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Monitoring the Formation of Thin Films by Photothermal Technique

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Abstract Evaporation is a widely used technique for developing thin films. In this study the formation of a film on top of a substrate is investigated using a photothermal technique. The configuration implies the illumination of an opaque substrate by modulated laser radiation and the detection of the heat at the illuminated zone. The system is considered as a two-layer system in which the non-illuminated layer presents a dynamic response, the thickness and thermophysical properties, which change as a function of time. Results of modeling such a system, which depend on the evaporation rate and concentration changes are presented. It was found that for the process in which evaporation constitutes a dominant contribution, one observes a stable long time process, and at a certain instant, the amplitude of the photothermal signal suddenly grows. On the other hand, additional contributions (such as the increase of concentration) involve processes that cause the amplitude of the photothermal signal to grow smoothly with time. The contributions of different mechanisms involved during the film formation are discussed.

Keywords Evaporation process · Photothermal technique · Polymers · Time evolution

1 Introduction

The dynamics of evaporation from a solution and the subsequent formation of a thin film on a substrate is a complex process, during which the system passes through a series of stages where it is originally thermally thick and eventually becomes ther-

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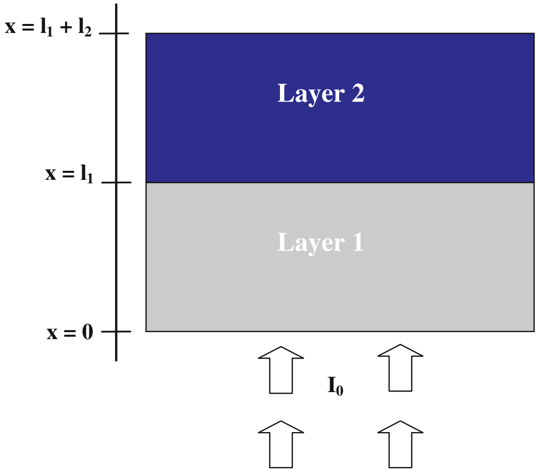


Fig. 1 Geometry of the configuration used in this study. Layer 1 is the substrate, and layer 2 is the liquid sample. The whole system is surrounded by the gas

mally thin [1,2]. The photothermal (PT) study of this process has been mainly devoted to the study of films that remain thermally thick during the formation. In this case, the thermal effusivity is the parameter that permits monitoring of the process [3,4]. However, the formation of thin films has not been fully explored. One of the reasons for this is that the process of the formation of thin films involves a complex dynamic process in which the evolution of both the thermal diffusivity and thermal effusivity are involved.

One of the main challenges during the formation of a thin film involves the clarification that not all the changes in the PT signal comprise a change of thermal effusivity. Progressive reduction of the sample's thickness during evaporation induces a change in the modulated temperature and could also induce effects related to thermal wave interference inside the film.

In order to clarify these questions, theoretical simulations of the temperature (under the conditions of a PT experiment) during the evaporation of a solution on a substrate are presented. It is shown that if the evaporation is the dominant contribution during the process, a long stable process is observed, and at a certain instant, a sudden growth in the amplitude of the photothermal signal occurs. It is also shown that the increase of the concentration of the solute in the solvent (as a consequence of evaporation) affects additionally the thermal properties, which is evident as a smooth growth of the PT signal with time.

2 Theory

Assuming that during the process of evaporation the liquid remains smooth, as in the case of experiments on liquids performed in thin ring containers, a one-dimensional configuration can be used [3,5]. Figure 1 shows the geometry of the configuration used here. The 20 μm aluminum substrate (layer 1) is illuminated with a periodic light source and the sample (layer 2) is atop the aluminum. The one-dimensional solution of the Fourier equation for the temperature at the face of the illuminated Al side is given by [2,6]:

$$T(x=0,t) = \frac{I_0\Gamma_{g1}}{2k_1\sigma_1}\frac{1+R'_{21}\mathrm{e}^{-2\sigma_1 l_1}}{1-R_{g1}R'_{21}\mathrm{e}^{-2\sigma_1 l_1}}\mathrm{e}^{i\omega t} \tag{1}$$

where

$$R'_{21} = \frac{R_{21}+R_{g2}\mathrm{e}^{-2\sigma_2 l_2}}{1+R_{21}R_{g2}\mathrm{e}^{-2\sigma_2 l_2}},$$

