re-emitted monomer to escape is just  $1 - \epsilon$ . Starting from Equation 3a, with a monomer of gram Molecular Weight MW, and inserting some proportionality constants to convert from g/s to sccm per m of web width, one finds the flow of monomer gas into the chamber and through the pumps to be:

$$F = \left( \frac{100 \cdot 60 \cdot 22,400}{MW} \right) [(1 - \epsilon) \cdot w_e + w_p] W(T_{sub}) \quad \text{Equation 6}$$

(sccm per m of web width)

For a vacuum pumping speed of  $S_v$  l/s, one then finds the monomer partial pressure, per m of web width, P to be:

$$P = \frac{F}{78.95 \cdot S_v} \quad (Torr \text{ per m of web width}) \quad \text{Equation 7}$$

## DISCUSSION AND RESULTS

The term VMT will be used to describe the process in which evaporated monomer gas emitted from a moderately warm reservoir/evaporator of liquid monomer condenses onto a substrate held at a lower temperature than the liquid reservoir. PML will refer to the process in which the monomer is flash evaporated. Resultant film thicknesses in VMT processes are determined by the temperature difference between the liquid reservoir and the substrate and the time that is required to move from the evaporator to the cure station. Film thickness in the PML process, ideally, is controlled by the rate of flow of liquid monomer into the flash evaporator, the temperature of the substrate, and the time that is required to move from the evaporator to the cure station.

With our spreadsheet model we can model all aspects of the performance of an evaporator/monomer combination, in either the VMT or PML configuration, or we can design an evaporator/monomer combination to meet any necessary performance specifications. This is done by entering geometric data, liquid and substrate temperatures, web speed, vacuum pump speed, and selecting the monomer. The only external data required are the vapor pressure versus temperature characteristics for the monomer (i.e. A, B, and C in Equations 1 and 2). When modeling a PML system there is still not a consistent procedure for compensating for the rate decrease due to monomer polymerizing within the evaporator.

We currently have measured vapor pressure data on 9 monomers of interest. Figures 1 and 2 show one sheet of the VMT workbook for the monomers Tripropyleneglycol Diacrylate (TRPGDA), with the substrate at 10°C, and Hexanediol Diacrylate (HDODA), with the substrate at 0°C. The substrate temperatures chosen are the minimum allowable for each monomer since, for substrate temperatures any lower, the monomer mobility becomes too low for proper polymerization. Figures 1 and 2 are for web coating processes, and we have analogous worksheets for modeling batch coaters. The main difference between the web and batch models is that the post evaporator monomer re-emitting area in the web model is the product of the web width and the evaporator-to-cure distance, while in the batch model the re-emission area is the actual area of the coated part. Figures 1 and 2 also indicate a maximum temperature for the liquid, above which there is a possibility that the liquid will polymerize within the evaporator.

Examination of Figures 1 and 2 shows that, for a VMT system, the difference between the liquid temperature and the substrate temperature must be large enough that there is still condensed monomer, of the correct thickness, on the substrate at the position of the cure station. Further work with the



$$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$$

T <sub>gas</sub> (°C)	$\frac{\partial d}{\partial w_e}$ (um/cm)	$\frac{\partial d}{\partial w_p}$ (um/cm)	$\frac{\partial d}{\partial \rho}$ (um/(g/cm <sup>3</sup> ))	$\frac{\partial d}{\partial t_c}$ (um/s)	$\frac{\partial d}{\partial t_p}$ (um/s)	$\frac{\partial d}{\partial C}$ (um/unitC)	$\frac{\partial d}{\partial B}$ (um/unitB)	f um evap um dep	Monomer Flow Into Chamber in (sccm per m web width)	Resultant Chamber Pressure Due To Flow (Torr)
-40	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-35	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-30	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-25	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-20	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-15	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-5	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
15	5.01E-03	-6.74E-03	-5.48E-05	8.35E-02	-1.12E-01	3.78E-02	-1.17E-04	6.72E-01	2.62E+01	6.62E-05
20	1.34E-02	-6.74E-03	-3.33E-04	2.23E-01	-1.12E-01	2.30E-01	-7.57E-04	2.52E-01	2.62E+01	6.62E-05
25	2.70E-02	-6.74E-03	-7.89E-04	4.50E-01	-1.12E-01	5.45E-01	-1.79E-03	1.25E-01	2.62E+01	6.62E-05
30	4.90E-02	-6.74E-03	-1.52E-03	8.17E-01	-1.12E-01	1.05E+00	-3.41E-03	6.87E-02	2.62E+01	6.62E-05
35	8.38E-02	-6.74E-03	-2.68E-03	1.40E+00	-1.12E-01	1.85E+00	-5.95E-03	4.02E-02	2.62E+01	6.62E-05
40	1.38E-01	-6.74E-03	-4.49E-03	2.30E+00	-1.12E-01	3.10E+00	-9.83E-03	2.44E-02	2.62E+01	6.62E-05
45	2.22E-01	-6.74E-03	-7.27E-03	3.69E+00	-1.12E-01	5.02E+00	-1.57E-02	1.52E-02	2.62E+01	6.62E-05
50	3.48E-01	-6.74E-03	-1.15E-02	5.80E+00	-1.12E-01	7.93E+00	-2.44E-02	9.68E-03	2.62E+01	6.62E-05
55	5.37E-01	-6.74E-03	-1.78E-02	8.95E+00	-1.12E-01	1.23E+01	-3.73E-02	6.27E-03	2.62E+01	6.62E-05
60	8.155E-01	-6.735E-03	-2.707E-02	1.359E+01	-1.123E-01	1.870E+01	-5.600E-02	4.130E-03	2.615E+01	6.625E-05
65	1.222E+00	-6.735E-03	-4.062E-02	2.037E+01	-1.123E-01	2.806E+01	-8.284E-02	2.756E-03	2.615E+01	6.625E-05
70	1.808E+00	-6.735E-03	-6.015E-02	3.013E+01	-1.123E-01	4.159E+01	-1.209E-01	1.863E-03	2.615E+01	6.625E-05
75	2.643E+00	-6.735E-03	-8.798E-02	4.405E+01	-1.123E-01	6.077E+01	-1.744E-01	1.274E-03	2.615E+01	6.625E-05
80	3.820E+00	-6.735E-03	-1.272E-01	6.367E+01	-1.123E-01	8.789E+01	-2.487E-01	8.815E-04	2.615E+01	6.625E-05

$\left(\frac{\partial d}{\partial T_{\text{gas}}}\right)$   
DepOverEvap

$\left(\frac{\partial d}{\partial T_{\text{gas}}}\right)$   
d

Figure 1b: Image of Right Hand Side of one worksheet from the VMT modeling workbook using Tripropyleneglycol Diacrylate monomer (TRGPDA) in a web coating application. For substrate temperatures below about 10 °C the mobility of TRGPDA becomes too low for proper polymerization, while for liquid temperatures above about 60 °C there is the increasing possibility that the TRGPDA monomer will polymerize within the VMT evaporator. The top four lines on the left display the structure of the TRGPDA monomer molecule. A variety of values and gradients are tabulated in the remainder of the sheet as a function of monomer gas temperature.





models shows that as the liquid temperature and velocity rise, or the substrate temperature drops, thickness control improves. However, the chamber pressure depends solely on the substrate temperature.

These spreadsheet models can be used to model PML processes too. For PML process modeling the liquid thickness on the substrate, at the point of leaving the evaporator position, is simply entered directly, and the re-emitted monomer is all that is calculated. We find that, for a web system where there is a short time (on the order of a few tenths of a second or less) between the evaporator and cure station positions, reasonable thickness control can be attained with relatively low chamber pressures ( $10^{-4}$  torr to  $10^{-5}$  torr) with either VMT or PML processes.