$$R_{mn} = \frac{1-e_m/e_n}{1+e_m/e_n},$$

$$\Gamma_{g1} = \frac{2}{1+e_g/e_1},$$

$$\sigma_i = (1+i)\sqrt{\frac{\pi f}{\alpha_i}},$$

I_0 is the intensity of the light source, f is the modulation frequency of the heating source, e_i is the thermal effusivity, l_i is the thickness, and α_i and k_i are the thermal diffusivity and thermal conductivity, respectively. The subscripts 1, 2, and g refer to layers 1 and 2, and the surrounding gas, respectively.

Considering that the transversal cross section of the system does not change in time, we assume that the evaporation rate follows the equation [1,7],

$$m(t) = m_0 - bt, \tag{2}$$

where m_0 is the initial mass and b is the rate of evaporation of the solvent.

As a consequence, the thickness $l(t)$ of the sample varies according to

$$l(t) = \left(\frac{m_\mathrm{p}}{\rho_\mathrm{p}} + \frac{m(t)}{\rho_\mathrm{s}}\right)\Big/ A, \tag{3}$$

with ρ_p and ρ_s being the densities of the solute and solvent, respectively, m_p is the constant mass of the solute, and A is the transversal cross-sectional area.

The concentration $\phi(t)$ of the solute is given by

$$\phi(t) = \frac{m_\mathrm{p}}{m_\mathrm{p}+m(t)}. \tag{4}$$

Taking into account the increasing concentration of the solute in the solution (due to the evaporation process), the evolution of the thermal properties must be considered.

For the case of volumetric heat capacity, it can be considered that

$$(\rho c)_{\text{eff}} = (\rho c)_{\text{p}}\, \phi + (\rho c)_{\text{s}}\, (1 - \phi)\,, \tag{5}$$

where $(\rho c)_{\text{eff}}$ is the effective volumetric heat capacity of the sample (layer 2) while $(\rho c)_{\text{p}}$, and $(\rho c)_{\text{s}}$ are volumetric heat capacities of the solute and solvent, respectively.

Two different effective models are considered for the thermal conductivity of the sample [8].

Linear model:

$$k_{\text{eff}} = k_{\text{p}}\phi + k_{\text{s}}\,(1 - \phi)\,, \tag{6a}$$

and the Maxwell model:

$$k_{\text{eff}} = \left(1 + \frac{3\phi\,(\beta - 1)}{(\beta + 2) - \phi\,(\beta - 1)}\right) k_{\text{s}}, \tag{6b}$$

where $\beta = \frac{k_{\text{p}}}{k_{\text{s}}}$, k_{p} and k_{s} are the thermal conductivities of the solute and solvent, respectively, and ϕ is the mass fraction.

The effective thermal conductivity and thermal effusivity can be obtained from

$$\alpha_{\text{eff}} = \frac{k_{\text{eff}}}{(\rho c)_{\text{eff}}} \text{ and } e_{\text{eff}} = \sqrt{(\rho c)_{\text{eff}}\, k_{\text{eff}}}. \tag{7}$$

Considering the evolution on the sample's thickness and thermal properties, one can obtain information about the evolution of temperature by using Eqs. 3–7 in Eq. 1. Given the complexity and length of the algebraic results, software developed in Mathematica (5.0 ©Wolfram Research, Inc.) has been used to perform the algebraic and numerical calculations.

3 Results and Discussion

Figure 2 shows the result of the simulation of temperature as a function of time for a sample consisting of acetone on an aluminum substrate (20 μm thick, $\alpha_1 = 0.9 \text{cm}^2 \cdot \text{s}^{-1}$, $\text{e}_1 = 2.3\,\text{W} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2} \cdot \text{K}^{-1}$) without solute. This is a process that includes only pure evaporation. The normalization was performed by dividing the temperature obtained from the sample by the temperature attained without the sample. The thermal conductivity, density, and heat capacity of acetone are $k_2 = 0.002\,\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$, $\rho_2 = 0.8\,\text{g} \cdot \text{cm}^{-3}$, and $c_2 = 2.8\,\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, respectively. The rate of evaporation $m = 0.0367 - 9 \times 10^{-5}\, t$ has been obtained experimentally using an analytical balance.