Figure 3 shows a schematic layout of the relative positions of the PML flash evaporator and electron beam cure station on the NRC PML vacuum roll coater at Spectrum Polytronics (SPI) in 1987 [1, 3].  $S_v$  for monomer was about 75,000 l/s (35" diffusion pump with cryo-coil with one right angle [3]). The effective distance between the PML evaporator and the electron-beam curing zone was about 6.3 inches [3]. The standard run at SPI produced 1  $\mu\text{m}$  of polymerized film at 200 linear feet per minute web speed, with  $T_{\text{sub}}=0^\circ\text{C}$  [3]. Experiments were run at SPI in which a constant monomer flow to the flash evaporator was used (the standard run flow), and the substrate temperature was varied with HDODA as the monomer [3]. Table I contains the rates of change of thickness with respect to both evaporator-to-cure station transit time and substrate temperature [3]. The two rates of change are not independent since the re-emission is actually dependent on the duration and the temperature. This is not immediately apparent from the gradients since the time and temperature gradients, respectively, shown in Table I (as calculated by Equations A10 and A2, respectively) assume the shared geometry and web speed of the SPI web coater while assuming zero for the temperature and time variations, respectively. While the time rates of change in Table I are rather large, the error in the times (due to web speed fluctuations) are very small, on the order of 0.002 seconds or around 0.01  $\mu\text{m}$ . Table I also contains the results from the spreadsheet model of the substrate temperature variation experiment on the SPI system. The model agreement with the measured thickness decrease due to monomer re-evaporation is about 20%, which is fairly good considering the uncertainties in the geometry. With a continuously moving web, thickness errors, due to time and temperature variations, are equivalent for both PML and VMT sources.

However, for batch coating tools (either central hub cluster or in-line configurations) there exist distinct thickness control differences between the PML and VMT process approaches. These differences are largely due to the increased time between condensation and cure that the PML process requires coupled with the fact that it is not practical to actively cool the

substrate during the process. The thickness rates of change with respect to time remain the same as for web coating as shown in Table I. However, since PML gas flow does not turn on instantly, there is a great deal of re-emitted monomer escaping the substrate while the, spatially homogeneous, shower-head builds up enough monomer on the substrate to then move on to the cure station. This increases housekeeping and particle problems. After monomer build-up is complete, with a PML process, the stationary part must then begin moving to the position of the cure station. When monomer loss is 10s of microns per second, the timing of these starts, stops, and traverses is extremely critical when sub-micron thick coatings, of controlled thickness, are required.

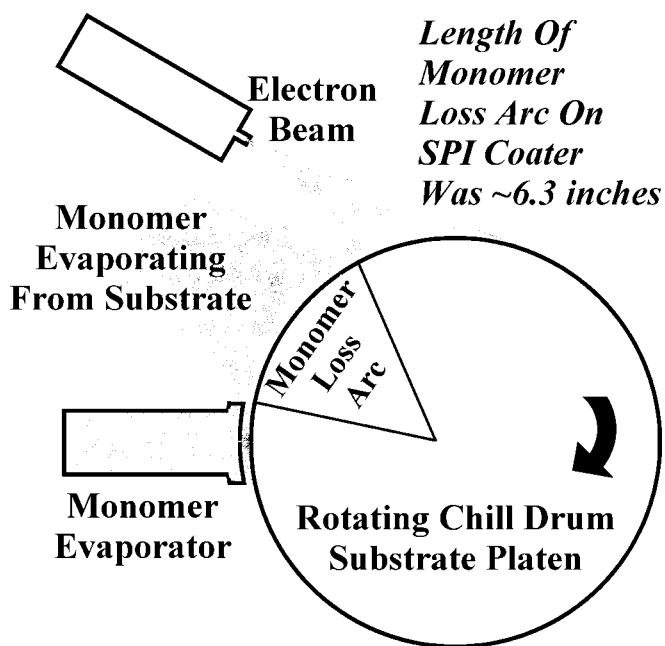


Figure 3: Schematic drawing of the 1987 SPI PML webcoater [1,3]. Monomer condenses onto the substrate at the evaporator position and the substrate immediately begins to re-emit monomer. The hot surface of the evaporator releases monomer back to the substrate, but once leaving the evaporator position the condensed film rapidly evaporates until it is cured at the electron-beam position.