In Fig. 2, the first stage before 50 s corresponds to the temperature without the sample. When the sample is deposited onto aluminum, the temperature decreases and remains constant for more than 350 s. Depending on the modulation frequency, a minimum in the temperature appears followed by a fast increase until the system reaches the initial temperature.

Fig. 2 Normalized temperature as a function of time for the aluminum/acetone system at different modulation frequencies

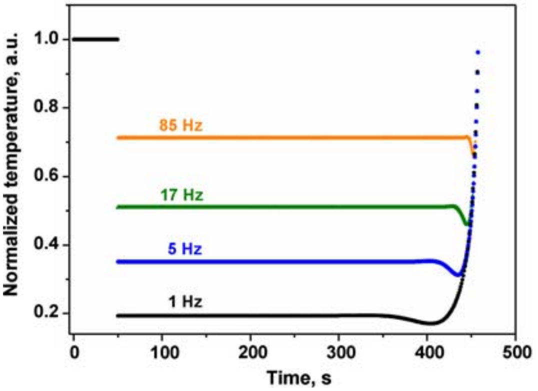
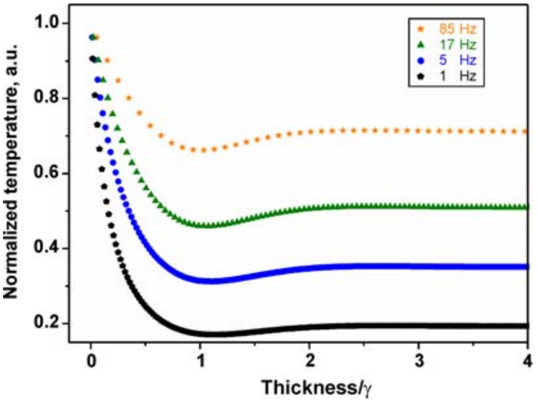


Fig. 3 Normalized temperature as a function of the ratio of the sample thickness and the thermal diffusion length



In order to investigate the origin of the minimum, the temperature was plotted as a function of the thickness of the sample divided by the thermal diffusion length of the sample ($\gamma = (\alpha/\pi f)^{1/2}$). Results for the temperature as a function of the sample thickness are shown in Fig. 3. It can be observed that the temperature remains constant up to the instant at which the length of the thermal wave becomes comparable to the thickness of the sample, with a minimum at the point $l_2(t) = \gamma$. This indicates that this effect is due to the interference, and consequently it is defined by the thermal diffusivity of the system. The minimum becomes sharper at higher frequencies.

The numerical values obtained by the effective models for the thermal conductivity, density, and volumetric heat capacity for acetone and a solute ($k = 0.001\,\mathrm{W\cdot cm^{-1}\cdot K^{-1}}$, $\rho = 0.8\,\mathrm{g\,cm^{-3}}$, $c = 1.6\,\mathrm{J\cdot g^{-1}\cdot K^{-1}}$, respectively) as a function of the mass fraction of the solute are shown in Fig. 4. It can be observed that the linear and Maxwell models give very similar values. This is due to the fact that the concentration of the solute in the solvent is very low and that both the solute and solvent have similar thermal properties.

The result for the amplitude of the modulated temperature for a system, in which the concentration changes as a function of the film's thickness, is shown in Fig. 5.

Fig. 4 (**A**) Effective thermal conductivity and (**B**) effective volumetric heat capacity for the solute–solvent system as a function of the mass fraction of the solute