One advertised in-line PML process tool design can be found on the World Wide Web [18]. This design shows the PML deposition station in one chamber and the cure station in a separate chamber, with a chamber length tunnel between the evaporator and cure chambers. Table II contains model results for a similarly constructed in-line PML tool for two different monomers (HDODA and TRPGDA) at two substrate temperatures. For Table II, pumping and line speed specifications were taken as higher and faster than those of the CPA 9900 series of in-line sputter tools [19]. Each monomer is calculated at  $20^\circ\text{C}$  and at the lowest possible temperature allowed before monomer mobility on the substrate would

interfere with polymerization. Table II assumes a 25 cm by 25 cm substrate area, 10,000 l/s pumping speed, and a 60 second transit time between the evaporator and cure positions. The volume of monomer that escapes to the chamber prior to starting the substrate moving from the deposition chamber toward the cure chamber is ignored. However, the effective monomer flow and chamber pressure during this ignored interval will be greater than that during the inter-chamber passage. Clearly, neither monomer in Table II will be adequate for deposition of 1 um thick coatings under the type of in-line PML tool configuration outlined above. The minimum variation of  $d$  with variations in  $T_{sub}$  is 70% of the target thickness per °C, and ranges as high as 1200%. The variations in  $d$  with variations in transit time are somewhat better (10% to 600% of target  $d$  per second). However, it is doubtful that  $T_{sub}$  could ever be controlled to even 1 °C in such a system, and  $\pm 1$  °C variations produce nearly 2d or 0d (Double or Nothing). This makes the time derivatives negligible compared with the temperature derivatives.

**TABLE I**  
**SPECTRUM POLYTRONICS (SPI) DATA**

Transit time between evaporator and cure positions is usually less than a second. However, for HDODA at 200 ft/min with ~6.3" between evaporator and e-gun (LIKE AT SPI), we find the following values for the derivatives:

$$\begin{aligned} \text{At } T_{sub}=0 \text{ }^\circ\text{C} \quad \quad \quad \text{At } T_{sub}=20 \text{ }^\circ\text{C} \\ \frac{\partial d}{\partial T_{sub}} = -0.021 \left( \frac{\mu\text{m}}{^\circ\text{C}} \right) \quad \quad \quad \frac{\partial d}{\partial T_{sub}} = -0.0378 \left( \frac{\mu\text{m}}{^\circ\text{C}} \right) \\ \text{and} \quad \quad \quad \text{and} \\ \frac{\partial d}{\partial t} = -3.03 \left( \frac{\mu\text{m}}{\text{s}} \right) \quad \quad \quad \frac{\partial d}{\partial t} = -6.31 \left( \frac{\mu\text{m}}{\text{s}} \right) \end{aligned}$$

PML Measurements at SPI (at 200 feet/min) with a 0.19 second transit time between evaporator and cure, show that  $d$  drops from 1 um to ~0.55 um as  $T_{sub}$  is varied from 0 °C to 21 °C and, at  $T_{sub}=0$  °C, the chamber pressure ran in the high  $10^{-5}$  torr range. The results of the spreadsheet model calculations for the Spectrum system, below, are seen to be very close to the measured values. Vacuum pumping speed was about 75,000 l/s.

$T_{sub}$ (°C)	Calculated Effective Re-Emitted Monomer Flow (scm)	Calculated Chamber Pressure (Torr)	MEASURED Chamber Pressure (Torr)	Calculated Monomer Thickness At Evaporator (um)	Calculated Polymerized Thickness (um)	MEASURED Polymerized Thickness (um)
0	366	6.2E-05	1E-4 to 5E-5	1.58	1	1
21	790	1.3E-04	Not Measured	1.51	0.45	0.55

**TABLE II**

**Model Results For In-Line Cluster Tool**

Condensed monomer required to be on the substrate at the time that it begins moving towards the cure position can exceed several hundred microns in order obtain a 1 um thick film with PML process.

MONOMER	$T_{sub}$ (°C)	Effective Re-Emitted Monomer Flow (scm)	Chamber Pressure (Torr)	Monomer Thickness At Evaporator (um)	Polymerized Thickness (um)	$\frac{\partial d}{\partial T_{sub}}$	$\frac{\partial d}{\partial t}$
						(um/°C)	(um/s)
HDODA	8	1156	1.48E-03	182.7	-1	-4.74	-3.03
	20	2390	3.02E-03	379.8	-1	-12.1	-8.31
TRPGDA	10	32.7	4.14E-05	7.735	-1	-0.747	-0.112
	20	87.5	1.24E-04	21.1	-1	-2.05	-0.335

**Common Parameters**

evap-to-cure time = 60 s      Substrate w = 25 cm  
pump speed = 10,000 l/s      substrate L = 25 cm

How would thickness control in a VMT batch process compare to that in a PML batch process? Mass balance calculations show the difference between  $T_{gas}$  in a VMT evaporator and  $T_{gas}$  of a closed system in equilibrium is dependent upon the ratio of the evaporator aperture area to the evaporator liquid area, or  $A_e/A_{liq}$ . For  $A_e < 5\%$  of  $A_{liq}$ , calculations show the difference between  $T_{gas}$  in an evaporator with an open aperture and the equilibrium system value of  $T_{gas} = T_{liq}$  for a closed evaporator at  $T_{liq} = 50$  °C is less than 0.25 °C. Under the conditions of Figures 1 and 2, this would mean an initial thickness error of 0.9% for HDODA and 2.2% for TRPGDA when the shutter is first opened. Further, kinetic arguments from the Moltech publications [16, 17] indicate that the time required for the gas to reach steady state, for such small perturbations from steady state, is much less than a second after the source shutter is opened. Thus, if a sealed evaporator is opened the change in  $T_{gas}$  between when it is first opened and the steady state value is small, and the time needed to reach this value is short. Therefore, the ideal VMT evaporator would be a sealed system with a variable area aperture. Since the temperatures are always less than about 80 °C, a simple o-ring sealed plate would be adequate for the aperture. Based upon the substrate speed and  $T_{gas}$ , the aperture can be opened to the desired width to produce the desired thickness. The above analysis of the SPI data indicates that the model fits the data reasonably well. Figures 1 and 2 show that VMT evaporators have reasonable net deposition rate and good process thickness control characteristics. Since VMT evaporators are "instant-on", the shower-head apertures and stop and go process required with a PML batch system are not needed. The substrate is simply moved past a close-coupled VMT evaporator/cure station at a constant speed. The aperture is opened just as the substrate arrives and is closed immediately after it passes. To minimize thickness variations due to process variations, the speed and  $T_{gas}$  are set as high as possible while  $T_{sub}$  and the evaporator-to-cure separation are set as low as possible. The maximum value of  $T_{gas}$  is the highest possible temperature at which there is no danger of polymerization within the evaporator (generally between about 50 °C and 80 °C, depending on the monomer). The minimum value of  $T_{sub}$  is the lowest temperature at which the monomer mobility remains high enough to permit proper polymerization (typically between 0 °C and 20 °C, depending on the monomer). Calculations then show thickness control in VMT batch processes is the same as in VMT, or PML, web processes (at equal substrate speeds), which is much better than in PML batch processes.

The advantages of VMT thermal evaporation over PML flash evaporation at the very low line speeds and film thickness' needed to match rates with slower processes, like sputtering, can now be discussed. In terms of the vapor pressure/re-emission calculations, there is no difference in the ability to control film thickness (the signal to noise ratio) between VMT and PML processes. However, there is a great difference between the mechanical constraints imposed by the two