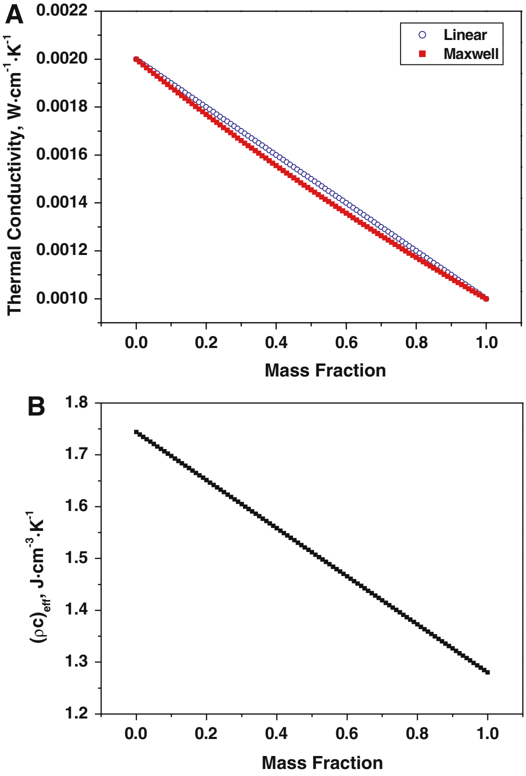
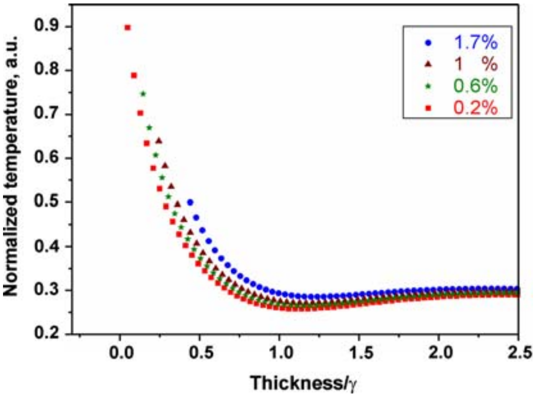


Fig. 5 Normalized temperature as a function of the ratio of the sample thickness and the thermal diffusion length for different initial concentrations of solvent



The Maxwell model was used to compute the temperature evolution. The temperature shows similar behavior to that observed in the case of pure evaporation; however, a systematic increase in time is observed. Such an increase in temperature is more pronounced for samples characterized by a higher solute concentration that results in thicker films at the end of the process. On the other hand, the process stops at different thicknesses, as expected.

Experimental results for the study of evaporation of liquids [1,9] and formation of polymers [5] using photothermal techniques have been previously reported. The evaporation of isopropanol droplets on an Al substrate using photoacoustics (PA) recorded at a 160 Hz modulation frequency has been studied by Miranda and Cella [1]. These authors analyzed the evolution of the PA signal as a function of time for monitoring the evaporation and contraction of a droplet wetting the flat Al surface. These experimental data are similar to simulations reported in this work (Fig. 2), and especially the minimum appearing during the time monitoring of the process can be understood as a consequence of thermal wave interference, as can be compared with our results (Fig. 3). This could be due to the fact that an isopropanol drop was evaporated without changing its radius during their experiment [1].

For the case of the solute/solvent system, where the solvent is evaporated and a thin film is formed on a substrate, our results predict the same behavior as shown by the experimental data reported by Bante et al. [5] based on the same experimental configuration. They have measured the time evolution of the PA signal amplitude for the process of evaporation-crosslinking in a sample of chitosan highly diluted in a solution of water–acetic acid at a constant modulation frequency of 4.17 Hz. The substrate was mica covered by silver paint. The experimental results show the same behavior as our simulation (Fig. 5), in particular, with the minimum appearing when the thickness of the sample is close to the thermal diffusion length of the sample (γ).

The agreement of our results with previous reported experimental data indicates that the simulations performed in this work take into account the most important factors involved in the process. In order to improve our models, it is important to consider three-dimensional effects involved in the process of evaporation as well as the additional increase of thermal properties taking place when polymeric films are developed.

4 Conclusions

The formation of thin films by evaporation was studied theoretically using the two-layer model of a PT technique. It was demonstrated that the theoretical model predicts the experimentally observed results. Reduction of the thickness generates interference phenomena that can help to analyze the formation of films with different solute/solvent proportions. It was also found that when the thermal properties of the solute and solvent are not very different, the results obtained by different effective models are very similar.

These results can be useful in the characterization of the thermal properties of pure liquids, when the evaporation rate is known, given that the initial sudden decrease, as well as the final rapid increase, depends only on the thermal effusivity of the sample. On the other hand, the minimum due to the interference effects can be used to determine the thermal diffusivity of the liquid. For more complex systems such as mixtures of a solvent and solute, which result in a thin layer at the end of the process, the technique can be useful in the real time analysis of the process. Given that our approach takes into account the evaporation, which is the dominant effect during almost the complete process of the formation of the layer, our results could be useful as the basis for monitoring of the different process occurring during polymer casting of films by evaporation.

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