methods of evaporation. The PML process requires that liquid monomer be pumped down a capillary, and through an ultrasonic (or other type of) atomizer, the fluid is atomized, then the atomized mist must strike as large a surface area as possible in order to flash evaporate. A simple calculation indicates that, on a 20 cm wide web, a flow of  $3.3 \times 10^{-5} \text{ cm}^3/\text{s}$  of monomer is required to deposit 1000 Angstroms at 1 m/min (without re-evaporation). Unfortunately, the lowest, smooth and continuous, flow specified for the lowest flow Sono-Tek atomizer is  $1.2 \times 10^{-2} \text{ cm}^3/\text{s}$  [20]. For lower flows the atomizer pulses and does not deliver a smooth output. In practice, lower flows are used by employing conductance limiting baffles placed within the PML evaporator. The baffles build up pressure within the evaporator and damp out fluctuations caused by the atomizer pulses to some extent. However, as the internal pressure rises due to the conductance limiting baffles, a point is reached when the monomer vapor pressure is high enough that the monomer residence time on the surface is long enough to permit polymerization to occur, and the monomer builds up inside the evaporator. Then the problem of surface cooling, followed by more internal polymerization, occurs. None of these problems are associated with the VMT source—the aperture is simply opened and gas escapes. The model calculations indicate that thickness variations of 10%, or less, can be obtained for 1000 Angstrom thick films of Propoxylated (3) Glyceryl Triacrylate at 1 m/min, while 2%-3% variations are easily attainable at higher line speeds.

### Multi-Component Monomer Mixtures

Implicit in the above analysis, but not yet explicitly discussed, is the problem of multi-component monomer mixtures. When two or more monomers are mixed, unless the mixture is an azeotropic composition, the reservoir liquid composition, and the composition of the evaporated material, is continuously changing. Each component will evaporate at a different rate, and these rates will be temperature dependent. To first order these rates can be determined by modified versions of Equations 3 and 4, with effective areas related to the relative volume percentages of each component in the mixture. This correction is analogous to a fugacity calculation [21]. With a VMT source, reservoir and evaporated composition, while possibly calculable, will be constantly changing as monomer evaporates. For multi-component mixtures in a PML process each component can be independently fed from its own atomizer into a common evaporator, but if a critical composition is required in the polymerized film, another problem arises with the PML process. The liquid composition on the substrate will be continuously changing (due to differential evaporation rates for each component) right up until polymerization occurs. Thus, very precise control of both substrate speed and temperature, and initial composition, are required for a multi-component PML process to be successful. The VMT process is not readily applicable to multi-component evaporation, unless an azeotropic composition is utilized within the evaporator.

### APPENDIX ON PROCESS GRADIENTS

$$\frac{\partial d}{\partial T_{\text{res}}} = \frac{\ln(10) \cdot 10^4 \cdot w_c \cdot W(T_{\text{res}})}{\rho \cdot V} \left[ \frac{B}{T_{\text{res}}^2} - \frac{0.5 \cdot \text{LOG}(10)}{T_{\text{res}}} \right] \left( \frac{60}{100} \right) \left( \frac{\text{mm}}{^\circ\text{C}} \right) \quad \text{Equation A1}$$

$$\frac{\partial d}{\partial T_{\text{sub}}} = - \frac{\ln(10) \cdot 10^4 \cdot (w_c + w_p)}{\rho \cdot V} \cdot W(T_{\text{sub}}) \cdot \left[ \frac{B}{T_{\text{sub}}^2} - \frac{0.5 \cdot \text{LOG}(10)}{T_{\text{sub}}} \right] \left( \frac{60}{100} \right) \left( \frac{\text{mm}}{^\circ\text{C}} \right) \quad \text{Equation A2}$$

$$\frac{\partial d}{\partial V} = - \frac{d}{V} \left( \frac{\text{mm}}{\text{m}} \right) \quad \text{Equation A3}$$

$$\frac{\partial d}{\partial w_c} = \frac{10^4}{\rho \cdot V} \cdot [W(T_{\text{res}}) - W(T_{\text{sub}})] \left( \frac{60}{100} \right) \left( \frac{\text{mm}}{\text{cm}} \right) \quad \text{Equation A4}$$

$$\frac{\partial d}{\partial w_p} = - \frac{10^4}{\rho \cdot V} \cdot W(T_{\text{sub}}) \left( \frac{60}{100} \right) \left( \frac{\text{mm}}{\text{cm}} \right) \quad \text{Equation A5}$$

$$\frac{\partial d}{\partial \rho} = - \frac{d}{\rho} \left( \frac{\text{mm}}{\frac{\text{g}}{\text{cm}^3}} \right) \quad \text{Equation A6}$$

$$\frac{\partial d}{\partial C} = \ln(10) \cdot d \left( \frac{\text{mm}}{\text{mm} \cdot \text{C}} \right) \quad \text{Equation A7}$$

$$\frac{\partial d}{\partial B} = - \frac{10^4 \cdot \ln(10)}{\rho \cdot V} \left[ \frac{W(T_{\text{res}}) \cdot w_c}{T_{\text{res}}} - \frac{W(T_{\text{sub}}) \cdot w_c}{T_{\text{sub}}} - \frac{W(T_{\text{sub}}) \cdot w_p}{T_{\text{sub}}} \right] \left( \frac{\text{mm}}{\text{mm} \cdot B} \right) \quad \text{Equation A8}$$

$$\frac{\partial d}{\partial t_c} = \frac{10^4}{\rho} \cdot [W(T_{\text{res}}) - W(T_{\text{sub}})] \left( \frac{\text{mm}}{\text{s}} \right) \quad \text{Equation A9}$$

$$\frac{\partial d}{\partial t_p} = - \frac{10^4}{\rho} \cdot [W(T_{\text{sub}})] \left( \frac{\text{mm}}{\text{s}} \right) \quad \text{Equation A10}$$

### CONCLUSIONS

It was found that, in a PML web coating process, the background monomer vapor pressure can be lowered by reducing the evaporator-to-cure station distance/time, lowering the substrate temperature, or by employing a monomer with lower vapor pressure at the substrate temperature. Analysis of the evaporation process did not lead to any viable method for construction/operation of an instant-on/instant-off PML flash evaporation source. This shortcoming is seen to limit the utility of PML sources in either central hub or in-line batch coating processes. Similarly, no technique for eliminating polymerization within the PML evaporator emerged from this work. Thus, continuous, and variable, deposition rate reduction over the duration of a run remains a problem with PML sources. The thickness control, in PML processes at low line

speeds, was seen to be limited more by the mechanical constraints of the liquid monomer delivery/atomization hardware than by the intrinsic vapor pressure characteristics of the monomer-substrate combination.

Detailed mathematical analysis of the evaporation process indicated that an entirely new process approach could be employed for delivering monomer gas to the substrate. This process, labeled the Vacuum Monomer Technique (VMT), is seen to overcome many of the process problems and stability issues associated with the PML process. The instant-on/instant-off nature of the VMT method should prove very effective for batch processes. Without the mechanical constraints of the capillaries and atomizers of PML sources, VMT sources should prove much more effective at the low substrate speeds, and low film thicknesses, required to match rates and line speeds for in-line deposition with lower rate processes like sputtering. For higher speed web coating processes the film thickness control issues/errors were seen to be manageable, and equivalent, in both VMT and PML processes.

Unless azeotropic compositions are employed, neither the VMT or PML processes is ideally suited to multi-component monomer mixtures – particularly at lower substrate speeds. Of the two processes, the PML approach is the better suited to multi-component mixtures since, with multiple atomizers, the flash evaporation process can at least, initially, deliver the correct monomer composition to the substrate. After condensation onto the substrate, detailed measurements and calculations are required in order to know what initial composition is required in order to attain the proper composition in the final polymerized film. This final composition will be a strong function of the substrate temperature, and evaporator-to-cure station distance/time, according to the rules outlined in Equations 1-7 and A1-A10.

## REFERENCES

1. A. Yializis, G.L. Powers, and D.G. Shaw, A New High Temperature Multilayer Capacitor With Acrylate Dielectrics, I.E.E.E. Transactions on Components, Hybrids, and Manufacturing Technology. Vol 13, #4, December 1990.
2. D.G. Shaw and M.G. Langlois in Proceedings of the Seventh International Vacuum Web Coating Conference, R. Bakish ed., Bakish Press, New Jersey, 1993, pg 268
3. Private written communication from Greg Lowe who, as a Process Engineer at Spectrum Polytronics in 1987, performed a series of PML experiments to measure re-evaporation rates of monomer fluids condensed on a substrate as a function of substrate temperature. Details and analysis of the experiments described in the communication are given in the text, Figure 3, and Table I of this paper.
4. J.D. Affinito, P.M. Martin, M.E. Gross, and W.D. Bennett, Vacuum Deposited Polymer/Silver Reflector Material, Proceedings of SPIE Optical Thin Films IV: New Developments, July 25-27, 1994, San Diego CA, pg 276.
5. J.D. Affinito, P.M. Martin, M.E. Gross, C.A. Coronado, and E.N. Greenwell, Vacuum Deposited Polymer/Metal Films for Optical Applications, Thin Solid Films 270 (1995) pg 43-48.
6. J.D. Affinito, M.E. Gross, C.A. Coronado, G.L. Graff, E.N. Greenwell, and P.M. Martin, A New Method for Fabricating Transparent Barrier Layers, TSF290-91 (1996) pg 63-67.
7. D.G. Shaw, M. Roehrig, M. Langlois, and C. Sheehan, Proceedings of the Ninth International Conference on Vacuum Web Coating, ed R. Bakish, Bakish Press 1995, pg 222.
8. J.D. Affinito, M.E. Gross, P.M. Martin, C.A. Coronado, and G.C. Dunham, High Rate Vacuum Deposition of Polymer Electrolytes, Journal of Vacuum Science and Technology A 14(3), May/June 1996, pg 733-738.
9. J.D. Affinito, Stephan Eufinger, M.E. Gross, G.L. Graff, and P.M. Martin, PML/Oxide/PML Barrier Layer Performance Differences Arising From Use of UV or Electron Beam Polymerization of the PML Layers, Thin Solid Films, Vol 308, 1997, pg 19-25.
10. J.D. Affinito, M. Shi, S. Stockhause, M.E. Gross, and P.A. Mounier, Molecularly Doped Polymer Composite Films for Light Emitting Polymer Applications Fabricated by the PML Process, 41st Annual Technical Conference Proceedings of the Society of Vacuum Coaters, 1998, pg 220-225.
11. J.D. Affinito, G.L. Graff, M-K. Shi, M.E. Gross, P.A. Mounier, and M.G. Hall, A New Hybrid Deposition Process, Combining PML and PECVD, for High Rate Plasma Polymerization of Low Vapor Pressure, and Solid, Precursors, 42nd Annual Technical Conference Proceedings of the Society of Vacuum Coaters, Chicago, Illinois, 4/17-22/99, pg 102-107.
12. J.D. Affinito, Hybridization of the Polymer Multi-Layer (PML) Deposition Process, Surface and Coating Technology 133-134, 2000, pg 528-534
13. J.O. Hirschfelder, C.F. Curtis, R.B. Bird, in Molecular Theory of Gases and Liquids, Chapter 4, pg 283, Wiley, New York, 1954.

- 
14. T. Earl Jordan, in Vapor Pressure of Organic Compounds, Interscience Publishers, Inc., New York, 1954.
  15. S. Dushman, in Scientific Foundations of Vacuum Technique, edited by J.M. Lafferty, John Wiley and Sons, chapter 10, pg 691-703, 1962.
  16. J.D. Affinito, M.J. McCann, and C. Sheehan, Thermal Evaporation of Li: Experiment and a Novel Thermodynamic Model, Proceedings of the Fourteenth International Conference on Vacuum Web Coating, ed R. Bakish, Bakish Press 2000, pg 77-94.
  17. J.D. Affinito, M.J. McCann, C. Sheehan and S. Bullock, Web Substrate Heating and a Thermodynamic Calculation Method for Li Film Thickness in a Thermal Evaporation System, 44th Annual Technical Conference Proceedings of the Society of Vacuum Coaters, pg. 492-497, 2001.
  18. <http://www.vitexsys.com/guardian.html>.
  19. <http://www.cpa-sputtering.com/>.
  20. Sono-Tek product literature, or [http://www.sono-tek.com/nozzles/nozzles\\_specs.html](http://www.sono-tek.com/nozzles/nozzles_specs.html).
  21. A.W. Adamson, in A Textbook Of Physical Chemistry, Chapter 6, pg 241-242, Academic Press, New York, 1973.